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. 33, No. 4, 349–458, October 1965

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

For 1965, *Analytica Chimica Acta* has six issues to the volume, two volumes will appear. Beginning in 1966, three volumes per year will be published, each consisting of four issues. Subscription prices: \$ 17.50 or £ 6.6.— or Dfl. 63.— per volume; \$ 52.50 or £ 18.18.— or Dfl. 189.— 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

Annual Surveys of Organometallic Chemistry

The upsurge of interest in organometallic chemistry which has taken place in little over a decade has found its natural outlet in an almost mushroom-like explosion of literature.

Notwithstanding the creation of periodicals devoted wholly to this field (notably **THE JOURNAL OF ORGANOMETALLIC CHEMISTRY)**, an all too large proportion of papers concerned with organometallic compounds remain scattered throughout the pages of almost 100 non-specialist journals. The chemist, of course, has neither the time nor the funds to keep abreast of his subject in this manner.

In recognition of this problem, and in an attempt to alleviate the situation, **ELSEVIER PUBLISHING COMPANY** has undertaken publication of this new book series **ANNUAL SURVEYS OF ORGANOMETALLIC CHEMISTRY.**

The series will provide a comprehensive (but not necessarily exhaustive) and critical summary of organometallic chemistry on a year-to-year basis, each volume being published as soon as possible after the end of the year.

This first volume deals with 1964. For this review an organometallic compound is defined by the editors as one "which contains at least one metal-to-carbon bond and we include metal carbonyls in this definition". The organic derivatives of some elements usually considered in discussions of organometallic chemistry, e.g. boron and silicon, are included. The survey consists of two parts; one, edited by D. Seyferth presents a discussion of organic compounds of the main group (non-transition) metals and the second, by R. B. King, discusses transition metal organometallic chemistry dealing first with general developments in transition metal chemistry in 1964 followed by a discussion of advances in the chemistry of specific groups of transition metals organized according to the Periodic Table.

Volume 1
covering the year 1964

by

DIETMAR SEYFERTH,

Department of Chemistry,
Massachusetts
Institute of Technology,
Cambridge, Mass., U.S.A.

and

R. BRUCE KING,

Senior Fellow, Mellon Institute,
Pittsburgh, Pa., U.S.A.

$6\frac{1}{2} \times 9\frac{1}{2}$"
ix + 312 pages
+ Author index
13 illustrations
over 1400 lit. refs.
September 1965

CONTENTS: Part I: Main Group Metals: 1. Introduction. 2. Group I (Lithium, Sodium, Potassium). 3. Group IIA (Beryllium, Magnesium). 4. Group IIB (Zinc, Cadmium, Mercury). 5. Group III (Boron, Aluminum, Gallium, Indium, Thallium). 6. Group IV (General comments; Silicon, Germanium, Tin, Lead). 7. Group V (Antimony, Bismuth). Part II: Transition Metals: 8. Introduction. 9. General. 10. Group III (Lanthanides and Actinides). 11. Group IV (Titanium, Zirconium, Hafnium). 12. Group V (Vanadium, Niobium, Tantalum). 13. Group VI (Chromium, Molybdenum, Tungsten). 14. Group VII (Manganese, Technetium, Rhenium). 15. Group VIII (A: Ferrocene, Ruthenocene, Osmocene; B: Iron, Ruthenium, Osmium; C: Cobalt, Rhodium, Iridium; D: Nickel, Palladium, Platinum). 16. Group I (Copper, Silver, Gold). List of Journals covered directly. Author Index.

PRELIMINARY ANNOUNCEMENT

Organometallic Chemistry Reviews

Editors: K. A. ANDRIANOV *(Moscow)*
C. EABORN *(Brighton)*
E. O. FISCHER *(Munich)*
H. NORMANT *(Paris)*

Co-ordinating Editor: D. SEYFERTH *(Cambridge, Mass.)*

When the *Journal of Organometallic Chemistry* appeared in 1963 on a bi-monthly basis, the intention was to publish both original papers and review articles. However, the pressure of papers submitted was such that even with the most rigorous editorial scrutiny, and the transfer to a monthly publication schedule, it was not possible to publish more than original papers.

Therefore it was decided to adopt another form of publication – **Organometallic Chemistry Reviews** – to exist side by side with the *Journal of Organometallic Chemistry,* and to comprise only reviews.

Contributions will fall into two categories:

(a) Reviews of certain areas of organometallic chemistry with thorough literature coverage; these can be a complete coverage of the field in question, or coverage of recent events only.

(b) Reviews by research workers, active in the organometallic area, of their own contributions to a certain aspect of organometallic chemistry; this type of review would serve to summarize and put in perspective research carried out over a period of years.

The volumes will be of the same format as the Journal with a semi-stiff cover. Publication will be irregular as each volume will appear when sufficient material has been received for 200—250 pages.

Some Reviews to appear in the first volume:

D. S. MATTESON (Pullman, Wash.) – Organofunctional boronic esters

H. HEANEY (Loughborough) – Grignard and organolithium reagents derived from di- and poly-halogen compounds

K. JONES (Cambridge) and M. F. LAPPERT (Brighton) – Organic tin-nitrogen compounds

R. H. CRAGG (Newcastle-upon-Tyne) and M. F. LAPPERT (Brighton) – Organic boron-sulphur compounds

R. STUART TOBIAS (Minneapolis, Minn.) – Sigma bonded organometallic cations in aqueous solutions and crystals

B. J. WAKEFIELD (Salford) – Recent advances in the chemistry of organomagnesium compounds. (a) The nature of the Grignard reagent; (b) New organomagnesium compounds

I wish to order .... copy/copies of **ANNUAL SURVEYS OF ORGANOMETALLIC CHEMISTRY, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

I wish to order .... copy/copies of **ORGANOMETALLIC CHEMISTRY REVIEWS, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

Name (please print) ....

Address ....

....

Name and address of bookseller ....

....

I wish to order .... copy/copies of **ANNUAL SURVEYS OF ORGANOMETALLIC CHEMISTRY, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

I wish to order .... copy/copies of **ORGANOMETALLIC CHEMISTRY REVIEWS, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

Name (please print) ....

Address ....

....

Name and address of bookseller ....

....

I wish to order .... copy/copies of **ANNUAL SURVEYS OF ORGANOMETALLIC CHEMISTRY, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

I wish to order .... copy/copies of **ORGANOMETALLIC CHEMISTRY REVIEWS, VOLUME 1**

I wish to enter .... continuation order/s for the above series.

Name (please print) ....

Address ....

....

Name and address of bookseller ....

ELSEVIER PUBLISHING COMPANY

335, Jan van Galenstraat

P.O. Box 211

AMSTERDAM
The Netherlands

ELSEVIER PUBLISHING COMPANY

335, Jan van Galenstraat

P.O. Box 211

AMSTERDAM
The Netherlands

ELSEVIER PUBLISHING COMPANY

335, Jan van Galenstraat

P.O. Box 211

AMSTERDAM
The Netherlands

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 33, No. 4, October 1965

CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF COBALT WITH α-NITROSO-β-NAPHTHOL

The co-crystallization of ultramicro quantities of cobalt with α-nitroso-β-naphthol, was investigated by radio-tracer techniques. More than 99% cobalt, even when carrier-free, could be recovered. The distribution was studied and appeared to follow the logarithmic distribution law. The interference of a large excess of zinc was almost negligible. The method was applied to the carrier-free separation of cobalt isotopes (^{55}Co, ^{56}Co, ^{57}Co, ^{58}Co) produced by deuteron bombardment of an iron target. Contamination by manganese (^{54}Mn, ^{52}Mn) and iron (^{59}Fe) was, even in the absence of manganese carrier, almost negligible.

R. DAMS,
Anal. Chim. Acta, 33 (1965) 349–359

MANOMETRIC SUBMICRO DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC MATERIALS

A method is described for the determination of carbon and hydrogen in quantities of organic material ranging from 5 to 50 μg. The method involves catalytic combustion of the sample in oxygen and measurement of the pressures of the resulting carbon dioxide and water. Special attention has been paid to the reduction of the effect of water adsorption in the apparatus. The present submicro method can be applied to non-volatile, non-hygroscopic samples and is free from interferences by nitrogen, sulphur and halogens (except fluorine). The standard deviation in the 50-μg sample range is 0.13% for carbon and 0.10% for hydrogen. The average duration per analysis when carried out in series is 20 min.

P. GOUVERNEUR, H. C. E. VAN LEUVEN, R. BELCHER AND A. M. G. MACDONALD,
Anal. Chim. Acta, 33 (1965) 360–372

THE NUCLEATION OF CALCIUM PHOSPHATE FROM SOLUTION

Dicalcium phosphate was precipitated from homogeneous solution in the pH range 5–6 by using the hydrolysis of cyanate to control the precipitation process. Turbidimetric determination of the onset of precipitation enabled the critical supersaturation to be determined. In this region the average critical supersaturation ratio was found to be 2.3.

T. HLABSE AND A. G. WALTON,
Anal. Chim. Acta, 33 (1965) 373–377

THE STABILITY CONSTANTS OF THE ALKALINE EARTH LACTATE AND α-HYDROXYISOBUTYRATE COMPLEXES

The stability constants of the lactate and α-hydroxyisobutyrate complexes of the alkaline earths were determined by potentiometric titration. The average ligand number exceeds a value of one, indicating the formation of ML^+ and ML_2 complexes; α-hydroxyisobutyrate forms stronger complexes than lactate. The stability constants β_2 increase as a function of decreasing atomic number for both ligands: $Ba < Sr < Ca < Mg$, although the constant β_1 is greater for Mg than for Ca.

F. Verbeek and H. Thun,
Anal. Chim. Acta, 33 (1965) 378–383

ANALYTICAL APPLICATIONS OF β-HETEROPOLY ACIDS

PART I. DETERMINATION OF ARSENIC, GERMANIUM AND SILICON

The existence of two forms of several heteropolymolybdates, differing in structure and stability, was confirmed. The unstable β-forms were stabilised by addition of comparatively large amounts of polar organic solvents, especially acetone, presumably because the solvent displaces water from the surface of the heteropoly anion and so inhibits any reorganisation of the structure of the anion. The organic solvent also intensifies the colour. The methods are rapid, sensitive, precise and accurate. Various applications are described.

R. A. Chalmers and A. G. Sinclair,
Anal. Chim. Acta, 33 (1965) 384–390

THE TITRIMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM IN SILICATE ROCKS

A cation-exchange scheme is described for the separation of calcium and magnesium from interfering elements in rapid silicate analysis. Interfering elements can be eluted from the ammonium form of Zeo-Karb 225 with a solution of the ammonium salt of ethylenediaminetetraacetic acid at pH 4.5. Calcium and magnesium are not eluted with this reagent but can be eluted consecutively with ammonium chloride solution and titrated photometrically with EDTA. Calcium and magnesium can be separated quantitatively from Al, Fe, Ti, Mn, Bi, Cd, Cr, Co, Cu, Pb, Mo, Ni, U, V, rare earths, and Zn.

M. I. Abdullah and J. P. Riley,
Anal. Chim. Acta, 33 (1965) 391–396

DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF TARTRATE WITH CHLORANILIC ACID

A differential spectrophotometric method for the determination of tartrate using chloranilic acid is described. Standard and sample solutions containing slightly more tartrate than the reference solution, are measured relative to it. The procedure is applicable to the determination of tartrate in baking powder; the results obtained compared favorably with the official A.O.A.C. method.

A. R. Johnson, Jr.,
Anal. Chim. Acta, 33 (1965) 397–402

THE POLAROVOLTRIC METHOD

GENERAL PRINCIPLES AND FUNDAMENTALS OF THE METHOD

(in French)

The various steps in the development of the polarovoltric method and its utilisation in an automatic titration apparatus employing 2 polarized platinum electrodes are described. The method is based on the use of 2 types of polarization relationships applied to different chemical systems. These relationships are of the type $I = \mathrm{f}(V)$ and $V = \mathrm{f}(U)$, where V is the potential measured at the electrodes and U the potential applied to the electrodes across a resistance R, and are obtained directly from 2 indicating electrodes without the need for a reference electrode.

The advantage of these relationships over the classic $I = \mathrm{f}(E)$ curves, where E is the potential of the indicating electrode with respect to a reference electrode, is to facilitate the prediction of the titration curves as a function of the resistance R and the applied voltage U. The use of these relationships has shown that a fixed applied voltage U of 3 V and a fixed series resistance R of 0.5 megohm are the most suitable for a differential polarovoltmeter for semi-automatic titrations.

A symbolic notation is described which indicates the origin of the observed variations in potential. This notation permits a simple interpretation of polarovoltric curves and the rational use of unsymmetrical electrode arrangements.

J. E. Dubois et P. C. Lacaze,
Anal. Chim. Acta, 33 (1965) 403–412

HIGH-SPEED CONTROLLED-POTENTIAL COULOMETRY

APPLICATION TO PRECISE DETERMINATION OF PLUTONIUM

An electrolysis cell for high-speed controlled-potential coulometric analysis with conventional magnetic stirring is described. The factors influencing the precision obtainable by this technique with platinum and gold electrodes are discussed with particular reference to the oxidation of Pu(III) to Pu(IV) in 0.5 M sulphuric acid.

G. C. Goode and J. Herrington,
Anal. Chim. Acta, 33 (1965) 413–417

DETERMINATION OF AMERICIUM BY CONTROLLED POTENTIAL COULOMETRY

(in French)

A coulometric determination of americium by reduction of Am(VI) to Am(V) at a potential of +1.3 V is proposed. The accuracy of the method was evaluated by analyzing ^{241}Am solutions prepared by weighing and dissolving AmO_2 of known purity. The results must be corrected by a factor of 1.017, in order to eliminate the systematic error due to autoreduction. After this correction, the relative standard deviation of the method ranged from 0.44% for americium concentrations of $3.125 \cdot 10^{-3}$ M to 0.96% for those of $1.25 \cdot 10^{-4}$ M.

G. Koehly,
Anal. Chim. Acta, 33 (1965) 418–425

METHOD FOR THE ISOLATION OF THORIUM FROM SILICEOUS MATERIALS

A method for the isolation from siliceous materials of carrier-free chemically and radiochemically pure thorium is described. The method was applied and tested on several shale and deep-sea sediment samples used in the application of the Thorium Isotopes Method to the Dating of Marine Sediments. The chemical procedure consistently produces pure thorium in good yields. Several samples can be prepared simultaneously in a few hours.

I. Almodóvar,
Anal. Chim. Acta, 33 (1965) 426–433

THE CHROMATOGRAPHIC SEPARATION OF CALCIUM AND STRONTIUM BY ELUTION WITH AMMONIUM SULPHATE SOLUTION

(in German)

A method is described for the chromatographic separation of calcium and strontium adsorbed on a cation-exchange resin, by means of elution with ammonium sulphate solution. The method is suitable for Ca : Sr ratios $\geqslant 1$. The separated elements can be determined directly in the eluate.

R. Christova and P. Ilkova,
Anal. Chim. Acta, 33 (1965) 434–437

FLAME-PHOTOMETRIC DETERMINATION OF SODIUM IN URANIUM ORES

A flame-photometric method of determining sodium in uranium, phosphate, carbonate, and silicate rocks has been developed. The mutual enhancement of the alkali metals is overcome by the addition of a radiation buffer added to both the sample and to the standards. The method is rapid and suitable for routine analysis. Results obtained are within $\pm 2\%$ of the sodium content.

H. Kramer and L. J. Pinto,
Anal. Chim. Acta, 33 (1965) 438–442

DETERMINATION OF MOLYBDENUM IN HAIR AND WOOL BY NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis was applied to the determination of molybdenum in hair and wool. Ashed samples of hair and wool were irradiated for 15 min at a flux of $5 \cdot 10^{13}$ n/cm^2/sec to produce ^{101}Mo. An acid solution of the ash was first boiled in the presence of sodium bromide and bromate to volatilize bromine (^{80}Br and ^{82}Br radioisotopes interfere) and then extracted with 0.1% α-benzoinoxime in chloroform to remove ^{101}Mo from other interfering radionuclides. The ^{101}Tc daughter from ^{101}Mo was measured over the 0.31-MeV γ-ray photopeak after allowing the separated ^{101}Mo to decay for 15 min. The molybdenum concentration in hair varied from 0.02 to 0.13 μg/g while wool was found to contain 0.04–0.58 μg/g.

W. B. Healy and L. C. Bate,
Anal. Chim. Acta, 33 (1965) 443–448

NON-DESTRUCTIVE NEUTRON ACTIVATION DETERMINATION OF SILVER AND ANTIMONY IN BISMUTH BY γ,γ-COINCIDENCE SPECTROMETRY

A non-destructive neutron activation method was developed for the determination of silver and antimony in high-purity bismuth; γ,γ-coincidence counting of ^{110m}Ag or ^{124}Sb was applied. The activity of the matrix or other impurities did not interfere. When 1-g samples were irradiated at a neutron flux of $4 \cdot 10^{11}$ n cm^{-2} sec^{-1} for 25 days, the sensitivity of the method was in the p.p.b. region.

J. I. Kim and J. Hoste,
Anal. Chim. Acta, 33 (1965) 449–458

REDUCTION OF AZO COMPOUNDS WITH ACIDIC REDUCING AGENTS

(Short Communication)

R. D. Tiwari and J. P. Sharma,
Anal. Chim. Acta, 33 (1965) 459–462

GRAVIMETRIC DETERMINATION AND SEPARATION OF THORIUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE BY DIRECT WEIGHING

(Short Communication)

B. Das and S. C. Shome,
Anal. Chim. Acta, 33 (1965) 462–464

CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF COBALT WITH α-NITROSO-β-NAPHTHOL*

R. DAMS
Laboratory of Analytical Chemistry, Ghent University, Ghent (Belgium)

(Received January 11th, 1965)

Co-crystallization with organic reagents is a new tool for the selective concentration of elements from greatly diluted solutions. In recent years many data[1-7] dealing with co-crystallization have been published. Organic co-precipitants have distinct advantages over inorganic co-precipitants; for instance they are easily removed by ashing or acid oxidation, and they possess a better and easily controlled selectivity. The method consists of introducing the organic reagent into the solution containing the microcomponent and crystallizing it by appropriate means.

In the present work α-nitroso-β-naphthol was selected as the cobalt reagent because of its insolubility in water compared with its solubility in organic solvents. After the organic reagent has been introduced, the organic solvent is evaporated and the α-nitroso-β-naphthol crystallizes. As the cobalt complex is less soluble than the reagent itself, FAJANS' Rule[8] is satisfied and the microcomponent is enriched in the crystalline phase. The co-crystallization of various trace elements with α-nitroso-β-naphthol has already been studied by WEISS *et al.*[4], who found that cerium, zinc, iron, cobalt, zirconium and uranium at different acidities are carried almost quantitatively at a rapid evaporation rate of the acetone solvent. No separation of a cobalt microcomponent from other micro- or macrocomponents was examined. In the present work, separation from an excess of zinc was of interest; slow evaporation of a small amount of ethanol was used to co-crystallize cobalt with α-nitroso-β-naphthol.

Studying the distribution of the cobalt between the liquid and solid phases, WEISS *et al.*[4] found a large deviation from the logarithmic distribution law, because of the changing solubility when acetone is evaporated. In the present work the author obtained a better agreement with the DOERNER–HOSKINS law, crystallizing the organic reagent by evaporation from a small amount of alcohol. This co-crystallization of cobalt was applied to a carrier-free separation of the cobalt isotopes from an iron target bombarded with deuterons.

EXPERIMENTAL

Reagents and tracers

α-Nitroso-β-naphthol was dissolved in ethanol at a concentration of 0.5%

---

* This work is part of the research sponsored by "Het Interuniversitair Instituut voor Kernwetenschappen".

(w/v). The buffer solution consisted of 10% (w/v) sodium acetate. The following radioactive tracers were used:

^{60}Co: β, γ-emitter, half-life 5.2 y, produced by irradiation of Co in the BR-1 reactor.

^{58}Co: β, γ-emitter, half-life 72 d, produced carrier-free by irradiation of cobalt-free nickel in the BR-1 reactor and separation on Dowex 1-X2 as described by KRAUS *et al.*[9].

^{65}Zn: β, γ-emitter, half-life 245 d, produced by irradiation of Zn in the BR-1 reactor.

^{54}Mn: γ-emitter, half-life 324 d, obtained carrier-free from the Radiochemical Centre, Amersham, England.

^{59}Fe: β, γ-emitter, half-life 45 d, produced by irradiation of Fe in the BR-1 reactor and purified on Dowex 1-X2[9].

The purity of the nuclides was controlled by γ-spectrometry.

Apparatus

Counting techniques: Integral γ-counting using a well-type NaI(Tl) detector.

Spectrophotometer: Beckman D.U. or D.K.-1 spectrophotometer with 1.00-cm Corex cuvettes.

Procedure

To approximately 30 ml of a slightly acidic (pH 1–6) solution, containing cobalt and 2 ml of buffer, add 10 ml of freshly prepared α-nitroso-β-naphthol reagent, and mix thoroughly in a beaker. Heat the solution on a hot water-bath to evaporate the alcohol, and after 1 h, transfer it to an ice-bath and cool for 20 min. Filter the crystallized reagent containing the microcomponent through a fine-porosity sintered glass filter and wash with 15 ml of cold water. Ash the precipitate, or bring it into solution with 10 ml of acetone or ethanol. The cobalt recovery was better than 99%.

Measuring techniques

The extent of the crystallization was measured by spectrophotometry of the organic reagent concentration in the filtrates as well as in the redissolved crystalline phase. α-Nitroso-β-naphthol was determined at 385 mμ, the wavelength of maximum absorption. The extinction of α-nitroso-β-naphthol at concentrations ranging from 2.0 to 30 p.p.m. was measured; it was in good agreement with BEER's law in this concentration range the specific extinction coefficient in 40% acetone was $k = 31.0 \pm 0.3$. The standard deviation of a single measurement was about 2%. To determine the amount of the organic reagent in the crystalline phase, the latter was dissolved in approximately 10 ml of acetone, 10 ml of 2 N hydrochloric acid, 10 ml of water and again 10 ml of acetone and eventually diluted to the mark. The quantity of cobalt carried by the crystals was determined by γ-ray scintillation counting. The count rates of the filtrates and of the dissolved crystals were compared with standard tracer solutions, diluted to the same volume. If very low count rates of the crystalline phase had to be measured, the sintered glass filter with the crystals was placed on top of the NaI(Tl) crystal and compared with standards prepared in the same way. The measurements were continued until at least 3,000 counts were registered.

RESULTS

Crystallization of α-nitroso-β-naphthol

Firstly the relationship between the crystallization of the organic reagent and the evaporation time was studied. At certain intervals after the beginning of the evaporation the samples were cooled, filtered and washed rapidly. Figure 1 demonstrates the crystallization of the organic reagent as a function of time on the hot water-bath; crystallization practically reached a maximum after 2 h. The solubility of α-nitroso-β-naphthol in cold water calculated from this figure was approximately 1.2 · 10^{-3} mol/l, which is in good agreement with the value obtained by WEISS *et al.*[4] (1.38 · 10^{-3} mol/l at 22.5°).

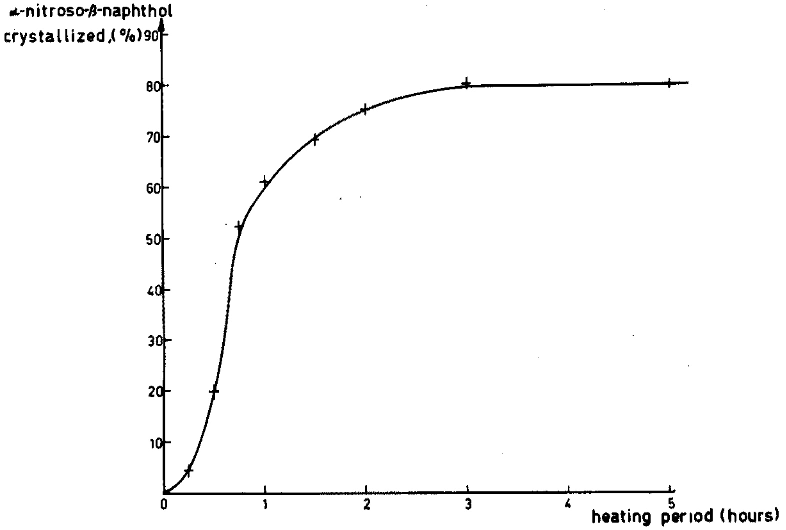


Fig. 1. Crystallization of α-nitroso-β-naphthol as a function of evaporation time.

Co-crystallization of cobalt

To a number of buffered samples of different acidities, 1 ml of ^{60}Co tracer containing 2.2 μg of cobalt carrier, and 5 ml of organic reagent solution were added; the heating period was 1 h. The results (Table I) show that cobalt was almost quantitatively co-crystallized from buffered solutions (pH 1–6).

The influence of the organic carrier concentration on co-crystallization of carrier-free ^{58}Co was also examined. The amount of organic reagent added was varied from 5 to 50 mg. The optimum results (Table I) were obtained with 10 ml of 0.5% α-nitroso-β-naphthol in alcohol.

In a check on the recovery of different amounts of cobalt varying from 4.4 μg to carrier-free ^{58}Co, 10 ml of 0.5% organic reagent solution were added. The recoveries (Table I) were found to be better than 99%, even at the most dilute concentrations.

TABLE I

CO-CRYSTALLIZATION OF COBALT WITH α-NITROSO-β-NAPHTHOL

Acidity (pH)	*Amounts added*			*Heating period (min)*	*Crystallized (%)*	
	Buffer (ml)	*Cobalt carrier (μg)*	*α-Nitroso-β-naphthol*		*α-Nitroso-β-naphthol*	*Cobalt*
2 *N* HCl	—	2.2	5 ml 0.5%	60	81.5	3·0
0.5 *N* HCl	—	2.2	5 ml 0.5%	60	68	97·4
1	2	2.2	5 ml 0.5%	60	65	99·6
2	2	2.2	5 ml 0.5%	60	56	99·8
4	2	2.2	5 ml 0.5%	60	52·5	99·85
6	2	2.2	5 ml 0.5%	60	53·5	99·9
3	2	Carrier-free	10 ml 0.5%	75	79·5	99·5
3	2	Carrier-free	10 ml 0.25%	75	34·5	79·3
3	2	Carrier-free	10 ml 0.1%	75	7	17·3
3	2	Carrier-free	5 ml 0.1%	120	15·5	5·2
3	2	4·4	10 ml 0.5%	60	70	99·95
3	2	2.2	10 ml 0.5%	60	75	100
3	2	1.1	10 ml 0.5%	60	72	99·85
3	2	0.44	10 ml 0.5%	60	70	99·65
3	2	0.22	10 ml 0.5%	60	74	99·1
3	2	Carrier-free	10 ml 0.5%	60	74	99·4
3	2	Carrier-free	10 ml 0.5%	60	75·5	99·4

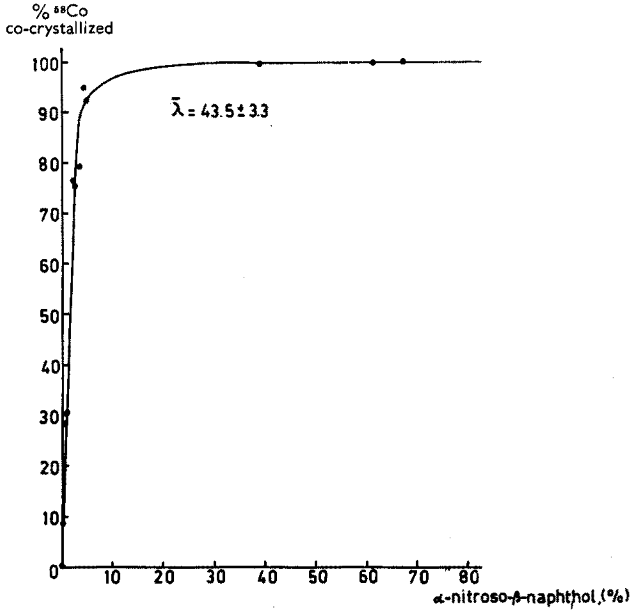


Fig. 2. Distribution of ^{58}Co on α-nitroso-β-naphthol.

Determination of the distribution coefficient

The distribution of carrier-free ^{58}Co between the aqueous and solid phases after crystallization of different quantities of the organic reagent is shown in Fig. 2. The amount of alcohol evaporated was varied between samples to provide for the crystallization of different quantities of α-nitroso-β-naphthol. The values of the distribution coefficients K, D and λ were calculated according to eqns. (1), (2) and (3), where x and y represent the respective amounts of co-precipitant and carrier separated, and a and b the initial concentrations.

Proportional distribution law[10] $$\frac{x}{y} = K\frac{a}{b} \qquad (1)$$

Homogeneous distribution law[11] $$\frac{x}{a-x} = D\frac{y}{b-y} \qquad (2)$$

Logarithmic distribution law[12] $$\ln\frac{a}{a-x} = \lambda \ln\frac{b}{b-y} \qquad (3)$$

TABLE II

DISTRIBUTION OF COBALT ON α-NITROSO-β-NAPHTHOL

Crystallized (%)		*Distribution coefficients*		
α-Nitroso-β-naphthol	*^{58}Co*	*K*	*D*	*λ*
0.25	8.5	34	37	34.5
0.80	28.3	35.5	49	41
1.2	30.5	25.5	36	30.5
2.8	76.5	27.5	114	51
3.0	75.5	25	99.5	46
4.0	79.3	20	92	38.5
4.85	94.9	19.5	365	58.5
5.15	92.1	18	215	48

As could be expected, because diffusion of ions within the crystal and recrystallization are almost negligible[13], it appears from Table II and Fig. 3 that DOERNER AND HOSKINS' logarithmic distribution law was followed. The values obtained for the logarithmic distribution coefficient (λ) were nearly constant, the mean value being 43.5 ± 3.3. The values calculated by WEISS *et al.*[4] for λ increased considerably as the concentration of acetone was reduced, because of the important change in the solubility of the organic reagent. In the present experiments the change in solubility was much lower. It can be seen from Fig. 3 that the values for λ showed only a negligible increase as a function of the degree of crystallization.

Interference of an excess of zinc

With a view to the separation of micro quantities of cobalt from a zinc matrix, the interference of zinc was studied. To a solution containing 0.4 μg of cobalt were added ^{65}Zn tracer and different amounts of inactive zinc carrier. The amount of zinc added and percent zinc contamination are given in Table III; even in presence of a large

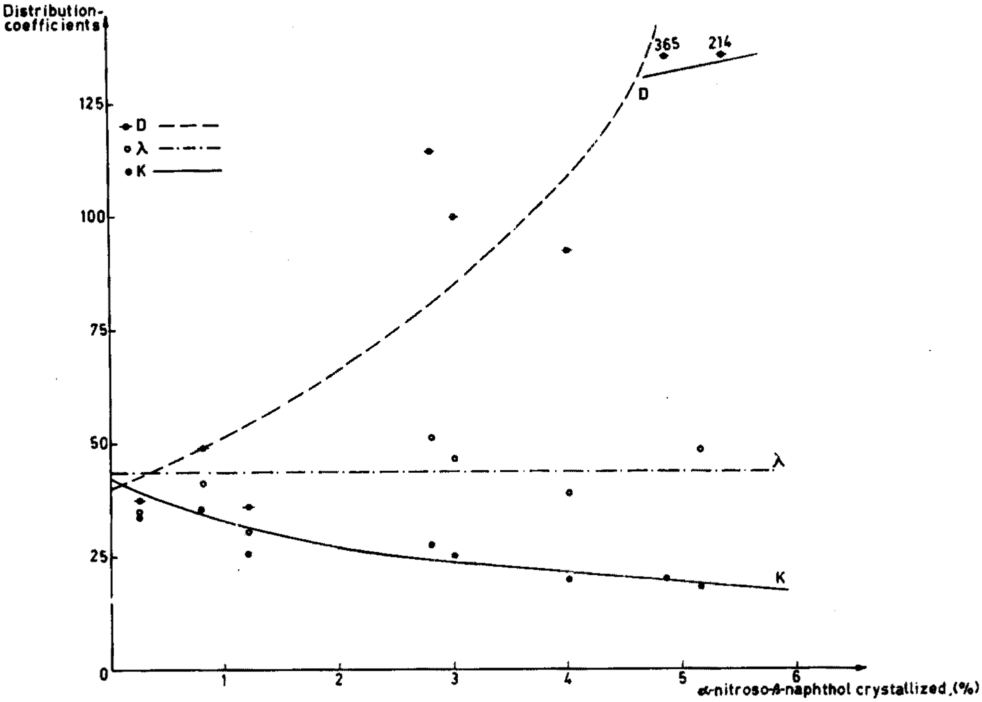


Fig. 3. Distribution coefficients.

TABLE III

CONTAMINATION BY ZINC WITH α-NITROSO-β-NAPHTHOL AND MICRO QUANTITIES OF COBALT

Zinc added (mg)	*Zinc contamination (%)*[a]	*Zinc in the crystalline phase (μg)*[a]
0.362	0.25	0.9
0.725	0.18	1.3
1.45	0.11	1.6
2.9	0.08	2.3
5.8	0.06	3.5
11.6	0.025	2.9
14.6	0.02	2.9
20.3	0.015	3.2
29.0	0.01	2.9
43.5	0.01	4.3
64.5	0.005	3.2
79.0	0.003	2.1
129.0	0.004	5.2
174.5	0.0028	4.9
229.0	0.002	4.6

[a] Mean values of 2 determinations.

excess of zinc the crystalline phase was only very slightly contaminated with zinc. When more than 50 mg of zinc were present, contamination was less than 0.01%.

SEPARATION OF CARRIER-FREE COBALT ISOTOPES FROM A DEUTERON-BOMBARDED IRON TARGET

Carrier-free cobalt can, for instance, be produced by deuteron bombardment of an iron target, giving rise through (d, n) and (d, 2n) reactions to ^{55}Co, ^{56}Co, ^{57}Co and ^{58}Co. Simultaneously a number of iron and manganese isotopes are produced through (d, p), (d, α) and (d, αn) reactions.

From data in the literature[14–18] it appears that the cobalt activity, produced by a bombardment with 18-MeV deuterons and after a waiting period of about 20 days, is at least twice as important as the manganese activity and 400 times more important than the iron activity. A carrier-free separation of the cobalt isotopes from an iron target has been described by MAXWELL *et al.*[18], but this method is tedious; it requires a double extraction of the bulk of iron, followed by a precipitation of iron with ammonia. Manganese is co-precipitated whilst the most important fraction of cobalt remains in solution.

The simplicity of the co-crystallization technique described above seemed to make it a useful and more rapid procedure for this separation. A double co-crystallization technique of the cobalt isotopes in the presence of a large excess of iron carrier was studied. The interference of iron and carrier-free manganese was examined.

Procedure

After bombardment, dissolve the exposed surface of the iron target in 6 *N* hydrochloric acid. Dilute the solution so as to contain *ca.* 15–20 mg Fe/ml. Add 5 ml of phosphoric acid (d = 1.7) to 20 ml of solution and oxidise carefully with 7 ml of 30% hydrogen peroxide. Boil until the peroxide has decomposed. Add 2.5 g of oxalic acid dihydrate and 2 ml of buffer, and adjust with ammonia solution to pH 1. Add 12 ml of the organic reagent solution, place the beaker on a hot water-bath for 1 h, and cool during 20 min. Separate the crystalline phase from the mother liquor. If required, reprecipitate by dissolving the crystals in 12 ml of alcohol, 5 ml of 1 *N* hydrochloric acid and 10 ml of water, add 0.5 g of oxalic acid dihydrate, 1 ml of phosphoric acid (d = 1.7) and 2 ml of buffer and adjust with ammonia solution to pH 1; only 5 ml of 1% organic reagent solution are required. A heating period of 2 h is necessary for this second crystallization. After cooling, filter, dissolve the precipitate quantitatively in 15 ml of hot 14 *N* nitric acid and evaporate. Take the residue to dryness twice with 5 ml of 12 *N* hydrochloric acid and dissolve in 10 ml of 6 *N* hydrochloric acid. If the organic precipitate is ashed at 500° for 45 min only 95% of the cobalt activity is dissolvable in 10 ml of 12 *N* hydrochloric acid.

The second crystallization must be carried out in a new beaker because the carrier-free cobalt and manganese activities tend to adhere to the beaker walls.

RESULTS

In the presence of 230 mg of inactive iron carrier the co-crystallization of 1 ml of carrier-free ^{58}Co was carried out as described above. Double crystallizations as well as single ones were performed. As can be seen from Table IV the filtrates showed only a low ^{58}Co activity.

TABLE IV

CO-CRYSTALLIZATION OF ^{58}Co IN PRESENCE OF AN EXCESS OF IRON

1st Crystallization		*2nd Crystallization*		*^{58}Co recovered (%)*
Time on bath (h)	*^{58}Co in filtrate (%)*	*Time on bath (h)*	*^{58}Co in filtrate (%)*	
1	1.4			98
1	1.3			99
1	1.5			98
1.25	1.1			99
1.5	3.3			96.5
1	6.2	1.75	1.0	92
1	0.9	2	1.1	98
1	1.5	2	0.95	96.5
1	1.5	2.25	0.1	98.5

TABLE V

CONTAMINATION BY ^{54}Mn

1st Crystallization		*2nd Crystallization*	
Mn carrier added (mg)	*^{54}Mn in crystalline phase (%)*	*Mn carrier added (mg)*	*^{54}Mn in crystalline phase (%)*
275	0.21		
55	0.23		
No	0.13		
No	0.10		
No	0.18		
55	0.18	No	0.18
No	0.10	No	0.11
No	0.19	No	0.20
No	0.28	55	0.20

TABLE VI

CONTAMINATION BY ^{59}Fe

1st Crystallization		*2nd Crystallization*		*Fe in crystalline phase (mg)*
Fe carrier present (mg)	*^{59}Fe in crystalline phase (%)*	*Fe carrier added (mg)*	*^{59}Fe in crystalline phase (%)*	
603	0.043			0.26
481	0.049			0.23
355.5	0.017			0.06
336	0.015			0.05
240.5	0.021			0.05
240.5	0.016			0.04
221	0.012			0.025
125.5	0.039			0.05
240.5	0.019	No	0.019	0.05
220	0.027	No	0.031	0.065
230	0.026	105	0.028	<0.09

To a series of samples, containing 230 mg of iron carrier, 0.4 μg of cobalt carrier and 1 ml of carrier-free ^{54}Mn were added, together with different amounts of manganese carrier. Single and double separations of cobalt were performed. To determine the degree of contamination by an excess of iron, ^{59}Fe tracer containing different amounts of iron carrier was added to a set of samples. The activities of the crystals were compared with the activities of standards. The amounts of carrier added and the contamination by both elements, for single and double crystallizations are given in Tables V and VI. It appears that the major manganese and iron activities remained in solution. To separate cobalt from carrier-free ^{54}Mn, addition of manganese carrier was not required. The amount of iron carrier added was limited, because only about 400 mg could be masked by 2.5 g of oxalic acid. A second crystallization did not improve decontamination.

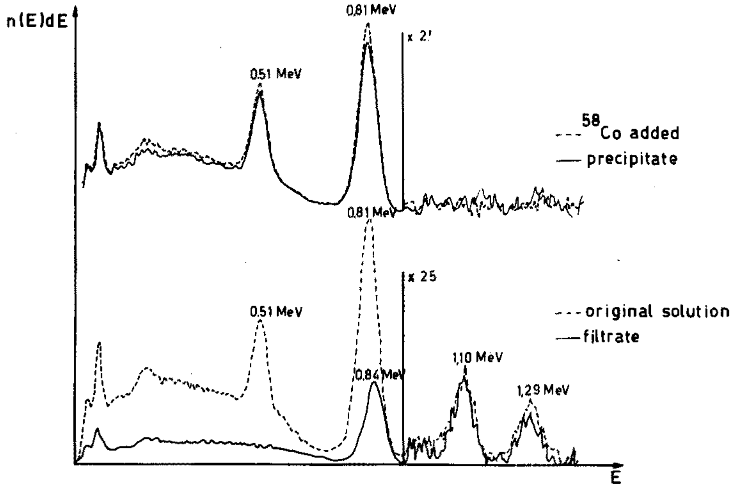


Fig. 4. γ-Spectra of ^{58}Co, ^{54}Mn, and ^{59}Fe before and after separation.

Figure 4 shows the γ-spectrum of a solution containing ^{58}Co ($1 \cdot 10^6$ counts/min), ^{54}Mn ($0.5 \cdot 10^6$ counts/min) and ^{59}Fe ($2 \cdot 10^4$ counts/min) before the separation and the γ-spectra of the filtrate and of the dissolved crystals after the crystallization. No contamination is perceptible in the spectrum of the separated ^{58}Co.

CONCLUSIONS

The co-crystallization technique with α-nitroso-β-naphthol permits an almost quantitative recovery of tracer quantities of cobalt within less than 2 h. Contamination by zinc is very slight. From determinations of the distribution coefficient it appears that reasonable agreement is obtained with the DOERNER–HOSKINS law.

The separation of cobalt isotopes from an iron target by this co-crystallization technique offers certain advantages over the method described by MAXWELL *et al.*[18]

as the separation is simple and rapid; it requires only one crystallization. Further, the crystals are easily collected, the organic matter can be removed by acid oxidation and the residue can be dissolved in a small volume of hydrochloric acid.

After dissolution of 300 mg of a bombarded iron target, one crystallization results in a recovery of about 98% carrier-free cobalt, contaminated with less than 0.06 mg of iron carrier. The radioactive contamination of ^{59}Fe is negligible and the ratio of the manganese activity to the cobalt activity is reduced to 0.001. The solution contains only a very small amount of extraneous salt.

The author wishes to express his grateful thanks to Prof. Dr. J. HOSTE for his continuous interest and useful criticisms. The author is also highly indebted to Mrs. J. GORLÉE-ZELS for technical assistance.

SUMMARY

The co-crystallization of ultramicro quantities of cobalt with α-nitroso-β-naphthol, was investigated by radio-tracer techniques. More than 99% cobalt, even when carrier-free, could be recovered. The distribution was studied and appeared to follow the logarithmic distribution law. The interference of a large excess of zinc was almost negligible. The method was applied to the carrier-free separation of cobalt isotopes (^{55}Co, ^{56}Co, ^{57}Co, ^{58}Co) produced by deuteron bombardment of an iron target. Contamination by manganese (^{54}Mn, ^{52}Mn) and iron (^{59}Fe) was, even in the absence of manganese carrier, almost negligible.

RÉSUMÉ

L'auteur a examiné, à l'aide de techniques avec radio-traceurs, la cocristallisation du cobalt (en ultramicroquantités) avec l'α-nitroso-β-naphtol. L'influence d'un gros excès de zinc est presque négligeable. Ce procédé a été appliqué à la séparation des isotopes du cobalt (^{55}Co, ^{56}Co, ^{57}Co, ^{58}Co), produits par le bombardement avec deutérons, d'une cible de fer.

ZUSAMMENFASSUNG

Die Mitfällung von Ultramikromengen Kobalt durch Auskristallisieren von α-Nitroso-β-naphtol wurde mit der Tracer-Technik untersucht. Mehr als 99% Kobalt, auch wenn sie trägerfrei sind, können zurückgewonnen werden. Die Verteilung wurde untersucht und scheint dem logarithmischen Verteilungsgesetz zu folgen. Störungen durch einen grossen Überschuss Zink sind meist vernachlässigbar. Die Methode wurde zur trägerfreien Trennung der Kobaltisotopen (^{55}Co, ^{56}Co, ^{57}Co, ^{58}Co) angewandt, die durch Deutronenbeschuss eines Eisen-Targets enzeugt waren. Verunreinigungen durch Mangan (^{54}Mn, ^{52}Mn) und Eisen (^{59}Fe) waren sogar in Abwesenheit eines Manganträgers meist vernachlässigbar.

REFERENCES

1 H. V. WEISS AND M. G. LAI, *Anal. Chem.*, 32 (1960) 475; 33 (1961) 39; 34 (1962) 1012.
2 H. V. WEISS AND M. G. LAI, *Talanta*, 8 (1961) 72.
3 H. V. WEISS AND M. G. LAI, *Anal. Chim. Acta*, 28 (1963) 242.

4 H. V. WEISS, M. G. LAI AND A. GILLESPIE, *Anal. Chim. Acta*, 25 (1961) 550.
5 H. V. WEISS AND W. H. SHIPMAN, *Anal. Chem.*, 33 (1961) 37; 34 (1962) 1010.
6 W. P. TAPPMEYER AND E. E. PICKETT, *Anal. Chem.*, 34 (1962) 1709.
7 K. SUDHALATHA, *Talanta*, 10 (1963) 934.
8 K. FAJANS AND P. BERR, *Ber. Deut. Chem. Ges.*, 46 (1913) 3486.
9 K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON AND J. S. JOHNSON, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy*, P 1832, Geneva, 23 (1958) 3.
10 N. RIEHL, *Z. Physik. Chem.*, A 177 (1936) 224.
11 L. M. HENDERSON AND F. C. KRACEK, *J. Am. Chem. Soc.*, 49 (1927) 738.
12 H. A. DOERNER AND M. HOSKINS, *J. Am. Chem. Soc.*, 47 (1925) 662.
13 A. C. WAHL AND N. A. BONNER, *Radioactivity Applied to Chemistry*, Wiley, New York, 1951.
14 W. M. GARRISON AND J. G. HAMILTON, *Chem. Rev.*, 49 (1951) 237.
15 A. F. REID AND A. S. NEIL, *U. S. Atomic Energy Commission Declassified Report*, AECD 2324.
16 J. W. IRVINE, JR., *Nucleonics*, 32 (1948) 5.
17 J. J. LIVINGOOD AND G. T. SEABORG, *Phys. Rev.*, 54 (1938) 391.
18 R. D. MAXWELL, J. D. GILL, W. M. GARRISON AND J. G. HAMILTON, *J. Chem. Phys.*, 17 (1949) 1340.

MANOMETRIC SUBMICRO DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC MATERIALS

P. GOUVERNEUR AND H. C. E. VAN LEUVEN
Koninklijke/Shell-Laboratorium, Amsterdam (The Netherlands)
R. BELCHER AND A. M. G. MACDONALD
Chemistry Department, University of Birmingham, Birmingham (Great Britain)

(Received March 1st, 1965)

Quite early in the development of the organic submicro technique, the determination of carbon and hydrogen was studied. Obviously, the conventional gravimetric micro-method could never be scaled down for 50-μg samples and many other possibilities were therefore examined.

Titrimetric procedures based on precipitation of barium carbonate were first tested for the determination of carbon dioxide formed by a combustion process; results were low and variable because of difficulties in absorbing the final few micrograms of carbon dioxide in a reasonable volume of absorbent, because of adsorption of barium hydroxide on to the carbonate precipitate and because of adsorption of acidic cleaning solutions on to the absorber surfaces, the final traces of acid being extremely difficult to remove[1]. The replacement of barium by strontium hydroxide was unsuccessful because of coprecipitation of the hydroxide with the carbonate; precipitation of lead carbonate and compleximetric titration of the excess lead or of the precipitate itself failed because of considerable adsorption of lead ions on all the filter materials tested[1]. Modifications of BLOM's method in which carbon dioxide is titrated with sodium methylate in non-aqueous medium[2] were unsatisfactory owing to indistinct end-points on the microgram scale[1]. Submicro modifications of the Karl Fischer titration for water also did not provide sufficiently clear end-points. Reaction of water with magnesium nitride to give titratable ammonia was unsatisfactory because of high blank values[1].

Because of the chemical and technical difficulties of straightforward combustion–titration methods for carbon and hydrogen, attention was given to various fusion procedures in which carbon was converted to cyanide rather than to carbon dioxide. Such procedures were much simpler in construction of apparatus and technique than the combustion processes, but the difficulties created by interfering side-reactions and by impurities in the various reagents proved to be insuperable[1].

None of these chemical methods showed any promise and recourse was therefore had to physical measurements. A manometric method for the determination of carbon was developed[3] and found quite satisfactory. However, a straightforward adaptation of this procedure for a simultaneous determination of hydrogen, by freezing out water and carbon dioxide separately and measuring their vapour pressure, failed because of adsorption of water on to the glass walls of the apparatus. Results for the water determination were repeatedly very low for the first 2–3 determinations; during the next determination, the accumulated water was desorbed to give a very high value.

It was then decided to examine various possibilities for the conversion of water to some gas which would be easy to measure manometrically or otherwise. Although none of these trials was successful, they are outlined here, for the information obtained may be useful to other workers. In view of the recurrent difficulties over blank values, it may be as well to stress initially that the amount of water formed from a 50-μg sample containing 5–10% of hydrogen is 22.5–45 μg which corresponds to a quarter or half the permissible variation in a normal micro-determination.

The obvious reagents to test first were the hydrides, which would react with water to form hydrogen. Lithium aluminium hydride, sodium borohydride and calcium hydride appeared to be the most promising[4]. However, lithium aluminium hydride proved very unstable under vacuum; high and variable blanks were obtained even after prolonged evacuation to remove impurities. When organic samples were burned, it was shown that there was no reaction of carbon dioxide or water with the hydride at −102° (ethanol–nitrogen bath); but the reaction of water with the hydride was far from quantitative at room temperature[1]. The instability of sodium borohydride under vacuum made any further investigation impossible[1]. Extensive tests[5,6] were made with calcium hydride which was much more stable under vacuum than lithium aluminium hydride; there was no apparent reaction with carbon dioxide, water or oxygen at −102° and no apparent reaction with carbon dioxide or oxygen at room temperature. The reaction of water with calcium hydride at room temperature appeared to be reasonably proportional though not complete for organic or inorganic samples containing about 3–6 μg of hydrogen provided that the hydride was fresh, but subsequent determinations were low and blank determinations were high; prolonged evacuation was needed to restore the initial blank values[6]. Probably, some water was retained on the calcium hydroxide formed by the reaction:

$$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$$

and desorbed only with difficulty. These tests were made by collecting the water in a trap containing the hydride at −102° and then bringing the trap to room temperature to allow the reaction to proceed. With this technique there was a distinct possibility of water being lost by adsorption on to glass between the combustion system and the trap. Further tests[6] were made in which the water was retained on a cooled layer of desiccant placed in the combustion tube itself; after the removal of excess of oxygen and the carbon dioxide formed from the sample, the water was heated into a layer of calcium hydride also placed in the combustion tube. This technique caused greater difficulties with blank values because the calcium hydride could not be readily protected from the various heaters on the other parts of the combustion tube; however, the behaviour found with the hydride in a separate trap was confirmed in all essentials, *i.e.* there was no apparent reaction with oxygen or carbon dioxide, but a considerable retention of water after one reasonably satisfactory determination. Possibly a method could have been developed in which fresh reagent was added for each determination, but this could never have formed a satisfactory basis for a routine process because of the long period needed to restore the vacuum after the system had been opened to the atmosphere.

The blank values with these hydrides were at best rather high (corresponding to about 25% of the expected hydrogen pressure from a sample) and attention was therefore diverted to the possibilities of metallic reductants.

The first metal tested was magnesium[1,7]. This was examined by collecting the water on to magnesium in a trap at −102°. After oxygen and carbon dioxide had been pumped off, the trap was heated at 80° and hydrogen was measured. Blank values were low and some good results for conversion of water to hydrogen were obtained, but the behaviour of magnesium was unpredictable from batch to batch, with occasional zero reduction of water. Many modifications were tested; it was eventually concluded that the magnesium became deactivated after a few determinations although there was no change in the physical appearance of the metallic layers.

Sodium metal was tested in a similar way. There was no reduction of the water at −102°; at room temperature or 80° the amounts of hydrogen formed bore little relationship to the amounts of water present[5]. Potassium initially gave more promising results[6,7]; there was no apparent reaction with oxygen or carbon dioxide at −102°, and blank values were reasonable (about 5–10% of the expected hydrogen value) after any surface film formed during the introduction of the metal into the trap had been removed by prolonged evacuation. Further, the amounts of hydrogen formed at 80° appeared to bear some relationship to the amounts of water introduced. However, after several runs a yellowish surface layer (K_2O_3?) appeared and the potassium was deactivated; the reduction to hydrogen did not proceed reproducibly with different batches of potassium. Many puzzling results were obtained; the complexity of the possible reactions is indicated by some work of TRAPNELL[8] who states that oxygen is adsorbed on to clean potassium under vacuum at −102 to 0° and that this oxygenated surface takes up hydrogen slowly at room temperature. However, when oxygen was removed on copper from the gas stream before the trap for water, blank values became very unpredictable.

In general, the reactions with these metals proceeded in an unpredictable fashion and few really coherent results were obtained. Although the blank values were rather better than those produced with metal hydrides, the reactions occurring on the metallic surfaces were obviously more complex and unreproducible.

Based on a qualitative test for hydrogen described by FEIGL AND JUNGREIS[9], attempts were made to pyrolyse the sample with sulphur to form hydrogen sulphide[10]. Although a variety of reaction conditions was tried, conversion was invariably incomplete, the maximum being 60% conversion for sucrose.

MALISSA[11] has utilized the reaction of water with N,N′-carbonyl-diimidazole[12] to form carbon dioxide, in an electrical conductivity method for the determination of organically bound hydrogen. The material proved to be quite stable under vacuum and there was little or no reaction[6] of the compound with oxygen at −102°. However, after reaction with water to form carbon dioxide and imidazole itself, extremely high blank values were obtained. These were caused by the volatility of imidazole under vacuum; a film of the compound spread throughout the vacuum line and attempts to trap it in one position at −30° failed[6].

Some tests were made with calcium carbide, but very high blank values corresponding to about 20 µg of hydrogen were obtained from oxygen or nitrogen streams[6]. At the time when this work was done, the carbide available was not of very high purity, which may account for some of the trouble.

The final tests in this series involved conversion of water to carbon dioxide by reaction with platinized carbon[13,14] and copper oxide at 900°. The water was absorbed on a cooled desiccant and after other reactants had been swept from the tube, the water was heated into the platinized carbon layer, the carbon monoxide formed then being oxidized to the dioxide with copper oxide. It was shown[6] that oxygen did not react with the platinized carbon at room temperature, but was tenaciously adsorbed and then reacted when the carbon was heated to the working temperature. When nitrogen was used as the sweeping gas with the carbon at 900°, some product was formed which made it impossible to obtain a vacuum holding for longer than 15 min after the carbon–copper oxide system had been cut off from the vacuum line. This phenomenon did not occur with the carbon and copper oxide at room temperature and the loss of vacuum was not caused by any gas condensable in liquid oxygen. The size of the vacuum loss corresponded to about 15 μg of hydrogen or 165 μg of carbon dioxide, which is oddly similar to the normal blank value on an oxygen determination on the microscale.* The precise cause of the trouble could not be discerned, but all the evidence tended to show that there was a reaction between carbon and nitrogen leading to some volatile product which could not readily be pumped from the vacuum line.

All these tests indicated that there was no relatively straightforward method of converting water to a readily measurable gas. It became apparent that for manometric purposes the only solution was to take the utmost precautions to prevent adsorption of water on (glass) surfaces. The further work along these lines was based on previous experience with a manometric method for carbon and hydrogen determination which allowed of very high precision with milligram samples[15]. In this previous work, soda glass components had been used where possible and the measuring system kept at 50° to reduce water adsorption. Furthermore, teflon membrane valves had been used instead of glass stopcocks to eliminate any possible effect of grease. In the present submicro study similar measures were found to be adequate and, although on this small scale the relative importance of the adsorption effect did become greater, a satisfactory precision for both carbon and hydrogen was attained.

PRINCIPLE OF THE METHOD

The sample was decomposed in a stream of oxygen and burned catalytically. Water and carbon dioxide thus formed were separately trapped by freezing at $-80°$ and $-196°$, and the excess oxygen was removed by pumping. After thawing and expanding the trapped gases into fixed volumes, their pressures were measured using the piston-type buret system and photoelectric level indicator previously described[15].

The present submicro version proved to be suitable for sample sizes of 5–50 μg and provisions were made to eliminate interference from oxides of nitrogen. The necessary modifications of the previously described milligram method concerned the reduction of the expansion volumes, the use of a modified combustion arrangement and the introduction of an absorption train for nitrogen oxides. Two separate mano-

---

* Dr. G. TÄLG from the Johannes Gutenberg University, Mainz, Germany, has recently been successful in developing a method for quantitatively measuring microgram amounts of organic hydrogen by combustion to water and conversion to hydrogen sulphide by reaction with carbon disulphide (private communication).

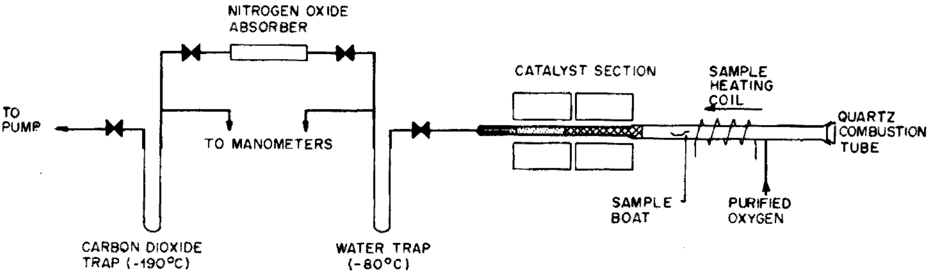


Fig. 1. Diagram of apparatus.

meter systems were used, one for water and one for carbon dioxide measurement. This was found more convenient than the use of only one manometer which — because of the presence of the nitrogen oxides absorber — would require a much more complicated valve system. A calibration graph was used to convert manometer readings into masses of carbon and hydrogen.

Figure 1 is a diagram of the apparatus.

EXPERIMENTAL

The apparatus consisted of a combustion system and a freezing and measuring system (Figs. 2 and 3); details of the measuring system are given in Fig. 4.

An Oertling model Q01 quartz-fibre torsion balance was used for all sample weighings.

The sample was decomposed in a narrow quartz combustion tube with the aid of a travelling heating coil. Together with a stream of oxygen, the resulting gases were contacted with platinum at 1100° for complete oxidation and next led through the decomposition product of silver permanganate (KÖRBL's catalyst)[16], at 500° to

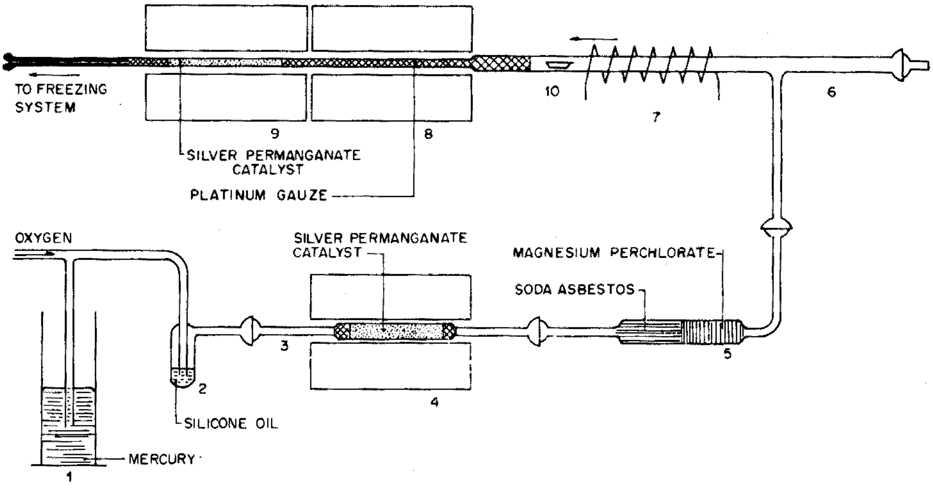


Fig. 2. Combustion system. (1) Blow-off flask; (2) bubble counter; (3) precombustion tube; (4) and (9) electric furnaces, 500°; (5) absorber; (6) quartz combustion tube; (7) travelling sample heating coil; (8) electric furnace, 1100°; (10) sample boat.

remove sulphur and the halogens. Water vapour, carbon dioxide and the excess oxygen were allowed to enter the evacuated freezing system through the capillary outlet of the combustion tube at a rate of *ca.* 10 ml (NTP) per min.

The water was collected by freezing at -80° (dry ice/ethanol mixture) and the carbon dioxide was trapped at -196° (liquid nitrogen). Between the traps an absorber was placed containing chromic/sulphuric acid on Sil-O-Cel (as described by Kirsten[17]) to oxidize any nitric oxide, and manganese dioxide to retain nitrogen dioxide. The freezing system was controlled by 4 teflon membrane valves.

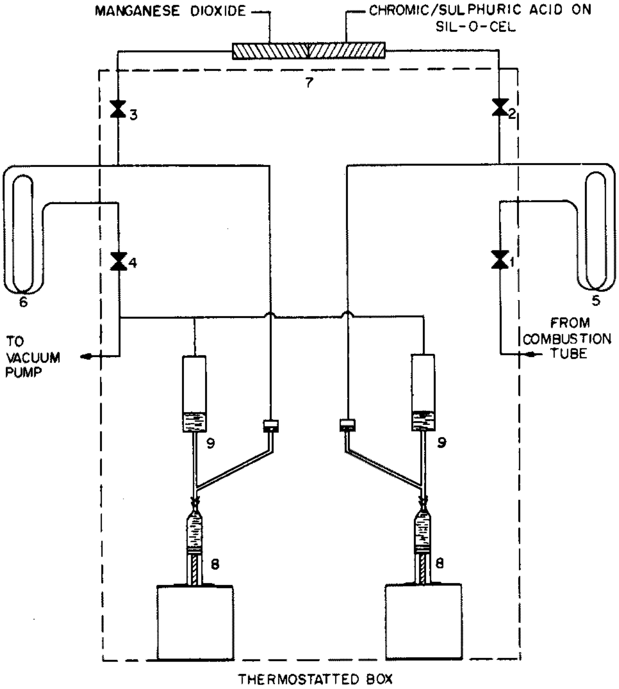


Fig. 3. Freezing and measuring system. (1)–(4) Teflon membrane valves; (5) water freezing trap; (6) carbon dioxide freezing trap; (7) nitrogen oxide absorber; (8) piston burets; (9) manometer tubes.

The measuring system and part of the freezing system were contained in a box in which the temperature was maintained at $50 \pm 0.1^\circ$. Each of the manometers consisted of a mercury-filled U-tube mounted on a piston buret (see Fig. 4). This type of manometer was operated as follows[15]: after the gas or vapour to be measured had been allowed to expand, the mercury level in the measuring leg was restored to its original position by adding mercury from the buret. The pressure rise was represented by the level rise in the reference leg. The latter being purely cylindrical, the pressure rise was proportional to the volume of mercury added, which could be read from the buret. A simple photoelectric device served as an indicator for the level adjustment in the measuring leg. In this way pressures could be measured to the nearest 0.02 mm Hg. A special feature of the manometer was that its own volume (dead space) was small and constant over the whole pressure range without capillary legs being required.

The total volumes into which the carbon dioxide and the water vapour expanded were 4 and 8 ml respectively. These volumes were those of the freezing traps and the manometers; no extra bulbs were used. Each microgram of carbon then corresponded to 0.4 mm Hg or 20 scale divisions on the piston buret and each microgram of hydrogen to 1 mm Hg or 50 scale divisions. Thus, carbon could be measured to the nearest 0.05 µg, and hydrogen to the nearest 0.02 µg.

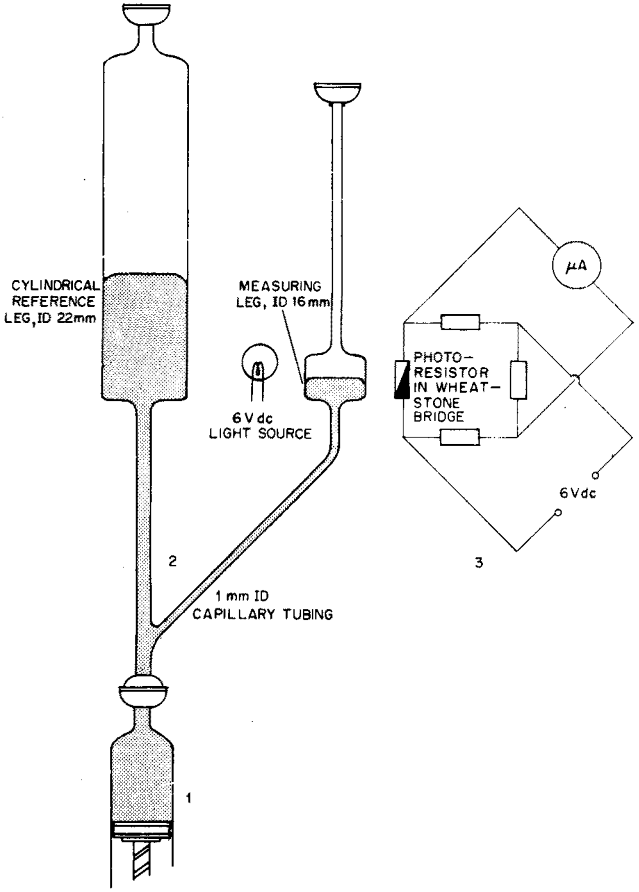


Fig. 4. Details of measuring system. (1) Piston buret; (2) manometer tube; (3) level indicator.

The normal stand-by position of the apparatus was with the freezing and measuring system evacuated (valve 1, Fig. 3, closed, and 2, 3 and 4 opened). Before combustion of a sample, valve 1 was opened, allowing oxygen to flow through the system. With the cooling media in position, the sample (weighed to the nearest 0.01 µg in a small platinum boat) was introduced in the combustion tube (Fig. 2) and the travelling sample heater switched on. Usually the combustion was complete and all water and carbon dioxide were trapped after 10 min. The excess of oxygen was then pumped off by closing valve 1. After 2 min the other valves (2, 3 and 4) were also closed, the manometers adjusted and their zero positions read. The water trap was then electrically heated to a fixed temperature (about 75°) and the carbon dioxide trap was brought to −80° using the dry ice/ethanol mixture from the water trap. After about 3 min the manometers could be readjusted and read again.

For calculations, a calibration graph was required relating manometer read-

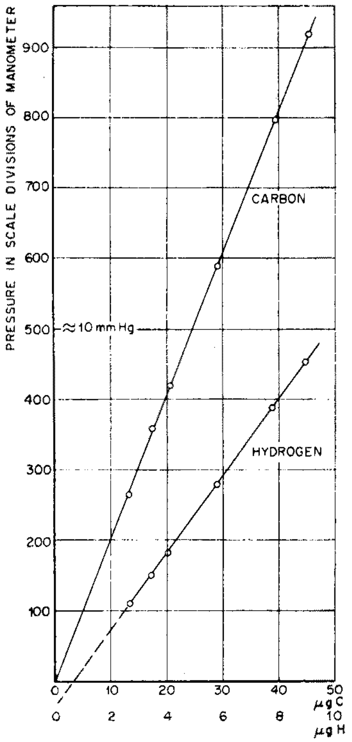


Fig. 5. Calibration of apparatus on mannitol test samples.

TABLE I

RESULTS OF MULTIPLE ANALYSES OF STANDARD COMPOUNDS

Compound	*Sample weight (µg)*	*% Carbon*		*% Hydrogen*	
		Theory	*Found*	*Theory*	*Found*
n-Hexadecane	42.63	84.86	85.02	15.14	15.08
	43.96		84.99		15.06
	41.72		84.94		15.22
	56.51		84.88		15.13
	52.19		84.60		15.24
		Mean	84.89	Mean	15.15
Benzoic acid	69.99	68.84	68.83	4.95	4.84
	67.01		68.61		5.16
	64.41		68.75		4.90
	50.16		68.52		5.08
	67.43		68.79		5.07
		Mean	68.70	Mean	5.01

ings to masses of carbon and hydrogen. Figure 5 shows such a graph based on the combustion of various amounts of mannitol.

RESULTS

Table I shows the results of multiple analyses of *n*-hexadecane and benzoic acid; a standard deviation of 0.13% carbon and 0.10% hydrogen was calculated. These values were confirmed for compounds which apart from carbon, hydrogen and oxygen also contained other elements (Table II). Table III illustrates the application to research samples of which such minute quantities were available that analysis would have been impossible without the present technique.

TABLE II

RESULTS OF DUPLICATE ANALYSES ON PURE COMPOUNDS CONTAINING OTHER ELEMENTS BESIDES C, H AND O

Compound	*% Carbon*		*% Hydrogen*	
	Theory	*Found*	*Theory*	*Found*
Iodobenzoic acid	33.90	33.55	2.03	2.03
		33.90		2.03
Sulfonal	36.82	36.66	7.06	7.20
		36.79		7.23
Nitroaniline	52.17	52.59	4.38	4.55
		52.62		4.63
Dinitrobenzene	42.86	42.52	2.40	2.34
		42.37		2.45
Melamine	28.57	28.94	4.80	5.20
		28.48		4.95
S-Benzylthiuronium chloride	47.40	47.23	5.47	5.16
		47.54		5.63

TABLE III

RESULTS FROM DUPLICATE ANALYSES ON RESEARCH SAMPLES

Sample type	*% Carbon*	*% Hydrogen*
Diels-Alder Product A	32.13	1.57
	32.28	1.47
Diels-Alder Product B	35.53	2.01
	35.94	2.15
Diels-Alder Product C	33.48	1.63
	33.54	1.54
Chlorinated Hydrocarbon A	54.13	5.76
	53.86	5.50
Chlorinated Hydrocarbon B	47.02	2.54
	47.54	2.54
Fuel Stability Test Deposit	65.08	5.99
	65.31	6.46
Radiolysis Product A	40.90	5.83
	40.87	5.91
Radiolysis Product B	41.82	6.25
	42.04	6.28
Radiolysis Product C	43.13	6.71
	43.00	6.72
Carbonaceous Deposit	32.00	2.66
	32.51	2.62

DISCUSSION

Adsorption of water vapour

As indicated before, the water adsorption effect is of greater relative importance on the present small scale than in the milligram method previously described[15]. This is mainly due to the down scaling of the apparatus, as a result of which the ratio of water mass to surface becomes less favourable. The adsorption effect is evident from Fig. 5 where the extrapolated hydrogen calibration line is seen not to pass through the origin, suggesting that a constant amount of water is adsorbed in the considered pressure range from 2 to 10 mm Hg (*ca.* 2–10 μg of hydrogen). The major part of this water appears to be adsorbed very quickly after its introduction in the measuring system. A small but perceptible pressure drop during the actual measurement of the water pressure (3 min after thawing) is taken to be a residual adsorption effect, whose influence can be minimized by careful timing of the readings. Figure 6 confirms that below a level of approximately 2 mm Hg (23 μg of water or 2.5 μg of hydrogen) the amount of water adsorbed varies with the amount present. The measured points were obtained by combustion of small quantities of iodobenzoic acid, which has a very low hydrogen content (2.03%); the experimental curve passes through the origin. With the aid of Fig. 6 even very small samples can be analysed. This is shown in Table IV where results are recorded which are based on sample weights of only 5 to 10 μg. For carbon the normal calibration line (Fig. 5) was valid in this range.

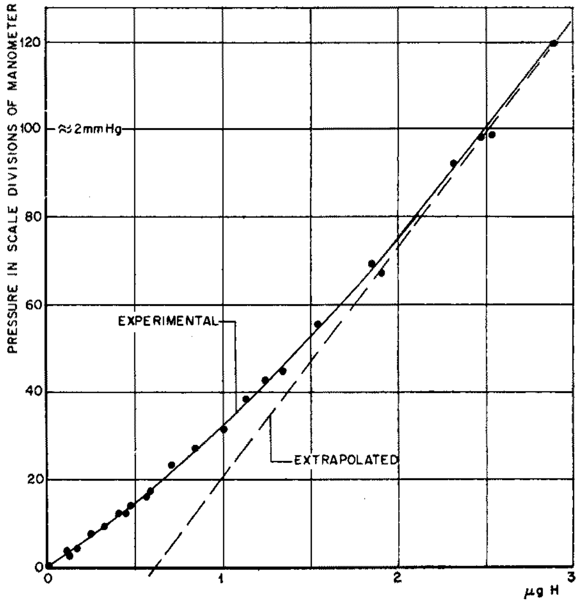


Fig. 6. Experimental and extrapolated calibration lines for hydrogen.

TABLE IV

RESULTS OF ANALYSES ON SAMPLES IN THE 5–10 μg RANGE

Compound	*Sample weight (μg)*	*% Carbon*		*% Hydrogen*	
		Theory	*Found*	*Theory*	*Found*
Hexaethylbenzene	8.12	87.73	87.0	12.27	12.4
	4.42		87.8		11.8
	6.14		88.3		12.7
	7.90		88.2		12.4
	4.15		87.5		12.5
		Mean	87.8	Mean	12.4
Iodobenzoic acid	4.80	33.90	34.2	2.03	2.0
	6.55		34.2		2.0
	4.25		34.0		2.0
	11.30		33.9		2.0
		Mean	34.0	Mean	2.0

Elimination of nitrogen interference

When nitrogen-containing compounds were analysed without provision for the elimination of nitrogen oxides, correct hydrogen values were found but carbon results were high. Obviously, interfering oxides passed through the water trap but condensed in the carbon dioxide trap. Initially, nitric oxide (NO) and nitrogen dioxide (NO_2) were not expected to be responsible for this interference; nitric oxide should pass through the carbon dioxide trap under the experimental conditions[18] and nitrogen dioxide — though trapped — remains solid at the temperature at which the carbon dioxide is measured ($-80°$). Still, a blue-coloured spot appearing in the trap above the carbon dioxide condensate did suggest the presence of both oxides, namely as nitrogen trioxide (N_2O_3). From this mixed oxide nitric oxide was liberated at $-80°$, causing high carbon results. A tube containing manganese dioxide was then inserted between the water and carbon dioxide traps, but this was insufficient. The reagent did remove the nitrogen dioxide but not the nitric oxide and the latter obviously gave rise to another NO/NO_2-equilibrium with the oxygen present so that the blue nitrogen trioxide was again formed. Next, chromic/sulphuric acid reagent on Sil-O-Cel carrier was inserted between the water and carbon dioxide traps, on the assumption that this reagent would not only oxidize any nitric oxide to nitrogen dioxide but also fix the latter. Unlike KIRSTEN[17], we found that the nitrogen dioxide was not quantitatively retained (presumably because of the low pressure in our system) and an additional section of manganese dioxide was necessary to bind all the nitrogen dioxide produced.

This arrangement was successfully used for a variety of nitrogen compounds, until compounds of the melamine type were analysed and high carbon figures were again found. Since similar effects were encountered when ammonium nitrate was heated in the apparatus, these results pointed to the formation of nitrous oxide (N_2O). Most probably the low-temperature catalytic KÖRBL-type combustion (500°) exclusively used until then was responsible for the nitrous oxide formation, since the effect disappeared when a high-temperature platinum section (1100°) was inserted upstream of the KÖRBL catalyst section. This combined arrangement has been giving satisfaction for over 8 months, now.

Sampling

The load capacity of the Oertling model Q01 balance is 250 mg on each pan and the sensitivity of the torsion head is such that one division is equivalent to approximately 0.1 μg whilst tenths of a division can be easily estimated. The total rotation allowed is equivalent to approximately 1 mg[19]. In previous investigations[10] we had found that the torsion-to-weight ratio (calibration factor) was linear to within 0.12% over a weight range 50–500 μg. It was also found that variations in ambient temperature and in load had moderate effects on the calibration factor. Although an apparent effect of 0.3 μg per degree temperature variation was calculated (higher ambient temperatures leading to higher torsion readings) an object's net weight indication (when obtained as difference between 2 weighings immediately following each other) was found to vary within only 0.1% in the investigated temperature range from 20 to 24°. A similar small variation in the calibration factor was found when the total load was varied between 25 and 50 mg.

The favourable properties of this balance were confirmed during the present study. Under controlled atmospheric conditions in the balance room (filtered air, 21 ± 1°, 50 ± 5% relative humidity) it was possible to determine combustion residues in the boat with satisfactory precision from weighings taken 30 min apart. A toolmakers' stereo-"zoom" microscope (magnification 7 to 30 ×) was found of great help in the handling of samples. The average time required to prepare and weigh a 50 μg sample was 5 min. Little experience has so far been gained with volatile or hygroscopic samples. These will, no doubt, require further development of weighing procedures and special attention should be given to light-weight boat containers, *e.g.* of the gelatine capsule type. It was noticed that some compounds which can be weighed in open containers on the microscale without significant weight loss due to volatility cannot be so weighed on the submicro scale owing to the unfavourable surface-to-mass ratio. Another potential problem is presented by possible inhomogeneity of the sample. This may also require special techniques but it is stressed that no unusual measures were taken prior to the analysis of any of the research samples listed in Table III.

SUMMARY

A method is described for the determination of carbon and hydrogen in quantities of organic material ranging from 5 to 50 μg. The method involves catalytic combustion of the sample in oxygen and measurement of the pressures of the resulting carbon dioxide and water. Special attention has been paid to the reduction of the effect of water adsorption in the apparatus. The present submicro method can be applied to non-volatile, non-hygroscopic samples and is free from interferences by nitrogen, sulphur and halogens (except fluorine). The standard deviation in the 50-μg sample range is 0.13% for carbon and 0.10% for hydrogen. The average duration per analysis when carried out in series is 20 min.

RÉSUMÉ

On décrit une méthode pour le dosage du carbone et de l'hydrogène dans des quantités de matière organique de 5 à 50 μg. La méthode comporte la combustion catalytique de l'échantillon dans l'oxygène et on détermine les pressions du dioxyde de carbone et de l'eau qui en résultent. On s'est efforcé en particulier de réduire l'effet de l'adsorption de l'eau dans l'appareil. La méthode submicro décrite s'applique aux échantillons qui ne sont ni volatils ni hygroscopiques; l'azote, le soufre et les halogènes (fluor excepté) ne causent pas de perturbation. Dans le cas des échantillons de 50 μg environ la déviation standard est de 0.13% pour le carbone et de 0.10% pour l'hydrogène. La durée moyenne d'une analyse faisant partie d'une série est de 20 min.

ZUSAMMENFASSUNG

Ein Verfahren zur Bestimmung von Kohlenstoff und Wasserstoff in organischen Substanzen in Substanzmengen von 5 bis 50 μg wird beschrieben. Dabei werden die Proben in Sauerstoff katalytisch verbrannt und die Drucke des sich ergebenden Kohlendioxyds und Wassers ermittelt. Man hat sich besonders bemüht, den Effekt der Wasseradsorption im Gerät zu beschränken. Das beschriebene Submikroverfahren lässt sich auf nichtflüchtige, nichthygroskopische Proben anwenden und wird von Stickstoff, Schwefel und Halogenen (mit Ausnahme von Fluor) nicht gestört. Die Standardabweichung im 50-μg Probenbereich ist 0.13% für Kohlenstoff und 0.10% für Wasserstoff. Die für eine Analyse benötigte durchschnittliche Zeit beträgt bei serienmässiger Ausführung 20 Min.

REFERENCES

1 C. W. Ayers, *Ph.D. Thesis*, University of Birmingham, 1958.
2 L. Blom and L. Edelhausen, *Anal. Chim. Acta*, 13 (1955) 120.
3 C. W. Ayers, R. Belcher and T. S. West, *J. Chem. Soc.*, (1959) 2582.
4 D. T. Hurd, *Chemistry of the Hydrides*, Wiley, New York, 1952.
5 R. Belcher and A. D. Campbell, unpublished work, 1962.
6 A. K. Awasthy, *M.Sc. Thesis*, University of Birmingham, 1964.
7 R. Belcher and B. Breen, unpublished work.
8 B. M. W. Trapnell, *Proc. Roy. Soc. (London), Ser. A*, 218 (1953) 566.
9 F. Feigl and E. Jungreis, *Mikrochim. Acta*, (1958) 812.
10 P. Gouverneur, *M.Sc. Thesis*, University of Birmingham, 1961.
11 H. Malissa, private communication.
12 H. A. Staab, *Angew. Chem.*, 68 (1956) 754.
13 J. Unterzaucher, *Chem. Ing.-Tech.*, 22 (1950) 39.
14 I. J. Oita and H. S. Conway, *Anal. Chem.*, 26 (1954) 600.
15 H. C. E. van Leuven and P. Gouverneur, *Anal. Chim. Acta*, 30 (1964) 328.
16 J. Körbl, *Mikrochim. Acta*, (1956) 1705.
17 W. J. Kirsten, *Mikrochim. Acta*, (1964) 487.
18 D. R. Christman, J. E. Stuber and A. A. Bothner-By, *Anal. Chem.*, 28 (1956) 1345.
19 F. A. Chappell, *Vacuum Microbalance Techniques*, Vol. 2, Plenum Press, New York, 1962, p. 19.

THE NUCLEATION OF CALCIUM PHOSPHATE FROM SOLUTION

T. HLABSE* AND A. G. WALTON
Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106 (U.S.A.)
(Received January 11th, 1965)

It is now well known that the precipitation of solids from homogeneous solution involves first the creation of supersaturation[1,2], followed by nucleation (usually heterogeneous) and crystal growth. The maximum stable supersaturation obtainable under such conditions is not entirely characteristic of the precipitating species, since removal of impurities present in solution affects the nucleation process. However, with reasonable generality it is found that the magnitude of the so-called "critical" supersaturation is related to the structure, and particularly the surface energetics, of the forming embryo.

The control of supersaturation in calcium phosphate systems and an understanding of the nucleation process are important in relation to the physiological deposition of bone mineral from blood serum. Since nothing seems to be known of calcium phosphate nucleation, there are few guidelines to follow. The main difficulties in dealing with phosphate systems are concerned with the many equilibria which have to be satisfied. In the following work is reported an investigation of the nucleation of calcium phosphate from aqueous solution in the pH range 5–6. In this region dicalcium phosphate, $CaHPO_4 \cdot 2H_2O$, is the stable product. In later work will be reported the relation between the nucleation of dicalcium phosphate, octocalcium phosphate, and bone mineral (hydroxyapatite). The transformations between these latter phosphates occur at higher pH.

EXPERIMENTAL

A technique was developed for this investigation, utilizing the solubility characteristics of the calcium phosphates in acidic solution. Because of the equilibria between the various phosphate ions and hydrogen ions, the calcium phosphate used, $CaHPO_4 \cdot 2H_2O$, has a solubility which increases rapidly as the acidity of its solvent rises. $CaHPO_4 \cdot 2H_2O$ was therefore dissolved in hydrochloric acid and the acidity was slowly destroyed by reaction with cyanate ion. The pH was raised in this manner until precipitation occurred. The process was followed in two ways. One part of the solution was placed in a cell of a Beckman DU spectrophotometer. Transmission measurements were repeatedly made at 5460 Å, and a sudden increase in absorbance marked with precision the onset of precipitation. The pH of the remainder of the solution was measured at frequent intervals to determine the pH at which precipitation occurred. If the solubility of $CaHPO_4 \cdot 2H_2O$ as a function of hydrogen ion concentration is known, the supersaturation at precipitation is easily calculated. The con-

---

* Present address: Chemistry Department, University of Chicago.

centration of calcium phosphate used was varied considerably, resulting in a range of pH values at which precipitation occurred.

The hydrolysis reaction used to raise the pH in this procedure deserves some mention here. The stoichiometry of the reaction is as follows:

$$OCN^- + 2H^+ \xrightarrow{H_2O} NH_4^+ + CO_2$$

This reaction has been analyzed by AMELL[3] and has been fairly well characterized. The rate of the reaction at room temperature is sufficiently fast for experimental convenience, yet slow enough to allow accurate determinations of pH at any particular time. For example, for the concentrations used the pH of a solution could be raised from 3 to 7 in about 45 min. All solutions of sodium cyanate were filtered before use.

Since very little reliable information is available in the literature on the solubility of dicalcium phosphate at specific hydrogen ion concentrations, solubilities were determined experimentally. Several properties of the calcium phosphate must be known to make the procedure used possible. The equilibrium constants, obtained from the literature for the following equilibria between various phosphate ions and hydrogen ions, are

$$HPO_4^{2-} \overset{K_1}{\rightleftarrows} PO_4^{3-} + H^+ \qquad K_1 = 2.2 \cdot 10^{-13}$$

$$H_2PO_4^- \overset{K_2}{\rightleftarrows} HPO_4^{2-} + H^+ \qquad K_2 = 6.23 \cdot 10^{-8}$$

$$H_3PO_4 \overset{K_3}{\rightleftarrows} H_2PO_4^- + H^+ \qquad K_3 = 7.52 \cdot 10^{-3}$$

Activity coefficients used were those published by KIELLAND[4]. The basic procedure was as follows. Solutions of hydrochloric acid were made up over a range of pH values. To each of these solutions was added a quantity of $CaHPO_4 \cdot 2H_2O$, a much larger amount than could completely dissolve. These solutions were placed in a constant temperature bath, periodically shaken, and allowed to come to equilibrium for about one week. At this time the solutions were filtered, and the pH of each measured again. The calculation of solubility from the data obtained was based on the following premise. The $CaHPO_4 \cdot 2H_2O$ dissolves in the acidic solution until all the possible equilibria are satisfied. This includes the 3 equilibria listed above for the phosphate ions, as well as the solubility product for the $CaHPO_4 \cdot 2H_2O$. In this process hydrogen ions are used in the conversion of some of the HPO_4^{2-} to $H_2PO_4^-$ and H_3PO_4. The equilibrium process whereby HPO_4^{2-} goes to PO_4^{3-} can be ignored since it is insignificant at lower pH values. With these assumptions solubility calculations can be made.

From the initial and final pH values a certain change in hydrogen ion concentration, $\Delta[H^+]$, is obtained. Clearly

$$\Delta[H^+] = [H_2PO_4^-] + 2[H_3PO_4]$$

since the only change in hydrogen ion concentration arises from the formation of these species. From the previously listed equilibria the following expressions are obtained:

$$\frac{\gamma_1 H_2PO_4^-}{\gamma_0 H_3PO_4} = \frac{7.52 \cdot 10^{-3}}{\gamma_H [H^+]}$$

$$\frac{\gamma_2 HPO_4^{2-}}{\gamma_1 H_2PO_4^-} = \frac{6.23 \cdot 10^{-8}}{\gamma_H [H^+]}$$

where γ indicates the activity coefficient.

Thus three equations with three unknowns, the three phosphate species, are available, and the concentration of each of these species can be calculated. The value for the solubility of the $CaHPO_4 \cdot 2H_2O$ at each of the final pH values is obtained by observing that

$$[Ca^{2+}] = [HPO_4{}^{2-}] + [H_2PO_4{}^{-}] + [H_3PO_4]$$

The concentration of calcium ions so calculated is identical to the solubility. Table I shows the solubility *vs.* pH that was obtained by this method.

The preparation of the $CaHPO_4 \cdot 2H_2O$ used was also undertaken. Solutions of analytical grade disodium hydrogen phosphate and calcium chloride were prepared and filtered. The calcium chloride solution was added, with magnetic stirring, to the sodium phosphate solution. The precipitate was washed repeatedly and dried for 2–3 days.

RESULTS

The data produced from the experimental determination of the solubility of calcium phosphate in aqueous solutions are shown in Table I.

The results of the precipitation studies on the calcium phosphate were consistent and reproducible. The onset of precipitation was readily observable with the Beckman DU spectrophotometer, and in high concentrations was easily visible to the naked eye, since it occurred suddenly. The precipitation occurred as finely dispersed,

TABLE I

DATA FOR THE SOLUBILITY OF $CaHPO_4 \cdot 2H_2O$ DETERMINED FROM CHANGE OF pH AT 25 ± 0.01°

Sample	*Initial pH*	*Final pH*	*$\Delta[H^+]$(mole/l)*	*Solubility (mole/l)*
1	1.10	3.77	$6.38 \cdot 10^{-2}$	$6.28 \cdot 10^{-2}$
2	1.34	4.05	$4.54 \cdot 10^{-2}$	$4.51 \cdot 10^{-2}$
3	1.77	4.94	$1.80 \cdot 10^{-2}$	$1.82 \cdot 10^{-2}$
4	2.08	5.68	$8.22 \cdot 10^{-3}$	$8.53 \cdot 10^{-3}$
5	2.35	6.04	$4.41 \cdot 10^{-3}$	$4.82 \cdot 10^{-3}$
6	2.56	6.14	$2.70 \cdot 10^{-3}$	$3.02 \cdot 10^{-3}$
7	3.15	6.49	$7.08 \cdot 10^{-4}$	$8.66 \cdot 10^{-4}$

TABLE II

SUPERSATURATIONS ATTAINED BEFORE THE ONSET OF PERCEPTIBLE CRYSTAL GROWTH

Run	*pH at precipitation*	*Average supersaturation ratio*
1,2	5.00	2.4
3,4	5.20	2.7
5	5.30	2.0
6,7	5.50	2.7
8,9	5.60	3.4
10	5.65	2.1
11	6.00	2.0
	Average	2.3

fairly large, white particles. The hydrolysis was slow enough so that the pH of precipitation could be determined with accuracy to better than 0.1 pH unit.

The parameter of most interest, the supersaturation, was then easily calculated. Since the solubility is known as a function of pH, the supersaturation ratio is obtained by dividing the actual concentration by the solubility at which precipitation occurred. As can be seen from Table II, the supersaturation ratios remained approximately constant throughout the pH range undertaken in this study.

DISCUSSION AND CONCLUSION

Although the accuracy of the results was limited by the simultaneous use of different techniques on different portions of the reaction mixture, there did not appear to be any consistent change of critical supersaturation with pH. Infrared spectra of the product showed that at all pH values, dicalcium phosphate formed a significant part of the precipitate. In the two most acid solutions significant amounts of NH_4^+ ion appeared in the product as characterized[5] by an infrared band at approximately 14 μ and one at 7 μ. It is conceivable therefore that calcium ammonium phosphate, $CaNH_4PO_4$, is involved in the formation process[6].

The nucleation of crystals from homogeneous solution is generally a heterogeneous process initiated by impurities. However, the supersaturation attained before the onset of nucleation and crystal growth does reflect a property of the new phase itself. Changes in structure of the initial nucleus should therefore cause major changes in the maximum stable supersaturation. Without knowing details of the lattice matching between impurity substrate and depositing phase, it is not possible to formulate a quantitative approach. Dicalcium phosphate is, however, a fairly soft material which presumably possesses a low interfacial energy against water and may thus support a low supersaturation. These deductions are consequently in agreement with the reported data.

The authors are pleased to acknowledge the partial support of the National Science Foundation and National Institutes of Health.

SUMMARY

Dicalcium phosphate was precipitated from homogeneous solution in the pH range 5–6 by using the hydrolysis of cyanate to control the precipitation process. Turbidimetric determination of the onset of precipitation enabled the critical supersaturation to be determined. In this region the average critical supersaturation ratio was found to be 2.3.

RÉSUMÉ

On a précipité le phosphate dicalcique, en solution homogène, à un pH de 5 à 6, en utilisant l'hydrolyse du cyanate pour contrôler le processus de précipitation. Un dosage turbidimétrique a permis de déterminer la supersaturation critique; dans ces conditions le rapport moyen de supersaturation est de 2.3.

ZUSAMMENFASSUNG

Dicalciumphosphat wurde aus homogener Lösung im pH-Bereich 5–6 gefällt. Die Hydrolyse von Cyanat wurde zur Kontrolle des Fällungsvorgangs verwendet. Die turbidimetrische Bestimmung des Niederschlages liess die kritische Übersättigung bestimmen. In diesem Bereich betrug das mittlere kritische Übersättigungsverhältnis 2.3.

REFERENCES

1 V. K. LAMER AND R. H. DINEGAR, *J. Am. Chem. Soc.*, 73 (1951) 380.
2 A. G. WALTON, *Science*, 148 (1965) 601.
3 A. R. AMELL, *J. Am. Chem. Soc.*, 73 (1956) 6234.
4 H. KIELLAND, *J. Am. Chem. Soc.*, 59 (1937) 1675.
5 K. H. BUTLER, private communication.
6 A. W. FRAZIER, J. R. LEHR AND J. P. SMITH, *J. Agr. Food Chem.*, 12 (1964) 198.

THE STABILITY CONSTANTS OF THE ALKALINE EARTH LACTATE AND α-HYDROXYISOBUTYRATE COMPLEXES

F. VERBEEK AND H. THUN
Laboratory of Analytical Chemistry, University of Ghent, Ghent (Belgium)

(Received February 28th, 1965)

The use of ammonium lactate and α-hydroxyisobutyrate solutions for alkaline earth separations by cation-exchange chromatography has been discussed by several investigators[1-6]. BAERG AND BARTHOLOMEW[3] and WISH[4] developed a procedure for the separation of calcium, strontium and barium from the rare earths and from each other by elution with ammonium α-hydroxyisobutyrate solutions. POLLARD *et al.* separated all 4 alkaline earth metals, magnesium included, using lactate[5] and α-hydroxyisobutyrate[6]. It was stated that the elution was in the order magnesium, calcium, strontium and barium.

This phenomenon can be explained by the decrease of the stability constants of the complexes involved with increasing atomic number, but only the K_1 values for the lactate–alkaline earth complexes are reported in the literature[7] and these values indicate a decrease of the stability in the order: calcium, magnesium, strontium and barium. To explain this disagreement between the elution order and stability of calcium and magnesium, and also to complete previous work on the stability of lactate and α-hydroxyisobutyrate complexes with the lanthanides[8], in this investigation the determination of the stability constants of both ligands with the alkaline earth metals is described.

EXPERIMENTAL

Apparatus

A Keithley 660 guarded differential voltmeter was used. Potentials were measured to 0.01 mV.

Other apparatus was as previously described[9].

Reagents

Alkaline earth perchlorate solutions. The solutions were prepared by dissolving the alkaline earth carbonates (Merck, analytical grade) in perchloric acid. The small amount of acid in excess (2–6 m*M*) was determined by potentiometric titrations in a nitrogen atmosphere. The concentrations of the alkaline earths (*ca.* 50 m*M*) were determined by EDTA titration.

Organic acid buffer solutions. These solutions were prepared as before[9].

The buffer ratio $\delta = C_{HL}°/C_L°$ was respectively:
lactate : $C_{HL}° = 0.971\ M, C_L° = 1.003\ M;\ \delta = 0.968$
α-hydroxyisobutyrate : $C_{HL}° = 1.011\ M.\ C_L° = 1.000\ M;\ \delta = 1.011$

Procedure

Some modifications were introduced in the procedure previously described. Instead of CHOPPIN's arrangement[10] with 3 half-cell compartments in series, FRONAEUS' technique[11] with 2 compartments was used. The potential differences, E_{AB} and E_{AC}, between the quinhydrone electrodes in the reference perchloric solution in compartment A (concentration H_A) and respectively the metal–ligand solution in compartment B, and the 1 M sodium perchlorate solution in compartment C were determined by 2 separate titrations. Every titration series was at least duplicated; the potentials were stable and could usually be reproduced within 0.05 mV.

E_{AB} potentials were corrected for change in ionic strength (ΔI) during the titration, due to complex formation in compartment B.

$$E_{AB}' = E_{AB} + \Delta E_{AB} \quad \text{where} \quad \Delta E_{AB} = k\,\Delta I \tag{1}$$

where k is a constant depending on the nature of the ligand.
For M^{2+}, ΔI is given by

$$\Delta I = 0.5\, C_M \bar{n}(5 - \bar{n}) \tag{2}$$

k was determined by adding known amounts of sodium perchlorate to cell B and measuring the potential differences involved[12].

E_{AB}, E_{AC}, k, H_A, δ, C_L°, C_M°, C_H° (concentration of perchloric acid in compartment B) and volume data were supplied to an IBM 1620 digital computer which gave the corresponding $[L]$ and $\bar{n}$ values. For the calculation of $[L]$ the full equation was used

$$[L] = \frac{[H]_C}{[H]_B}\left[\frac{\delta C_L + C_H - [H]_B + [H]_C\left[\delta + \dfrac{C_H - [H]_B}{C_L}\right]}{\delta - \dfrac{[H]_C}{C_L}}\right] \tag{3}$$

Although calculation of $[L]$ according to eqn. (3) does not require the numerical value of the dissociation constant of the organic acid, K_A values were calculated from the E_{AC} potentials

$$K_A = [H]_C \frac{C_L + [H]_C}{C_{HL} - [H]_C} \tag{4}$$

Other conditions ($t = 25.0 \pm 0.1°$; $I = 1$), and the calculations of the stability constants by means of an IBM 1620 computer were as before[9].

RESULTS AND DISCUSSION

Table I presents an example of the experimental data and the calculated values of ΔE_{AB}, K_A, $[L]$ and $\bar{n}$ for the calcium–lactate complex system as a function of added buffer solution. All other titrations were performed in the same manner. The K_A value of α-hydroxyisobutyric acid varied from $1.73 \cdot 10^{-4}$ to $1.39 \cdot 10^{-4}$ during the titration.

The formation curves, representing $\bar{n}$ as a function of $pL(= -\log[L^-])$ of the alkaline earth complexes with lactate and α-hydroxyisobutyrate are reproduced in

TABLE I

DETERMINATION OF $[L]$ AND $\bar{n}$ FOR THE CALCIUM LACTATE SYSTEM

($C_M^\circ = 25.00$ mM, $C_L^\circ = 1003$ mM, $[H]_A = 11.57$ mM, $C_H^\circ = 2.47$ mM, $\delta = 0.9680$, $k = 2.0$, initial volume = 10 ml)

Volume of titrant (ml)	$E_{AB}(mV)$	$\Delta E_{AB}(mV)$	$E_{AC}(mV)$	$K_A \cdot 10^4$	$[L](mM)$	$\bar{n}$
0.10	86.05	0.007	102.95	2.268	6.51	0.056
0.20	91.19	0.015	102.09	2.297	14.61	0.121
0.30	93.18	0.021	101.82	2.305	22.78	0.179
0.40	94.28	0.027	101.69	2.308	30.91	0.232
0.50	95.02	0.032	101.63	2.309	38.99	0.282
0.60	95.54	0.037	101.60	2.308	46.95	0.329
0.70	95.97	0.041	101.59	2.306	54.87	0.373
0.80	96.31	0.044	101.58	2.306	62.70	0.414
0.90	96.61	0.048	101.59	2.303	70.43	0.453
1.00	96.87	0.051	101.60	2.301	78.09	0.489
1.20	97.29	0.056	101.61	2.298	93.12	0.556
1.40	97.66	0.060	101.63	2.295	107.87	0.611
1.60	97.96	0.063	101.66	2.292	122.16	0.664
1.80	98.23	0.066	101.70	2.288	136.08	0.712
2.00	98.47	0.068	101.74	2.283	149.63	0.755
2.25	98.73	0.070	101.79	2.278	166.02	0.806
2.50	98.97	0.072	101.84	2.273	181.91	0.848
3.00	99.37	0.074	101.94	2.264	212.00	0.926
3.50	99.71	0.075	102.03	2.256	240.20	0.985
4.00	100.00	0.076	102.12	2.247	266.52	1.037
4.50	100.26	0.075	102.21	2.239	291.19	1.080
5.00	100.49	0.075	102.31	2.230	314.16	1.126
5.50	100.69	0.074	102.39	2.223	335.81	1.161
6.00	100.88	0.073	102.47	2.216	356.26	1.187
7.00	101.20	0.071	102.61	2.204	393.64	1.233
8.00	101.47	0.069	102.75	2.192	426.80	1.284
9.00	101.70	0.067	102.87	2.181	456.61	1.323
10.00	101.92	0.064	102.99	2.171	483.66	1.345
12.00	102.25	0.060	103.18	2.155	530.19	1.407
14.00	102.52	0.056	103.34	2.141	569.17	1.450
16.00	102.80	0.051	103.50	2.128	602.99	1.405
18.00	102.98	0.049	103.64	2.116	630.72	1.500
20.00	103.17	0.046	103.77	2.105	655.43	1.514

TABLE II

STABILITY CONSTANTS OF THE ALKALINE EARTH–LACTATE COMPLEX SYSTEMS AT 25.0°

Element	*Bjerrum Half $\bar{n}$ method*		*Fronaeus*		*Computer*	
	log β_1	*log β_2*	*log β_1*	*log β_2*	*log β_1*	*log β_2*
Ba	0.49	0.49[a]	0.34	0.44	0.34 ± 0.015	0.42 ± 0.025
Sr	0.68	0.74[a]	0.54	0.71	0.53 ± 0.015	0.69 ± 0.035
Ca	1.09	1.29	0.95	1.16	0.90 ± 0.01	1.24 ± 0.015
Mg	1.00	1.31	0.76	1.26	0.73 ± 0.03	1.30 ± 0.06

[a] Extrapolated value.

Figs. 1 and 2. The $\bar{n}$ values exceeding 1, except for barium, indicate the formation of ML^+ and ML_2 complexes in the investigated pL range.

Approximate values of the stability constants were obtained directly from the formation curves, using BJERRUM's half $\bar{n}$ method[13]: the logarithms of the stepwise formation constants K_1 and K_2 are approximately given by the pL values at $\bar{n}=0.5$ and 1.5 respectively. The corresponding log β values, together with the constants and standard deviations calculated by the computer are listed in Tables II and III. These deviations were in general about 2% on K_1 and about 5% on K_2, except for the magnesium complexes, where deviations of respectively 5% and 7% were found. To check the computer values, the stability constants were determined by FRONAEUS' graphical method[8].

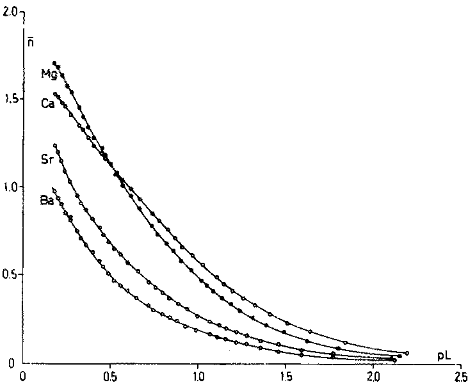


Fig. 1. Formation curves of the alkaline earth–lactate complex systems at 25.0°.

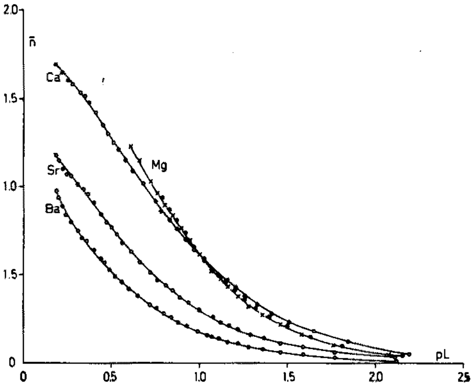


Fig. 2. Formation curves of the alkaline earth–α-hydroxyisobutyrate complex systems at 25.0°. Mg: ●, 24 mM; ×, 12 mM.

TABLE III

STABILITY CONSTANTS OF THE ALKALINE EARTH–α-HYDROXYISOBUTYRATE COMPLEX SYSTEMS AT 25.0°

Element	*Bjerrum Half $\bar{n}$ method*		*Fronaeus*		*Computer*	
	log β_1	*log β_2*	*log β_1*	*log β_2*	*log β_1*	*log β_2*
Ba	0.51	0.53[a]	0.38	0.52	0.36 ± 0.01	0.51 ± 0.02
Sr	0.72	0.77[a]	0.58	0.74	0.55 ± 0.01	0.73 ± 0.025
Ca	1.11	1.44	0.96	1.38	0.92 ± 0.015	1.42 ± 0.025
Mg	1.10	1.52	0.83	1.43	0.81 ± 0.02	1.47 ± 0.04

[a] Extrapolated value.

The solubility of the neutral magnesium-α-hydroxyisobutyrate complex (MgL_2) was rather small because it precipitated at $\bar{n}=1$, when an initial metal concentration of 24 mMol was used. In a second titration series at a metal concentration of 12 mMol the precipitation of MgL_2 began at $\bar{n}=1.2$.

For the computer calculation only the $\bar{n}$ values smaller than 1.20 of the second series were used. β_2 was obtained with good precision. The formation curves, being exactly the same for $\bar{n} \leqslant 1$ at both metal concentrations, indicated that no polynuclear complexes were formed in solution. Under the same conditions the neutral magnesium–lactate complex was soluble.

The K_1 or β_1 values of the magnesium lactate and α-hydroxyisobutyrate are smaller than the corresponding constants of the calcium complexes, whereas the K_2 values and also the overall stability constants β_2 are greater for magnesium. This phenomenon corresponds with the literature data for K_1 of the calcium and magnesium lactate complexes, and also with the elution experiments of POLLARD *et al.*[5,6].

The log β_2 values plotted in the order of decreasing atomic number increase more for the α-hydroxyisobutyrate complexes than for the lactate complexes. This shows that, as for the rare earths, α-hydroxyisobutyrate is a better eluent for ion-exchange separation of the alkaline earths, which conforms to the elution experiments of POLLARD *et al.*[5,6].

In the literature the only stability constants reported at the same temperature (25°) and a comparable ionic strength (0.16) are the K_1 values of the strontium and calcium lactate complexes determined by SCHUBERT AND LINDENBAUM[14], using cation-exchange methods. These authors found values of 0.5 and 0.8 respectively; this is in fair agreement with the constants in Table II, as is the K_1 value of 0.82 for the calcium lactate complex determined by JOSEPH[15], from EMF measurements.

The formation of ML_2 complexes is not in disagreement with SCHUBERT's conclusion that only 1:1 species would exist at lactate concentrations ranging from 0.04 to 0.08 ($pL = 1.4$–1.1). As can be seen from the formation curves (Fig. 1) at $pL = 1.1$ the value of $\bar{n}$ is 0.23 for strontium and 0.50 for calcium, indicating that almost only ML^+ complexes are in solution.

The authors wish to express their thanks to Prof. Dr. J. HOSTE for his kind interest in this work, to Mr. W. VANDERLEEN for his help with the IBM computer, and to Mrs. VAN DEN ABEELE for technical assistance.

SUMMARY

The stability constants of the lactate and α-hydroxyisobutyrate complexes of the alkaline earths were determined by potentiometric titration. The average ligand number exceeds a value of one, indicating the formation of ML^+ and ML_2 complexes. α-Hydroxyisobutyrate forms stronger complexes than lactate. The stability constants β_2 increase as a function of decreasing atomic number for both ligands: $Ba < Sr < Ca < Mg$, although the constant β_1 is greater for Mg than for Ca.

RÉSUMÉ

On a déterminé les constantes de stabilité de complexes: lactates et α-hydroxyisobutyrates alcalino-terreux (du type ML^+ et ML_2), par titrage potentiométrique. Les α-hydroxyisobutyrates sont des complexes plus forts que les lactates. Les constantes de stabilité augmentent lorsque le nombre atomique du métal diminue ($Ba < Sr < Ca < Mg$).

ZUSAMMENFASSUNG

Durch potentiometrische Titration wurden die Stabilitätskonstanten der Lactat- und α-Hydroxyisobutyrat-Komplexe der Erdalkalien bestimmt. Die durchschnittliche Ligandenzahl überstieg den Wert von 1, was auf die Bildung von ML^+- und ML_2-Komplexen hinweist. Die α-Hydroxyisobutyrate bilden stärkere Komplexe als die Lactate. Die Stabilitätskonstanten β_2 steigen bei beiden Liganden mit abnehmender Ordnungszahl: $Ba < Sr < Ca < Mg$, obwohl die Konstante β_1 beim Magnesium grösser ist als beim Calcium.

REFERENCES

1 H. Lerner and W. Rieman, *Anal. Chem.*, 26 (1954) 610.
2 G. M. Milton and W. E. Grummitt, *Can. J. Chem.*, 35 (1957) 541.
3 A. P. Baerg and R. M. Bartholomew, *Can. J. Chem.*, 35 (1957) 980.
4 L. Wish, *Anal. Chem.*, 33 (1961) 53; *U.S. Naval Radiological Defense Lab. Rept., US NRDL-TR-341*, 1959.
5 F. H. Pollard, G. Nickless and D. Spincer, *J. Chromatog.*, 10 (1963) 215; 11 (1963) 542.
6 F. H. Pollard, G. Nickless and D. Spincer, *J. Chromatog.*, 13 (1964) 224.
7 L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Spec. Public. no. 17, Chem. Soc., Burlington House, London, 1964.
8 H. Deelstra and F. Verbeek, *Anal. Chim. Acta*, 31 (1964) 251.
9 L. Eeckhaut, F. Verbeek, H. Deelstra and J. Hoste, *Anal. Chim. Acta*, 30 (1964) 369.
10 G. R. Choppin and J. A. Chopoorian, *J. Inorg. & Nucl. Chem.*, 22 (1961) 97.
11 S. Fronaeus, *Acta Chem. Scand.*, 4 (1950) 72; 5 (1951) 139; 6 (1952) 100, 1200.
12 A. Sonesson, *Acta Chem. Scand.*, 12 (1958) 165, 1937; 13 (1959) 998.
13 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, P. Haase, Copenhagen, 1941.
14 J. Schubert and A. Lindenbaum, *J. Am. Chem. Soc.*, 74 (1952) 3529.
15 N. R. Joseph, *J. Biol. Chem.*, 164 (1946) 529.

ANALYTICAL APPLICATIONS OF β-HETEROPOLY ACIDS

PART I. DETERMINATION OF ARSENIC, GERMANIUM AND SILICON

ROBERT A. CHALMERS AND ALAN G. SINCLAIR
Chemistry Department, University of Aberdeen, Aberdeen (Great Britain)

(Received April 7th, 1965)

It is now generally realised that the existence of two forms (α and β) of silicomolybdic acid, first postulated by STRICKLAND[1], necessitates the formation of one form exclusively if a spectrophotometric method is to be used to determine the amount of heteropoly acid. Until STRICKLAND's discovery was fully appreciated, colorimetric methods for silicon continued to appear in which the conditions were such that both forms of silicomolybdate were present in mixtures that varied in composition with time, since the β-form spontaneously changed into the α-form. Later, however, care was taken to ensure that only the more stable α-form was obtained[2,3]. The present work is based on the idea that it would be quicker to use the β-form if it could be stabilised, and more advantageous because of its higher extinction coefficient. It was found that several polar organic solvents effectively stabilised β-silicomolybdic acid, and could also be applied to the determination of arsenic, germanium, and phosphorus as their heteropoly acids.

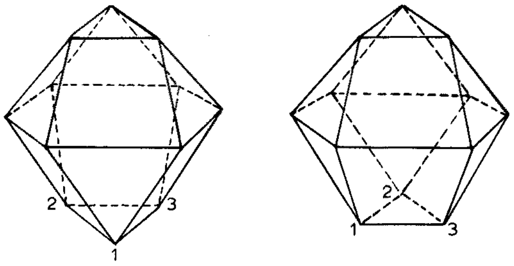
EFFECT OF ACIDITY ON HETEROPOLY ACID FORMATION

The optical densities of silicomolybdic acid solutions made from fixed amounts of sodium silicate and ammonium molybdate and varying amounts of acid were measured in 1-cm cells at 440 mμ after various intervals of time. In agreement with other workers, it was found that β-silicomolybdic acid was formed when the ratio $[H^+] : [MoO_4^{2-}]$ exceeded the critical value 1.5. Similar behaviour was found for germanomolybdic acid, which supports STRICKLAND's suggestion that KRUMHOLTZ's observations on the fading of the colour of this compound[4] could be explained in terms of a spontaneous transformation of an unstable β-form into a stable α-form. It was further found that reduction of the two forms of germanomolybdic acid to molybdenum blue had the same kind of spectral change as found by STRICKLAND for the silicomolybdic acids.

Phosphomolybdic acid is formed so quickly that it proved possible to investigate its formation by means of a spectrophotometric titration of a mixture of phosphate and an excess of molybdate with 5 M sulphuric acid. A plot of optical density against $[H^+] : [MoO_4^{2-}]$ showed breaks at ratios of 1.5 and about 1.8, indicating the existence of two forms of phosphomolybdic acid. A similar method was used to investigate the colourless arsenomolybdic acid, except that a wavelength of

390 mμ was used and a correction was made for the optical density of the excess of isopolymolybdate. A similar result was obtained except that the arsenomolybdic acid formed at high acid concentration had a lower extinction coefficient than the arsenomolybdate formed at low acid concentration.

It seems probable that all heteropoly acids can exist in a stable α-form or an unstable β-form that reverts spontaneously to the α-form. The ratio of base to heteropoly acid in such compounds as quinoline or pyridine silicomolybdate was found to be the same for both the α- and β-forms (though the X-ray powder diagrams are different). Strickland's suggestion that the heteropoly anions may condense to form bigger units can be discounted since it implies an alteration in the charge per molybdenum atom in the anion, and it seems probable that the formulae of the two forms are the same and that they differ only in structure. Chalmers[5] has suggested that the simplest structural change would be the rotation through 60° of molybdenum atoms 1, 2, and 3 in the Keggin structure[6] for the α-form (Fig. 1), which changes the symmetry from cubic to hexagonal, and involves the breaking and making of 6 oxygen–molybdenum bonds. Comparison of the domains of formation of the α- and β-heteropoly acids with the degree of condensation of isopolymolybdates at the same degree of acidification shows that the α-form is obtained from an octamolybdate, whereas the β-form is produced from a deca- or dodecamolybdate. The β-form might then revert to the α-form by a mechanism involving water molecules bridging between the oxygen atoms that are singly-coordinated to molybdenum atoms. The β-form might then be stabilised if the water molecules were displaced by polar organic molecules of the right length. This hypothesis will be developed more fully elsewhere.



1 2

Fig. 1. (1) Keggin's structure for α-phosphomolybdate; (2) proposed structure for β-phosphomolybdate.

THE EFFECT OF SOME POLAR ORGANIC SOLVENTS ON HETEROPOLYMOLYBDATES

The heteropolymolybdates of silicon, phosphorus, and arsenic can all be extracted into organic solvents from strongly acidic solutions and show no sign of fading in these solvents. Moreover, the arsenomolybdic acid is coloured yellow in organic media. Saint-Chamant and Vigier[7] concluded that an ethereal solution of phosphomolybdic acid contained a coordination complex of the solute and solvent. Vigier[8] extended this work and found evidence for the existence of an acetic acid–

phosphomolybdic acid complex in aqueous solution. Ordinarily the phosphomolybdic acid is partly dissociated into phosphate and molybdate ions (unless the equilibrium is shifted by precipitation or reduction) but VIGIER found that if excess of molybdate is added all the phosphate is converted into the heteropoly acid. The colour is intensified and the ammonium salt cannot be precipitated. BERNHART AND WREATH[9] found similar behaviour in the presence of acetone. The extinction coefficient is the same in aqueous acetone as it is in ether solution, and the conclusion is that the water molecules in the solvation shell have been replaced by organic molecules. The character of the oxygen atom in the solvent is most important—furan, in which the oxygen atom has a completely delocalised unshared pair of electrons, does not extract heteropoly acids at all.

Arsenomolybdic acid

It was found that when acetone was added to the colourless arsenomolybdic acid, a yellow colour appeared. The effect of the acetone was to shift the absorption spectrum towards longer wavelengths. At 440 mμ the absorbance was unaffected by less than 16% (v/v) of acetone but rose steeply as the acetone concentration was increased to 25% and remained constant when more than 30% of acetone was present. The large amount of acetone required implies competition between the acetone and water for coordination sites on the heteropoly anion. For a given amount of arsenate the absorbance measured against a reagent blank was constant over a range of concentrations of the other components of the system. The molybdate could be varied from 1.0–1.2%, the acetone from 32–40%(v/v), and the acidity from 0.8–1.9 *N*. It was best to keep the acid concentration above 1 *N* to prevent interference from silicomolybdic acid and to prevent formation of a yellow colour in the reagent blank. The colour formed very quickly, but faded slightly for about 30 min and then became stable.

Silicomolybdic acid

In a search for reagents that would stabilise β-silicomolybdic acid, it was found that methanol, ethanol, propan-1-ol, acetone, and acetic acid all possessed stabilising power, but the alcohols caused some reduction of the silicomolybdate, and acetic acid slowed its formation. Acetone not only stabilised the system but also increased the rate of reaction and intensified the colour. With fixed amounts of molybdate and silicate present and 10% (v/v) of acetone, the acidity could vary from 0.04 to 0.4 *N* without effect on the optical density. The full colour took 15 min to develop and then the rate of fading was 0.4% per h. The concentrations of molybdate and acetone were not critical and could vary from 0.6–1.0% and 10–15% respectively without effect on the results. The system obeyed Beer's law for silicate concentrations up to the equivalent of 3.6 mg SiO_2/50 ml of solution. The range could be extended (and the results made more precise) by applying a differential method using the permanent standard recommended by SWANK AND MELLON[10]. As the absorption spectrum of the standard was almost parallel to that of the silicomolybdate, the wavelength setting was not critical, and 416 mμ was chosen as giving the least error. The calibration curve showed only a slight deviation from linearity over the range 3.5–6.0 mg SiO_2/50 ml solution, and a precision of 2 parts per thousand was attainable.

Germanomolybdic acid

The determination of germanium as germanomolybdate[11] or its reduced form[12] was regarded by BOLTZ AND MELLON[13] as unsatisfactory because of the stringent reaction conditions required; the main source of error was the rapid conversion of the β- into the α-form. SHAW AND CORWIN[14] found that the time factor in the reduction method was critical to 25 sec. KITSON AND MELLON[15] achieved a considerable degree of stabilisation by forming the germanomolybdate in 5 N acetic acid solution. In the present work, acetone was found to be an excellent stabiliser. As with silicon, the reaction was faster and the colour stable and more intense. Systematic variation of the conditions showed that the final concentrations could range from 0.8–1.6% of molybdate, 20–40% (v/v) of acetone, and 0.08–0.24 N for the acidity. The system obeyed Beer's law up to a concentration of 6 mg GeO_2/50 ml of solution, and the rate of fading was 1.5% per h. The sensitivity was only about a tenth that of the molybdenum blue method, but the latter suffers from the uncertainty about the amounts of the two forms of heteropoly acid present. It was found that the stabilised β-form could be reduced satisfactorily with iron(II) ammonium sulphate, but that it was then better to use a slightly higher acidity for the initial formation of the unreduced form. More acid had to be added before the reduction in order to prevent reduction of the excess of molybdate, but the acetone stabilised the β-form sufficiently for the extra acid to have no effect on it in the short time needed to add the reductant. Beer's law was obeyed for amounts up to 140 μg GeO_2/50 ml of solution, and the method was more sensitive than the customary one.

EXPERIMENTAL

Reagents

8% (w/v) ammonium molybdate solution. This reagent should be prepared and stored in polythene.

Standard arsenic solution. Weigh accurately about 2 g of disodium hydrogen arsenate heptahydrate (checked gravimetrically for its water content, which is variable), dissolve in water and dilute to 1 l.

Standard silicate solution. Weigh accurately about 0.3 g of pure dry finely-ground quartz into a platinum crucible and fuse it with about 3 g of M.A.R. grade sodium carbonate. Cool the melt, dissolve in water, dilute to 500 ml and store in polythene.

Standard germanium solution. Dissolve 0.3180 g of pure GeO_2 in dilute ammonia (silica-free), neutralise with dilute sulphuric acid and dilute to 500 ml.

Permanent standard for the differential silicon method. Dissolve 0.4528 g of potassium chromate and 20 g of sodium metaborate in water and dilute to 1 l.

Procedure for arsenic

Make a solution of the material to be tested and ensure that the arsenic is present as As(V). For organic compounds a Kjeldahl digestion with 1 ml of concentrated sulphuric acid is satisfactory, and 4 ml less of the 8 N sulphuric acid should be used in the subsequent procedure. Take an aliquot of sample solution containing not more than 7 mg of arsenic and place it in a 50-ml standard flask. Add 6–12 ml of 8 N sulphuric acid, 6–7.5 ml of molybdate solution and 16–20 ml of acetone, dilute to the mark with water, and mix. After 30 min measure the absorbance in a 1-cm cell against a reagent blank at 440 mμ. Phosphate interferes but silicate does not. Construct a calibration curve, using the standard arsenate solution. The slope is 0.00565/μg As/ml, and Beer's law is obeyed up to 140 μg As/ml.

Procedure for silicon

If silicon is to be determined in rocks or glasses, decompose the sample by fusion with sodium hydroxide in a silver crucible[16], cool the melt, leach it with water, and add it to enough dilute sulphuric acid to yield a slightly acidic solution. Transfer the solution to a standard flask and dilute to volume and mix. Sulphuric acid is used instead of the usual hydrochloric acid in order to prevent interference by chloro-complexes of iron. If the sample contains a large amount of calcium, the formation of the heteropoly acid is very slow, and colour development must be allowed to continue until a steady value of the absorbance is reached.

In a 50-ml standard flask place 10 ml of a 1:1 mixture of 8% ammonium molybdate solution and 2 *N* sulphuric acid, and add to it 5 ml of acetone and an aliquot of sample solution containing not more than 3 mg of silicon. Dilute to the mark with water, mix well, let stand for 15 min and during the next 30 min measure the absorbance in a 1-cm cell, at 430 mμ against a reagent blank for less than 2 mg of silicon, and at 416 mμ against the permanent chromate standard for more than 2 mg. Construct a calibration curve, using the standard silicon solution. In this method it is essential to avoid polymerisation of silicic acid, and the sample solution must therefore be slightly alkaline or freshly acidified. If the sample solution is not far from neutral the range of acidity permissible is wide enough to deal with a small excess of acid or alkali in the sample solution. Distilled water often contains a little silicate but this will be compensated for in the reagent blank or in the calibration curve. A blank should be done on the reagents used to dissolve the sample if they are different from those used in the rest of the procedure. Phosphate, arsenate, and germanate will also be measured as their heteropoly acids if they are present, and must either be removed (see Part II[17]) or corrected for.

Procedure for germanium

In a 50-ml standard flask place 6–7 ml of ammonium molybdate solution, 10–12 ml of acetone, and 2–4 ml of 2 *N* sulphuric acid. Add an aliquot of sample solution containing not more than 4 mg of germanium, dilute to the mark with water, mix, and let stand for 5 min. During the next 20 min measure the absorbance in a 1-cm cell at 430 mμ against a reagent blank. Construct a calibration curve; Beer's law is obeyed and the slope is 0.00864/μg Ge/ml.

Organo-germanium compounds can often be simply analysed by adding 5–20 mg of sample to a mixture of 10–12 ml of acetone and 4 ml of 2 *N* sulphuric acid in a 50-ml standard flask, shaking until the sample has dissolved, and then adding 6–7 ml of molybdate solution, diluting, and measuring as before.

For smaller amounts of germanium, take 4 ml of molybdate solution, 5 ml of 2 *N* sulphuric acid, and 6 ml of acetone in a 50-ml standard flask. Add an aliquot of sample solution containing not more than 100 μg of germanium and not more than 10 ml in volume. Mix and let stand for 2–15 min, then add 12–15 ml of 2 *N* sulphuric acid and mix; 1–5 min later, add 6 ml of freshly prepared 10% (w/v) iron(II) ammonium sulphate solution in 0.1 *N* sulphuric acid, dilute to the mark and mix. Between 2 and 30 min later, measure the absorbance in a 1-cm cell at 805 mμ against a reagent blank. Beer's law is obeyed and the slope of the calibration curve is 0.418/μg Ge/ml.

RESULTS

The methods described were used to analyse various organic and inorganic compounds and some glasses. The results are given in Table I, and compare favourably with those obtained by standard methods. An advantage of the methods is their rapidity: three germanium samples were analysed in 25 min.

TABLE I

RESULTS OBTAINED BY THE METHOD

Compound	*Amount of species present (%)*	
	Theory	*Observed*
Arsenic		
Triphenylarsinic sulphide	19.3	19.5, 19.2, 19.5
o-Aminophenylarsonic acid	34.5	34.4, 34.5, 34.8
Triphenylarsinoxide	23.3	23.5, 23.1
Potassium arsenite	51.4	51.9, 52.0
Sodium arsenite	57.7	57.6, 58.0
Triphenylarsine	24.8	24.7, 25.0
Sodium arsenate	25.7	25.7
Silica		
Standard glass No. 2	80.1	79.8, 80.2, 79.9 80.2, 79.9
Standard glass No. 3	55.3	55.5, 55.6, 55.6, 55.5
Germanium		
$C_{14}H_{28}O_8Ge$	18.3	18.1
$C_{16}H_{32}O_8Ge$	17.1	17.2
$C_{18}H_{32}O_6Ge$	17.4	17.4
$C_{18}H_{36}O_8Ge$	16.0	16.0
$C_{20}H_{40}O_8Ge$	15.1	15.1
$C_{24}H_{48}O_8Ge$	13.5	14.0

We thank Miss R. SALES of the British Glass Industry Research Association for samples of standard glasses, Dr. E. R. CLARK of Birmingham College of Advanced Technology for the germanium samples, MAHOMMED BASIT for analysing the arsenic samples, and D.S.I.R. for a grant to one of us (A.G.S.).

SUMMARY

The existence of two forms of several heteropolymolybdates, differing in structure and stability, was confirmed. The unstable β-forms were stabilised by addition of comparatively large amounts of polar organic solvents, especially acetone, presumably because the solvent displaces water from the surface of the heteropoly anion and so inhibits any reorganisation of the structure of the anion. The organic solvent also intensifies the colour. The methods are rapid, sensitive, precise and accurate. Various applications are described.

RÉSUMÉ

Les auteurs ont confirmé l'existence de deux formes de plusieurs hétéropolymolybdates, différant par leur structure et leur stabilité. Les formes β instables ont été stabilisées par addition de solvants organiques polaires, spécialement l'acétone, vraisemblablement en raison du déplacement de l'eau par le solvant à la surface de l'hétéropolyanion. Le solvant organique intensifie aussi la couleur. Ces méthodes sont rapides, sensibles, précises et exactes. Diverses applications sont décrites.

ZUSAMMENFASSUNG

Die Existenz von 2 Formen verschiedener Heteropolymolybdate, die sich in Struktur und Stabilität unterscheiden, wurde festgestellt. Die unstabilen β-Formen wurden durch Zugabe vergleichsweise grosser Mengen polarer organischer Lösungsmittel, besonders von Aceton, stabilisiert; vermutlich weil das Lösungsmittel das Wasser von der Oberfläche des Heteropolyanions verdrängt und dadurch eine Reorganisation der Struktur des Anions verhindert. Das organische Lösungsmittel intensiviert die Farbe. Die Methoden sind schnell, empfindlich, genau und richtig. Verschiedene Anwendungen werden beschrieben.

REFERENCES

1 J. D. H. STRICKLAND, *J. Am. Chem. Soc.*, 74 (1952) 862, 868, 872.
2 L. H. ANDERSSON, *Acta Chem. Scand.*, 12 (1958) 495.
3 A. RINGBOM, P. E. AHLERS AND S. SIITONEN, *Anal. Chim. Acta*, 20 (1959) 78.
4 P. KRUMHOLTZ, *Z. Anorg. Allgem. Chem.*, 212 (1933) 1.
5 R. A. CHALMERS, *Proc. IIIrd Conf. Anal. Chem., Prague, 1959.*
6 J. F. KEGGIN, *Proc. Roy. Soc. (London), Ser. A*, 144 (1934) 75.
7 H. SAINT-CHAMANT AND R. VIGIER, *Bull. Soc. Chim. France*, (1953) 344.
8 R. VIGIER, *Bull. Soc. Chim. France*, (1954) 702.
9 D. H. BERNHART AND A. R. WREATH, *Anal. Chem.*, 27 (1955) 440.
10 H. W. SWANK AND M. G. MELLON, *Ind. Eng. Chem. (Anal.)*, 6 (1934) 348.
11 I. P. ALIMARIN AND B. N. IVANOV-EMIN, *Mikrochemie*, 21 (1936) 1.
12 W. FISHER AND H. KEIM, *Z. Anal. Chem.*, 128 (1948) 443.
13 D. F. BOLTZ AND M. G. MELLON, *Anal. Chem.*, 19 (1947) 872.
14 E. R. SHAW AND J. F. CORWIN, *Anal. Chem.*, 30 (1958) 1314.
15 R. E. KITSON AND M. G. MELLON, *Ind. Eng. Chem. (Anal.)*, 16 (1944) 128.
16 J. P. RILEY, *Anal. Chim. Acta*, 19 (1958) 413.
17 R. A. CHALMERS AND A. G. SINCLAIR, *Anal. Chim. Acta*, in the press.

THE TITRIMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM IN SILICATE ROCKS

M. I. ABDULLAH AND J. P. RILEY
Department of Oceanography, The University, Liverpool, 3 (Great Britain)

(Received February 18th, 1965)

The accurate determination of calcium and magnesium is probably the most troublesome problem in the analysis of silicate rocks for their major components. This arises largely from the difficulty of separating these elements quantitatively from iron, aluminium, titanium and manganese which interfere in both gravimetric and titrimetric procedures for their determination.

In classical gravimetric rock analysis procedures[1-3] the interfering elements are removed by precipitation with ammonium hydroxide in the presence of ammonium chloride; subsequently, calcium and magnesium are precipitated consecutively as their oxalates and ammonium phosphates respectively. At the pH value prevailing during the precipitation of the hydroxides of the interfering elements (*ca.* 8) considerable amounts of calcium and magnesium are co-precipitated. Double or even triple precipitations are necessary to separate calcium. and magnesium quantitatively. Because of the gelatinous nature of the precipitate the separation is very time-consuming, and appreciable amounts of aluminium are usually present in the solution owing to the amphoteric nature of this element. The solution will in addition contain much of the manganese present in the sample unless steps have been taken to oxidize it to insoluble manganese dioxide in the precipitation stage. The manganese then precipitates in part with both calcium and magnesium, and whereas the small amounts of manganese present in igneous rocks do not produce significant errors, the large quantities present in many marine siliceous sediments may cause appreciable errors. The classical silicate procedures are made even more tedious by the necessity for precipitating both calcium and magnesium at least twice if pure precipitates are to be obtained; such multiple precipitations can lead to considerable losses of both elements.

In several schemes for the rapid analysis of silicates[4,5], separation of the interfering elements is carried out by a single precipitation of the hydroxides at pH 6. While the use of this lower pH considerably reduces the amounts of calcium and magnesium co-precipitated, it also reduces the efficiency of the precipitation of aluminium; manganese is not removed at all. Both of these elements interfere seriously in the subsequent titrimetric determination of calcium and magnesium with EDTA. In order to avoid separation processes employing precipitation, with their associated co-precipitation phenomena, solvent extraction has been used for the removal of interfering elements; for example, oxinates of these elements have been extracted in a continuous extractor[6,7]. Although these procedures give cleaner separations than precipitation, not all interfering elements are removed; thus, in the examples cited, manganese is not extracted. As an alternative to removal of the interfering elements, attempts have been made to mask the latter with complexing agents (such as triethanolamine[8]) before the titration of calcium and magnesium with EDTA is carried out. Unfortunately none of the complexing agents at present available is sufficiently strong and selective to mask completely the effect of major amounts of the interfering elements and consequently the end-points of the titrations tend to be indistinct.

In all the rapid titrimetric methods for the determination of calcium and magnesium in rocks, the titrations yield the calcium and total calcium + magnesium, and magnesium is estimated by difference. The titration of calcium is generally carried out at a pH of 12 or more in order to precipitate magnesium as its hydroxide. This precipitate may carry down considerable amounts of calcium and large errors may result in the determination of small amounts of calcium in the presence of much magnesium. Further, the indicators available for the titration of calcium at this pH do not give as sharp an end-point as those used at pH 10 for the titration of total calcium + magnesium.

This paper describes a simple ion-exchange method for the separation of calcium and magnesium from the major elements of silicate rocks (including manganese), from many other elements, and from one another. It is based on the finding that practically all interfering elements can be eluted from a column of Zeo-Karb 225 cation exchanger (ammonium form) by means of a solution of the ammonium salt of ethylenediaminetetraacetic acid at pH 4.5. Calcium and magnesium are not removed at this pH and may be eluted successively with ammonium chloride solution. Although the separation process takes several days, very little manipulation time is required, and if the solution of the rock sample is applied to the ion-exchange column at the start of the general rapid analysis scheme, the separated calcium and magnesium will be ready for titration by the time the other determinations are complete.

Other ion-exchange procedures for the determination of calcium and magnesium in silicates have been described by Japanese workers[9,10]; in these processes the elution was carried out by means of mineral acids and the elements were therefore only separated into groups for titration.

The optimum conditions for the elution of interfering elements from a column of the ammonium form of Zeo-Karb 225 (34 cm in length and 8 mm in diameter) were investigated and it was established that calcium and magnesium were not eluted from the column with 500 ml of 0.22% ethylenediaminetetraacetic acid brought to pH 4.5–4.6 with ammonia. Above a pH value of 6.0 appreciable amounts of both elements were eluted with 500 ml of this reagent. Tests were then carried out in which interfering elements (*ca.* 30 mg) were adsorbed onto the column and then eluted with successive 50-ml portions of the EDTA solution of pH 4.5. The eluates were analysed for the adsorbed element in an appropriate manner. It was found that the following elements were quantitatively removed with 150 ml of EDTA: Al, Fe(III), Ti, Mn(II), Bi, Cd, Cr, Cu, Pb, Mo(VI), Ni, U(VI), V(V), rare earths and Zn. Cobalt required *ca.* 300 ml of EDTA to elute it completely.

If the solution applied to the column was appreciably acid, small amounts of the rather insoluble ethylenediaminetetraacetic acid were precipitated in the column. It was therefore necessary to wash the column with *ca.* 1 l of water before eluting magnesium and calcium. Tests showed that if 200 ml of 0.5 *M* ammonium chloride were then passed through columns containing calcium and magnesium, neither of these elements was eluted. However, a further 240 ml of this reagent eluted magnesium quantitatively. Elution of calcium did not commence until a further 350 ml of the reagent had been passed through the column. In order to speed up the elution of calcium, 1 *M* ammonium chloride was used immediately after the elution of magnesium was complete; 240 ml of this reagent were required for the complete elution of calcium. After calcium had been removed, strontium and barium were still retained on the column, and could if desired presumably be eluted with 2 *N* ammonium chloride and determined by flame photometry.

EXPERIMENTAL

Equipment

An Eel Quantitrator was employed for the photometric titration of calcium and magnesium with EDTA.

Ion-exchange column

Fill an ion-exchange column having an internal diameter of 8 mm with a 34-cm column of Zeo-Karb 225 (52–100 mesh, 8% cross-linked) cation exchanger. Wash the column with 250 ml of 2 *M* hydrochloric acid and then with 50 ml of water. Convert the resin to the ammonium form by passing 200 ml of 2 *M* ammonium chloride solution through it, and then wash with 50 ml of water.

Reagents

Eluting reagents. Prepare ammonium chloride solutions having the following molarities: 0.5, 1 and 2.

Ammonium ethylenediaminetetraacetate eluting agent. Suspend *ca.* 2.2 g of ethylenediaminetetraacetic acid (free acid) in *ca.* 900 ml of water. Add 1 *M* ammonium hydroxide gradually from a buret to the vigorously stirred solution until all the solid has just dissolved. Continue the addition dropwise until the pH of the solution is 4.5. Dilute with water to 1 l.

Standard EDTA solution. Dissolve 1.0 g of ethylenediaminetetraacetic acid (disodium salt) in water, add *ca.* 100 mg of magnesium chloride hexahydrate and dilute to 1 l.

Eriochrome black T indicator. Dissolve 0.1 g of Eriochrome black T in 50 ml of ethanol. Store the solution in an amber bottle and renew at weekly intervals.

Standard calcium solution. Dissolve 0.8925 g of calcium carbonate (A.R.; dried at 110°) in a slight excess of dilute hydrochloric acid. Dilute to 1 l. 1 ml of this solution is equivalent to 500 μg of CaO.

Standard magnesium solution. Dissolve 0.3015 g of "Specpure" magnesium in dilute hydrochloric acid. Dilute to 2 l. 1 ml of this solution is equivalent to 250 μg of MgO.

Determination of calcium and magnesium in silicates

Solution of rock sample. Weigh out 0.5 g of the sample, ground to pass an 80-mesh sieve, into a 25-ml platinum crucible. Add 4 ml of 60% (w/w) perchloric acid and 15 ml of 40% (w/w) hydrofluoric acid and heat the covered crucible on the water bath overnight. On the following morning, remove the crucible lid and evaporate the hydrofluoric acid on the water bath. When no fumes of hydrofluoric acid are visible, place the crucible under an infrared heater and heat until most of the perchloric acid has evaporated but do not bake. Add a further 2 ml of perchloric acid, stir with a platinum rod and then repeat the evaporation. Add 2 ml of perchloric acid and 15 ml of water and heat the covered crucible on the water bath, stirring occasionally with a platinum rod, until the cake has dissolved. Dilute the solution to 500 ml. If the cake resists dissolution, transfer it to a silica flask using *ca.* 100 ml of water, and boil until solution is complete; dilute to 500 ml. The solution corresponds to the solution B of the rapid silicate analysis scheme of RILEY[6], except that the acidity is halved. Prepare a reagent blank solution in the same manner, but omitting the sample.

Ion-exchange separation of calcium and magnesium. Dilute 100 ml of the solution of the rock to *ca.* 200 ml and allow the solution to pass through the ion-exchange column at a flow-rate of 40 ml/h. Maintain the same flow-rate in subsequent operations. Wash the column with *ca.* 200 ml of water and elute the interfering elements with 250 ml of ammonium ethylenediaminetetraacetate reagent. If cobalt is present, 400 ml of the eluting agent should be used. Wash the column with 1 l of water to remove all traces of ethylenediaminetetraacetic acid and follow this with 200 ml of 0.5 M ammonium chloride; reject the washings.

Pass 240 ml of 0.5 M ammonium chloride through the column, dilute the effluent to 250 ml and retain for the titration of magnesium. Pass a further 50 ml of 0.5 M ammonium chloride through the column, and add a few drops of eriochrome black T and 10 ml of ammonium hydroxide (s.g. 0.880); the resultant solution should have a pure blue colour, showing that all magnesium was eluted by the 240 ml of ammonium chloride. If the solution has a pink tinge, titrate it with standard EDTA solution as described below.

Elute calcium from the column with 240 ml of 1 M ammonium chloride and dilute the eluate to 500 ml. After completion of the analysis, regenerate the ion-exchange column by passing 100 ml of 2 M ammonium chloride through it to remove traces of strontium, and wash it well with water.

Titration of calcium and magnesium. Pipet 50 ml of the 0.5 M ammonium chloride eluate containing the magnesium into a titration beaker, and add 150 ml of water, 10 ml of 10 M ammonium hydroxide and 5 drops of eriochrome black T indicator. Titrate the solution photometrically with the standard EDTA solution using an orange filter (maximum transmission at *ca.* 500 mμ, such as Ilford Filter No. 607). If a photoelectric titration apparatus is not available, the titration may be carried out visually, the titration being continued until the solution has attained a pure blue-green colour, free from all traces of pink. The titration of calcium in the 1 M ammonium chloride eluate is carried out in the same fashion using a 100-ml aliquot of the eluate. Standardize the EDTA solution by titrating, as described above, 2-ml and 4-ml aliquots of the standard magnesium and calcium solutions respectively. Carry blank determinations through the whole procedure.

RESULTS

In order to test the efficiency of the analytical process, solutions containing known amounts of calcium and magnesium, together with elements known to interfere in the titration with EDTA, were prepared and analyzed as described above. The results of these analyses (Table I) show that satisfactory recoveries of both calcium and magnesium were achieved in the presence of all the interfering elements tested.

The accuracy of the procedure for the analysis of rocks was tested by analysing the U.S. Geological Survey Standard granite G1 and diabase W1[11] and the Warren Spring Laboratory standard granite R 117[12]. The concentrations of calcium and magnesium found agreed well in each case with the recommended values (Table II).

TABLE I

DETERMINATION OF CALCIUM AND MAGNESIUM IN THE PRESENCE OF INTERFERING ELEMENTS

Interfering element	*Weight (mg)*	*Weight taken (mg)*		*Weight found (mg)*	
		Ca	*Mg*	*Ca*	*Mg*
—	—	20	20	19.99	20.02
Al^{3+}	10	20	20	19.90	19.96
Bi^{3+}	5	10	20	9.97	19.97
Cd^{2+}	5	10	20	9.92	19.99
Cr^{3+}	5	20	20	19.90	19.95
Co^{2+}	5	10	20	10.01	20.12
Cu^{2+}	5	20	20	20.05	19.94
Fe^{3+}	40	20	20	19.92[a]	19.94[a]
Pb^{2+}	2.6	20	20	19.98	19.94
Mn^{2+}		20	20	20.02	20.08
Mo^{6+}	2	20	20	19.96	20.02
Ni^{2+}	5	20	20	20.03	20.04
Ti^{4+}	4	20	20	19.85	19.95
UO_2^{2+}	5	20	20	20.05	19.92
Yb^{3+}	10	20	20	19.91	20.02
Zn^{2+}	5	20	20	19.94	20.06

[a] Mean of 3 determinations.

TABLE II

DETERMINATION OF CALCIUM AND MAGNESIUM IN STANDARD ROCK SAMPLES (% wt.)

	Granite G1		*Diabase W1*		*Granite R 117*	
	Found	*Recommended value*[11]	*Found*	*Recommended value*[11]	*Found*	*Recommended value*[12]
Calcium (as CaO)	1.48		10.90		0.35	
	1.49		10.79		0.32	
	1.49		10.89		0.33	
	Ave 1.49	1.38	10.79		0.35	
			Ave 10.84	10.96	Ave 0.34	0.30
Magnesium (as MgO)	0.43		6.62			
	0.43		6.64			
	0.44		6.66			
	Ave 0.43	0.41	6.67			
			Ave 6.65	6.61	0.024	0.06

The authors wish to thank Dr. P. G. JEFFERY for supplying granite R 117 and the Director of the Warren Spring Laboratory for permission to publish the average calcium and magnesium contents found in this rock in a collaborative test.

SUMMARY

A cation-exchange scheme is described for the separation of calcium and magnesium from interfering elements in rapid silicate analysis. Interfering elements can be eluted from the ammonium form of Zeo-Karb 225 with a solution of the ammonium salt of ethylenediaminetetraacetic acid at pH 4.5. Calcium and magnesium are not eluted with this reagent but can be eluted consecutively with ammonium chloride solution and titrated photometrically with EDTA. Calcium and magnesium can be separated quantitatively from Al, Fe, Ti, Mn, Bi, Cd, Cr, Co, Cu, Pb, Mo, Ni, U, V, rare earths, and Zn.

RÉSUMÉ

Une méthode est proposée pour la séparation du calcium et du magnésium d'avec des éléments gênants dans une analyse rapide de silicates. Les éléments gênants sont élués (de la forme ammonium de Zeo-Karb 225), à l'aide d'une solution d'éthylènediaminetétracétate d'ammonium, au pH 4.5. Ca et Mg sont élués avec une solution de chlorure d'ammonium et titrés photométriquement avec EDTA. Calcium et magnésium peuvent être séparés quantitativement d'avec Al, Fe, Ti, Mn, Bi, Cd, Cr, Co, Cu, Pb, Mo, Ni, U, V, terres rares et Zn.

ZUSAMMENFASSUNG

Zur Abtrennung des Calciums und Magnesiums von störenden Elementen bei der Silikatanalyse wird ein Kationenaustauscher-Schema beschrieben. Störende Elemente können von der Ammoniumform des Zeo-Karb 225 mit einer Lösung des Ammoniumsalzes der Äthylendiamintetraessigsäure beim pH-Wert 4.5 eluiert werden. Calcium and Magnesium werden dabei nicht eluiert, sondern mit Ammoniumchloridlösung und photometrisch mit EDTA titriert. Calcium und Magnesium werden von folgenden Elementen quantitativ getrennt: Al, Fe, Ti, Mn, Bi, Cd, Cr, Co, Cu, Pb, Mo, Ni, U, V, Seltene Erden und Zn.

REFERENCES

1 H. S. WASHINGTON, *Chemical Analysis of Rocks*, 4th Ed., J. Wiley, New York, 1930.
2 A. W. GROVES, *Silicate Analysis*, T. Murby, London, 1938.
3 W. F. HILLEBRAND AND G. E. F. LUNDELL, *Applied Inorganic Analysis*, J. Wiley, 1929.
4 L. SHAPIRO AND W. W. BRANNOCK, *U. S. Geol. Surv. Bull. 1036 C*, 1956.
5 G. LEDENT, *Congo Belge Ruanda-Urundi Dir. Gen. Affaires Econ. Serv. Geol. Bull.*, 6 (1956) 1.
6 J. P. RILEY, *Anal. Chim. Acta*, 19 (1958) 413.
7 J. P. RILEY, *Anal. Chim. Acta*, 21 (1959) 317.
8 K. ARCHER, D. FLINT AND J. JORDAN, *Fuel*, 37 (1958) 421.
9 Y. OKI, S. OKI, H. SHIBATU AND Y. SAKAKIBARA, *Chishitsugaku Zasshi*, 68 (1962) 329.
10 J. YOSHIMURA AND H. WAKI, *Bunseki Kagaku*, 6 (1957) 362.
11 R. E. STEVENS AND W. E. NILES, *U.S. Geol. Surv. Bull. 1113*, 1960.
12 *D.S.I.R. Warren Spring Laboratory Report No. RR/PCS/43*, March 1963.

DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF TARTRATE WITH CHLORANILIC ACID

ARNOLD R. JOHNSON, JR.
*Department of Chemistry, University of Wyoming, Laramie, Wyo. (U.S.A.)**

(Received February 8th, 1965)

A differential spectrophotometric method for the determination of tartrate using chloranilic acid has been developed. Although chloranilic acid has been widely used for various colorimetric metal ion determinations and metal chloranilates have been used for certain anion analysis, no application of chloranilic acid to the determination of tartrate has previously been made. The method is dependent on the difference in absorbance between a reference solution containing a known amount of tartrate and a series of standard solutions containing slightly greater concentrations of tartrate. The reaction is carried out in hydrochloric or perchloric acid media. Differential spectrophotometric techniques have been discussed in the literature[1].

The method developed was applied to the determination of tartrate in tartrate baking powders with good results. The methods presently available[2–4] for total tartrate or tartaric acid in baking powders are generally based on gravimetric procedures, which may give satisfactory results but are often inconvenient and time-consuming. The method described in this paper has the advantage of being rapid while giving results similar to those obtained by the official A.O.A.C. method.

EXPERIMENTAL

Apparatus and reagents

A Beckman Model DU Spectrophotometer equipped with hydrogen lamp, photomultiplier and electronic power supply was used for all absorbance measurements. Matched silica cells were used.

Chloranilic acid reagent. A 0.1% solution was prepared by dissolving 0.5000 g of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone, m.p. 283–284°, Matheson, Coleman and Bell) in distilled water, filtering and finally diluting to 500 ml in a volumetric flask.

Standard tartrate solutions. A 1.000 M solution was prepared by dissolving 115.03 g of reagent-grade sodium tartrate dihydrate and diluting to 500 ml with distilled water. A 0.1000 M solution was prepared by diluting exactly 10.00 ml of the 1.000 M solution to 100 ml in a volumetric flask.

Development of method

Absorption spectra. Absorption curves were constructed for solutions containing: (*a*) chloranilic acid, (*b*) chloranilic acid and hydrochloric acid, (*c*) chloranilic

---

* Present address: Department of Chemistry, Minot State College, N.D., U.S.A.

acid and tartrate, and (*d*) chloranilic acid, hydrochloric acid and tartrate. These curves are shown in Fig. 1. It can be seen from this Fig. that the chloranilic acid and chloranilic acid plus tartrate spectra were essentially identical but the chloranilic acid plus hydrochloric acid curve maximum was shifted to a lower wavelength. With a high concentration of tartrate present, the chloranilic acid–hydrochloric acid curve was shifted to the right and was again similar to the original chloranilic acid and chloranilic acid–tartrate curves. The effect of smaller concentrations of tartrate is discussed below. From these spectra a wavelength of 330 mμ was selected for subsequent quantitative measurements.

Optimum conditions. The concentration of the tartrate reference solution which gave the greatest sensitivity was found by preparing a series of solutions containing increasing concentrations of tartrate and measuring the absorbances relative to each other. The results (Table I) show that the greatest sensitivity was obtained by using 6.00 ml of 1.000 *M* tartrate solution in the reference cell. The optimum concentration of acid was found to be about 0.250 *M* for both perchloric and hydrochloric acids. It was found that although small deviations from this concentration were permissible, the sensitivity was greatly decreased in solutions with significantly higher or lower acid concentrations.

TABLE I

OPTIMUM CONCENTRATION OF TARTRATE

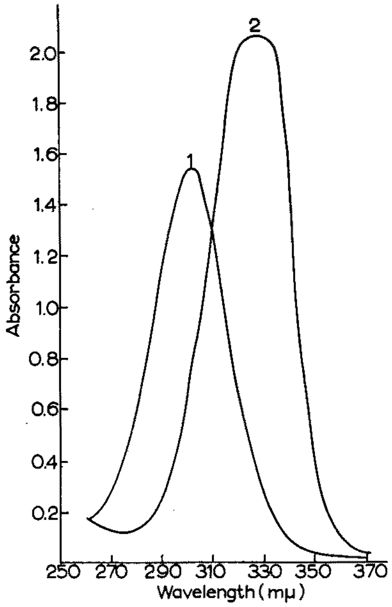
Soln.[a] *no.*	*Tartrate added (1.000 M) (ml)*	*Soln. no.*		*Differential absorbance (ΔA)*
		Set 100	*Read*	
1	0.00	1	2	0.048
2	1.00	3	4	0.093
3	5.00	4	5	0.600
4	6.00	5	6	0.258
5	7.00	7	8	0.110
6	8.00			
7	9.00			
8	10.00			

[a] All solutions were 0.250 *M* in perchloric acid and contained 1.00 ml 0.10% chloranilic acid plus the amount of 1.000 *M* sodium tartrate shown in the Table. Total volume was 50.00 ml. Wavelength was 330 mμ.

Three ml of 0.10% chloranilic acid was considered to be a good compromise concentration for this reagent. This was based on the fact that, although slightly greater sensitivity could be realized by using higher concentrations, it also meant using greater instrumental sensitivities and/or slit widths.

Effect of tartrate concentration on absorption spectra. Absorption curves of solutions containing various concentrations of 0.1000 *M* tartrate were determined; 1.00 ml of 0.10% chloranilic acid was used in these solutions as the absorbance with 3.00 ml, at some wavelengths, was too great to be measured other than by a differential technique. However, it is felt that these curves are analogous to those that would be obtained at the higher chloranilic acid concentrations if they could be determined directly. Several of these curves are shown in Fig. 2.

Examination of Figs. 1 and 2 shows that at the lower concentrations of tartrate added to the chloranilic acid–hydrochloric acid system, a region existed between the 2 spectra maxima extremes shown in Fig. 1, where a significant shift in spectra was obtained with small increases in the tartrate concentration. This shift formed the basis for the procedure developed. It should be apparent from these spectra that only differential measurements held any promise of being successfully applied for analytical purposes. This was of course especially true for greater chloranilic acid concentrations where the absorbance was so great that it could not be measured except by a differential technique.



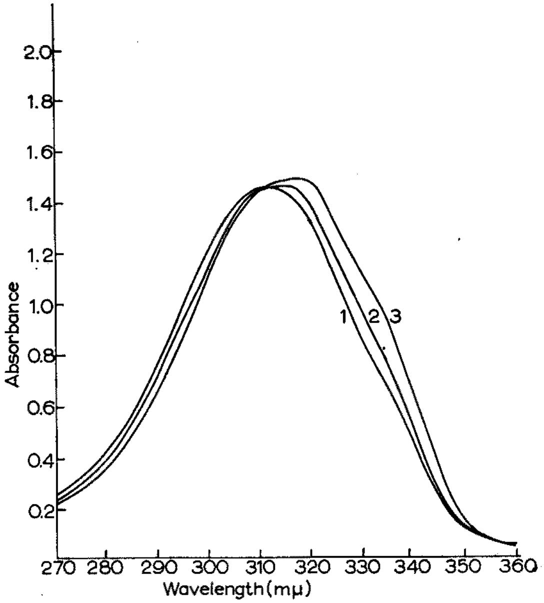
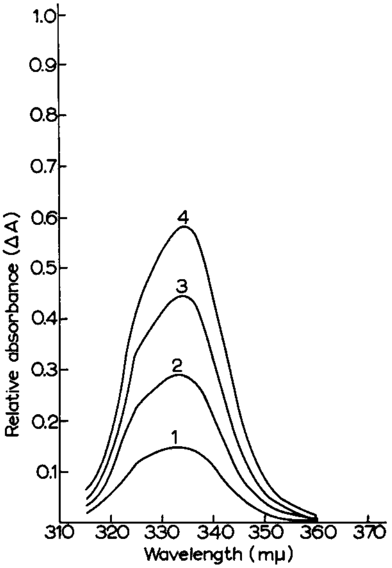


Fig. 1. Absorption spectra. (1) Chloranilic acid–hydrochloric acid (1.00 ml 0.10% chloranilic acid, 0.240 *M* in hydrochloric acid, total volume 50.00 ml); (2) chloranilic acid (1.00 ml 0.10% solution diluted to 50.00 ml), chloranilic acid–tartrate (1.00 ml 0.10% chloranilic acid, 6.00 ml 1.000 *M* sodium tartrate, total volume 50.00 ml), and chloranilic acid–hydrochloric acid–tartrate (1.00 ml 0.10% chloranilic acid, 0.240 *M* in hydrochloric acid, 25.00 ml 1.000 *M* sodium tartrate, total volume 50.00 ml). These 3 curves listed under Curve 2 were all essentially identical and are, therefore, shown as a single curve.

Fig. 2. Absorption spectra of tartrate–chloranilic acid system. (1) 0.240 *M* in hydrochloric acid, 1.00 ml 0.10% chloranilic acid, 6.00 ml 1.000 *M* sodium tartrate, total volume 50.00 ml; (2) same as 1, except that 2.00 ml of 0.1000 *M* sodium tartrate were added; (3) same as 1, except that 5.00 ml of 0.1000 *M* sodium tartrate were added.

Differential absorption curves. Differential absorption curves obtained for standard solutions containing 1.00, 2.00, 3.00 and 4.00 ml of 0.1000 *M* tartrate *versus* a reference solution containing 0.00 ml of 0.1000 *M* tartrate are shown in Fig. 3. When the ΔA values from these curves at 330, 335 and 340 mμ plus others not plotted above, were plotted against concentration, straight-line calibration curves were obtained in each case (Fig. 4). Other wavelengths between 330 and 340 mμ



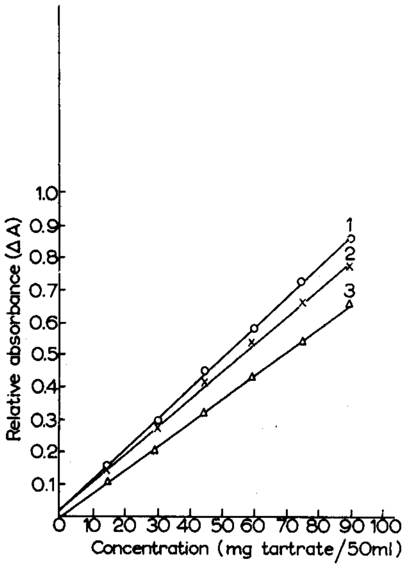


Fig. 3. Differential absorption spectra for tartrate–chloranilic acid system. (1) 0.240 *M* in hydrochloric acid, 3.00 ml 0.10% chloranilic acid, 6.00 ml 1.000 *M* sodium tartrate, 1.00 ml 0.1000 *M* sodium tartrate, total volume 50.00 ml; (2), (3), (4) same as (1) except that 2.00 ml, 3.00 ml and 4.00 ml, respectively of 0.1000 *M* sodium tartrate was added. Reference solution was same as (1), except that no 0.1000 *M* sodium tartrate was added.

Fig. 4. Calibration curves. (1) wavelength 335 mμ; (2) wavelength 330 mμ; (3) wavelength 340 mμ.

would probably give equally good calibration curves. At lower and higher wavelengths, the curves became non-linear or showed greatly decreased sensitivity. It later appeared that perhaps a wavelength of 333 to 335 mμ would have been a better choice than 330 mμ, as the differential absorbance measurements would be less affected by slight errors in setting the wavelength. However, there is no reason to believe that any significant differences in the analytical results would have been obtained.

Calibration curve. As previously mentioned, a linear calibration curve was obtained for standard solutions containing from 1.00 to 7.00 ml of 0.1000 *M* tartrate solution (Fig. 4). Once a calibration curve had been established for a given set of reagents, it was fairly reproducible from day to day. It was, of course, necessary to construct a new calibration curve when any reagent was newly prepared; also for best accuracy, the calibration curve should be checked periodically. Absorbance measurements could be made immediately after preparing solutions or after several hours, as the color developed rapidly and seemed to be quite stable. Detailed directions for the construction of a standard curve are given below.

The reagents are listed in the order in which they were added in this investigation. This order was found to be convenient, but it seems likely that others would be equally satisfactory.

Procedure. Pipet 2.00-ml aliquots of 6.00 *M* hydrochloric acid and 6.00 ml of 1.000 *M* sodium tartrate solution into 50.00-ml volumetric flasks. Next measure accurately 0.00 to 7.00 ml aliquots of the standard 0.1000 *M* sodium tartrate solution into these flasks and then pipet exactly 3.00 ml of 0.10% chloranilic acid solution into each flask and dilute to volume with distilled water. Mix the solutions thoroughly and measure the absorbance of each solution relative to the solution containing 0.00 ml of 0.1000 *M* tartrate solution as reference. Construct the calibration curve to read mg of tartrate per 50.00 ml of solution.

Tartrate could be determined by this method only when present as the tartrate ion and not as the acid tartrate ion or as tartaric acid; when it was present as either of these latter two species it had first to be neutralized with base.

TARTRATE IN BAKING POWDER

The preceding method was applied to the determination of total tartrate or tartaric acid and compared with the results obtained by the official A.O.A.C. method for total tartaric acid.

Procedure

Weigh 2.500-g samples of baking powder into 250-ml volumetric flasks, add 100 ml of distilled water at about 50° and allow to stand at room temperature for at least 30 min with occasional shaking. Cool the solutions, dilute to volume with distilled water, shake vigorously and filter through large Whatman No. 42 filter papers. Filter again to obtain a clear filtrate. The procedure up to this point is essentially the A.O.A.C. procedure. (For the remainder of the A.O.A.C. procedure see ref. 1.)

Prepare the solutions as described in the "*Calibration curve*" section and pipet 10.00-ml aliquots of the clear baking powder solutions into the flasks in place of the standard 0.1000 *M* tartrate solution. Complete the procedure as described previously. Determine the number of mg of tartrate in 50.00 ml from a standard curve and calculate the percent total tartaric acid.

Results

The analytical results obtained are summarized in Table II. The commercial

TABLE II

DETERMINATION OF TARTARIC ACID IN BAKING POWDER

Sample	*Total tartaric acid added (%)*	*Total tartaric acid found (%)*	
		A.O.A.C.	*Differential method*
Synthetic samples			
1	31.69	31.80	31.98
2	27.52	27.90	27.48
3	28.96	—	29.07
Commercial baking powder		29.69, 30.00, 30.05, 29.78, 29.85, 29.93, 29.85 Mean=29.87 Standard deviation 0.12%	29.90, 29.95, 29.80, 29.90, 30.00, 30.20, 30.25 Mean=30.00 Standard deviation 0.17%

tartrate baking powder contained sodium bicarbonate, starch, potassium acid tartrate and tartaric acid. Synthetic baking powder No. 1 contained sodium bicarbonate, starch and potassium acid tartrate; no. 2 contained sodium bicarbonate, starch, potassium acid tartrate and tartaric acid; no. 3 contained sodium bicarbonate, tartaric acid and starch.

It can be seen from these data that the proposed method compares favorably with the A.O.A.C. method. Although the A.O.A.C. method gives good results, it has the disadvantages previously mentioned. It is believed that the proposed method could be further refined to give even better precision and accuracy by development of a permanent reference standard.

Appreciation is expressed to the University of Wyoming Graduate Research Council for support of this research.

SUMMARY

A differential spectrophotometric method for the determination of tartrate using chloranilic acid is described. Standard and sample solutions containing slightly more tartrate than the reference solution, are measured relative to it. The procedure is applicable to the determination of tartrate in baking powder; the results obtained compared favorably with the official A.O.A.C. method.

RÉSUMÉ

Une méthode spectrophotométrique différentielle est décrite pour le dosage des tartrates au moyen d'acide chloranilique. Ce procédé est applicable au dosage de tartrates dans la levure. Les résultats obtenus sont avantageusement comparables à ceux de la méthode de l' "Association of Official Agricultural Chemists".

ZUSAMMENFASSUNG

Es wird eine differentialspektralphotometrische Methode zur Bestimmung von Tartrat unter Anwendung von Chloranilsäure beschrieben. Standard- und Probenlösungen, die etwas mehr Tartrat als die Vergleichslösung enthalten, werden relativ dazu gemessen. Das Verfahren ist für die Bestimmung von Tartrat in Backpulver anwendbar. Die erhaltenen Ergebnisse stimmen gut mit der offiziellen A.O.A.C.-Methode überein.

REFERENCES

1 D. F. BOLTZ AND G. H. SCHENK, in L. MEITES, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963.
2 ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, *Methods of Analysis*, 9th Ed., Washington, D. C., Association of Official Agricultural Chemists, 1960, p. 98–99.
3 C. H. MANLEY, *Analyst*, 62 (1937) 526.
4 I. SARDI AND G. HERTELENDI, *Z. Lebensm. Untersuch.-Forsch.*, 95 (1952) 179; *C.A.*, 46 (1952) 11477i.

LA METHODE POLAROVOLTRIQUE

PRINCIPES GÉNÉRAUX ET BASES DE LA MÉTHODE

J. E. DUBOIS ET P. C. LACAZE
Laboratoire de Chimie Organique Physique, Faculté des Sciences, Paris, 5e (France)

(Reçu le 7 Avril, 1965)

Une méthode analytique très générale, qui utilise les propriétés d'électrodes de platine plongées en milieu liquide, et entre lesquelles est appliquée une tension électrique extérieure, en série avec une résistance, a été proposée dès 1952 par DUBOIS ET WALISCH[1]. Cette méthode dont nous nous proposons de rappeler le principe a reçu le nom de *polarovoltrie*[2,3].

Sa mise au point, réalisée par l'étude expérimentale de plusieurs circuits électriques entre électrodes de platine ainsi que par l'étude de réseaux de courbes de polarisation particuliers, a conduit à la construction de divers appareillages[4-6], ainsi qu'au choix d'un circuit de polarisation. Ce dernier, inclus dans la construction du polarovoltmètre standard, permet d'accomplir d'une manière semi-automatique la plupart des dosages rencontrés.

Les applications analytiques de la méthode sont multiples, tant dans le domaine de la chimie minérale que celui de la chimie organique: dosage des acides et des bases[1], dosage d'oxydo-réduction[2,7,8], précipitation des halogénures par le nitrate d'argent[9], dosage du carbonyle[10], dosage de l'eau par la méthode de KARL FISCHER[11], dosage de bases organiques faibles dans des solvants non aqueux (nitrobenzène, méthanol, acétonitrile, acide acétique et méthylisobutylcétone)[12], et récemment des applications plus complexes relatives à l'asservissement de concentrations de brome dans un solvant organique, à l'aide d'un coulomètre, ce qui a permis la réalisation de "concentrostats" utilisés dans la mesure de cinétique rapide[13,14].

PRINCIPE DE LA MÉTHODE

Considérons le circuit électrique représenté sur la Fig. 1, où U représente la source de tension extérieure, R la résistance en série avec les électrodes A et C placées dans la solution à doser, V la tension mesurée entre ces électrodes, et I l'intensité du courant d'électrolyse. La loi d'Ohm appliquée à ce circuit donne la relation $U = RI + V$.

Lorsque U et R ont des valeurs moyennes, les variations relatives de I et de V sont comparables, comme le montre la relation:

$$\frac{\Delta I}{I} = -\frac{\Delta V}{RI} = -\frac{\Delta V}{V}\left(\frac{V}{U-V}\right)$$

Dans le cas de la polarovoltrie, où la variable mesurée est la tension V aux électrodes, et où $U = 3$ V et R = 0.5 mégohm, les variations relatives de I sont comprises entre 10 et 50%. Ceci correspond à des valeurs de ΔV comprises entre 0.2 et 1 V, pour une valeur initiale de V égale à 1 V. (Les faibles valeurs de ΔV correspondent généralement au domaine des solutions aqueuses, alors que les fortes variations de V se produisent fréquemment dans les solvants organiques.)

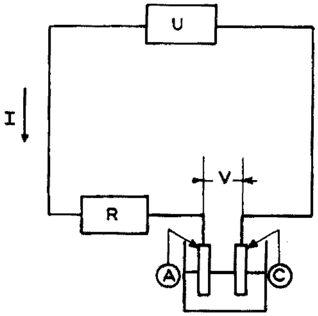


Fig. 1. Circuit d'électrolyse. U, source de tension (3 V); R, résistance (0.5 mégohm); I, intensité du courant d'électrolyse; A, anode; C, cathode; V, tension aux électrodes.

Les cas limites de la méthode apparaissent pour: (*a*) U et R très grands ($U=$ 100 V, $R=50$ ou 100 mégohms), et (*b*) U faible ($U < 0.5$ V), et $R=0$.

Dans le premier cas, I est sensiblement constant, ($\Delta I/I \sim 1\%$ pour $U = 100$ V), la seule variable qui peut être mesurée est V. Ce cas limite est celui de la potentiométrie à "intensité constante" ou encore selon une classification récente, celui de la "bipotentiométrie à intensité constante"[15].

Dans le deuxième cas, où U est faible et R nul, la tension V aux électrodes est constante et égale à U, la variable utilisable est I. Ce dernier cas limite correspond à celui de l'ampérométrie.

Dans le cas général où V et I sont variables, la mesure de I peut également être utilisée à des fins analytiques, et dans ce cas nous avons l'équivalent d'une méthode ampérométrique à tension variable, que l'un d'entre nous a précédemment nommé polarammétrie[2].

UTILISATION DES RÉSEAUX DE COURBES DE POLARISATION À LA PRÉVISION DES COURBES DE DOSAGE ENTRE 2 ÉLECTRODES DE PLATINE

La forme d'une courbe de dosage entre 2 électrodes de platine identiques, peut être facilement, dans le cas de la potentiométrie à intensité constante, déduite du réseau classique des courbes de polarisation $I = \mathrm{f}(E)$, obtenu à l'aide d'un montage à 3 électrodes.

En fait, le passage du réseau de ces courbes de polarisation à la courbe de dosage n'est valable que pour des solutions peu résistantes. La courbe de polarisation $I=\mathrm{f}(E)$ donne en effet le potentiel de l'électrode par rapport à une électrode de référence, alors que la tension V mesurée au cours d'un dosage est égale à $(E_A - E_C) + rI$, où E_A et E_C désignent les potentiels respectifs de l'anode et de la cathode, r la résistance de la solution, et I l'intensité du courant.

Or, dans des solvants organiques peu conducteurs, la résistance r peut atteindre des valeurs très élevées, et par suite l'écart entre V et $E_A - E_C$ est également grand.

Aussi pour éviter ces difficultés, et afin de se placer dans des conditions d'emploi des électrodes identiques à celles du dosage, nous avons préféré utiliser 2 types de réseaux, pour lesquels les grandeurs mesurées ne font par intervenir le potentiel de chaque électrode, mais seulement la tension entre ces 2 électrodes.

C'est ainsi que nous avons tracé les réseaux:

$V = \mathrm{f}(U)$ pour R déterminée

et $I = \mathrm{f}(V)$

où V, tension résultante aux électrodes est mesurée directement en l'absence d'électrode de référence.

Afin de rendre ceci plus explicite, nous étudierons 2 exemples:

(*a*) courbe de dosage de l'acide sulfanilique par le nitrite de sodium, déduite du réseau $I = \mathrm{f}(V)$ (Fig. 2).

(*b*) courbe de dosage de l'aniline par le brome, déduite du reseau $V = \mathrm{f}(U)$, pour $R = 0.5$ mégohm (Fig. 3).

(On a posé Z = degré d'avancement de la réaction de neutralisation = rapport de la quantité de réactif titrant versé à la quantité de corps à titrer.)

(a) Utilisation du réseau $I = \mathrm{f}(V)$. Le réseau $I = \mathrm{f}(V)$ des courbes de diazotation a été obtenu entre 2 électrodes de platine dissymétriques: une électrode tournante (1000 t/min), constituée par un fil de platine cylindrique de 8/10 mm de diamètre et de 5 mm de longueur, et une électrode fixe, cylindrique et coaxiale à la première, constituée par une grille de platine irridié de 2 cm de diamètre et de 12 mm de hauteur.

Le tracé des courbes $I = \mathrm{f}(V)$ a été effectué en présence d'un barbotage d'azote, et les électrodes ont été préalablement nettoyées à l'aide de l'acide nitrique bouillant et concentré.

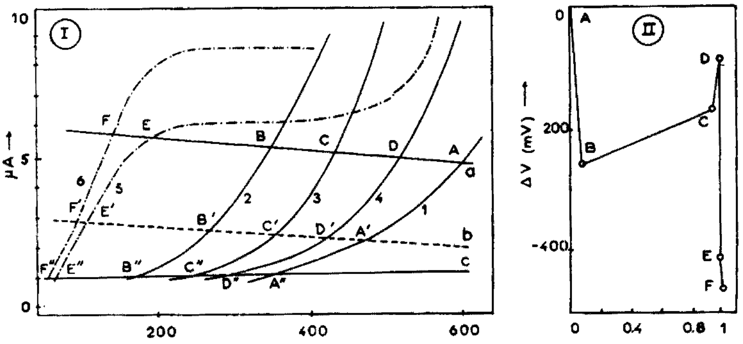


Fig. 2. Réseau de courbes $i = \mathrm{f}(V)$ de l'acide sulfanilique neutralisé par le nitrite de sodium (I) L'acide sulfanilique est dissout dans 100 ml d'acide chlorhydrique 6 N. Sa concentration initiale est 0.01 N, celle du réactif 0.1 N. Les courbes correspondent à différents degrés d'avancement de la réaction de neutralisation: $Z_1 = 0$; $Z_2 = 0.05$; $Z_3 = 0.96$; $Z_4 = 1$; $Z_5 = 1.006$; $Z_6 = 1.009$. La droite (*a*) est définie pour les valeurs $U = 3$ V et $R = 0.5$ mégohm (Polarovoltmètre standard); les droites (*b*) et (*c*) sont respectivement définies pour les couples de valeurs: $U = 1.5$ V et $R = 0.5$ mégohm; $U = 50$ V et $R = 50$ mégohms. (II) Courbe de dosage polarovoltrique déduite du réseau I.

L'électrode tournante fonctionne en cathode et la variation de la tension entre les 2 électrodes est linéaire en fonction du temps, et égale à 5.5 V/h.

Les courbes 1, 2, 3 et 4 de la Fig. 2 correspondent à la disparition progressive de l'acide sulfanilique, et les courbes 5 et 6 à un excès du réactif $NaNO_2$.

A partir de ce réseau, on peut facilement choisir les paramètres électriques U et R qui donneront la meilleure courbe de dosage. Il suffit de tracer les droites d'équation $V = U - RI$, dans le même système d'axes V, I. Les paramètres U et R définissent 2 familles de droites: D_1 (U) pour R constant, et D_2 (R) pour U constant. Les points d'intersection de ces droites avec les courbes du réseau précédent représentent le "point figuratif du dosage" pour différentes valeurs de Z.

Dans le cas de la polarovoltrie, nous avons tracé les droites AF, correspondant à $U = 3$ V et $R = 0.5$ mégohm, et A'F', correspondant à $U = 1.5$ V et $R = 0.5$ mégohm. Un exemple de potentiométrie à intensité constante (1 μA) est donné par la droite A''F''.

La valeur du saut de potentiel après le point équivalent correspond dans chaque cas à la projection des segments DE, D'E' et D''E'' sur l'axe des tensions.

D'après ce graphique, nous voyons que s'il y a intérêt à augmenter la tension appliquée U, pour une même valeur de R, afin d'accroître la valeur du saut lié à l'intervalle DE, on note également que l'erreur de titrage devient plus importante. Aussi l'obtention simultanée d'un saut de potentiel élevé et d'une erreur de titrage faible, implique pour le cas de la diazotation un choix raisonnable des valeurs $U = 3$ V et $R = 0.5$ mégohm, auquel correspond un courant d'électrolyse compris entre 5 et 6 μA.

(b) Utilisation du réseau $V = \mathrm{f}(U)$. Le deuxième type de réseau, d'interprétation plus simple que le précédent, présente cependant l'inconvénient d'imposer un choix préalable et arbitraire de R, ce qui limite son utilisation à une valeur particulière de la résistance.

Ainsi le réseau $V = \mathrm{f}(U)$, représenté sur la Fig. 3, et relatif au dosage de l'aniline par bromation n'est valable que pour $R = 0.5$ mégohm.

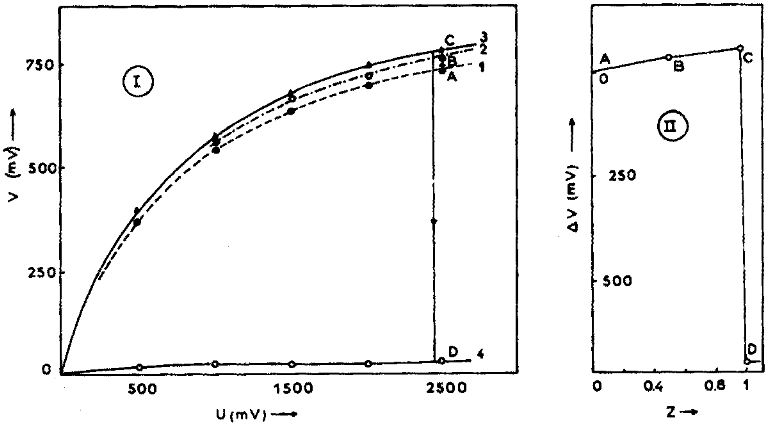


Fig. 3. Réseau $V = \mathrm{f}(U)$ ($R = 0.5$ mégohm). (I) Dosage de l'aniline $2.5 \cdot 10^{-3}$ M par le mélange bromure–bromate de potassium $1.5 \cdot 10^{-2}$ M. Solvant = 25 ml eau + 25 ml méthanol; HCl 1.2 N; KBr 0.33 N. Les courbes correspondent à différentes valeurs de Z: $Z_1 = 0$; $Z_2 = 0.5$; $Z_3 = 0.99$; $Z_4 = 1.006$. A, B, C et D représentent le point figuratif du dosage pour les valeurs de Z correspondantes. (II) Courbe de dosage polarovoltrique déduite du réseau I.

Les courbes de ce réseau, tracées point par point, ont été obtenues dans des conditions expérimentales différentes de l'exemple précédent: les électrodes sont 2 fils de platine de 10 mm de long et distants de 5 mm l'un de l'autre; la solution est agitée au moyen d'un barreau aimanté entraîné magnétiquement à la vitesse de 600 t/min.

L'évolution du "point figuratif du dosage" en fonction de Z est représentée par les points A, B, C, et D. La valeur du saut de potentiel au point équivalent, correspondant à CD croît rapidement avec la tension pour les faibles valeurs de U. Une limite est pratiquement atteinte lorsque $U = 3$ V, et le saut de potentiel est alors supérieur à 750 mV.

C'est à la suite d'essais systématiques de ce genre, pour différents types de dosages (oxydo-réduction, acidimétrie, chélation et précipitation) qu'ont été adoptées pour U et R, les valeurs standard de 3 V et 0.5 mégohm, qui permettent ainsi d'effectuer un très grand nombre de dosages, avec une précision comprise entre 0.5 et 0.2%, dans le cas de solutions 0.01 et 0.05 N et par des réactifs 0.1 et 0.2 N.

A partir des valeurs électriques de U et R précédemment choisies, et en tenant compte des propriétés particulières aux électrodes de platine, et plus généralement des électrodes métalliques, on peut alors envisager simplement la construction d'un titrimètre automatique.

CONSTRUCTION D'UN TITRIMÈTRE AUTOMATIQUE À ELECTRODES DE PLATINE POLARISÉES (POLAROVOLTMÈTRE DIFFÉRENTIEL)

Il est bien connu que les indications de potentiel d'une électrode de platine dépendent de multiples facteurs, dont essentiellement des effets de surface. Ainsi le recouvrement de l'électrode par des films organiques ou par des oxydes peut être une cause de non réproductibilité.

Ces effets peuvent être minimisés, comme par exemple pour le tracé des courbes de polarisation, en utilisant chaque fois le même mode de nettoyage de l'électrode et une courte durée de fonctionnement.

Dans le cas des dosages, ces conditions sont plus difficiles à réaliser, et par suite on ne peut espérer obtenir des indications de potentiel très reproductibles.

Heureusement, la seule indication pratique qui soit reproductible, et indépendante de l'état des électrodes, est la position par rapport à Z du saut de potentiel au moment du virage, bien que son amplitude puisse également subir des variations pouvant atteindre jusqu'à 10%.

Ainsi, entre plusieurs dosages consécutifs, dont les conditions chimiques sont identiques, on observe statistiquement à l'endroit du point équivalent ($Z = 1 \pm \varepsilon$), une plage de potentiel, pour laquelle les courbes sont confondues et dont l'étendue représente les 7 à 9/10 de la valeur totale du saut de potentiel.

Cette dernière propriété justifie à elle seule l'emploi des électrodes de platine en chimie analytique, par le fait que leur utilisation, qui est d'une grande simplicité, peut s'étendre aux solvants organiques, et que par ailleurs, ces électrodes ont l'avantage de permettre, par rapport à l'électrode à goutte de mercure, l'étude de toute une série de dosages faisant intervenir des systèmes chimiques situés en zone anodique éloignée.

Ces dernières remarques nous amènent à envisager la construction d'un titrimètre à électrodes métalliques dans un but différent de celui de la potentiométrie classique, et pour laquelle la notion de précision absolue n'apparaît plus justifiable.

La seule grandeur utilisable étant la variation de V au point équivalent, l'opposition d'un potentiel V_0 variable, dont la valeur n'est pas nécessairement connue, permettra de suivre cette variation avec une "échelle de mesure dilatée", et de négliger la non reproductibilité des électrodes entâchant inévitablement la mesure de cette différence de potentiel V en début de dosage.

L'appareil connu sous le nom de polarovoltmètre différentiel, réunit en un seul ensemble, 3 éléments distincts, représentés sur la Fig. 4:

(*1*) le circuit de polarisation des électrodes: tension U, résistance R, électrodes A et C.

(*2*) le circuit de mesure de la différence de potentiel aux électrodes, c'est-à-dire le voltmètre différentiel. (L'appareil de mesure comporte 5 sensibilités, qui font correspondre aux 100 divisions du cadran les tensions respectives de 5, 1, 0.5, 0.25 et 0.125 V.)

(*3*) un dernier élément, constitué par une bascule de Schmitt qui commande la fermeture ou l'ouverture d'une valve électromagnétique de burette, afin de rendre les dosages automatiques.

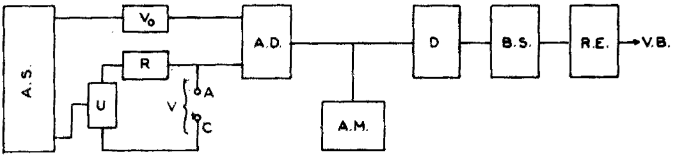


Fig. 4. Schéma de principe. *A.S.*, alimentation stabilisée. (I) *circuit d'électrolyse*: U, tension appliquée aux électrodes par l'intermédiaire de la résistance R, égale à 3 V; R, résistance égale à 0.5 mégohm; A, anode; C, cathode; V, tension aux électrodes. (II) *circuit de mesure*: *A.D.*, amplificateur différentiel; *A.M.*, appareil de mesure; V_0, tension de référence variable. (III) *circuit de commande de la valve électromagnétique de burette*: D, diviseur de tension; *B.S.*, bascule de Schmitt; *R.E.*, relais électromagnétique; *V.B.*, valve de burette.

Le nom de polarovoltmètre a été choisi d'une part pour souligner qu'il ne s'agit pas de prétendre faire des mesures absolues de potentiométrie, au sens propre du mot, et d'autre part pour rappeler par la contraction des mots "polaro" et "voltmètre", que l'appareil effectue des mesures de d.d.p. entre électrodes, polarisées par une source de tension extérieure.

Par ailleurs, au lieu de prévoir un circuit de polarisation avec de multiples possibilités électriques, c'est-à-dire, U et R laissées au choix de l'utilisateur, nous avons préféré fixer U et R à 2 valeurs standard de 3 V et 0.5 mégohm, et montrer qu'il reste encore à jouer sur le milieu chimique, pour obtenir des modifications de courbes bien plus importantes que celles que l'on peut espérer obtenir en ne faisant varier que les paramètres électriques.

MORPHOLOGIE DES COURBES. NOTATION SYMBOLIQUE

La forme de ces courbes au voisinage du point équivalent peut être soit un S (droit ou renversé), lorsque une seule électrode est indicatrice, soit un V renversé plus ou moins déformé, qui se produit chaque fois que les 2 électrodes sont indicatrices.

Ces courbes de dosages polarovoltriques ne permettent cependant pas d'identifier directement les réactions électrochimiques qui ont lieu aux électrodes, car la tension mesurée n'est pas une grandeur absolue, mais seulement une grandeur différentielle.

Elles s'opposent en cela aux courbes de dosages potentiométriques à courant nul, en forme de S, pour lesquelles des mesures de potentiel absolu peuvent être effectuées, et à partir desquelles l'identification des systèmes électrochimiques est rendue possible, dans le cas il est vrai seulement de systèmes rapides.

Aussi pour rémédier à cet inconvénient des courbes polarovoltriques, nous avons introduit une notation symbolique, déduite de l'étude des réseaux de courbes de polarisation classiques, et dont le but précisément est de nous renseigner sur la nature des réactions électrochimiques qui ont lieu aux électrodes au voisinage du point de virage.

Afin d'expliciter cette dernière proposition, nous examinerons à titre d'exemple le dosage des amines aromatiques par l'acide perchlorique, en milieu acétique. Les courbes polarovoltriques ont la forme d'un S. Le cas typique est celui de la N,N-diéthylaniline, dont nous avons montré précédemment les applications analytiques de son perchlorate dans différents solvants[12].

L'anode est la seule électrode indicatrice, et d'après la Fig. 5, la variation de la tension au point équivalent correspond au passage du potentiel de cette électrode, du réseau des courbes d'oxydation de l'amine à celui de l'amine perchloratée.

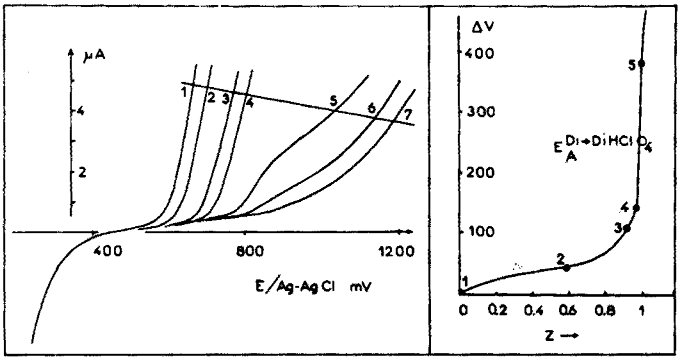


Fig. 5. Réseau de courbes de polarisation de la N,N-diéthylaniline neutralisée par $HClO_4$. Courbe polarovoltrique déduite du réseau. Les courbes numérotées de 1 à 7 correspondent à différentes valeurs de Z. La solution initiale (non dégazée) contient 56.8 mg d'amine dans 40 ml d'acide acétique saturé en perchlorate de N,N-diéthylanilinium. $Z_1 = 0$; $Z_2 = 0.58$; $Z_3 = 0.9$; $Z_4 = 0.97$; $Z_5 = 0.995$; $Z_6 = 1.02$; $Z_7 = 1.04$. L'électrode de travail est une électrode de platine tournante: 1000 t/min, 5 mm de long, 0.8 mm de diamètre. Elle est nettoyée au moyen de l'acide nitrique avant chaque tracé.

Nous avons représenté cette variation de potentiel par la notation $E_A^{Di\rightarrow DiH^+ClO_4^-}$; elle rappelle sur la courbe de dosage que la variation de tension (E) se produit à l'anode (A), et qu'elle correspond au passage de transition des courbes d'oxydation de la N,N-diéthylaniline (Di), à celles de son perchlorate ($DiH^+ClO_4^-$).

Outre la possibilité d'interprétation de la courbe de dosage, cette notation présente également l'avantage d'indiquer à l'utilisateur, les facteurs déterminants du titrage.

Ainsi dans le cas présent, nous savons que c'est l'anode qui est l'électrode indicatrice, et qu'elle est seule responsable du saut de potentiel au point équivalent.

Comme cependant elle est indicatrice dans une zone de potentiel anodique élevé, nous pouvons dans certains cas nous attendre à rencontrer des phénomènes de passivation d'électrode, qui auront pour effet d'annuler le saut de potentiel à l'endroit du virage.

C'est précisément ce qui se produit pour certaines amines aromatiques comme l'aniline. Celle-ci est en effet très facilement oxydable, et pendant tout le temps de l'électrolyse, la surface de l'électrode se recouvre de films organiques qui peuvent la rendre inutilisable pour le dosage suivant[16].

L'origine de ce phénomène étant connue, il suffit alors de nettoyer l'anode à l'aide de l'acide nitrique pour régénérer sa surface, et permettre à nouveau son fonctionnement normal.

La pleine utilité de cette notation est également mise en évidence dans l'étude des dosages de diacides carboxyliques en milieu N,N-diméthylformamide, pour lesquels nous avons rencontré différentes formes de courbes, qui peuvent être en fait ramenées à quelques types fondamentaux[17,18].

La détection des deux acidités est rendue possible par l'intermédiaire de deux réactions électrochimiques distinctes, se produisant pour $Z = 1/2$ et $Z = 1$. Le premier signal d'électrode correspondant à la disparition de H^+ ($Z = 1/2$) ou ($Z = 1$), est dû à la transition de passage du potentiel de la cathode, des courbes de réduction des ions H^+ à celles du solvant, et a été caractérisé par la notation $E_C{}^{H^+ \rightarrow S}$. Le second signal d'électrode, noté $E_A{}^{S \rightarrow OH^-}$, dû à un excès de réactif basique en solution, correspond à la transition de potentiel de l'anode, des courbes d'oxydation du solvant à celles du réactif titrant. L'existence de ces 2 signaux distincts permet alors de prévoir la possibilité théorique de 4 types fondamentaux de courbes.

Le signal $E_A{}^{S \rightarrow OH^-}$ qui correspond à un excès de réactif, ne peut en effet se produire qu'après le signal $E_C{}^{H^+ \rightarrow S}$. Lorsque $E_C{}^{H^+ \rightarrow S}$ se produit pour $Z = 1/2$, $E_A{}^{S \rightarrow OH^-}$ peut apparaître pour $Z = 1/2$ ou $Z = 1$. Si $E_C{}^{H^+ \rightarrow S}$ se produit pour $Z = 1$ (2 protons équivalents), $E_A{}^{S \rightarrow OH^-}$ ne peut avoir lieu que pour $Z = 1$.

Enfin le cas où le signal $E_C{}^{H^+ \rightarrow S}$ n'apparaît pas du fait de la trop faible dissociation des hydrogènes, alors que le signal $E_A{}^{S \rightarrow OH^-}$ continue de subsister pour $Z = 1$, nous permet effectivement d'envisager 4 possibilités de dosage différentes.

Cette dernière proposition sera démontrée et analysée lors de l'étude des dosages polarovoltriques de quelques diacides organiques, de même que sera donnée une interprétation des modifications de courbes apportées par des effets de sels et de réactifs titrants[17].

Par ces quelques exemples, nous voyons dès maintenant que l'utilisation de cette notation transforme les courbes polarovoltriques en des courbes facilement interprétables, susceptibles de donner des renseignements pratiques dans la conduite d'un dosage entre électrodes de platine.

Cette notation présente également l'avantage, de permettre une classification cohérente des différents types de courbes qui peuvent être rencontrées dans le cas d'une série de dosages faisant intervenir les mêmes types de réactions électrochimiques.

Nous remercions Mademoiselle M. QUINTIN, Professeur à la Faculté des Sciences de Paris et Monsieur I. EPELBOIN, Directeur de Recherches au CNRS pour les observations et les conseils qu'ils ont bien voulu nous donner au cours de la rédaction de ce travail.

RÉSUMÉ

Nous avons rappelé les différentes étapes qui ont conduit à la méthode polarovoltrique et à la conception d'un nouveau titrimètre automatique, utilisant les propriétés de 2 électrodes de platine polarisées. Les bases de la méthode ont été déduites de l'utilisation systématique de 2 types de réseaux de polarisation appliqués à différents systèmes chimiques. Ces réseaux de polarisation du type $I = \mathrm{f}(V)$ et $V = \mathrm{f}(U)$ sont obtenus directement entre 2 électrodes indicatrices, et sans électrode de référence (V, tension aux électrodes; U, tension appliquée aux électrodes par l'intermédiaire d'une résistance R).

Ils présentent l'avantage par rapport au réseau classique $I = \mathrm{f}(E)$, où E représente le potentiel d'une électrode indicatrice par rapport à une électrode de référence, de faciliter la prévision des courbes de dosage en fonction du choix de la résistance R et de la tension U. Leur emploi a montré que les paramètres électriques du polarovoltmètre différentiel pouvaient être fixés aux valeurs standard $U = 3$ V et $R = 0.5$ mégohm, adaptés à la réalisation de dosages semi-automatiques.

Une notation symbolique a été définie afin de rappeler l'origine des différentes variations de tension. Elle permet une interprétation simple des courbes polarovoltriques, et une utilisation rationnelle d'électrodes dissymétriques.

SUMMARY

The various steps in the development of the polarovoltric method and its utilisation in an automatic titration apparatus employing 2 polarized platinum electrodes are described. The method is based on the use of 2 types of polarization relationships applied to different chemical systems. These relationships are of the type $I = \mathrm{f}(V)$ and $V = \mathrm{f}(U)$, where V is the potential measured at the electrodes and U the potential applied to the electrodes across a resistance R, and are obtained directly from 2 indicating electrodes without the need for a reference electrode.

The advantage of these relationships over the classic $I = \mathrm{f}(E)$ curves, where E is the potential of the indicating electrode with respect to a reference electrode, is to facilitate the prediction of the titration curves as a function of the resistance R and the applied voltage U. The use of these relationships has shown that a fixed applied voltage U of 3 V and a fixed series resistance R of 0.5 megohm are the most suitable for a differential polarovoltmeter for semi-automatic titrations.

A symbolic notation is described which indicates the origin of the observed variations in potential. This notation permits a simple interpretation of polarovoltric curves and the rational use of unsymmetrical electrode arrangements.

ZUSAMMENFASSUNG

Die verschiedenen Etappen, die uns zur Polarovoltrie sowie zur Entwicklung eines neuen automatischen Titrationsapparates mit 2 polarisierten Elektroden geführt haben, werden beschrieben. Die Methode beruht auf der Anwendung zweier Polarisationsbeziehungen auf verschiedene chemische Systeme. Diese Polarisationsbeziehungen sind: $I=f(V)$ und $V=f(U)$. Sie werden ohne Anwendung einer Bezugselektrode direkt zwischen 2 Indikationselektroden gemessen (V=Spannung an den Elektroden, U=angewandte Spannung unter Zwischenschaltung eines Widerstandes R).

Gegenüber der klassischen Beziehung $I=f(E)$ (E=Potential zwischen Indikator- und Bezugselektrode) haben diese den Vorteil, die Form der Titrationskurven in Abhängigkeit vom Widerstand R und der Spannung U leichter vorauszusagen.

Die Untersuchung dieser Polarisationsbeziehungen hat gezeigt, dass für eine halbautomatische Titration mit einem differentiellen Polarovoltmeter Standardwerte benutzt werden können ($U=3$ V, $R=0.5$ Megohm).

Um den Ursprung der jeweiligen Spannungsänderungen aufzuzeigen, wurden Symbole definiert. Sie erlauben eine einfache Erklärung der polarovoltrischen Kurven und als Folge davon eine rationelle Anwendung unsymmetrischer Elektroden.

BIBLIOGRAPHIE

1 J. E. Dubois et W. Walisch, *Ann. Univ. Saraviensis*, 1 (1952) 326.
2 J. E. Dubois, *Mises au point de Chimie Analytique pure et appliquée d'Analyses bromatologiques*, 5° série, 1957, Masson, p. 135.
3 W. Walisch, *Chim. Anal. (Paris)*, 2 (1957) 63.
4 J. E. Dubois, P. Maroni et W. Walisch, *Ann. Univ. Saraviensis*, 1 (1952) 237.
5 J. E. Dubois, P. Maroni et W. Walisch, *Ann. Univ. Saraviensis*, 1 (1952) 319.
6 J. E. Dubois et W. Walisch, *Compt. Rend.*, 242 (1956) 1289.
7 J. E. Dubois, M. R. F. Ashworth et W. Walisch, *Compt. Rend.*, 242 (1956) 1452.
8 J. E. Dubois et Graser-Capuano, *Bull. Soc. Chim. France*, (1961) 2216.
9 W. Walisch et M. R. F. Ashworth, *Anal. Chim. Acta*, 18 (1958) 632.
10 W. Closs, *Dipl. Ing. Chim.*, Sarrebruck, 1954.
11 J. E. Dubois et S. Beech, *Ann. Univ. Saraviensis*, 2 (1953) 363.
12 J. E. Dubois et P. C. Lacaze, *Compt. Rend.*, 252 (1961) 748.
13 J. E. Dubois et G. Mouvier, *Compt. Rend.*, 255 (1962) 1104.
14 J. E. Dubois et G. Mouvier, *Tetrahedron Letters*, (1963) 1325.
15 P. Delahay, G. Charlot et H. A. Laitinen, *J. Electroanal. Chem.*, 1 (1959–60) 425.
16 J. E. Dubois et P. C. Lacaze, *Anal. Chim. Acta*, sous presse.
17 J. E. Dubois et P. C. Lacaze, *Anal. Chim. Acta*, sous presse.
18 J. E. Dubois, P. C. Lacaze, M. Marie de Ficquelmont et A. Guihaumé, *Compt. Rend.*, 260 (1965) 564.

HIGH-SPEED CONTROLLED-POTENTIAL COULOMETRY

APPLICATION TO PRECISE DETERMINATION OF PLUTONIUM

G. C. GOODE AND J. HERRINGTON
Atomic Weapons Research Establishment, Aldermaston, Berkshire (Great Britain)
(Received February 6th, 1965)

Controlled-potential coulometry is now a highly developed technique, and its wide range of analytical applications has been recently summarised by RECHNITZ[1]. Since it is a method capable of high precision even at milligram levels and has the advantage of being absolute it has found many applications in the nuclear field, in particular to the determination of plutonium. An excellent review of controlled-potential coulometric methods for this element has been presented by SHULTS[2].

In controlled-potential coulometry it is advantageous to reduce the electrolysis time to a minimum. Quite apart from time considerations in routine analysis, short electrolysis times should lead to an improvement in overall precision owing to a reduction in background current corrections and the minimisation of chemical side effects. BARD[3] has discussed the factors controlling the rate of electrolysis and has described a high-speed coulometric cell with a large ratio of electrode area to electrolyte volume. This cell incorporates a large spiral platinum working electrode and uses a combination of ultrasonic and nitrogen stirring. It is clear from the results obtained however that ultrasonic stirring, though efficient, is not essential for achieving a high rate of electrolysis, and in this work a simpler cell with conventional magnetic stirring has been developed. In this establishment there is considerable interest in the determination of plutonium and the methods described by SHULTS[2] have been applied. The work described in this paper was undertaken primarily to determine the precision obtainable using the high-speed technique.

EXPERIMENTAL

Electrolysis cell

In designing an electrolysis cell with a large ratio of electrode area to electrolyte volume, the technique of BARD[3] who used a tightly wound spiral of platinum gauze which occupied almost the entire volume of electrolyte, was considered most suitable. With such a system, however, problems arise due to difficulties in providing efficient stirring. Preliminary experiments with cells of various design showed that a very low stirring efficiency is obtained by merely raising the electrode from the base of the cell to allow free rotation of the magnetic stirring bar beneath it. Considerable improvement results, however, if the electrode is made annular in shape, the central hole being approximately 8 mm in diameter. The final cell design adopted is shown in Fig. 1. The glass cell is 26 mm internal diameter, being fitted with a machined polythene cap. This supports two unfired Corning 7930 Vycor tubes, $\frac{1}{8}''$ in diameter, one containing an Ag/AgCl, saturated KCl, reference electrode and the other a 16-SWG platinum wire auxiliary electrode immersed in 0.5 *M* sulphuric acid, and a nitrogen inlet tube. The working electrode is formed from 48-mesh expanded platinum or gold sheet, approximately 150 × 1 cm by tightly winding around a glass tube 8 mm in diameter; the outer diameter of the spiral is 22 mm. The working electrode is supported on an outer cylinder of expanded platinum or gold sheet 20 mm deep which is spot-welded to a 16-SWG platinum or gold wire to make electrical contact through the polythene cap. The volume of electrolyte required just to immerse electrode and support is 7 ml.

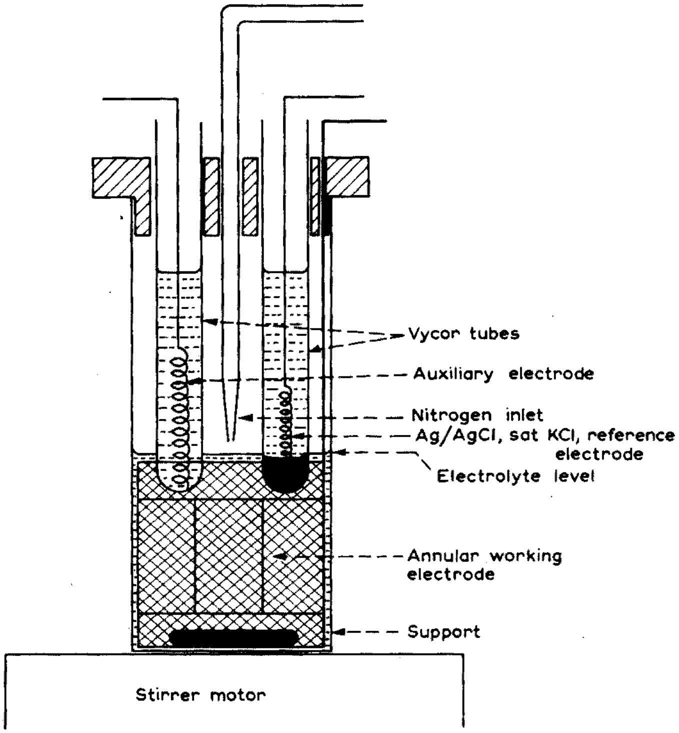


Fig. 1. High-speed electrolysis cell.

Apparatus

The potentiostat and electronic integrator have been described previously[4]. The potentiostat, although capable of providing a current of 300 mA at 25 V was calibrated only up to 100 mA and the ammeter indicating the cell current was thus modified accordingly. The inclusion of the potential overshoot circuit in the instrument prevented electrolysis current measurements being made within the first 7 sec.

Current–time behaviour

In preliminary experiments the current–time behaviour of various designs of electrolysis cell was investigated using iron(III) solutions. Iron(III) was reduced to iron(II) at +0.25 V *vs.* Ag/AgCl, saturated KCl, in 0.5 *M* sulphuric acid and the rate of electrolysis for the oxidation of iron(II) to iron(III) at +0.48 V measured.

With the cell shown in Fig. 1, for oxidation of 1.5–2.0 mg of iron(II) an initial current of approximately 250 mA was obtained which decayed to 1.0% of its initial value in 66 sec and 0.1% in 82 sec. Calculation of the overall effective constant k for the single electrode reaction involving mass transport according to the equation $i = i_0 e^{-kt}$, where i_0 and i represent the current at zero and time t sec, gave a value of 0.11/sec. The very high initial electrolysis rate observed by BARD was confirmed and current–time plots during the later stages of electrolysis gave a slope of 0.052/sec. Both these values are in good agreement with this author. In all experiments oxygen-free nitrogen was used to deoxygenate the electrolyte, the gas stream being blown over the surface to avoid splashing.

Determination of plutonium

SHULTS[2] has summarised the methods available for the coulometric determination of plutonium and has critically examined the alternative electrolytes available. We have confirmed that 1.0 *M* perchloric acid is most suitable for routine determination of plutonium by oxidation of plutonium(III) but in this work 0.5 *M* sulphuric acid was used because of the presence of large quantities of plutonium(VI). In this electrolyte iron(II) interferes and corrections for small amounts of iron in the plutonium solutions are necessary. For electrolysis times as short as 2 min, corrections for background currents and integrator drift become insignificant but a correction of 1–2 millicoulombs for the double-layer charging contribution would be expected. With large electrode areas, however, surface phenomena become important and oxidation or reduction of the electrode surface itself can give rise to much larger corrections. Thus if a very high precision is to be achieved an inert and highly reproducible electrode surface must be chosen. Several investigators have noted and studied the formation of oxide surfaces on platinum and gold electrodes[5,6], and recently PETERS AND SHULTS[7] have encountered difficulties in the chronopotentiometric determination of plutonium(III) due to concomitant electro-oxidation of the platinum surface. It was thus necessary to investigate the reproducibility of "blank" determinations at the plutonium(III) oxidation potential using large electrode surfaces. The platinum electrode was cleaned by igniting to red heat followed by washing with 6 *M* nitric acid and water. Seven ml of 0.5 *M* sulphuric acid were placed in the cell, most of the oxygen was removed by blowing oxygen-free nitrogen over the surface for 5 min and the solution was then electrolysed at +0.33 V *vs.* Ag/AgCl, saturated KCl for 2 min, giving a background current of less than 20 μA. After zeroing the integrator an oxidation blank at +0.69 V was determined for the same period. It was found that abnormally high blanks were obtained immediately following the cleaning treatment but subsequent blanks became more constant and gave a mean value of 31.8 millicoulombs. This represents approximately 1.5% of the current consumed in the oxidation of 5 mg of plutonium(III). Analysis of a large number of blanks determined over a period of several weeks gave a coefficient of variation of 14.2% which would limit the overall precision obtainable for a determination of 5 mg of plutonium to 0.23%. When this technique was used for the determination of plutonium in a solution prepared from metal of known purity, an actual precision of 0.20% was obtained for 10 determinations, which is considerably lower than SHULTS[2] has obtained with a small working electrode. In an attempt to obtain a more inert surface a gold electrode was examined as above, and it was found that lower background currents were obtained (<10 μA in 2 min). The mean blank with this electrode for a 2-min electrolysis was 14.8 millicoulombs with a coefficient of variation of 6.0%, and this would limit the final precision for a 5-mg plutonium determination to 0.04%. This was confirmed in the analysis of the plutonium solution used previously when a coefficient of variation of 0.05%, with zero bias, was obtained.

Results for blank and plutonium determinations using platinum and gold electrodes are summarised in Table I. All results given are calculated from integrated current readings recorded after 2 min, no corrections being applied. Plutonium results are corrected for small amounts of iron present.

TABLE I

PRECISION OBTAINABLE WITH PLATINUM OR GOLD ELECTRODES

Electrode	*Blank determination*				*Pu determination*		
	Mean (mC)	*No. of detns.*	*Coeff. of variation (%)*	*Limiting precision (%)*	*% Pu found*	*No. of detns.*	*Coeff. of variation (%)*
Platinum	31.8	50	14.2	0.23	99.90	10	0.20
Gold	14.8	20	5.95	0.044	99.99	10	0.05

CONCLUSIONS

The results in Table I show that a very high precision is obtainable by the high-speed controlled-potential coulometric technique using a gold working electrode. In addition, up to a 10-fold saving of time can be achieved. Although relatively low precision is obtained with a platinum electrode because of the poor reproducibility of the blank, chemical pretreatment of the electrode is clearly extremely important and it may be possible to improve precision considerably by more careful standardisation of conditions.

Investigations were restricted to sulphuric acid electrolyte by the nature of the plutonium species present; some difficulties might arise if hydrochloric or perchloric acid solutions were used with gold electrodes at the more positive potentials required for oxidation of plutonium(III). This aspect of the problem was not investigated.

We thank Mr. T. DOWNHAM for carrying out some of the plutonium determinations.

SUMMARY

An electrolysis cell for high-speed controlled-potential coulometric analysis with conventional magnetic stirring is described. The factors influencing the precision obtainable by this technique with platinum and gold electrodes are discussed with particular reference to the oxidation of Pu(III) to Pu(IV) in 0.5 *M* sulphuric acid.

RÉSUMÉ

Les auteurs décrivent une cellule d'électrolyse pour analyse coulométrique à potentiel contrôlé, rapide. On examine les facteurs influençant la précision obtenue par cette technique, avec électrodes de platine et d'or, en se référant particulièrement à l'oxydation de Pu(III) en Pu(IV), en milieu acide sulfurique 0.5 *M*.

ZUSAMMENFASSUNG

Es wird eine Elektrolysezelle für die coulometrische Analyse mit einem sehr schnellen, kontrollierten Potential und einer konventionellen magnetischen Rührung beschrieben. Es werden die Faktoren diskutiert, die die Genauigkeit beeinflussen, die bei dieser Technik mit Platin- und Goldelektroden erhalten werden unter besonderer Berücksichtigung der Oxydation von Pu(III) zu Pu(IV) in 0.5 *M* Schwefelsäure.

REFERENCES

1 G. A. RECHNITZ, *Controlled Potential Analysis*, International Series of Monographs on Analytical Chemistry, Vol. 13, Pergamon Press, 1963.
2 W. D. SHULTS, *Talanta*, 10 (1963) 833.
3 A. J. BARD, *Anal. Chem.*, 35 (9) (1963) 1125.
4 G. C. GOODE, J. HERRINGTON AND G. HALL, *Anal. Chim. Acta*, 30 (1964) 109.
5 F. C. ANSON AND J. J. LINGANE, *J. Am. Chem. Soc.*, 79 (1957) 1015, 4901.
6 J. J. LINGANE, *J. Electroanal. Chem.*, 1 (1959) 379.
7 D. G. PETERS AND W. D. SHULTS, *J. Electroanal. Chem.*, 8 (1964) 200.

DOSAGE DE L'AMERICIUM PAR COULOMETRIE A POTENTIEL IMPOSE

G. KOEHLY

Services de Chimie des Combustibles Irradiés, Section d'Etudes Chimiques et Radioactives, Centre d'Etudes Nucléaires, Fontenay-aux-Roses (France)

(Reçu le 5 février, 1965)

Les méthodes analytiques utilisées actuellement pour doser l'américium se limitent à la spectrophotométrie d'absorption[1-3], d'émission[4] et à la radiométrie par comptage α ou γ[5,6]. Il nous a paru intéressant de mettre au point une méthode électrochimique permettant de déterminer l'américium en présence d'autres éléments sans séparation préalable. Le choix de la coulométrie s'explique par la réputation de sélectivité, de précision et de sensibilité de cette méthode directe utilisant le coulomb comme étalon.

Le dosage coulométrique ne peut être réalisé par oxydation directe de Am^{3+} car les potentiels d'oxydo-réduction des divers couples de l'américium sont trop élevés[7] mais le processus suivant peut être envisagé: oxydation quantitative de Am^{3+} en AmO_2^{2+}, puis réduction coulométrique en AmO_2^{+}. Pour faciliter l'oxydation il est préférable d'opérer à faible acidité et en présence d'ions SO_4^{2-} complexant AmO_2^{2+}. Nous avons étudié le rendement chimique de l'oxydation en milieu sulfate et le rendement en courant de la réduction.

PARTIE EXPÉRIMENTALE

Préparation d'une solution étalon

Une solution étalon $1.25 \cdot 10^{-2}$ *M* en américium a été préparée par pesée d'oxyde AmO_2 * et dissolution sulfurique à chaud. Le titre exact en Am a été calculé en tenant compte des impuretés dosées par spectrophotométrie d'émission et indiquées par le fournisseur. Toutes les autres solutions ont été préparées par dilution de la solution étalon.

Tous les assais ont été faits sur des solutions d'américium-241.

Appareillage

Le montage potentiostatique classique (Fig. 1) a été réalisé avec les appareils suivants: un potentiostat Tacussel type PRT 2000, un millivoltmètre électronique Tacussel du type S6, et les cellules d'électrolyse de la Fig. 2. Les électrodes de travail et auxiliaires étaient en platine. Pour éviter la présence d'ions Cl^-, l'électrode de référence utilisée était constituée par la chaîne $Hg/Hg_2SO_4/K_2SO_4$ saturé.

Tous les potentiels cités dans ce texte sont exprimés par rapport à l'électrode normale à hydrogène.

---

* Cet oxyde de l'isotope ^{241}Am nous a été fourni par l'U.S.A.E.C.

Pour intégrer le courant nous avons utilisé un intégrateur numérique MECI dont l'étude détaillée a été faite par SCHOEDLER[8]. Cet appareil permet d'obtenir une précision de 0.3% sur une quantité d'électricité même si le courant varie dans un rapport de 100 à 1.

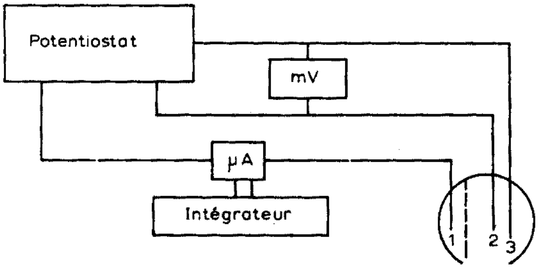


Fig. 1. Coulométrie à potentiel contrôlé; schema type. (1) électrode auxiliaire; (2) électrode de travail; (3) électrode de référence.

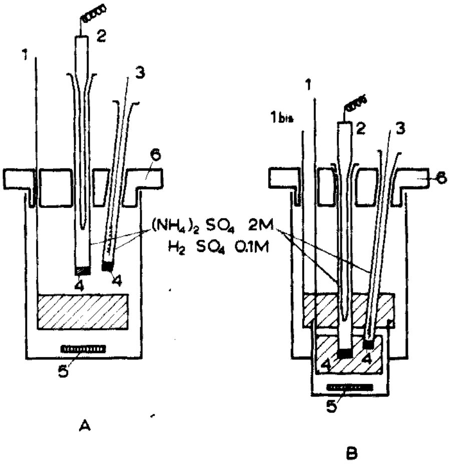


Fig. 2. Cuves d'électrolyse. (1) et (1 bis) électrode de travail; (2) électrode de référence au mercurosulfate; (3) électrode auxiliaire; (4) séparations des compartiments en verre fritté; (5) barreau magnétiq (6) chapeau en téflon.

Les contrôles spectrophotométriques des formes ioniques en solution ont été effectués avec un spectrophotomètre enregistreur Spectromatic JOUAN.

Essais et résultats

Oxydation électrolytique. L'oxydation de Am^{3+} en AmO_2^{2+} peut être obtenue soit par voie chimique, soit par voie électrolytique[2,7,9,10]. GUNN[2] signale pour l'oxydation électrolytique un rendement chimique supérieur à 90% en quelques heures en utilisant une cathode de 0.2 cm², une anode de 2 cm² et un courant anodique de 50 mA/cm². Ce rendement est supérieur à 95% en une heure en opérant sur un bain de glace.

Il s'est avéré utile de reprendre quelques essais d'oxydation pour vérifier, dans nos conditions expérimentales, le temps nécessaire à l'obtention du meilleur rendement.

Ces conditions étaient les suivantes: 10 ml de solution 2 *M* $(NH_4)_2SO_4$ et 0.1 *M* H_2SO_4, électrode en platine poli, de surface ≃ 20 cm². La faible acidité facilite l'oxydation de Am^{3+} en AmO_2^{2+} comme le montre la réaction:

$$Am^{3+} + 2\ H_2O - 3\ e \rightleftarrows AmO_2^{2+} + 4\ H^+$$

La présence d'ions sulfates complexant principalement AmO_2^{2+} abaisse le potentiel redox du couple Am^{3+}/AmO_2^{2+}.

L'ion ammonium, ion indifférent, participe au transport du courant et évite un appauvrissement du compartiment anodique en américium car, durant l'oxydation électrolytique, les cations migrent vers le compartiment cathodique. Nous avons choisi l'ammonium de préférence à K^+ ou Na^+ qui forment avec Am^{3+} des sulfates doubles relativement peu solubles[11].

Après avoir vérifié que la spectrophotométrie d'absorption permet de déceler 1% d'Am^{3+} en présence de AmO_2^{2+} pour une concentration totale en américium de $5 \cdot 10^{-3}$ *M*, nous avons utilisé cette méthode pour vérifier le rendement chimique de l'oxydation électrolytique.

En utilisant un potentiel anodique compris entre +1.9 V et +2.0 V par rapport à l'électrode normale à hydrogène le rendement en AmO_2^{2+} est au moins égal à 99%, mais le temps nécessaire à l'obtention de ce rendement est fonction de l'âge de la solution de ^{241}Am: pour une solution d'Am^{3+} fraîchement préparée par dissolution de l'oxyde ou de l'hydroxyde, l'oxydation est complète en 80 min alors que la même solution ayant séjourné 2 mois ne peut être oxydée qu'en 120 min (Fig. 3). Ceci s'explique par l'accumulation, dans les solutions d'Am^{3+}, d'eau oxygénée, produit de radiolyse de l'eau par les rayons-α de l'américium-241. Sur les courbes intensité–potentiel (Fig. 4) on voit que pour les solutions fraîchement préparées il n'y a qu'une barrière de potentiel à environ +1.6 V correspondant à l'oxydation de l'eau, tandis que pour les solutions âgées il apparaît une vague d'oxydation à +1.0 V correspondant à la réaction:

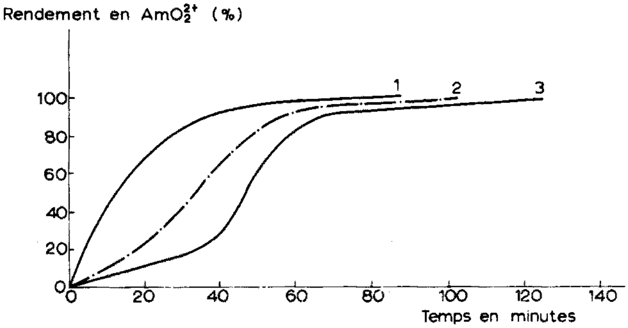


Fig. 3. Oxydation électrolytique de Am^{3+}; rendement en fonction du temps. (1) solution fraîche; (2) solution après 1 mois; (3) solution après 2 mois.

$$H_2O_2 \rightarrow O_2 + 2\ H^+ + 2\ e$$

Pour éviter la présence d'eau oxygénée il est proposé dans le mode opératoire type une évaporation de la solution avant oxydation.

Il est essentiel de ne pas prolonger inutilement l'oxydation électrolytique pour éviter une perte en américium par migration.

La dissipation d'énergie par effet joule étant importante durant l'oxydation il s'est avéré nécessaire de thermostater la cuve d'électrolyse à 15 ± 1° pour éviter que la solution se concentre. La puissance dissipée dans les verres frittés séparant les compartiments anodique et cathodique peut s'évaluer à 1 W puisque la résistance de ces frittés variait entre 180 et 280 ohms et que le courant d'oxydation était compris entre 0.05 et 0.10 A. La chute ohmique était de l'ordre de 14 à 18 V.

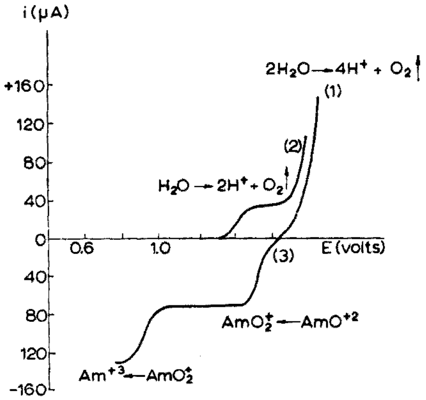


Fig. 4. Courbes $i = f(E)$. (1) solution Am^{3+} fraîchement préparée (oxydation); (2) solution âgée de Am^{3+} (oxydation); (3) réduction de AmO_2^{2+}.

Réduction coulométrique. La réduction de AmO_2^{2+} en Am^{3+} nécessite une surtension importante: le dosage réalisé de cette façon n'est plus sélectif car les ions tels PuO_2^{2+} et NpO_2^{2+} sont réduits en même temps que l'américium. Par contre, la réduction en AmO_2^{+} débute dès que le potentiel cathodique devient inférieur à +1.55 V (Fig. 4). En fixant le potentiel de la cathode à +1.3 V la réduction en AmO_2^{+} est quantitative en 20 min pour une prise d'essai de 25 ml et une surface d'électrode d'au moins 30 cm². Les résultats moyens obtenus lors de coulométries réalisées sur ce couple à +1.3 V pour des prises d'essai de 5 ml de solution 2 M $(NH_4)_2SO_4$ et 0.2 M H_2SO_4 sont groupés dans le Tableau I.

Le titre moyen pour chaque concentration correspond à la moyenne de 10 résultats de dosages. Pour diminuer l'erreur dûe au courant résiduel, ces dosages ont été réalisés de la façon suivante: pendant la dernière demi-heure d'oxydation une

TABLEAU I

RÉSULTATS MOYENS OBTENUS POUR 2 M $(NH_4)_2SO_4$ ET 0.2 M H_2SO_4

Titres des solutions étalons (M)	*Titres moyens trouvés par coulométrie (M)*	*Erreur (%)*	σ %
$3.125 \cdot 10^{-3}$	$3.075 \cdot 10^{-3}$	−1.61	0.44
$1.25 \cdot 10^{-3}$	$1.23 \cdot 10^{-3}$	−1.60	0.41
$6.25 \cdot 10^{-4}$	$6.14 \cdot 10^{-4}$	−1.76	0.51
$3.125 \cdot 10^{-4}$	$3.07 \cdot 10^{-4}$	−1.75	0.62
$1.25 \cdot 10^{-4}$	$1.229 \cdot 10^{-4}$	−1.68	0.96
$6.25 \cdot 10^{-5}$	$6.10 \cdot 10^{-5}$	−2.4	2.58

deuxième cuve d'électrolyse contenant 20 ml de l'électrolyte support a été mise sous tension, le potentiel de l'électrode de travail étant fixé à $+1.3$ V. Après 20 min le courant résiduel, qui est un courant d'oxydation prend une valeur faible et constante. Ce n'est qu'à ce moment que les 5 ml de solution d'AmO_2^{2+} sont ajoutés dans la cuve de réduction. L'erreur par défaut introduite dans le dosage par le courant résiduel devient ainsi très faible.

Nous donnons dans le Tableau II les résultats obtenus, pour une série de 10 mesures coulométriques d'une solution $1.25 \cdot 10^{-3}$ M, avec la cuve d'électrolyse B de la Fig. 2.

TABLEAU II

RÉSULTATS DE 10 MESURES COULOMÉTRIQUES

(Solution étalon $1.25 \cdot 10^{-3}$ M)

Concentration trouvée par coulométrie (M)	Σ	Σ^2
$1.232 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-12}$
$1.227 \cdot 10^{-3}$	$4 \cdot 10^{-6}$	$16 \cdot 10^{-12}$
$1.225 \cdot 10^{-3}$	$6 \cdot 10^{-6}$	$36 \cdot 10^{-12}$
$1.236 \cdot 10^{-3}$	$5 \cdot 10^{-6}$	$25 \cdot 10^{-12}$
$1.238 \cdot 10^{-3}$	$7 \cdot 10^{-6}$	$49 \cdot 10^{-12}$
$1.239 \cdot 10^{-3}$	$8 \cdot 10^{-6}$	$64 \cdot 10^{-12}$
$1.228 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	$9 \cdot 10^{-12}$
$1.226 \cdot 10^{-3}$	$5 \cdot 10^{-6}$	$25 \cdot 10^{-12}$
$1.229 \cdot 10^{-3}$	$2 \cdot 10^{-6}$	$4 \cdot 10^{-12}$
$1.230 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-12}$

Titre moyen $= 1.231 \cdot 10^{-3}$ M $\quad \sum \Sigma^2 = 229 \cdot 10^{-12}$

$\sigma = 5.06 \cdot 10^{-6}$ $\quad \sigma\,\% = 0.41$

Avec cette cuve, l'oxydation et la réduction se font dans le même vase ce qui élimine toute erreur dûe à une éventuelle variation de volume de la prise d'essai par évaporation. L'oxydation se fait dans la partie inférieure du vase avec l'électrode 1. Puis l'électrolyte support, réduit dans une autre cuve avec l'électrode 1 bis est ajouté sur la solution oxydée. La réduction coulométrique est faite par l'électrode 1 bis.

DISCUSSION

Dispersion des résultats et précision

Les valeurs moyennes $\bar{x}$, citées Tableau I correspondent, pour chaque concentration à la moyenne arithmétique de 10 résultats

$$\bar{x} = \frac{\Sigma x}{10}$$

D'après ces 10 résultats nous avons pu estimer l'écart type σ défini par:

$$\sigma = \sqrt{\frac{\Sigma\,(\bar{x} - x_i)^2}{n-1}}$$

où x_i représente le résultat de la *i*ème mesure, $\bar{x}$ le résultat moyen et n le nombre de mesures.

Nous pouvons de même définir un écart type relatif

$$\sigma\% = 100\,\frac{\sigma}{\bar{\bar{x}}}$$

dont la valeur pour chaque concentration est donnée dans le Tableau I.

Les résultats de tous les dosages mentionnés dans ce Tableau comportent une erreur par défaut de 1.68% en moyenne et atteignant parfois 2% qui trouve son explication dans l'influence de l'autoréduction de AmO_2^{2+}: la réduction des états de valence supérieurs de l'américium-241 sous l'action des rayons α en solution acide a été étudiée par plusieurs auteurs[1,2,11–14]. ASPREY ET STEPHANOU[15] ont observé que Am(VI) disparaît proportionnellement au temps et que la vitesse d'autoréduction est proportionnelle à la concentration totale d'américium.

$$-\frac{\mathrm{d}\,C_{\mathrm{Am(VI)}}}{\mathrm{d}t} = kC_{\mathrm{Am}_{\mathrm{total}}}$$

YAKOVLEV ET KOSSIAKOV[11] ont étudié l'autoréduction de Am(VI) en milieu perchlorique et sulfurique. Les résultats qu'ils ont obtenus permettent de conclure que l'autoréduction varie dans le sens inverse de l'acidité et de la teneur en ions sulfate. Ces auteurs trouvent pour kn (constante de diminution du nombre moyen d'oxydations "n") une valeur de $2.42 \cdot 10^{-2}$/h pour le milieu correspondant au dosage coulométrique, ce qui équivaut à une erreur de 1.21% par défaut pour une coulométrie de 30 min. Cette erreur est, en grande partie, dûe à l'intense activité-α de l'américium-241 et il est probable que pour l'américium-243 l'erreur du dosage pourrait être notablement diminuée.

Peuvent contribuer également à cette erreur par défaut: une oxydation incomplète et un courant résiduel d'oxydation.

Il ressort de l'analyse des variations de l'erreur systématique et de l'écart type en fonction de la concentration en américium que:

(*1*) l'erreur systématique dûe à l'autoréduction, au défaut d'oxydation et au courant résiduel pour des concentrations en américium comprises entre $3.125 \cdot 10^{-3}\,M$ et $1.25 \cdot 10^{-4}\,M$ varie entre -1.60 et -1.76%. Nous proposons dans ce cas d'affecter le résultat d'un facteur correctif $f = 1.017$.

(*2*) l'écart type relatif augmente lorsque la concentration diminue. Ceci est dû à l'interférence du courant résiduel non reproductible et qui correspond à $\simeq 3.5 \cdot 10^{-8}$ équivalent dans les 5 ml de la prise d'essai.

(*3*) la limite de concentration pour un dosage précis est comprise entre $1.25 \cdot 10^{-4}$ et $6.25 \cdot 10^{-5}\,M$. En deçà de $6.25 \cdot 10^{-5}$ l'interférence du courant résiduel devient trop importante.

Sélectivité

L'avantage de cette méthode réside dans sa sélectivité. Peu de couples possèdent un potentiel redox aussi élevé que Am(VI)/Am(V) et parmi ceux qui possèdent un tel potentiel la plupart sont irréversibles.

Les éléments qui en général se trouvent en présence de l'américium sont: l'uranium et le plutonium, les éléments obtenus par irradiation de ces corps (Np et Cm) et les produits de fission dont les plus importants sont les lanthanides. Parmi tous ces éléments deux sont gênants pour ce dosage: le cérium qui a un potentiel redox très proche de celui du couple AmO_2^{2+}/AmO_2^+ et le curium qui, par son activité-α très intense provoque la réduction de AmO_2^{2+} en AmO_2^+ (les activités-α de ^{242}Cm et de ^{244}Cm sont respectivement environ 1000 et 25 fois plus élevées que celles de ^{241}Am).

Il est possible d'éliminer ces deux éléments en ajoutant à la solution d'américium avant oxydation 1 à 2 mg de La^{3+} par ml de solution et après oxydation de Am^{3+}, en précipitant les fluorures insolubles (LaF_3, CmF_3 et CeF_3) par addition de 1 ml de solution saturée de NH_4F. Après décantation AmO_2^{2+} est dosé sur une aliquote de la solution surnageante.

En opérant de cette façon sur une solution contenant 8.3 mg/l d'un mélange de curium-242 et -244*, le facteur de décontamination a été trouvé égal à 150; le rapport:

$$\frac{\text{activité de } |^{241}\text{Am}|}{\text{activité de: } |^{242}\text{Cm}| + |^{244}\text{Cm}|}$$

était passé de 4.46 à 678. La concentration du cérium est passée de $1.2 \cdot 10^{-3}$ *M* à $1.9 \cdot 10^{-5}$ *M*. La quantité d'américium entraîné par le précipité de fluorure de lanthane était de 0.022 mg pour 20 ml d'une solution 10^{-3} *M* en Am.

La présence de quantités importantes de ^{242}Cm limite probablement le domaine d'utilisation de cette méthode de dosage du fait de la formation des produits de radiolyse de l'eau qui peuvent limiter le rendement chimique d'oxydation de l'américium et provoquer une réduction rapide de AmO_2^{2+}. Il ne nous est pas possible d'indiquer le rapport limite des concentrations $^{242}Cm/^{241}Am$ au-dessus duquel le dosage n'est plus possible; cependant les résultats de coulométries effectuées sur des solutions où l'activité initiale du curium était 30 fois supérieure à l'activité de ^{241}Am étaient pleinement satisfaisants.

MODE OPÉRATOIRE

Introduire une aliquote de la solution à doser dans la cuve d'électrolyse. Amener à sec, puis reprendre par 1 ml H_2SO_4 1 *M* à chaud. Ajouter 10 ml d'une solution 2 *M* en $(NH_4)_2SO_4$. Oxyder sous agitation durant 2 h avec un potentiel anodique de +1.9 à 2.0 V en thermostatant pour éviter une concentration par évaporation.

Prélever 5 ml de la solution oxydée et l'introduire dans une cuve contenant 20 ml d'électrolyte support préalablement électrolysé +1.3 V durant 20 min et procéder à la réduction coulométrique, sous agitation, en utilisant un potentiel cathodique de +1.3 V, la réduction est quantitative en un temps maximum de 40 min pour une surface d'électrode de 2 cm^2 par ml de solution.

La concentration en Am est donnée par:

$$c = \frac{2.2\,Q}{96.5\,v}$$

c = molarités,
Q = coulombs,
v = volume de la prise d'essai en ml.

RÉSUMÉ

Un dosage coulométrique de l'américium par réduction de Am(VI) en Am(V) à +1.3 V est proposé. La précision de la méthode a été évaluée en dosant des solu-

---

* Mélange isotopique obtenu par traitement chimique de plutonium irradié. Contrat Euratom-CEA no. 4428/R.

tions de ^{241}Am préparées par pesée et dissolution de AmO_2 de pureté connue. Les résultats des dosages doivent être affectés d'un facteur correctif $f = 1.017$ pour éliminer l'erreur systématique dûe à l'autoréduction. L'écart type relatif varie entre 0.44% et 0.96% lorsque la concentration en américium de la prise d'essai passe de $3.125 \cdot 10^{-3}$ *M* à $1.25 \cdot 10^{-4}$ *M*.

SUMMARY

A coulometric determination of americium by reduction of Am(VI) to Am(V) at a potential of +1.3 V is proposed. The accuracy of the method was evaluated by analyzing ^{241}Am solutions prepared by weighing and dissolving AmO_2 of known purity. The results must be corrected by a factor of 1.017, in order to eliminate the systematic error due to autoreduction. After this correction, the relative standard deviation of the method ranged from 0.44% for americium concentrations of $3.125 \cdot 10^{-3}$ *M* to 0.96% for those of $1.25 \cdot 10^{-4}$ *M*.

ZUSAMMENFASSUNG

Eine coulometrische Bestimmung von Americium durch Reduktion von Am(VI) zu Am(V) bei einem Potential von +1.3 V wird vorgeschlagen. Durch Analysen von ^{241}Am-Lösungen, die durch Einwägen und Lösen von AmO_2 von bekannter Reinheit hergestellt wurden, konnte die Genauigkeit der Methode berechnet werden. Die Ergebnisse müssen mit einem Faktor von 1.017 korrigiert werden, um den systematischen Fehler durch Autoreduktion zu eliminieren. Nach dieser Korrektur schwankt die relative Standardabweichung der Methode von 0.44% für Americiumkonzentrationen von $3.125 \cdot 10^{-3}$ *M* bis 0.96% für eine Konzentration von $1.25 \cdot 10^{-4}$ *M*.

BIBLIOGRAPHIE

1 G. R. Hall et P. D. Hernimann, *J. Chem. Soc.*, (1954) 2214.
2 S. R. Gunn, *Thermodynamics of the Aqueous Ions of Americium*, Thèse, Université de Californie, U.C.R.L. 2541, 1954.
3 S. E. Stephanou, R. A. Penneman et J. P. Nigon, *J. Chem. Phys.*, 21 (1953) 42.
4 A. W. Wenzel et C. E. Pietri, *Quantitative Spectrographic Determination of Americium in Plutonium*, N.B.L. 210, 1964.
5 F. L. Moore, *Anal. Chem.*, 35 (1963) 715.
6 J. Bubernek, M. S. Lew et G. N. Matlack, *Anal. Chem.*, 30 (1958) 1759.
7 R. A. Penneman et L. B. Asprey, *Review of Americium and Curium Chemistry, 1ère Conf. Genève*, 1955, P/838.
8 C. Schoedler, *J. Electroanal. Chem.*, 3 (1962) 390.
9 L. B. Asprey, S. E. Stephanou et R. A. Penneman, *J. Am. Chem. Soc.*, 73 (1951) 5715.
10 M. Ward et G. A. Welch, *J. Chem. Soc.*, (1954) 4038.
11 G. N. Yakovlev et V. N. Kossiakov, *Recherches sur la Chimie de l'Américium, 2ième Conf. Genève*, 1958, P/2127.
12 G. N. Yakovlev et V. N. Kossiakov, *Etudes Spectrophotométriques du Comportement des Ions Américium en Solution, 1ère Conf. Genève*, 1955, P/676.
13 G. R. Hall et T. L. Markin, *J. Inorg. & Nucl. Chem.*, 4 (1957) 296.
14 A. A. Zaitsev, V. N. Kossiakov, A. G. Rykov, I. P. Sobolev et G. N. Yakovlev, *Etudes de Diverses Réactions d'Oxydo Réduction de l'Américium, Actes de la Conférence, Les Isotopes et les Rayonnements en Chimie, Moscou*, 1958, p. 326.
15 L. B. Asprey et S. E. Stephanou, *The Autoreduction of Am(VI) and Am(V)* in A.E.C.D. 924, 1950.

METHOD FOR THE ISOLATION OF THORIUM FROM SILICEOUS MATERIALS

ISMAEL ALMODÓVAR

Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico, Mayaguez (Puerto Rico)

(Received January 28th, 1965)

The inorganic and analytical chemistry of thorium as well as its radiochemistry have been studied extensively since its discovery by BERZELIUS in 1828. General reviews of the chemistry of thorium have been given by HYDE[1] and VERMA[2]. Many analytical procedures for the determination of traces of thorium involve well-known precipitation and/or solvent extraction purification steps, ion exchange, etc. with a final determination of thorium by means of colorimetry[3–15]. For those assay methods the thorium need not be isolated from solution and small amounts of many other elements can be tolerated as long as they do not form colored complexes with reagents or other anions present.

Several methods for the isolation of thorium from silicate rocks, sediments and other materials have also been developed which employed γ-spectrometric measurements, gross α-activity measurements and neutron activation analysis for the final determination of thorium[16–20]. In some of these methods the final sample need not be radiochemically pure. In addition the sensitivity of these methods is limited because of the complex spectra obtained.

The chemical procedure presented here was designed to produce good yields of carrier-free, chemically pure thorium, which is especially radiochemically pure. The thorium samples were used in the application of the thorium isotopes method to the dating of marine sediments[21]. The procedure involves precipitation steps coupled with well-known anion-exchange purification steps. The gelatinous nature of the precipitates makes centrifugation more convenient than filtration. The precipitates remain in the same tube during most of the separation procedure, thus minimizing the losses usually incurred during transfers or filtrations.

Carrier-free thorium is obtained as the chloride and is deposited as a thin adherent film on platinum plates. Four samples can be processed simultaneously in about 16 h.

EXPERIMENTAL

Chemicals, carriers, and ion-exchange resins

All chemicals used throughout the procedure were of reagent quality. The sodium dihydrogen hypophosphate used in the coprecipitation of thorium with bismuth carrier was prepared by oxidizing red phosphorus with sodium chlorite[22], following the modification of REMY AND FALIUS[23]. All water was freshly distilled and passed through a bed of Dowex 50-X4 cation resin in the H^+-form for further purification.

All carriers were repurified by standard analytical purification steps. TTA was very useful in the purification of lanthanum[24]. Some carriers were tested individually for radiochemical purity after purification. Samples were prepared by taking an appropriate amount of carrier and precipitating out any thorium impurities in a form suitable for α- and β-counting.

Several blanks were run starting with 10 ml of 6 *M* hydrochloric acid and using the appropriate amounts of reagents and carriers as indicated in the chemical procedure. The α-spectra showed no thorium or uranium present in the blank samples. No β-activity outside the standard deviation for 1-day counts was observed during a period of 12 days from the isolation of the blank samples.

All purified standard carrier solutions, water, and reagents were stored in polyethylene containers rather than glass, to avoid possible contamination through exchange from the walls.

Ion-exchange resins were washed several times with distilled water. The fines and other floating matter were discarded. Burets (50 ml) were used to prepare ion-exchange columns 15 cm in length with an internal diameter of 1.2 cm. The ion-exchange resin occupied a volume of about 10 ml, and the resin was supported in the column by means of glass wool. The column was then washed with 5–10 column-volumes of the eluent to be used before the sample was put through. Since the ion-exchange resin columns used were small the resin was discarded after each use in order to avoid possible contamination of succeeding samples.

Chemical separation techniques

The procedure which was developed for the isolation of traces of thorium from siliceous materials is shown in diagram form in Fig. 1. The various steps are as follows.

Sample preparation and solution. The sample of siliceous material or sediment was ground until it passed through a 200-mesh sieve. Sufficient amounts of samples were taken, depending on the uranium and thorium content of the material to be processed.

Two methods of sample dissolution were used, depending on the chemical composition of the material to be analyzed. Samples of granitic material could be decomposed with sodium peroxide. In the case of sediments and shales leaching with hydrochloric acid was more convenient.

Sodium peroxide treatment. The sample (1–2 g) was mixed with a 6-fold quantity of sodium peroxide in a nickel or platinum crucible and heated for 1 h at 350–400°. The cake was extracted with hot water to destroy any unreacted peroxide. The mixture was centrifuged and the residue was washed twice with water after the supernatant liquid had been discarded. The cake contained all the thorium while the bulk of the Si, U, Pb, and many other elements were extracted and eliminated. The cake was then dissolved in 10 ml of 6 *M* hydrochloric acid.

Hydrochloric acid leaching. Leaching the sample with 6 *M* hydrochloric acid was more convenient when larger amounts of clay or shale were handled. This procedure brought most of the thorium into solution, leaving many other impurities in the residue[25]. About 10 g of material were treated with 50 ml of 6 *M* hydrochloric acid in

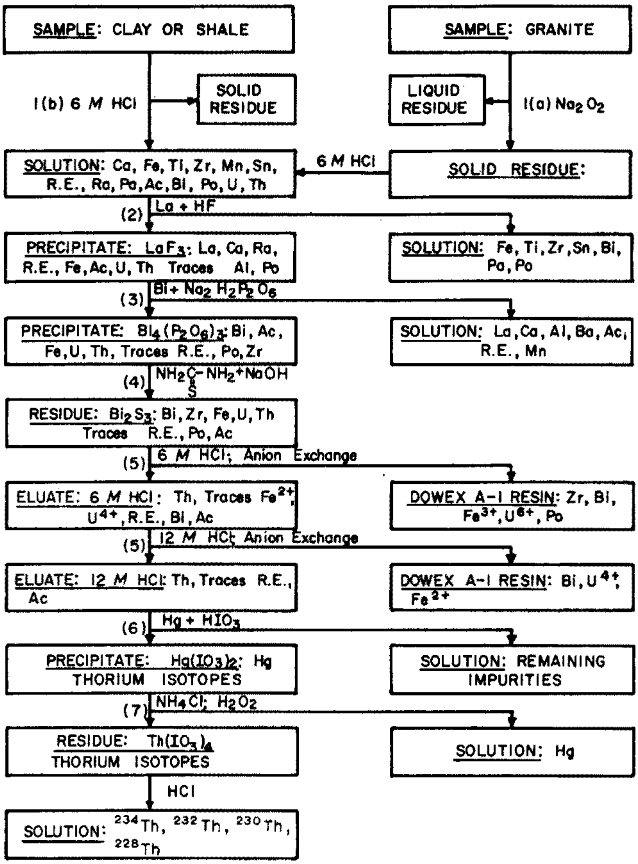


Fig. 1. Outline of chemical procedure.

a teflon beaker. The mixture was heated for 1 h at 90° and centrifuged after cooling. The supernatant liquid was separated from the residue by decantation. The residue was washed twice with a few ml of water. The supernatant liquid and water washings were then combined and evaporated to a volume of about 10 ml.

Coprecipitation with lanthanum carrier by fluoride

A 5-ml portion of a solution of lanthanum nitrate containing 3 mg La/ml was added to the 6 *M* hydrochloric acid solution obtained in the leaching procedure, and the fluorides were precipitated with 10 ml of 5 *M* hydrofluoric acid. The mixture was heated to boiling and centrifuged. The supernatant solution was discarded and the precipitate was washed with two 10-ml portions of 0.5 *M* hydrofluoric acid. The precipitate was dissolved by adding 4 ml of perchloric acid and heating to strong fumes of perchloric acid to expel hydrogen fluoride. The solution was made 2 *M* in perchloric acid by adding 24 ml of water.

Thorium is coprecipitated quantitatively with lanthanum as the fluoride from highly acidic solutions[26]. The coprecipitation of rare earths impurities is complete but several radioactive and stable impurities are eliminated in the centrifugate.

Coprecipitation of thorium with bismuth by sodium dihydrogen hypophosphate

A 2-ml portion of a solution of bismuth nitrate containing 6 mg Bi/ml was pipetted into the centrifuge tube and the hypophosphates precipitated with 8 ml of 0.06 *M* $Na_2H_2P_2O_6$. The precipitate was heated for 15 min at about 90° upon which it coagulated. The mixture was centrifuged and the precipitate was washed with two 10-ml portions of warm 0.5 *M* perchloric acid after the supernatant liquid had been decanted.

The high insolubility of thorium and bismuth hypophosphate in water and highly acidic solutions and the limited number of ions which react under similar conditions provide an excellent method for the removal of trace amounts of thorium from aqueous solutions[27]. Bismuth and thorium coprecipitate quantitatively from a 2 *M* perchloric acid medium of the elements still present and this precipitation is fairly specific for thorium.

Destruction of hypophosphate

The $Bi_4(P_2O_6)_3$ was treated with 5 ml of 2 *M* sodium hydroxide and with 1 ml of a solution containing 5 mg of thiourea. The mixture was heated for 15 min at about 90° with occasional stirring. The black bismuth sulfide precipitate was washed with 10 ml of 1 *M* sodium hydroxide and with 10 ml of 0.1 *M* ammonia solution. The hypophosphate went into solution and was removed by centrifugation.

Since thorium was converted to the hydroxide during the thiourea–sodium hydroxide treatment, while bismuth was converted to the sulfide, 3 mg of zirconium in solution could be added to help coagulate the bismuth sulfide and to insure that the thorium was insoluble. Slightly higher yields could be obtained when zirconium was added; however, it was not necessary to use zirconium provided that care is taken to keep the Bi_2S_3 and $Th(OH)_4$ precipitates in a slightly basic medium.

It was necessary to destroy the hypophosphate precipitate because of its high insolubility. The solubility of $ThH_2P_2O_6$ in 6 *M* hydrochloric acid is only $2.1 \cdot 10^{-4}$ mole/l.

Removal of carriers and impurities by anion exchange

The bismuth sulfide and thorium hydroxide precipitate was dissolved in about 5 ml of 6 *M* hydrochloric acid and heated to eliminate hydrogen sulfide. The solution was passed through a Dowex A-1 anion-exchange column, which had been previously washed with several column volumes of 6 *M* hydrochloric acid and eluted with 6 *M* hydrochloric acid. About 25 ml of 6 *M* hydrochloric acid from the column was collected and evaporated to dryness. Bi^{3+}, Zr^{4+}, Fe^{3+}, U^{6+}, and many other cations were retained by the column, but thorium(IV) passed through in a fairly pure condition[28].

The hydrochloric acid residue was treated with 1 ml of 15 *M* nitric acid in order to oxidize any iron(II) and uranium(IV) present. The nitrate ion was then eliminated by successive evaporations with 12 *M* hydrochloric acid. The residue was then mixed with 5 ml of 12 *M* hydrochloric acid and the solution was put through a Dowex A-1 anion-exchange column which had been previously washed with the 12 *M* acid. Iron, chromium, and any traces of bismuth were completely eliminated by adsorption on the column while thorium passed through.

Final purification: coprecipitation with mercury by iodate

The chloride eluate from the second ion-exchange column was evaporated to dryness and converted to the nitrate by successive evaporations to dryness with 15 M nitric acid. The nitrate residue was taken up with 8 ml of 15 M nitric acid and 10 drops of 3% hydrogen peroxide were added followed by 5 ml of a solution of mercury(II) nitrate containing 1 mg Hg/ml. The solution was warmed and 20 ml of 0.35 M iodic acid were added slowly with constant stirring. The solution was cooled in an ice bath for 45 min with occasional stirring. The solution was centrifuged and the precipitate washed twice with 10-ml portions of 0.03 M iodic acid plus 0.25 M hydrogen peroxide after the mother liquor had been separated by decantation.

Thorium and mercury precipitate quantitatively as iodates from a hydrogen peroxide–nitric acid medium. Rare earth elements, Ac, U, and other traces of impurities are eliminated[29] upon washing the precipitate with 0.03 M iodic acid.

Isolation of carrier-free thorium

The iodate precipitate was treated with 1 ml of 3 M ammonium chloride and centrifuged. The centrifugate contained the mercury carrier and was discarded. The residue (thorium iodate) was washed with 2 ml of 0.2 M hydrogen peroxide. The precipitate was then dissolved in a few drops of 10 M hydrochloric acid by bubbling sulfur dioxide which destroyed the iodate ion with subsequent liberation of iodine upon heating. The solution containing carrier-free thorium as the chloride was then ready to be deposited on platinum plates for α- or β-counting.

DISCUSSION

The isolated thorium samples were checked for radiochemical purity by α-spectra measurements and by β-counting. Complete purification from uranium and all other α-emitting radionuclides was achieved.

Beta-counting of thorium samples isolated from reagent salts and natural materials was done with a system of low-level β-counters as described elsewhere[30], since the specific activity of ^{232}Th is only 4,010 dis/sec/g and the thorium concentration in sediments is typically about $5 \cdot 10^{-6}$ g/g dry material[31,32].

The β-activity is mainly due to the presence of two sub-series, ^{234}Th + ^{234}Pa, and ^{228}Th + decay products.

Figure 2 shows the calculated β-activity as a function of time due to the various sub-chains having thorium parents following isolation of thorium from an equilibrium mixture of natural uranium and thorium. These parents are ^{234}Th (from ^{238}U), ^{231}Th (from ^{235}U), ^{228}Th (from ^{232}Th), and ^{232}Th itself. The ^{231}Th and ^{232}Th components are relatively insignificant, and are furthermore present in constant proportion to the ^{234}Th and ^{228}Th components, respectively, so they can be considered as merely perturbing the latter two components. Figure 2 also shows the course of the total β-activity under the assumption that the uranium and thorium are present in the source material in such a proportion that the ^{238}U : ^{232}Th activity ratio is unity. This corresponds to a U : Th weight ratio of 0.328 which is not far from the average U : Th ratio in the earth's crust[33,34].

Figure 3 shows the β-counting rate observed for the thorium fraction isolated from a reagent uranium salt several years old (curve A). It can be seen that the activ-

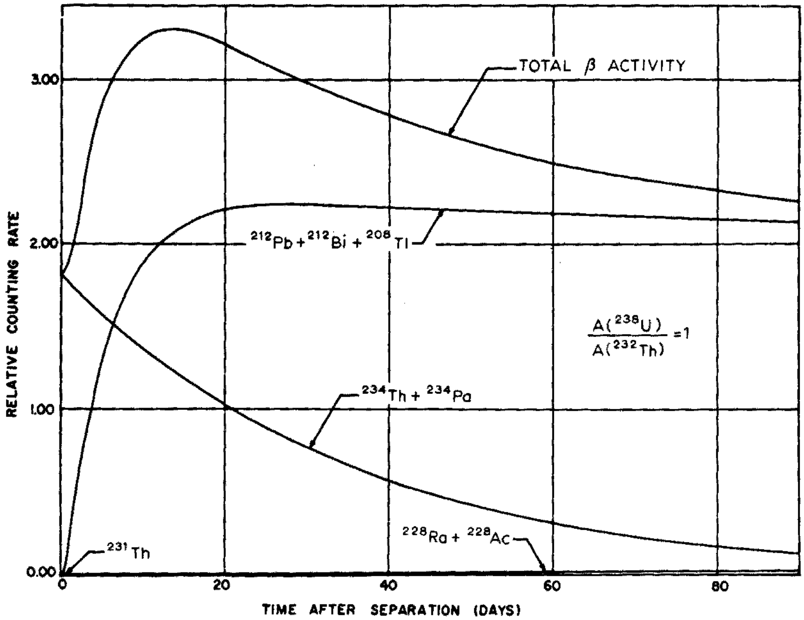


Fig. 2. Expected β-counting rate *vs.* time for thorium fraction isolated from an equilibrium mixture of ^{238}U, ^{235}U, and ^{232}Th families showing the contribution of the several sub-series to the total counting rate.

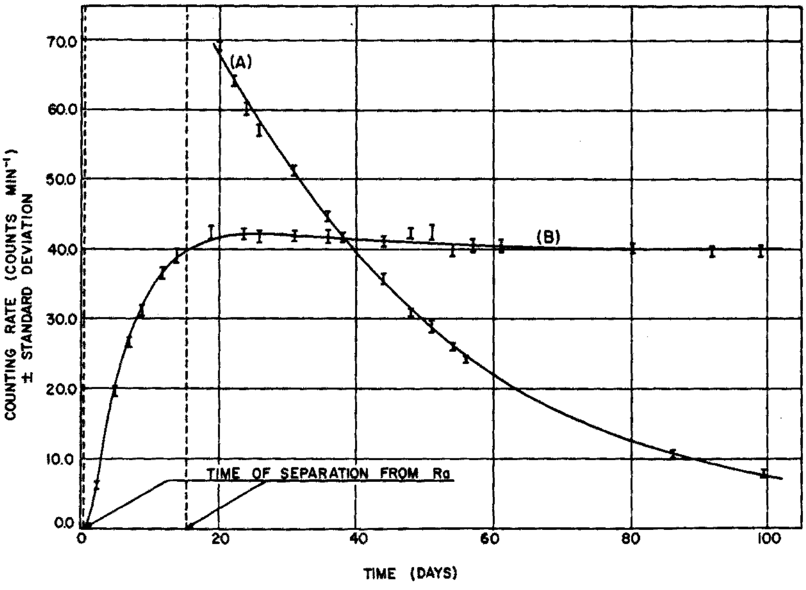


Fig. 3. Observed β-activity *vs.* time for thorium fraction isolated from reagent uranium salt (A) and thorium salt (B), each several years old.

ity is pure and decays exponentially with the half-life of ^{234}Th (24.1 days). Curve B represents the growth of activity from a thorium fraction isolated from a reagent thorium salt several years old. Curves A and B compare favorably with analogous calculated curves such as those shown in Fig. 2, indicating that the thorium fractions isolated by the proposed method are radiochemically pure, with respect to β-active contaminants.

Chemical yield

The nature of the Thorium Isotopes Method for which this chemical procedure was developed requires no knowledge of chemical yields. Nevertheless, the procedure was controlled by the use of ^{234}Th (UX$_1$) tracer prepared in the laboratory in order to achieve the highest possible yields. Experimental chemical yields were determined by adding a known amount of ^{234}Th activity and finally counting the tracer in the isolated thorium. The ratio of the isolated activity after correction for decay to that of the added activity represented the chemical yield. The overall chemical yield was always better than 85%.

SUMMARY

A method for the isolation from siliceous materials of carrier-free chemically and radiochemically pure thorium is described. The method was applied and tested on several shale and deep-sea sediment samples used in the application of the Thorium Isotopes Method to the Dating of Marine Sediments. The chemical procedure consistently produces pure thorium in good yields. Several samples can be prepared simultaneously in a few hours.

RÉSUMÉ

Une méthode est proposée pour isoler un thorium chimiquement et radiochimiquement pur, de matières silicieuses. Ce procédé a été appliqué à divers échantillons de sédiments marins. Le procédé chimique permet d'obtenir de bons rendements en thorium pur. Plusieurs échantillons peuvent être préparés simultanément en quelques heures.

ZUSAMMENFASSUNG

Es wird eine Methode zur Abtrennung von trägerfreien, chemisch und radiochemisch reinem Thorium von Silikatmaterialien beschrieben. Die Methode wurde an verschiedenen Schiefern und Tiefseesedimenten angewandt und geprüft, bei denen die Thoriumisotopenmethode zur Zeitbestimmung von Seesedimenten benutzt wird. Das chemische Verfahren erzeugt reines Thorium in guter Ausbeute. Verschiedene Proben können gleichzeitig in einigen Stunden hergestellt werden.

REFERENCES

1 E. K. Hyde, *Report UCRL-8703*, 1959; *Report NAS-NS 3004*, 1960.
2 M. R. Verma, *J. Sci. Ind. Res. (India)*, 20 A Suppl. (1961) 1.

3 F. Feigl, P. Krumholz and E. Reiman, *Mikrochim. Acta*, 2 (1931) 395.
4 P. F. Thomason, M. A. Perry and V. M. Byerik, *Anal. Chem.*, 21 (1949) 1239.
5 M. H. Fletcher and R. G. Milkey, *Science*, 119 (1954) 445.
6 J. Clinch, *Anal. Chim. Acta*, 14 (1956) 162.
7 V. T. Athavale, K. P. Oke and M. Tillu, *Anal. Chim. Acta*, 21 (1959) 528.
8 V. I. Kuznetsov and I. V. Nikol'skaya, *Zh. Analit. Khim.*, **15** (1960) 299.
9 J. Korkisch and P. Antal, *Z. Anal. Chem.*, 173 (1960) 126.
10 A. L. Arnfelt and I. Edmundson, *Talanta*, 8 (1961) 473.
11 Y. S. Wei and K'uo Li, *T'ai-wan Ta Hsueh Kung Cheng Hsueh Kan*, 7 (1962) 118.
12 S. Katiyar and S. N. Tandon, *Mikrochim. Ichnoanal. Acta*, 1 (1964) 55.
13 Y. V. Kuznetsov, V. K. Legin and Z. N. Simonyak, *Radiokhimiya*, 5 (1963) 189.
14 F. Hecht, *Fortschr. Geol. Rheinland Westfalen*, 10 (1963) 193.
15 S. Abbey, *Anal. Chim. Acta*, 30 (1964) 176.
16 P. Kehler and R. Monaghan, *USAEC T.I.D. 18125*, 1962, 16 pp.
17 I. E. Starik and Yu. V. Kuznetsov, *Tr. Inst. Okeanol. Akad. Nauk SSSR*, 55 (1962) 121.
18 S. A. Reynolds, *Talanta*, 10 (1963) 611.
19 J. F. Lovering and J. W. Morgan, *Nature*, 197 (1963) 138.
20 H. Siemes and E. Schwarz, *Z. Erzbergbau Metallhuettenw.*, 17 (1964) 233.
21 I. Almodóvar, *Thorium Isotopes Method for Dating Marine Sediments*, Thesis, Carnegie Institute of Technology, U.S.A.E.C. Report NYO-8919, 1960.
22 E. Leininger and T. Chulsky, *J. Am. Chem. Soc.*, 71 (1949) 2385.
23 H. Remy and H. Falius, *Naturwissenschaften*, 43 (1956) 177.
24 F. Hagemann, L. I. Katzin, M. H. Studier, G. T. Seaborg and A. Ghiorso, *Phys. Rev.*, 79 (1950) 435.
25 E. D. Goldberg and M. Koide, *Science*, 128 (1958) 1003.
26 L. Kosta, *Rept. J. Stefan Inst.*, 3 (1956) 163.
27 L. Kosta, *Energia Nucl. (Milan)*, 5 (1) (1957) 37.
28 K. A. Krauss and F. Nelson, *Proc. Intern. Conf. Peaceful Uses At. Energy*, 7 (1955) 113.
29 C. K. MacLane and S. Peterson, in G. T. Seaborg and J. J. Katz, *The Transuranium Elements*, Nat. Nucl. Energy Ser. 14B, Div. IV, paper 19.3, McGraw-Hill, New York, 1949, p. 1371.
30 W. D. Ehman and T. P. Kohman, *Geochim. Cosmochim. Acta*, 14 (1958) 340.
31 T. P. Kohman, D. P. Ames and J. Sedlet, *The Transuranium Elements*, Nat. Nucl. Energy Ser. 14B, Div. IV, paper 22.60, McGraw-Hill, New York, 1949, p. 1675.
32 B. Mason, *Principles of Geochemistry*, John Wiley, New York, 1958, p. 44.
33 K. Rankama and T. G. Sahama, *Geochemistry*, University of Chicago Press, 1950, p. 570, 632.
34 H. Petterson, in H. Faul, *Nuclear Geology*, John Wiley, New York, 1954, p. 115, 329.

CHROMATOGRAPHISCHE TRENNUNG VON CALCIUM UND STRONTIUM DURCH ELUTION MIT AMMONIUMSULFATLÖSUNG

R. CHRISTOVA UND P. ILKOVA
Lehrstuhl für analytische Chemie, chemische Fakultät der Universität, Sofia (Bulgarien)

(Eingegangen den 21. Januar, 1965)

Zur Trennung von Calcium und Strontium mit Ionenaustauschern werden als Elutionsmittel Lösungen organischer Säuren und ihrer Salze verwendet[1-3]. Bei dieser Methode müssen in den meisten Fällen die organischen Calcium- und Strontiumkomplexe vor der Analyse im Eluat zerstört werden. Um diesen Nachteil zu vermeiden, wurde die eluierende Wirkung der Lösungen von Nitraten, Chloriden und von Salz- und Salpetersäure auf am Kationit festgehaltene Erdalkalimetalle untersucht[4-6], ohne dass es hierbei zu brauchbaren Trennungen gekommen wäre.

Eine Trennung des Calciums vom Strontium mit einem Ionenaustauscher sollte gelingen, wenn man die unterschiedliche Stabilität ihrer Sulfatkomplexe berücksichtigt. Calciumsulfat ist in Ammoniumsulfatlösung weitgehend, Strontiumsulfat dagegen nur schwer löslich. Aus diesem Grunde stellten wir Versuche an, das am Sulfokationit absorbierte Calcium bzw. Strontium durch Elution mit Ammoniumsulfatlösung zu trennen.

Um die Grenzen festzustellen, innerhalb derer die Änderung der Konzentration des Ammoniumsulfats im Elutionsmittel zweckmässig erscheint, stellten wir folgende Berechnungen an:

$$x + y = A \quad ; \quad \frac{x \cdot [\mathrm{SO_4}^{2-}]}{y} = K$$

Hierbei ist: x die Konzentration der freien Calciumionen, y die Konzentration der komplexgebundenen Calciumionen, A die Ansatzmenge des Calciums (alle Konzentrationsangaben in Grammionen/l), $K = 4.9 \cdot 10^{-3}$ die Dissoziationskonstante des Calciumsulfats. Die Berechnungen wurden mit Calciummengen von 0.1 mMol und Konzentrationen der Sulfationen von 0.1 mMol bis 10 Mol durchgeführt. Die Ergebnisse sind in Tabelle I wiedergegeben.

Untersuchungen mit Sulfationenkonzentrationen über 0.5 Mol sind offensichtlich zwecklos, da bei diesen Konzentrationen die Elutionskurven alle ungefähr dasselbe Aussehen haben.

Da die Dissoziationskonstante des Strontiumsulfats nicht bekannt ist, wurde die geeignetste Konzentration durch Versuche ermittelt und zwar für Sulfationenkonzentrationen zwischen 0.2–0.5 Mol.

TABELLE I

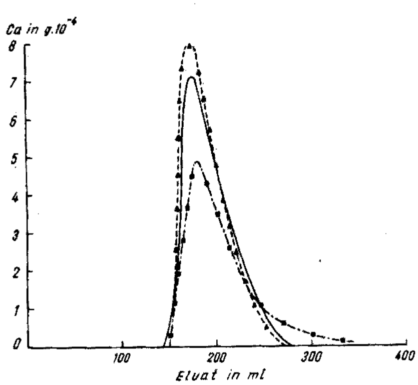
Konzentration der Sulfationen in g-Ionen/l	*Konzentration des komplexgebundenen Calciums*	
	in g-Ionen/l·10^{-6}	*in % der Gesamtmenge*
0.0001	2.0	2.0
0.001	16.0	16.0
0.01	67.1	67.1
0.1	95.3	95.3
0.5	99.0	99.0
1.0	99.5	99.5
10.0	99.9	99.9

EXPERIMENTELLER TEIL

Die Versuche wurden mit einer Sulfokationitkolonne Wofatit KPS-200 durchgeführt. Das Eluat wurde in Portionen von je 10 ml gesammelt. Nach Verdünnung auf 50 ml bestimmten wir das Calcium und Strontium mikrokomplexometrisch mit Thimolfluorexon als Indikator. Strontiummengen unter 0.05 mMol wurden spektralphotometrisch mit *o*-Kresolphthaleinkomplexon bestimmt[7].

Beträgt die Konzentration der Sulfationen 0.5 Mol, dann fallen die Anfänge der Elutionskurven von Calcium und Strontium fast zusammen. Sie werden mit sinkender Sulfationenkonzentration nach höheren ml-Werten verschoben, wobei die Verschiebung beim Strontium grösser ist. Die Trennung fiel am besten aus bei einer Sulfationenkonzentration von 0.26 Mol entsprechend einer 3.4%igen Ammoniumsulfatlösung.

Die zweckmässigste Korngrösse des Austauscherharzes ist 0.10–0.16 mm. Bei grösseren Korngrössen wird das Calcium in einem um 100 ml grösseren Volumen eluiert und seine Elutionskurve von der des Strontiums überdeckt. Ist die Korngrösse geringer, so sinkt die Durchlaufgeschwindigkeit unter 1 ml/sec und führt zu langen Trennzeiten. Die Abhängigkeit der Form der Elutionskurve des Calciums von der Durchlaufgeschwindigkeit zeigt die Fig. 1. Als geeignete Durchlaufgeschwindigkeit ergab sich 1 ml/min.



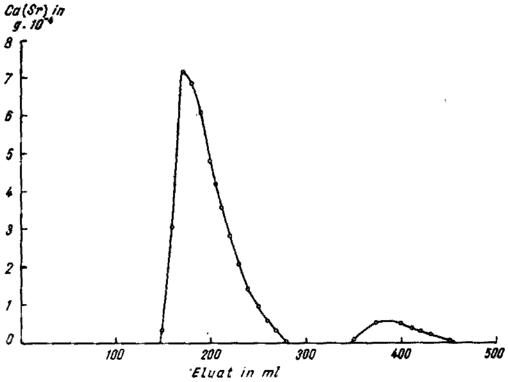


Fig. 1. Abhängigkeit der Art der Elutionskurven des Calciums von der Durchlaufgeschwindigkeit: ■—■—■ 1 ml/30 sec, ——— 1 ml/60 sec, –▲–▲– 1 ml/120 sec.

Fig. 2. Elutionskurven von Calcium und Strontium beim Molarverhältnis Ca : Sr = 20.

Es wurde festgestellt, dass eine vollständige Trennung des Calciums vom Strontium bei Konzentrationen von 0.1 mMol für jedes Element zu erreichen ist, wenn bei der angegebenen Korngrösse die Kolonnenhöhe 20 cm beträgt.

Unter den so ermittelten optimalen Bedingungen wurden Elutionskurven mit einem Konzentrationsverhältnis Calcium zu Strontium von 1 bis 100 aufgenommen. In Fig. 2 sind die Elutionskurven beim Molverhältnis Ca : Sr = 20 : 1 dargestellt. Die Kurven ergaben, dass das Ende der Elutionskurve des Calciums bei höherer Calciumkonzentration nach rechts verschoben wird, z.B. bei zehnfacher Erhöhung der Konzentration um etwa 12 ml. Andererseits wird der Beginn der Elutionskurve des Strontiums mit sinkender Konzentration nach rechts verschoben und zwar um etwa 30 ml bei zehnfacher Konzentrationserniedrigung. Konzentriertere Lösungen lassen sich also dann gut trennen, wenn grosse Mengen Calcium neben kleinen Mengen Strontium vorliegen.

ARBEITSVORSCHRIFT

Eine Kolonne von 20 cm Höhe, 0.7 cm Diameter und einer Korngrösse des Austauscherharzes von 0.10–0.16 mm wird mit 2 *N* HNO_3 durchspült, bis das Eluat frei von Calcium ist. Nach dem Auswaschen mit Wasser, wurden Calcium und Strontium in 0.1 *N* Salzsäure oder 3.4%iger $(NH_4)_2SO_4$-lösung aufgegeben. Das Calcium wird mit 320 ml 3.4%iger $(NH_4)_2SO_4$-lösung (von dem die ersten 70 ml verworfen werden) und das Strontium anschliessend mit 100 ml 2 *N* HNO_3 eluiert, in beiden Fällen bei einer Durchlaufgeschwindigkeit von 1 ml/min.

Zur Bestimmung des Calciums verdünnt man 25 ml des $(NH_4)_2SO_4$-Eluats mit 100 ml Wasser, gibt 4 ml 6 *N* KOH hinzu und titriert mit 0.002 Mol EDTA-Lösung. 20 ml des Strontiumeluats werden zur Trockne verdampft, mit Wasser aufgenommen und das Strontium je nach Menge mikrokomplexometrisch oder spektralphotometrisch mit *o*-Kresolphthaleinkomplexon bestimmt. Bei der Bestimmung des Calciums beträgt der mittlere relative Fehler 1%, bei der des Strontiums 5%.

TABELLE II

Probe	*Calcium in mg*		*Strontium in mg*	
	Gegeben	*Gefunden*	*Gegeben*	*Gefunden*
1	1.00	0.96	0.19	0.18
2	2.00	2.00	0.19	0.19
3	4.00	4.01	0.095	0.090
4	5.00	4.98	0.095	0.092

In der Tabelle II sind die Ergebnisse, wie sie mit der beschriebenen Methode mit künstlichen Gemischen erhalten wurden, dargestellt.

Zur Zeit laufen weitere analoge Versuche zur Trennung der Elemente Mg, Ca, Sr, und Ba sowie dreiwertiger Metalle.

ZUSAMMENFASSUNG

Es wurde ein Verfahren entwickelt zur chromatographischen Trennung von an

Sulfokationit adsorbierten Calcium und Strontium durch Elution mit Ammoniumsulfatlösung. Das Verfahren ist anwendbar beim Konzentrationsverhältnis des Calciums zum Strontium $\geqslant 1$. Sein Vorteil besteht darin, dass unmittelbar im Eluat eine quantitative Analyse getrennter Elemente möglich ist.

SUMMARY

A method is described for the chromatographic separation of calcium and strontium adsorbed on a cation-exchange resin, by means of elution with ammonium sulphate solution. The method is suitable for Ca : Sr ratios $\geqslant 1$. The separated elements can be determined directly in the eluate.

RÉSUMÉ

Une méthode est décrite pour la séparation chromatographique du calcium et du strontium, adsorbés sur résine, échangeur de cations, avec élution au moyen d'une solution de sulfate d'ammonium. Ce procédé convient pour des rapports Ca : Sr $\geqslant 1$. Les éléments séparés peuvent être dosés directement dans l'éluat.

LITERATUR

1 M. LERNER UND W. RIEMAN, *Anal. Chem.*, 26 (1954) 610.
2 P. POVONDRA, Z. SULCEK, R. PRIBIL UND R. STANGL, *Talanta*, 8 (1961) 705.
3 N. A. MAYERS, *Nature*, 183 (1959) 1807.
4 S. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 23 (1960) 441.
5 S. K. MAJUMDAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 356.
6 S. K. MAJUMDAR AND A. K. DE, *Anal. Chim. Acta*, 25 (1961) 452.
7 F. H. POLLARD AND J. V. MARTIN, *Analyst*, 81 (1956) 384.

FLAME-PHOTOMETRIC DETERMINATION OF SODIUM IN URANIUM ORES*

H. KRAMER** AND L. J. PINTO
U.S. Atomic Energy Laboratory, New Brunswick, N. J. (U.S.A.)

(Received February 8th, 1965)

A rapid routine method has been developed for the determination of sodium in siliceous uranium ores. The method is also applicable to the other types of silicates such as glasses, phosphate rocks and argillaceous limestones. Separations are not required, and the results compare favorably with values found by standard gravimetric procedures. The lower limit of sensitivity is 0.001%.

The flame-photometric determination of sodium in constant matrix material is well documented, but only a few general procedures regarding the application, without separation, to ores containing a variety of elements in different concentrations have been reported. BRODERICK AND ZACK[1] have described a method of variance for the determination of sodium, potassium, and lithium in the presence of each other. JENKINS[2] has used a correction curve for the enhancing effect of potassium on sodium emission. WEST *et al.*[3] prepared a radiation buffer which is added to both standards and sample to minimize the effect of diverse ions in the determinations of sodium, potassium, and lithium. KRAMER[4] used a more complex radiation buffer which was also added to the standards and sample to eliminate interference effects in the determination of calcium.

In this study, a radiation buffer was also used. Spectrographic analyses of the representative ore samples, Canadian, South African, and Colorado, were used to determine the elements to be included in the buffer.

Interference studies were carried out to determine the effects of the elements in the buffer. Initially, increasing amounts of perchloric acid were added to 10 p.p.m. of sodium and the effect on the emission at 589 mμ with the oxy–hydrogen flame was measured. Although the perchloric acid suppressed the emission slightly at higher concentrations, the effect of the desired 3% (v/v) concentration was insignificant. Next, the effect of increasing concentrations of uranium was tested with 10 p.p.m. sodium in 3% perchloric acid. Up to an arbitrary limit of 425 p.p.m., there was no effect. In this way, successive elements were added in the concentration range and in the order indicated in Table I.

Molybdenum, lead, chromium, cobalt, antimony, titanium and tin were omitted from consideration because these elements are usually present in only trace quantities. Arsenic was also eliminated because of the danger of aspirating it into the air.

These interference tests were used in determining the radiation buffer composition. Although with most of the elements there appeared to be little individual

---

[*] Work performed under the auspices of the U.S. Atomic Energy Commission.
[**] Now at Brookhaven National Laboratory, Upton, L.I., New York.

interference when studied in the order given in Table I, all of the elements except those mentioned above were included. When this buffer, which contained high concentrations of diverse ions, was added to both standards and sample, small variations in concentrations within the samples themselves had little or no effect upon the sodium emission. The visible effect of the buffer was to flatten out the usual parabolic transmission *vs.* concentration curve obtained for simple sodium solutions into a curve

TABLE I

ELEMENTS STUDIED FOR RADIATION BUFFER

Element	*Concentration range added to Na (p.p.m.)*	*Concentration in final standard solution (p.p.m.)*	*Effect on Na emission*
U	0–425	425	None
V	0–200	10	None
Ca	0–200	20	None
Fe	0–200	20	None
S (SO_4^{2-})	0–170	3.3	None
P (PO_4^{3-})	0–500	200	Slight suppression leveling off at 200 p.p.m.
Mg	0–400	200	Enhancement leveling off at 200 p.p.m.
Al	0–400	100	None
K	0–400	200	Enhancement leveling off at 200 p.p.m.
Mn	0–200	10	None
B	0–200	10	None
As	0–200	—	None
Mo	0–200	—	None
Cu	0–200	10	None

TABLE II

COMPARATIVE ANALYSIS OF TYPICAL ORES

Sample	*Sodium oxide (%)*	
	Gravimetric	*Flame photometric*
Colorado Uranium Ore	12.5	12.5
Colorado Uranium Ore	8.09	7.98
Canadian Uranium Ore	3.05	3.04
South African Uranium Ore	(0.0087)[a]	0.0070
South African Uranium Ore	(0.012)[a]	0.013

[a] Analysed by the "dilution technique"[5].

TABLE III

COMPARATIVE ANALYSES OF SYNTHETIC SAMPLES

Samples	*Sodium oxide (%)*	
	Calculated	*Flame photometric*
75 mg U_3O_8 + 25 mg NBS #97	0.11	0.09
50 mg U_3O_8 + 20 mg NBS #1A + 30 mg NBS #98	0.21	0.22
50 mg U_3O_8 + 50 mg NBS #120	0.12	0.12
50 mg U_3O_8 + 15 mg NBS #78 + 5 mg NBS #120 + 15 mg NBS #99 + 15 mg NBS #88	1.69	1.84
50 mg U_3O_8 + 25 mg NBS #29A + 25 mg NBS #78	0.09	0.09

that was nearer a straight line, even in the presence of large amounts of potassium which caused considerable enhancement of sodium emission.

The results obtained by analyzing the 3 types of ores are shown in Table II.

In Table III are given results obtained on a sample of U_3O_8 to which were added known amounts of sodium based on the addition of definite amounts of various National Bureau of Standards (NBS) standard samples as noted.

The scope of the method was further evaluated by analyzing various National Bureau of Standards standard samples (Table IV).

TABLE IV

COMPARATIVE ANALYSES OF NBS STANDARD SAMPLES

NBS sample	*Sodium oxide (%)*	
	Certified value	*Flame photometric*
Argillaceous Limestone #1A	0.39	0.43
Phosphate Rock #120	0.14	0.13
Glass #80	16.65	16.46
Pb–Ba Glass #89	5.70	5.74
Borosilicate Glass #93	4.16	4.26
Fluorspar #79	0.06	0.02
Plastic Clay #98	0.28	0.26

These data show that with some samples a considerable concentration latitude exists for certain elements, *e.g.*, lead or calcium, present in concentrations far greater than in the radiation buffer. The data also bear out the fact that some of the mentioned elements, when present in either trace or minor amounts, can be omitted from the radiation buffer.

EXPERIMENTAL

Apparatus and reagents

Flame photometer. A Beckman model DU spectrophotometer with a model 9220 flame photometer attachment and a model 4300 photomultiplier were used.

All reagents were reagent grade.

Radiation buffer. To prepare this solution, the following materials were placed in a 400-ml beaker: 10.00 g of sodium-free black uranium oxide (U_3O_8), 0.46 g of ammonium metavanadate, 1.00 g of calcium carbonate, 0.40 g of iron wire, 4.00 g of magnesium metal, 2.00 g of aluminum metal, 7.63 g of potassium chloride, 0.72 g of manganous chloride tetrahydrate, 1.14 g of boric acid, 0.54 g of cupric chloride dihydrate. About 100 ml of water was added to the beaker, the beaker was covered with a watch glass and 200 ml of 70% perchloric acid was added carefully in small increments. Some salts may precipitate at this point, but they were disregarded. To the beaker were then added 0.20 g of sulfate (20.0 ml of a solution made by diluting 5.77 ml of concentrated sulfuric acid to 1 l), and 12.25 g of phosphate (100.0 ml of a solution made by diluting 22.00 ml of 85% orthophosphoric acid to 250 ml). The solution and salts were then transferred to a 4-l volumetric flask and diluted to about 3.5 l. The salts were dissolved by agitation, and the solution was diluted to the mark and transferred to a polyethylene bottle.

Stock sodium solution. A stock solution containing 1 mg/ml was prepared by dissolving 5.084 g of sodium chloride, previously fused in a platinum dish and subsequently ground, in water and diluting to 2 l in a volumetric flask.

Standard sodium solutions. Standard solutions containing 50, 40, 30, 20, 10, 5, 1 and 0 p.p.m. of sodium were prepared by first diluting 50 ml of the stock solution (1 mg/ml) to 500 ml and then adding by buret 50.00, 40.00, 30.00, 20.00, 10.00, 5.00 and 1.00 ml of this diluted stock solution to 100-ml volumetric flasks. No aliquot was added to one volumetric flask for the 0 p.p.m. solution. To each flask was added 3 ml of 70% perchloric acid, 20.00 ml of the radiation buffer and water to volume.

Procedure

Sample preparation. Weigh a 0.1-g sample or less into a 125-ml platinum dish. Add 3 ml of 70% perchloric acid and about 3 ml of 48% hydrofluoric acid. Heat on the steam bath until the appearance of the first fumes of perchloric acid. Wash down the sides of the dish with water and evaporate again to the first fumes of perchloric acid. If the sample is not completely dissolved, repeat the addition of the hydrofluoric acid and the double evaporation.

Add about 25 ml of water to the dish and digest to effect complete solution. Transfer the solution to a 100-ml volumetric flask and cool. Add 20.00 ml of the radiation buffer and dilute to volume with water.

If the sample contains over 5% sodium, make an appropriate dilution of the dissolved sample before adding the radiation buffer so that the sodium concentration in the final solution is less than 50 p.p.m.

If the sample contains less than 0.1% sodium, prepare a reagent blank along with the sample.

Optical measurement. Adjust the flame photometer to the following settings: wavelength, 589 mμ; sensitivity control, 5 turns from clockwise limit; selector switch, 0.1; phototube, blue, with 22 megohm resistor; slit width, 0.02 to 0.1 mm; photomultiplier sensitivity, sufficient so that the above slit width can be used; hydrogen pressure, 4 p.s.i.; oxygen pressure, 10 p.s.i.

Turn on the spectrophotometer and allow for a 5-min warm-up period. Adjust the oxygen cylinder pressure regulator to 20 p.s.i. and the hydrogen cylinder pressure regulator to 10 p.s.i. Now adjust the oxygen pressure in the flame photometer to 10 p.s.i. and the hydrogen to 4 p.s.i. Carefully light the burner and allow for a 5-min warm-up.

With the wavelength set at 589 mμ and the 50-p.p.m. standard being aspirated, adjust the slit width so that the transmission is about 50%. Now slowly move the wavelength dial to either side of 589 mμ to obtain maximum transmission with a minimum slit width. Balance the dark current. Set the transmission to 100% and with the 50-p.p.m. standard being aspirated, adjust the slit width and sensitivity to balance the galvanometer. After the adjustment is made, correct any drift by means of the hydrogen pressure control.

Remove the 50-p.p.m. standard and aspirate the unknown. Open the shutter and balance the galvanometer with the transmission dial by turning slowly at a constant rate in a counter clockwise direction.

Select the standard solution with the next higher concentration to the unknown and the standard with next lower concentration so that the sample is bracketed between the two standards. Record 3 readings for the higher standard, 3 for the unknown and 3 for the lower standard. The readings must agree within 1% for each level. Calculate the sodium content of the unknown by assuming that the transmission *vs.* concentration plot is linear within each 10 p.p.m. increment.

For samples with sodium values below 0.5% but above 0.1%, set the 5-p.p.m. standard solution to 100% transmission and record readings of the 0 p.p.m. and the sample so that the sample is bracketed. For samples below 0.1%, set the 1-p.p.m. standard at 100% transmission and record readings of the 0-p.p.m. standard and the sample. For the samples below 0.1%, run a reagent blank, and subtract from the sample transmission the difference between the blank reading and 0-p.p.m. standard reading.

Note. If rapidity is desired at the sacrifice of some accuracy and precision, a standard curve may be prepared by means of the standard solutions. A single reading of the sample is then recorded and the sodium value is determined from this standard curve. A check of at least 2 points on the standard curve should be carried out with each set of unknowns.

SUMMARY

A flame-photometric method of determining sodium in uranium, phosphate, carbonate, and silicate rocks has been developed. The mutual enhancement of the alkali metals is overcome by the addition of a radiation buffer added to both the sample and to the standards. The method is rapid and suitable for routine analysis. Results obtained are within ±2% of the sodium content.

RÉSUMÉ

Une méthode photométrique de flamme est proposée pour le dosage du sodium dans les minerais d'uranium, les roches phosphatées, carbonatées et silicatées. L'augmentation mutuelle des métaux alcalins est évitée par addition d'un tampon de radiation à l'échantillon et aux étalons. La méthode est rapide et convient à l'analyse courante. L'erreur est de ±2% de la teneur en sodium.

ZUSAMMENFASSUNG

Eine flammenphotometrische Methode zur Bestimmung von Natrium in Uran, Phosphat, Carbonat und Silikatgesteinen wurde entwickelt. Die gegenseitige Anregung der Alkalien wurde durch Zugabe eines Strahlungspuffers sowohl zur Standardlösung als auch zur Probelösung verhindert. Die Methode ist schnell auszuführen und wird für Routine-Analysen empfohlen. Natrium kann mit einem Fehler von ±2% bestimmt werden.

REFERENCES

1 E. J. Broderick and P. G. Zack, *Anal. Chem.*, 23 (1951) 1455.
2 L. Jenkins, *U.S. Geological Survey TEI-45*, 1954.
3 P. W. West, P. Folse and D. Montgomery, *Anal. Chem.*, 22 (1950) 667.
4 H. Kramer, *Anal. Chim. Acta*, 17 (1957) 521.
5 Beckman Instruments, Inc., *Instruction Manual #334-A*, 1954.

DETERMINATION OF MOLYBDENUM IN HAIR AND WOOL BY NEUTRON ACTIVATION ANALYSIS*

W. B. HEALY** AND L. C. BATE

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)

(Received October 16th, 1964)

Neutron activation analyses of human hair and wool samples from 2 New Zealand areas were performed at Oak Ridge National Laboratory. Since molybdenum was of particular interest in this work but present only in submicrogram quantities, it was necessary to develop a method for the separation of molybdenum in amounts of 0.1 μg or less, from interfering radionuclides. A standardized procedure involving irradiation, separation, and measurement of molybdenum in samples of hair and wool ash was devised.

The ashed samples were irradiated for 15 min in the ORR (Oak Ridge Research Reactor) pneumatic tube at a flux of $5 \cdot 10^{13}$ n/cm²/sec to produce ^{101}Mo with subsequent measurement of the ^{101}Tc daughter. ^{101}Tc has a higher percentage abundance of the 0.31-MeV γ-ray per disintegration than any of the ^{101}Mo γ-rays and offered the most sensitive and convenient method of determining molybdenum. Under these conditions, however, the Compton and bremsstrahlung effects from radionuclides, such as ^{69m}Zn, ^{64}Cu, ^{56}Mn, ^{80}Br, ^{82}Br, ^{24}Na, ^{37}S, and ^{32}P, made measurement of the 0.31-MeV ^{101}Tc γ-ray photopeak impossible. The use of α-benzoinoxime in chloroform as an extractant for molybdenum, together with tungsten and vanadium, has been reported[1]. The effectiveness of this reagent in separating submicrogram quantities of molybdenum from interfering radionuclides in wool and hair and the subsequent measurement of ^{101}Mo as the ^{101}Tc daughter was therefore studied.

EXPERIMENTAL

Reagents

Distilled water and reagent-grade chemicals were used in the preparation of all solutions. α-Benzoinoxime (No. 1877 Eastman, Rochester, N.Y.) was used as a 0.1% (w/v) solution in chloroform. Molybdenum metal wire (General Electric), 99.8+% pure, annealed and cleaned, bright finish, 0.015″ diameter. A stock solution was prepared by dissolving 2 mg of the metal in concentrated nitric acid and sulfuric acid and diluting to 1 l.

---

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

** Present address: Soil Bureau, Department of Scientific and Industrial Research, Private Bag, Lower Hutt, New Zealand.

Procedure

Hair or wool samples were washed[2] 3 times and shaken for 15 min each time in an aqueous solution of a non-ionic detergent, KyroEO (alkylphenol ethylene oxide condensate type, supplied by Proctor and Gamble) and dried. Approximately 2 g of dried hair was ashed at 480° for about 6 h and irradiated for 15 min in the ORR pneumatic tube at a flux of $5 \cdot 10^{13}$ n/cm²/sec. Following irradiation, the sample was transferred to a beaker containing 1 ml of sulfuric acid and 1 ml of nitric acid, with approximately 5 ml of water. About 0.5 g of sodium bromide was added to the ash solution and dissolved, and then *ca.* 0.5 g of sodium bromate was added. Free bromine was boiled off to remove most of the ^{80}Br and ^{82}Br, and the solution was evaporated down to fumes of sulfur trioxide. The solution was diluted, cooled, and transferred to a separatory funnel, and the *ca.* 30 ml aqueous phase was extracted twice with 5-ml portions of 0.1% α-benzoinoxime in chloroform.

The first extraction was made between the 9th and 10th minute out of the reactor, followed immediately by a second 1-min extraction. The 10th minute out of the reactor, *i.e.*, at the completion of the first extraction, was taken as zero post-extraction time. The 10 ml of chloroform phase was counted on a 3″ × 3″ NaI crystal with 1/2″ polyethylene absorber, using a 200-channel analyzer, to measure the 0.31 MeV ^{101}Tc γ-ray photopeak. The extracted sample was counted for 5 min starting 15 min after extraction (corresponding to 25 min after reactor discharge).

A molybdenum wire of 2.0 mg was used for each standard. After the 15-min irradiation, the molybdenum standard was dissolved in 1 ml of concentrated sulfuric acid and 1 ml of nitric acid and the solution was diluted to 1 l. A 50-μl aliquot was processed and counted in the same manner as the samples. Since vanadium and tungsten were also extracted by this procedure, ^{52}V and ^{187}W were measured 5 min after the extraction and approximately 24 h later, respectively, to measure the ^{52}V and ^{187}W radioactivity at optimum conditions in relation to the interfering radioactivity.

RESULTS

Typical results of extracting molybdenum from neutron-irradiated wool ash are given in Table I. A typical γ-ray spectrum of the irradiated and cleaned wool ash on which no separation has been made is shown in Fig. 1, curve A. In this γ-ray spectrum, there is no indication of a photopeak at the energy (0.31 MeV) of the ^{101}Tc γ-ray. This spectrum was taken between 25 and 30 min after removal from the reactor. However, in Fig. 1, curve B, which shows the α-benzoinoxime extract of the wool ash,

TABLE I

TYPICAL RESULTS FOR DETERMINATION OF MOLYBDENUM IN HAIR AND WOOL

Sample no.	*A*	*B*	*C*	*D*	*E*	*F*
Mo in hair[a] µg/g	0.06	0.04	0.09	0.10	0.13	0.02
Mo in wool[a] µg/g	0.04	0.25	0.20	0.58	0.08	0.11

[a] Cleaned and dried.

the γ-ray photopeak of ^{101}Tc can be clearly observed and measured. It appears that ^{198}Au (0.41 MeV) is also extracted by this procedure although no checks were made on extraction efficiency. The ^{52}V (1.43 meV) γ-ray photopeak is very near the ^{24}Na (1.37 MeV) γ-ray photopeak and is measured by analyzing 2 or more decay curves in this region. The ^{187}W is measured the next day after the ^{56}Mn has decayed out and

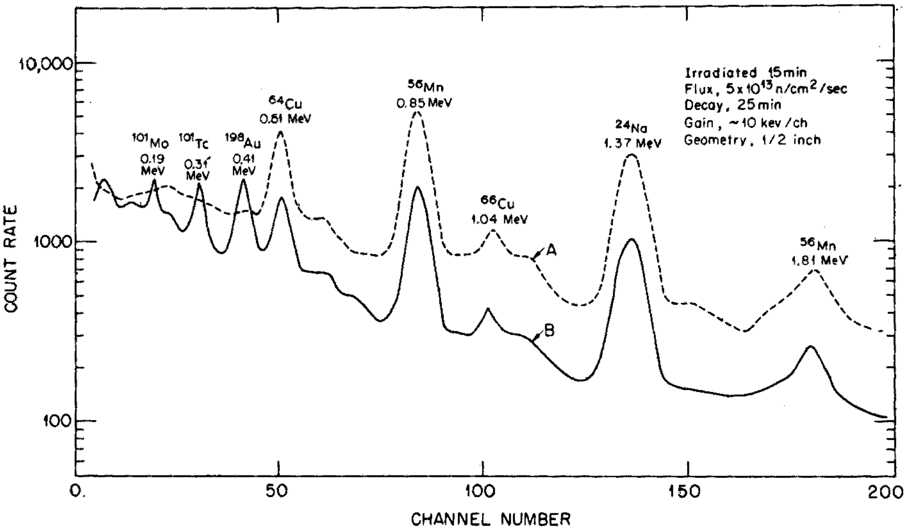


Fig. 1. γ-Ray spectra of irradiated wool ash. Curve A: 1/6000 of original sample. Curve B: α-benzoinoxime extract.

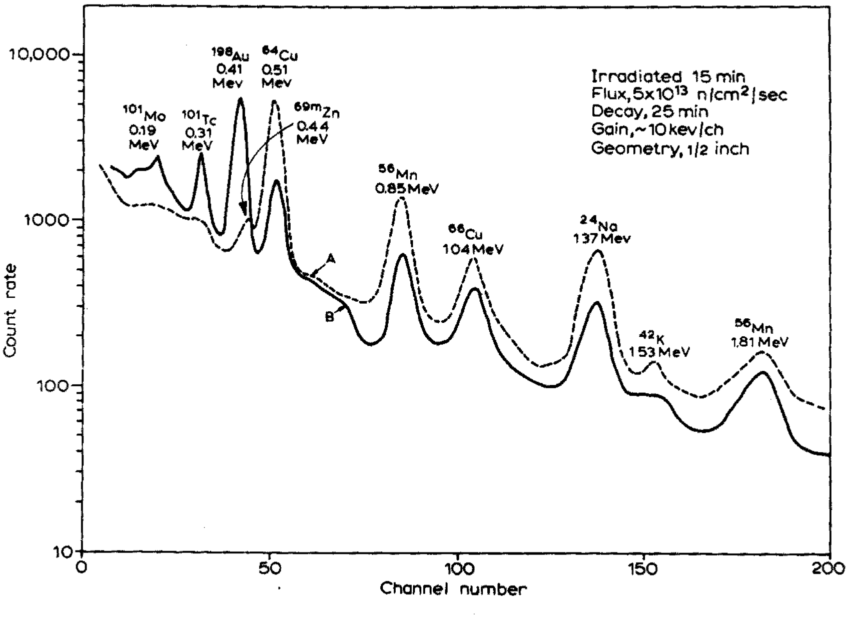


Fig. 2. γ-Ray spectra of irradiated hair ash. Curve A: 1/1000 of original sample. Curve B: α-benzoinoxime extract.

the ^{64}Cu has decayed about two half-lives. The ^{187}W is measured over the 0.68-MeV γ-ray photopeak.

Typical molybdenum data from neutron-irradiated hair ash are given in Table I. In Fig. 2, curve A, is a γ-ray spectrum of irradiated hair ash; curve B is the γ-ray spectrum of the separated ^{101}Mo. All the γ-ray spectra were taken between 25 and 30 min after removal from the reactor.

After the ^{101}Mo separation, the ^{101}Tc daughter was allowed to grow in for 15 min before the radioactivity was measured over the 0.31-MeV γ-ray photopeak of ^{101}Tc.

Extraction efficiency

Table II gives the results of successive 5-ml extractions of 2.2 μg and 0.11 μg of Mo from 30 ml of 1 *N* aqueous sulfuric acid solution by the above procedure. The counts were taken over the 0.30–0.32 MeV γ-ray photopeak area after background correction.

TABLE II

EXTRACTION EFFICIENCY OF MOLYBDENUM FROM 1 *N* H_2SO_4 WITH α-BENZOINOXIME–$CHCl_3$
(30 ml—aqueous; 5 ml—organic)

	2.2 μg Mo (counts/min)[a]		*0.11 μg Mo (counts/min)*[a]
Extraction (1)	8278	9739	488
Extraction (2)[b]	1461		
Extraction (3)[b]	243		11
Total	9982		499
Percent activity in extractions (1) plus (2)	97.6		97.8

[a] Counts/min over the 0.30–0.32-MeV γ-ray photopeak area after background correction.
[b] Fresh α-benzoinoxime–$CHCl_3$ used in each extraction.

Growth of ^{101}Tc daughter

Approximately 2 mg of Mo metal was irradiated for 7 sec in the ORR pneumat-

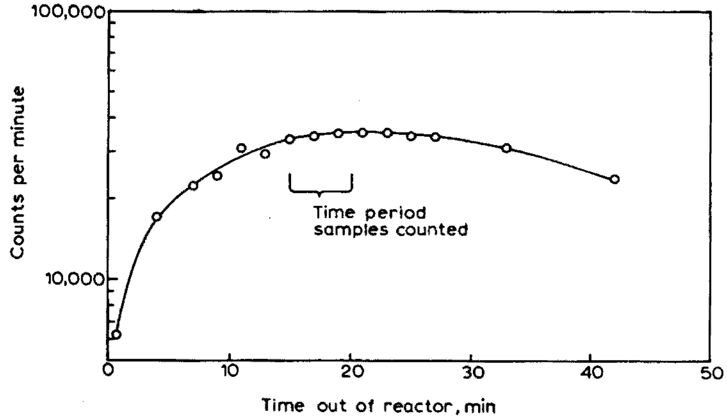


Fig. 3. Growth of ^{101}Tc in ^{101}Mo. Energy range 0.30–0.32 MeV.

ic tube at a flux of $5 \cdot 10^{13}$ n/cm²/sec. The activity of this sample was counted directly without separation to observe the growth of the ^{101}Tc daughter, which would be present at only very low levels at the end of the 7-sec irradiation period. The ^{101}Tc growth is shown in Fig. 3.

It can be seen that there was very little change in radioactivity from about 15 to 25 min after the sample came out of the reactor. The same result was obtained with a 0.124-μg molybdenum standard which was extracted as above; the radioactivity from 0.30–0.32 MeV was essentially the same over the period 15–25 min after extraction. It was on the basis of these results that a 5-min count over the 15–20-min period following extraction was adopted.

DISCUSSION

Although this method was developed for the determination of molybdenum in hair and wool, it is applicable to other biological samples containing Zn, Cu, Mn, S, P, Na, and Br. Separations of ^{101}Mo at submicrogram levels from the bulk of interfering radionuclides appeared to be efficient. In some cases, probably depending on the levels originally present, traces of bromine, manganese and sodium were detected in the chloroform phase. It is not known if this was actual extraction or some mechanical carry-over, but the amounts were not sufficient to interfere with determinations of molybdenum. The time required for the dissolution of the ash and separation of the molybdenum was about 12 min; this allowed the use of the 14.6-min ^{101}Mo radionuclide. The radioactivity measurements were made after the ^{101}Tc daughter had been permitted to grow in. The sensitivity of the molybdenum determination was thus increased, as the ^{101}Tc has a higher percentage abundance of 0.31-MeV γ-rays per disintegration than is present in the ^{101}Mo decay. This method, also, could be employed for the separation of the short-lived molybdenum radionuclides from fission products. The ashing temperature of 480° was chosen to prevent losses of molybdenum[3] and also to leave the ash, which was very fine, in a form reasonably easy to transfer. Some organic matter usually remained, but the bromate–bromide treatment helped to destroy this and ensured that the molybdenum was in the hexavalent state.

This work was carried out by one of the authors (W.B.H.) under a U.S. Public Health Fellowship.

SUMMARY

Neutron activation analysis was applied to the determination of molybdenum in hair and wool. Ashed samples of hair and wool were irradiated for 15 min at a flux of $5 \cdot 10^{13}$ n/cm²/sec to produce ^{101}Mo. An acid solution of the ash was first boiled in the presence of sodium bromide and bromate to volatilize bromine (^{80}Br and ^{82}Br radioisotopes interfere) and then extracted with 0.1% α-benzoinoxime in chloroform to remove ^{101}Mo from other interfering radionuclides. The ^{101}Tc daughter from ^{101}Mo was measured over the 0.31-MeV γ-ray photopeak after allowing the separated ^{101}Mo to decay for 15 min. The molybdenum concentration in hair varied from 0.02 to 0.13 μg/g while wool was found to contain 0.04–0.58 μg/g.

RÉSUMÉ

L'analyse par activation au moyen de neutrons a été appliquée au dosage du molybdène dans les cheveux et la laine. Les échantillons sont irradiés pendant 15 min après incinération, avec un flux de $5 \cdot 10^{13}$ n/cm^2/sec pour produire ^{101}Mo. La solution acide des cendres est portée à ébullition, en présence de bromure de sodium et de bromate, puis extraite au moyen d'une solution de benzoinoxime dans le chloroforme pour éliminer ^{101}Mo d'autres radioéléments. La concentration de molybdène dans les cheveux varie de 0.02 à 0.13 μg/g, tandis que celle dans la laine est de 0.04 à 0.58 μg/g.

ZUSAMMENFASSUNG

Mit der Neutronenaktivierungsanalyse wurde Molybdän in Haaren und Wolle bestimmt. Haar- und Wollaschen wurden 15 Min mit einem Fluss von $5 \cdot 10^{13}$ n/cm^2/sec bestrahlt, um ^{101}Mo zu erzeugen. Eine saure Lösung der Asche wurde zuerst in Gegenwart von Natriumbromid und -bromat gekocht um das Brom zu verdampfen (^{80}Br und ^{82}Br stören) und dann mit 0.1%iger Lösung von Benzoinoxim in Chloroform extrahiert, um das ^{101}Mo von anderen störenden Radionukliden abzutrennen. Nachdem das ^{101}Mo 15 Min lang zerfallen war, wurde von der Tochter ^{101}Tc der 0.31-MeV γ-Photopeak gemessen. Die Molybdänkonzentration im Haar liegt zwischen 0.02 und 0.13 μg/g, während Wolle 0.04–0.58 μg/g enthält.

REFERENCES

1 G. GOLDSTEIN, D. L. MANNING AND O. MENIS, *Anal. Chem.*, 30 (1958) 539.
2 L. C. BATE, *J. Forensic Sci.*, 10 (1) (1965) 60.
3 W. B. HEALY AND W. J. MCCABE, *Anal. Chem.*, 35 (1963) 2117.

NON-DESTRUCTIVE NEUTRON ACTIVATION DETERMINATION OF SILVER AND ANTIMONY IN BISMUTH BY γ,γ-COINCIDENCE SPECTROMETRY

J. I. KIM* AND J. HOSTE
Laboratory for Analytical Chemistry, Ghent University, Ghent (Belgium)
(Received February 19th, 1965)

Non-destructive activation analysis for the determination of silver by means of ^{110}Ag has been investigated by many authors[1-5]. For antimony, ADAMS AND HOSTE have developed a non-destructive method using ^{122}Sb and an internal standard technique[6], or ^{124}Sb and dual-channel γ-spectrometry[7] or sum-coincidence spectrometry[8].

Activation analysis for silver and antimony in various matrices, with chemical separation, has been studied by numerous workers, as is apparent from the surveys of BOCK-WERTHMANN[9-11]. When ^{110m}Ag and ^{124}Sb are used they all resort to a chemical separation, especially in the simultaneous determination of both elements. In bismuth, OKADA[1] and NAKAI *et al.*[4] determined silver by a non-destructive method using ^{110}Ag, whereas ALIMARIN AND YAKOVLEV[12] and KAMEMOTO AND YAMAKISHI[13] used a destructive technique for the determination of antimony.

In the present paper, a simultaneous, non-destructive determination of silver and antimony is described by γ,γ-coincidence spectrometry of ^{110m}Ag and ^{124}Sb. Up to now, activation analysis by means of coincidence spectrometry has been used in a number of cases, such as the determination of selenium by FINEMAN *et al.*[14], copper by PERKINS[15] and PETIT AND ENGELMAN[16], praseodymium by FUJII *et al.*[17], nickel by MALVANO AND FASOLO[18], antimony by ADAMS AND HOSTE[8] and manganese by BORG *et al.*[19]. Moreover, the utility of fast coincidence spectrometry has been demonstrated by LJUNGGREN[20] on scandium-46, selenium-75, copper-64 and cobalt-60.

MEASURING TECHNIQUE

Neutron activation of silver and antimony produces a number of radioisotopes, of which silver-110m and antimony-124 were chosen, as these nuclides are long-lived and have complex decay schemes in which convenient γ,γ-coincidence cascades exist, as appears from the decay schemes given in Fig. 1.

As both species have relatively long half-lives of 270 days and 60 days respectively, a long cooling period is possible. This insures the decay of all species with short half-lives which might interfere. Moreover, a long counting time is possible, which is desirable because of the low detection efficiency and extremely low silver and antimony contents of some samples.

The measuring technique consisted essentially of two 3 × 3" NaI(Tl) detectors, associated with their respective preamplifiers, linear amplifiers, pulse-height analyz-

---

* On leave from A.E.R.I. of the Republic of Korea.

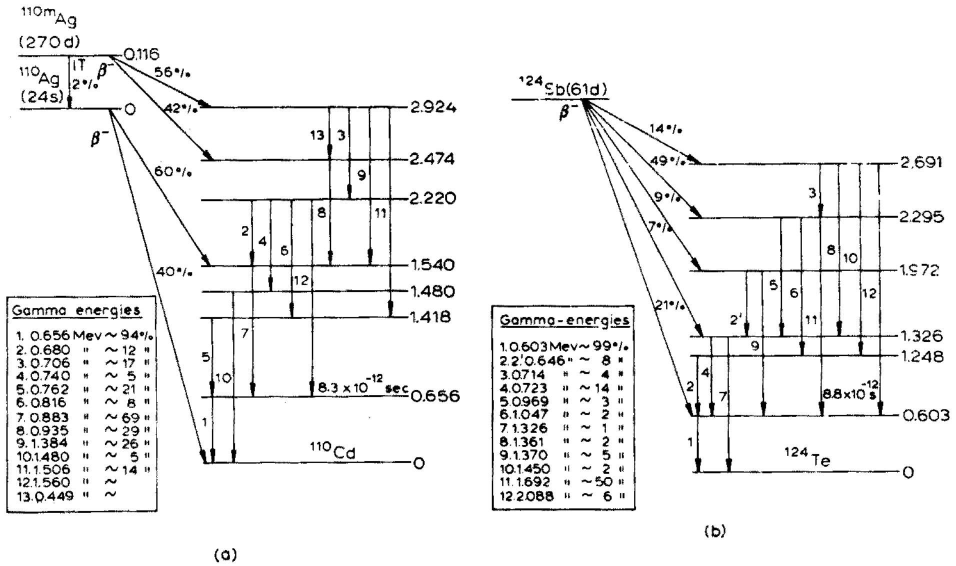


Fig. 1. (a) Decay scheme of ^{110m}Ag; (b) decay scheme of ^{124}Sb.

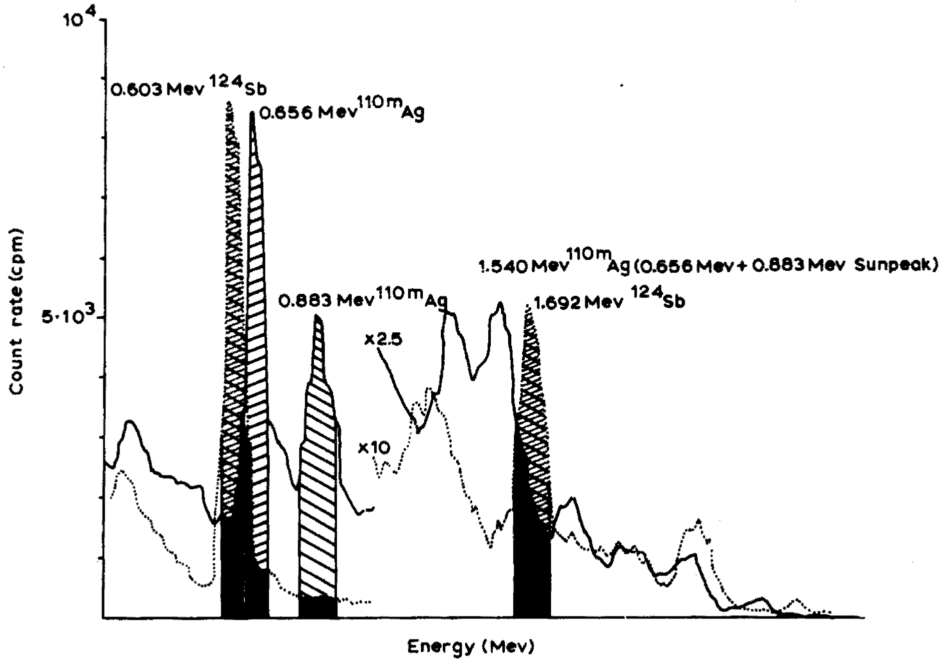
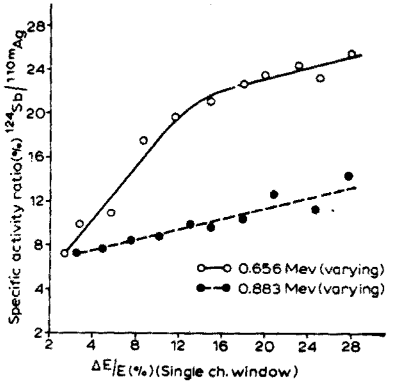


Fig. 2. Complex γ-ray spectra of ^{110m}Ag and ^{124}Sb.

ers and a coincidence circuit with a resolution time of 0.58 μsec as already described (KIM *et al.*[21]).

To obtain a reasonably high counting efficiency, together with good specificity, γ-rays which occurred in a high percentage of the decay modes were chosen, namely at 0.656 MeV (94%) and 0.883 MeV (69%) in the case of ^{110m}Ag, and at 0.603 MeV (99%) and 1.692 MeV (50%) for ^{124}Sb. As appears from Fig. 2 a small reciprocal interference can be expected, due to the respective γ-rays at 0.603 and 0.656 MeV which are not completely resolved. Moreover ^{110m}Ag gives rise to a sum peak at 1.540 MeV, which interferes with the 1.692-MeV peak of ^{124}Sb. The degree of interference is, of course, largely dependent upon the window width of the pulse-height analyzers, and was investigated experimentally with silver and antimony standards containing 12 μg Ag and 1 μg Sb, irradiated for 15 days in the BR-1 reactor at a flux of $4 \cdot 10^{11}$ n cm^{-2} sec^{-1} and a cooling time of 25 days. For the measurement of the silver activity the window widths of the photopeaks at either 0.656 MeV or 0.883 MeV were varied between 1% and 28%, the other being kept constant at 1%; these pulses were used as signal, the gate pulse being kept constant. It appeared that the antimony interference, under the concentration, irradiation and decay conditions stated above, varied between 7% and 26% in the first case and between 7 and 14% in the second (Fig. 3). The interference of ^{110m}Ag on the measurement of ^{124}Sb was studied on the same standard samples, by varying between 1% and 16% the window widths of the photopeaks at 0.603 MeV or 1.692 MeV, which were again chosen as signal pulses, the gate pulse being kept constant at 1%. The results are given in Fig. 4; clearly the interference was smaller and varied between 0.9% and 2.7% in the first case, and between 0.9% and 1.6% in the second.



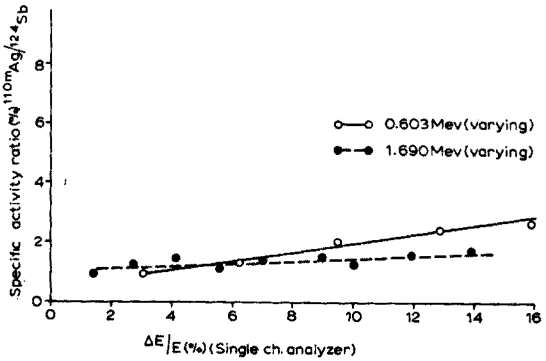


Fig. 3. Interference of ^{124}Sb on the measurement of ^{110m}Ag.

Fig. 4. Interference of ^{110m}Ag on the measurement of ^{124}Sb.

Although these reciprocal interferences were quite small if narrow windows were used, they could not be neglected, especially as the ratio of antimony/silver, in high-purity bismuth, was sometimes as high as 1:26. Double measurement was therefore required, once in the optimum ^{110m}Ag coincidence condition, and once in the optimum ^{124}Sb condition. The net silver and antimony activities were then given by eqns. (1) and (2).

$$R_{Ag} = (R_1 - R_2 \cdot f_2)/(1 - f_1 \cdot f_2) \tag{1}$$

$$R_{Sb} = (R_2 - R_1 \cdot f_1)/(1 - f_1 \cdot f_2) \tag{2}$$

where

R_{Ag} = net ^{110m}Ag count rate (^{110m}Ag coincidence condition),
R_{Sb} = net ^{124}Sb count rate (^{124}Sb coincidence condition),
R_1 = measured count rate (^{110m}Ag coincidence condition),
R_2 = measured count rate (^{124}Sb coincidence condition),
f_1 = ratio of count rates of ^{110m}Ag measured in the ^{124}Sb and ^{110m}Ag conditions, respectively,
f_2 = ratio of count rates of ^{124}Sb measured in the ^{110m}Ag and ^{124}Sb conditions, respectively.

The values of f_1 and f_2 were determined with the window widths indicated in Fig. 2, *i.e.* 2.9% at 0.656 MeV and 5.1% at 0.883 MeV in the ^{110m}Ag measuring condition, and 3.1% at 0.603 MeV and 4.1% at 1.692 MeV for ^{124}Sb. The experimental values are given in Table I.

The linearity of the count rate as a function of the activity was also investigated. As appears from Fig. 5, losses due to total dead time of the counting system were negligible up to 15 μg Sb and 27 μg Ag respectively. As these quantities were far higher than those found in high-purity bismuth, corrections for counting losses were not taken into account.

TABLE I

f_1 AND f_2 VALUES

Number of expt.	f_1	f_2
1	0.01605	0.06351
2	0.01625	0.06421
3	0.01653	0.06356
4	0.01630	0.06275
5	0.01626	0.06343
6	0.01645	0.06406
Mean value	0.01631 ±0.00016	0.06358 ±0.00052
S.D.	0.98%	0.82%

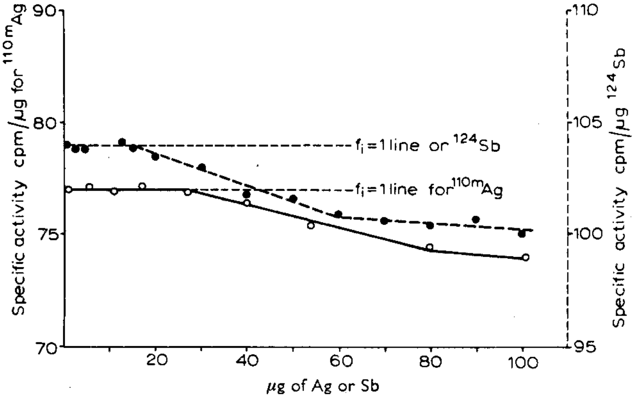
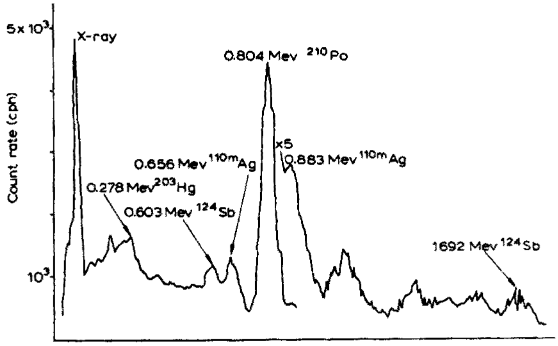


Fig. 5. Linearity of coincidence count rate.

SELECTIVITY AND SENSITIVITY

As already stated by numerous other authors, coincidence techniques offer the advantage of high selectivity, as the counting rates of other radioactive nuclides, which have no gamma cascades in the considered energy bands, are reduced to random coincidence events. As data on the impurity content of the bismuth samples were not available, it was not possible to determine experimentally how random coincidences of individual activated species influenced the true coincidence rate of ^{110m}Ag or ^{124}Sb. The γ-spectrum of bismuth, also irradiated for 15 days and cooled for 25 days, gave no indication of possibly interfering isotopes (Fig. 6). Although the γ-rays of ^{110m}Ag and of ^{124}Sb are clearly defined, the only other γ-rays appearing in the spectrum are located at 0.28 MeV, due to ^{203}Hg, and at 0.804 MeV due to ^{210}Po, daughter of the activated matrix, as appears from the decay scheme (Fig. 7).



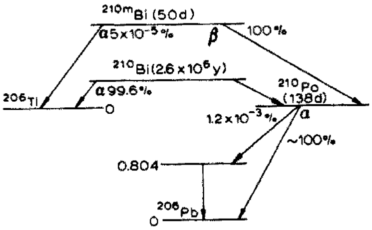


Fig. 6. γ-Ray spectra of sample B-2.

Fig. 7. Decay scheme of ^{210m}Bi and ^{210}Po.

Two criteria however make it possible to determine if other nuclides contribute to the coincidence rate.

(*1*) The total coincidence count rate R_t is the sum of the "true" coincidence rate R_c of two interrelated γ-rays, the random coincidence rate R_r and the background rate R_b, thus $R_c = R_t - R_r - R_b$. On irradiated bismuth samples it is possible to compute the random coincidence rate R_r from the equation:

$$R_r = R_I \cdot R_{II} \cdot 2\tau \tag{3}$$

where R_I and R_{II} are the individual count rates of the channels used for the respective coincidence measurements of ^{110m}Ag and ^{124}Sb, and τ is the time constant of the coincidence circuit. The latter was determined experimentally and appeared to be 0.58 μsec. From Table II it seems that the random to true coincidence rate is smaller than 1%. Consequently, random coincidence cannot contribute substantially to the total coincidence rate.

(*2*) Spiking the samples with known amounts of silver and antimony gave rise to the same specific activities of the elements added and originally present, as is described in detail below.

Coincidence counting not only reduces interferences, but can also increase

TABLE II

SELECTIVITY OF MEASUREMENT

Nuclide	*Sample*	$R_r = R_I \cdot R_{II} \cdot 2\tau$ R_I[a]	 R_{II}[a]	 R_r[b]	R_b[b]	R_t[b]	R_c[b]	R_r/R_t (%)	R_r/R_c (%)
^{110m}Ag	B-1	3545	3552	243.5	40	28469.4	28185.9	0.86	0.86
	B-2	276	268	1.4	40	857.6	816.2	0.16	0.17
	B-3	102	104	0.2	40	169.6	129.4	0.12	0.15
^{124}Sb	B-1	1235	158	3.8	8	1488.6	1476.8	0.26	0.26
	B-2	298	78	0.4	8	222.6	214.2	0.18	0.19
	B-3	674	119	1.5	8	54.2	44.7	2.77	3.36

[a] Counts/min. [b] 10^{-3} counts/min.

the sensitivity of activation analysis to a considerable extent. All other parameters being equal, the sensitivity is determined more by the signal-to-background ratio, than by the absolute count rate. As the background rate is drastically reduced, a large increase in the signal-to-background ratio is obtained (Table III).

TABLE III

RATIO OF ACTIVITY TO BACKGROUND

	^{110m}*Ag*			^{124}*Sb*		
	Act. (counts/min/μg)	*BKD (counts/min)*	*BKD/Act.*	*Act. (counts/min/μg)*	*BKD (counts/min)*	*BKD/Act.*
γ-Spectrometry	8205	131	$1.6 \cdot 10^{-2}$ [a]	16726	127	$7.8 \cdot 10^{-3}$ [b]
Two-channel coinc. spectra		$4 \cdot 10^{-2}$	$5.2 \cdot 10^{-4}$	104	$8 \cdot 10^{-3}$	$7.6 \cdot 10^{-5}$

[a] Counts/min under 0.656 MeV plus 0.883-MeV photopeak.
[b] Counts/min under 0.603 MeV plus 1.692-MeV photopeak.

In the present case, the sensitivities of the silver and antimony determinations could be estimated at 10^{-3} and 10^{-4} μg respectively, for the stated irradiation and measuring conditions, as these quantities gave activities of the same order of magni-

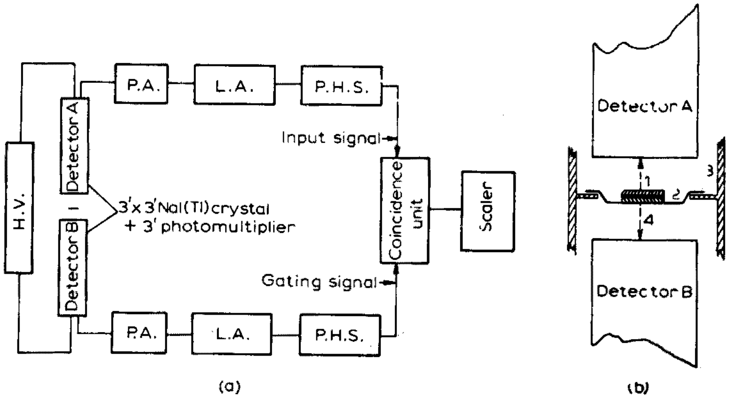


Fig. 8. (a) Block diagram of coincident counting system; (b) sample mounting.

tude as the background. The sensitivity is of course also dependent on the silver–antimony ratio, as there is a mutual interference.

EXPERIMENTAL

Equipment

Two 3 × 3″ NaI(Tl) crystals with EMI no. 9531A photomultipliers. Resolution for ^{137}Cs: 9%. White cathode followers and Fairstein-type linear amplifiers.

Nuclear Enterprises Pulse Height analyzers NE-5102.

Tracerlab coincidence-anticoincidence unit RCA-6A.

Bell Telephone Mfg Co scaler.

Castle of lead bricks (10 cm thickness); inside dimensions: 50 cm, Cd and Cu lined.

The temperature of the counting room was kept constant at 20 ± 0.5°. A block diagram is given in Fig. 8a.

Irradiation and counting

Sample (2 g) and standards of silver (1 μg) and antimony (0.1 μg) were irradiated in the BR-1 reactor for a period of 15 days at a flux of *ca.* $4 \cdot 10^{11}$ n cm^{-2} sec^{-1} and left to cool for 25 days. All samples were sliced to 1-mm thickness so as to avoid neutron flux attenuation, and packed in aluminium foil. After irradiation, all the samples were thoroughly washed with 3 *N* nitric acid to remove surface contamination, dried, weighed and mounted on aluminium planchets.

To prepare the standard samples, spectrographically pure silver metal and antimony pentoxide were used, the silver being dissolved in nitric acid (10 μg per ml) and the antimony in hydrochloric acid (1 μg per ml). After irradiation of the standard solutions, sealed into quartz ampoules, 0.1 μg of silver and 0.01 μg of antimony were pipetted onto inactive bismuth slices (0.5 mm thickness), dried under the infrared lamp and covered with another slice of inactive bismuth; the whole was mounted on an aluminium planchet in order to obtain uniform counting conditions in samples and standards.

As coincidence counting gives a low efficiency and as the matrix was ultra-pure (the certified purity of the B-1 sample was 99.999%, B-3 was 99.9999% pure, and B-2 unknown), counting for at least 2 h for silver and 4 h for antimony was necessary.

Since the distance between the detectors and the sample (see Fig. 8b) influenced the coincidence counting efficiency, the shortest practicable distance, *i.e.* 1 cm, was chosen.

RESULTS AND DISCUSSION

The results of a number of analyses are given in Table IV. It is apparent that reproducible results were obtained for the samples B-2 and B-3, whereas the results varied between large limits for the B-1 samples. Whereas the B-2 and B-3 samples were taken from metal rods, the B-1 metal consisted of metal chips. It is therefore believed that the irregular results were due to an inhomogeneous distribution of the trace elements, rather than to a lack of reproducibility in the technique.

An addition method of analysis was performed on the B-2 bismuth metal by

TABLE IV

ACTIVATION METHOD FOR SILVER AND ANTIMONY

Sample	*Number of times counted*	*Silver*		*Antimony*	
		Ag found (p.p.b.)	*S.D.(%)*	*Sb found (p.p.b.)*	*S.D.(%)*
B-1 1	4	9.70 ± 0.62	6.4	0.43 ± 0.08	18.6
2	4	71.70 ± 4.80	6.8	2.06 ± 0.25	9.6
3	4	13.70 ± 1.67	12.2	3.40 ± 0.50	14.7
4	4	1464.80 ± 56.00	3.8	64.80 ± 2.30	3.5
5	4	14.10 ± 0.84	6.0	2.40 ± 0.41	17.0
6	4	622.30 ± 24.60	4.0	12.10 ± 2.20	18.2
		Mean value 336.05		Mean value 14.20	
B-2 1	4	10.20 ± 0.25	2.5	2.92 ± 0.17	5.8
2	4	10.50 ± 1.10	10.5	1.30 ± 0.17	13.0
3	4	11.10 ± 0.63	5.7	2.00 ± 0.21	10.5
4	4	10.60 ± 0.68	6.4	1.90 ± 0.21	11.1
		Mean value 10.60 ± 0.67		Mean value 2.06 ± 0.19	
B-3 1	5	1.38 ± 0.15	10.9	0.34 ± 0.06	17.0
2	5	1.46 ± 0.31	21.2	0.20 ± 0.06	30.0
3	5	1.82 ± 0.23	12.6	0.37 ± 0.07	18.9
4	5	1.85 ± 0.16	8.7	0.49 ± 0.07	14.3
5	5	1.80 ± 0.24	13.4	0.60 ± 0.10	16.7
6	5	1.78 ± 0.23	12.9	0.55 ± 0.04	7.8
		Mean value 1.68 ± 0.22		Mean value 0.43 ± 0.07	

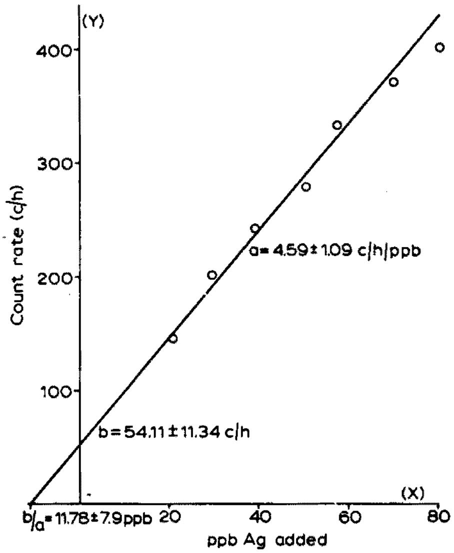


Fig. 9. Calibration curve of ^{110m}Ag.

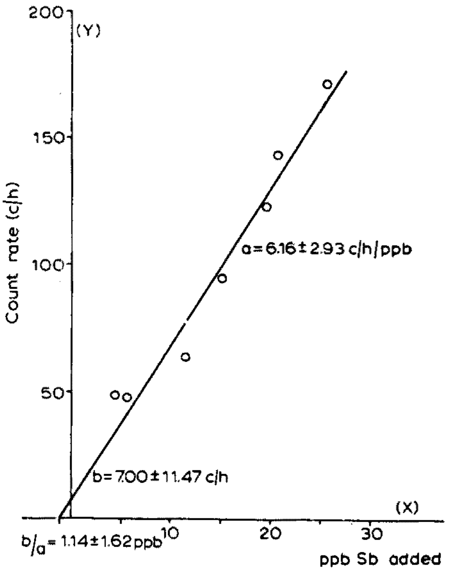


Fig. 10. Calibration curve of ^{124}Sb.

spiking 1–1.5 g samples with respectively 20.4, 29.5, 39.5, 50.4, 57.4, 70.2 and 80.0 p.p.b. of silver and 4.0, 6.2, 13.0, 15.3, 18.8, 21.2 and 26.1 p.p.b. of antimony.

The method of the least squares was applied to fit the most probable straight line through the experimental points obtained. The results are represented in Figs. 9 and 10, where the activity Y of silver or antimony is plotted against the added quantity X. The slope a gives the specific activity of the element, whereas the intercept b of the ordinate represents the activity of the element originally present. For silver, $a = 4.59 \pm 1.09$ counts/h/p.p.b. and $b = 54.11 \pm 11.34$ counts/h, whereas for antimony, $a = 16 \pm 2.93$ counts/h/p.p.b. and $b = 7.00 \pm 11.47$ counts/h.

The original content of the elements present in the sample is thus given by b/a, *i.e.* 11.8 ± 7.9 p.p.b. silver and 1.1 ± 1.6 p.p.b. antimony. As the amounts spiked were much larger than the amounts present the results allow no reliable estimate of the original content. However, for very low concentrations of both silver and antimony the values thus derived for a were in fair agreement with the specific activity of standard samples, *i.e.* 4.59 ± 1.09 counts/h/p.p.b. *vs.* 4.56 ± 0.21 counts/h/p.p.b. for silver, and 6.16 ± 2.93 counts/h/p.p.b. *vs.* 6.23 ± 0.32 counts/h/p.p.b. for antimony. Moreover, when small amounts such as 10^{-2}–10^{-3} μg are treated, an important source of error in this addition method is probably the spiking procedure itself.

One of the authors (J.I.K.) gratefully acknowledges the financial support of the University of Ghent, and of the Ministry of Foreign Affairs and Exterior Commerce. Thanks are also due to Dr. DE SOETE for help with the counting equipment.

SUMMARY

A non-destructive neutron activation method was developed for the determination of silver and antimony in high-purity bismuth; γ,γ-coincidence counting of ^{110m}Ag or ^{124}Sb was applied. The activity of the matrix or other impurities did not interfere. When 1-g samples were irradiated at a neutron flux of $4 \cdot 10^{11}$ n cm^{-2} sec^{-1} for 25 days, the sensitivity of the method was in the p.p.b. region.

RÉSUMÉ

Une méthode non-destructive par activation au moyen de neutrons est proposée pour le dosage de l'argent et de l'antimoine dans un bismuth de grande pureté. Le comptage de coïncidence-γ,γ de ^{110m}Ag ou ^{124}Sb est appliqué. L'activité de la matrice ou d'autres impuretés ne gêne pas. Lorsqu'un gramme d'échantillon est irradié avec un flux de neutrons de $4 \cdot 10^{11}$ n cm^{-2} sec^{-1}, pendant 25 jours, la sensibilité de la méthode est de l'ordre de p.p.b.

ZUSAMMENFASSUNG

Es wurde eine zerstörungsfreie Neutronenaktivierungsmethode zur Bestimmung von Silber und Antimon in hochreinem Wismuth entwickelt. Für das ^{110m}Ag oder das ^{124}Sb wurde die γ,γ-Koinzidenzmethode angewandt. Die Aktivität der Matrix oder andere Verunreinigungen störten nicht. Bei der Bestrahlung von 1 g Probe mit einem Neutronenfluss von $4 \cdot 10^{11}$ n cm^{-2} sek^{-1} für 25 Tage ergab sich eine Empfindlichkeit im p.p.b.-Bereich.

REFERENCES

1 M. Okada, *Nature*, 187 (1960) 57.
2 O. W. Anders, *Anal. Chem.*, 33 (1961) 1707.
3 F. Adams, J. Hoste and A. Speecke, *Talanta*, 3 (1963) 34.
4 T. Nakai, S. Yajima, M. Okada, Y. Kamemoto and K. Shiba, *Nippon Kagaku Zasshi*, 81 (1960) 1422.
5 Y. Kusaka, *Japan Analyst*, 8 (2) (1959) 111.
6 F. Adams and J. Hoste, *Talanta*, 9 (1962) 827.
7 F. Adams and J. Hoste, *Talanta*, 10 (1963) 1093.
8 F. Adams and J. Hoste, *Nucleonics*, 22 (1964) 55.
9 W. Bock-Werthmann and W. Schulze, *AED-C-14-1*, 1961.
10 W. Bock-Werthmann, *AEC-C-14-02*, 1963.
11 W. Bock-Werthmann, *AEC-C-14-03*, 1964.
12 I. P. Alimarin and Yu. V. Yakovlev, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958*, P/2023.
13 Y. Kamemoto and S. Yamagish, *Nippon Kagaku Zasshi*, 82 (1961) 1653.
14 I. Finenman, K. Ljunggren, H. G. Forsberg and L. G. Erwell, *J. Appl. Radiat. Isotop.*, 11 (1961) 10.
15 R. W. Perkins, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958*, P/2377.
16 L. Petit and Ch. Engelman, *Proc. Siminar Practical Application Short lived Radioisotopes produced in small research reactors, I.A.E.A., Vienna, 1962*, Vol. II, p. 29.
17 I. Fujii, A. Tani, H. Muto, K. Ogawa and M. Sato, *J. At. Energy Soc. Japan*, 5 (1963) 218.
18 R. Malvano and G. B. Fasolo, *Anal. Chim. Acta*, 30 (1964) 223.
19 D. C. Borg, R. E. Segel, P. Kienle and L. Campbell, *J. Appl. Radiat. Isotop.*, 3 (1958) 156.
20 K. Ljunggren, *Proc. Intern. Conf. Use of Radioisotopes in the Physical Sci. and Industry, I.A.E.A., Copenhagen, 1960*, RICC-79.
21 J. Kim, A. Speecke and J. Hoste, *Anal. Chim. Acta*, 33 (1965) 123.

SHORT COMMUNICATIONS

Reduction of azo compounds with acidic reducing agents

The reduction of azo compounds with acidic reducing agents in general, is supposed to proceed through the following steps, requiring 4 equivalents of the reducing agent per azo group for the complete reduction.

$$\mathrm{Ar'\text{-}N{=}N\text{-}Ar''} \xrightarrow{2\mathrm{H}} \mathrm{Ar'\text{-}NH\text{-}NH\text{-}Ar''} \xrightarrow{2\mathrm{H}} \mathrm{Ar'\text{-}NH_2 + Ar''\text{-}NH_2} \quad (1)$$

However, when the reduction of azobenzene is carried out with solutions of tin(II) or titanium(III) (in about 3 *M* hydrochloric or sulphuric acid), only 2 equivalents of the reducing agent per mole of the azo group are consumed. In the case of other azo compounds containing substituents in the benzene rings or containing naphthalene systems (*e.g.* Congo red), almost 4 equivalents per azo group are required under similar conditions. Results obtained for azobenzene and a few other azo compounds in the present work are shown in Table I.

TABLE I

REDUCTION OF AZO COMPOUNDS WITH ACIDIC REDUCING AGENTS

Compounds	*Azo group (%)*[a]				*No. of equiv. of reductant consumed*[b]
	Calcd.	*Found with*			
		Sn^{2+}	Ti^{3+}	Cr^{2+}	
Azobenzene	15.38	8.40	8.45	8.62	2
Congo red	8.59	8.27	8.30	8.42	4[c]
Methyl orange	9.18	8.47	8.98	8.92	4
Methyl red	10.40	10.03	10.17	10.28	4
1-(*o*-Tolylazo)-2-naphthol	10.68	10.19	10.23	10.30	4

[a] Values are average of 3 determinations.
[b] The values are expressed as the nearest whole numbers to the figures obtained by calculation from the results found with Sn^{2+}, Ti^{3+} and Cr^{2+}.
[c] Per azo group.

In a recent communication BOTTEI[1] pointed out that unlike the other azo compounds which were studied, azobenzene was not cleaved by chromium(II) chloride; only 2 equivalents of reductant per mole of azobenzene were consumed, while other azo compounds required 4 equivalents per mole. He further stated, "why azobenzene should behave so differently is not understood and will be further investigated". His attempts to reduce hydrazobenzene (an intermediate product in the reduction of azobenzene) with chromium(II) chloride were also unsuccessful.

In the present paper, an attempt is made to explain this unusual behaviour of azobenzene when reduced in acidic solutions with tin(II) chloride, titanium(III) sulphate or chromium(II) sulphate as observed by us, or with chromium(II) chloride as observed by BOTTEI. It was also shown that the reduction of azobenzene with titanium(III) solution in a concentrated solution of potassium citrate requires 4 equivalents for complete reduction.

Experimental

Reagents. Tin(II) chloride and titanium(III) sulphate solutions (0.5 N and 0.05 N respectively) were prepared as described earlier[2,3], the latter being prepared from a technical grade concentrated solution (B.D.H., Ltd., England). Chromium(III) sulphate solution (0.05 N) was prepared by the method of LINGANE AND PECSOK[4]. All 3 solutions were stored under an atmosphere of nitrogen.

All the reagents, except titanium(III) sulphate solution, were prepared from analytical grade materials.

Procedures. The percentage of azo group (and hence the number of equivalents of reductant consumed) was determined by procedures similar to those described for the determination of nitro groups in aromatic compounds[2,3]. The procedure involving chromium(II) sulphate was similar to the titanium(III) procedure, except that the reaction mixture was not heated. All these determinations were carried out under an atmosphere of nitrogen. For each set of determinations, separate blanks were determined.

Potential measurements were done with a Student's Potentiometer (Leeds & Northrup Co., Philadelphia, Cat. No. 7645) using platinum electrodes.

Identification of benzidine. After the reduction was complete, a few ml of sulphuric acid were added and the mixture was allowed to cool. The whitish precipitate of benzidine sulphate which separated was filtered off. The precipitate was treated with concentrated alkali to obtain the free base and was again filtered. The free base was thoroughly washed with distilled water and repeatedly crystallised from aqueous ethanol to a constant melting point (127–128°). The characteristic greyish white flakes obtained gave all the tests of benzidine (90% yield).

Identification of aniline. A portion of the filtrate was diazotized and coupled with β-naphthol. A brilliant red azo dye was obtained which clearly indicated the presence of an aromatic primary amine in the filtrate. The rest of the filtrate was made alkaline and steam-distilled. After salting out, the free base was recovered from the distillate by extraction with ether and subsequent removal of ether in the usual manner. The liquid so obtained (b.p. 182–184°) showed all the characteristics of aniline (yield about 8–9%).

Discussion

The percentage of azo group in azobenzene is 15.38. The values obtained in acidic media on the basis of the amount of the reducing agents consumed were of the order of 8.4–8.6% in most cases. To explain these results it would not be reasonable to assume that the reaction stops at the hydrazobenzene stage (eqn. (2)), as it proved impossible to isolate any hydrazobenzene as the final product using any of the 3 reductants mentioned above.

$$\text{Ph–N=N–Ph} \xrightarrow{2\text{H}} \text{Ph–NH–NH–Ph} \xrightarrow{2\text{H}} 2\ \text{PhNH}_2 \qquad (2)$$

Separate reductions of larger samples (about 2 g) of azobenzene with the 3 reducing agents and isolation of the final reaction products led to the identification of benzidine as the chief product and aniline as a very minor product in every case. Attempts to reduce hydrazobenzene were also fruitless as the reaction mixture contained not hydrazobenzene but benzidine as the major constituent. Actually when hydrazobenzene is treated with mineral acids, it undergoes an intramolecular rearrangement and a mixture of diaminodiphenyl compounds is obtained, *p,p'*-diaminodiphenyl (benzidine) being the main product[5]. Similar reactions occur with several other hydrazo compounds[6]. Thus, hydrazobenzene as such, or obtained as the intermediate product of azobenzene on reduction with any of the 3 reducing agents, may follow 2 reaction routes. Firstly, it may give aniline by consuming another 2 equivalents of the reductant, and secondly, it may give benzidine as the chief product by undergoing rearrangement; of course, it may give a mixture of the two depending upon the relative speeds of steps (*i*) and (*ii*) in the equation (3).

$$C_6H_5\text{–}NH\text{–}NH\text{–}C_6H_5 \xrightarrow[\text{acid}]{\text{Reductant}} \left| \begin{array}{l} \xrightarrow{(i)} 2C_6H_5NH_2\text{(aniline)} \\ \xrightarrow{(ii)} NH_2C_6H_4\cdot C_6H_4NH_2 \\ \qquad\qquad\qquad\text{(benzidine)} \end{array} \right. \tag{3}$$

The results obtained force us to conclude that step (*ii*) is the main course of reaction, and that step (*i*) is very slow. In acidic solutions azobenzene is mainly reduced only to the hydrazobenzene stage, consuming about 2 equivalents of the reductant and hydrazobenzene cannot be reduced under similar conditions (except for the cleavage of a very small proportion to aniline).

In the case of other hydrazo compounds containing substituents in the benzene ring, the transition state (during the rearrangement) involves an additional step[7] with a second rearrangement for which it has to survive for a sufficiently long time. This additional step makes the rearrangement very slow in comparison to the reduction of the hydrazo compounds to the primary bases.

In addition to the above fact, the probability that the hydrazo compound obtained from Congo red, which has 2 azo groups and naphthalene systems with substituents, would rearrange more slowly than it would undergo further reduction, is further increased by the voluminous structure of the compound.

The presence of large amounts of potassium citrate solution (75%) has a profound effect on the course of the reaction. Since the rate of the benzidine transformation is directly proportional to the square of the hydrogen ion concentration[8], anything which decreases the hydrogen ion concentration, will also decrease the rate of rearrangement. The presence of potassium citrate decreases the hydrogen ion concentration by forming potassium sulphate and weakly dissociated citric acid. Furthermore, potential measurement of the Ti^{3+}–Ti^{4+} couple in presence of potassium citrate shows that the redox potential of the system is considerably increased. These two effects conjointly make the process of reduction of hydrazobenzene to aniline much faster than the benzidine transformation.

Department of Chemistry,
University of Allahabad,
Allahabad (India)

R. D. TIWARI
J. P. SHARMA

1 R. S. Bottei, *Anal. Chim. Acta*, 30 (1964) 6.
2 R. D. Tiwari, J. P. Sharma and P. C. Gangwar, *Proc. Nat. Acad. Sci. India*, 32 (1962) 119.
3 R. D. Tiwari and J. P. Sharma, *Z. Anal. Chem.*, 191 (1962) 329.
4 J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, 20 (1948) 425.
5 See *e.g.* A. W. Hofmann, *Proc. Roy. Soc. (London)*, 12 (1863) 576; R. Fittig, *Ann.*, 124 (1862) 282.
6 P. Jacobson, *Ann.*, 428 (1922) 76.
7 E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart and Winston, New York, 1959, p. 659.
8 G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.*, 72 (1950) 220.

(Received February 28th, 1965)

Anal. Chim. Acta, 33 (1965) 459–462

Gravimetric determination and separation of thorium with N-benzoyl-N-phenylhydroxylamine by direct weighing

Thorium can be determined[1] by igniting the precipitate formed with N-benzoyl-N-phenylhydroxylamine (BPHA) and weighing the metal as dioxide; the precipitate obtained from cold solution is of indefinite composition and is contaminated with the organic reagent so that ignition is essential. Later, Alimarin and Chish[2] studied gravimetrically and by extraction methods the determination of thorium with BPHA; ignition of the precipitate to the dioxide before weighing, was again found necessary. In the present investigation a detailed study was made on the precipitation of thorium with BPHA under controlled conditions of temperature, and it was found that a granular precipitate of definite composition was formed at 50–55°. Thorium could be determined by direct weighing of the metal–BPHA complex after drying at 105–110°; the composition of the complex was $Th(C_{13}H_{10}O_2N)_4$. The thorium precipitate was, however, slightly soluble in water above 70° and if the precipitation was carried out from a hot solution above 80°, a gummy mass was obtained.

This method was applied for the separation of thorium from many other metals by pH adjustment or by using masking agents.

Metal solutions

A standard thorium nitrate solution was prepared by the usual method.

Standard solutions of iron(III) chloride, uranyl nitrate, aluminium sulphate, beryllium nitrate, ceric ammonium nitrate, zirconium chloride, titanium sulphate, sodium vanadate, ammonium molybdate, gallium chloride, indium chloride and lanthanum chloride were prepared separately. All the reagents used were of A.R. quality.

Procedure

An aliquot of the thorium solution was diluted to 200 ml and heated to 50–55°. The ethanolic reagent solution (about 2–2.5 times the theoretical amount) was added and the pH of the solution was raised to 4.0–5.0 by the addition of a 10% solution of sodium or ammonium acetate. The precipitate was digested on a water bath (50–55°) until the solution was clear and the precipitate assumed a granular form.

TABLE I

DETERMINATION OF THORIUM BY DIRECT WEIGHING OF Th–BPHA COMPLEX

Th taken (mg)	*Weight of complex (mg)*	*Th found (mg)*	*Error (mg)*
5.8	26.80	5.75	−0.05
11.6	54.00	11.60	−0.00
13.92	64.85	13.93	+0.01
18.56	86.45	18.57	+0.01
23.20	108.00	23.19	−0.01

It was then filtered through a sintered glass crucible (No. 4), washed with hot (40–45°) distilled water, dried at 110° for 1 h, cooled and weighed. Results are shown in Table I.

Properties and composition of the complex

The thorium–BPHA complex obtained in the above procedure was dirty white in colour; it was slightly soluble in water above 70° and completely soluble in 50% ethanol, as well as in other organic solvents such as chloroform, ether, benzene and ethyl acetate. It decomposed at 129–130°. The thorium content was established by igniting a known weight of the complex and weighing as ThO_2 (Th found, 21.46%; theoretical, 21.47%); nitrogen was determined by the Dumas method (N found, 5.18%; theoretical, 5.17%). The results indicate that the composition of the complex is $Th(C_{13}H_{10}O_2N)_4$.

TABLE II

SEPARATION OF THORIUM FROM OTHER METALS

Foreign ion	*Amount added (mg)*	*Th taken (mg)*	*Th found (mg)*	*Foreign ion*	*Amount added (mg)*	*Th taken (mg)*	*Th found (mg)*
Ce^{4+}	17.4	5.80	5.85	Fe^{3+}	15.0	5.80	5.75
	8.7	11.60	11.62		10.0	11.60	11.58
	4.35	11.60	11.60		5.0	11.60	11.62
Be^{2+}	33.0	5.80	5.80	Al^{3+}	13.5	5.80	5.70
	16.5	11.60	11.58		9.0	11.60	11.55
	5.5	11.60	11.60		4.5	11.60	11.60
$(UO_2)^{2+}$	40.0	5.80	5.85	Ti^{4+}	12.0	5.80	5.70
	20.0	11.60	11.65		9.0	11.60	11.58
	11.0	11.60	11.60		6.0	11.60	11.60
La^{3+}	25.92	5.80	5.75	Zr^{4+}	20.0	5.80	5.70
	12.96	11.60	11.60		10.0	11.60	11.60
	5.20	11.60	11.60		5.0	11.60	11.60
VO_3^-	14.0	5.80	5.82	MoO_4^{2-}	18.0	5.80	5.75
	7.0	11.60	11.60		9.0	11.60	11.55
	4.2	11.60	11.58		4.5	11.60	11.60
Ga^{3+}	5.76	11.60	11.59	In^{3+}	20.00	5.80	5.56
	11.52	11.60	11.58		10.00	11.60	11.58

Separation of thorium from Ce, Be, U, La, Fe, Al, V, Ti, Zr, Ga and In

Thorium was separated previously from cerium[1] by reducing the latter to cerium(III) with hydroxylamine and carrying out the precipitation of thorium at pH 5.0. In the present research, it was found that ascorbic acid was a better reducing agent to avoid contamination of the precipitate with cerium, and that thorium could be determined by precipitating the metal with BPHA at pH 4.8 in the presence of cerium(IV) provided that ascorbic acid was added before BPHA.

When thorium was precipitated at pH 4.5 in the presence of ammonium acetate, uranium did not interfere with the determination even when present in an amount 10 times that of thorium. Thorium was estimated in the presence of trivalent rare earths also at pH 4.5.

Thorium was separated from iron, aluminium and vanadium by prior precipitation of these metals with BPHA in the presence of tartrate at pH 4.5, 5.1 and 3.8 respectively; thorium was subsequently precipitated from the filtrate after the pH had been raised to 6.2. Molybdenum and tungsten[3] were separated from thorium by precipitating these metals in the presence of tartrate at pH 3.0.

Titanium[4], zirconium[5] or hafnium[6] was precipitated from an acid solution (0.5 *N* with respect to sulphuric acid) and gallium[7] at pH 2.0; thorium was then determined in the filtrate as before. Thorium was separated from indium by complexing the latter with thioglycollic acid and precipitating thorium with BPHA at pH 4.8. Thorium was precipitated at pH 6.2 in presence of beryllium using tartrate as masking agent.

The results of these separations are shown in Table II.

Phosphates, fluorides, citrates and EDTA, however, interfered with the determination of thorium.

The authors are indebted to the Council of Scientific and Industrial Research for a fellowship awarded to B.D.

Chemical Laboratory,
Presidency College,
Calcutta (India)

B. DAS
S. C. SHOME

1 S. K. SINHA AND S. C. SHOME, *Anal. Chim. Acta*, 21 (1959) 415.
2 I. P. ALIMARIN AND Y.-H. CHIEH, *Vestn. Mosk. Univ., Ser. II, Khim.*, 15 (No. 2) (1960) 53.
3 V. R. M. KAIMAL AND S. C. SHOME, *Anal. Chim. Acta*, 31 (1964) 268.
4 V. R. M. KAIMAL AND S. C. SHOME, *Anal. Chim. Acta*, 29 (1963) 286.
5 D. E. RYAN, *Can. J. Chem.*, 38 (1960) 2488.
6 J. DAS AND S. C. SHOME, unpublished work.
7 H. R. DAS AND S. C. SHOME, *Anal. Chim. Acta*, 27 (1962) 545.

(Received February 4th, 1965)

BOOK REVIEWS

ARNE E. NIELSEN, *Kinetics of Precipitation*, International Series of Monographs on Analytical Chemistry, Vol. 18, Pergamon Press, Oxford, 1964, x + 154 pp., price 40 s.

This book is an extended account of the CHRISTIANSEN–NIELSEN theory of the nucleation process in precipitation. As one has come to expect from the Scandinavian schools of chemistry, it seeks to provide a rigorous mathematical presentation of the theories it is discussing. It is all the more disappointing therefore to find that the table of symbols is not only incomplete but is self-contradictory. For example, the symbols θ and χ are introduced in the text but are not given in the list of symbols; r is given two meanings; the superscript $'$ denotes "surface", but primes are used to modify symbols in ways other than that associated with a phenomenon occurring at a surface. Worst of all, especially at a time when thermodynamicists are striving to standardise their symbolism, is the use of S' for entropy—a usage forced on the author by his use of S (almost the only universally accepted thermodynamic symbol!) for the saturation ratio. One could point to other difficulties arising from the symbols used, but those already quoted will suffice.

In spite of these strictures, let it be said at once that this book is a brave attempt to provide a sound and adequate theory for one of the more intractable problems facing the physical chemist, and is likely to prove useful to those kineticists who are interested in precipitation phenomena. Whether it is justifiable to include the book in a series of monographs on analytical chemistry is another matter altogether; it seems very doubtful whether the book is of any help at all to the practising analyst who wants to obtain purer precipitates that are more easily filtered, and is not the least bit interested in mathematical wizardry. To sum up, one would say that this is an interesting account of one approach to the problem of the nature of the precipitation process.

R. A. CHALMERS (Aberdeen)

ROLF K. FREIER, *Wasseranalyse; physiko-chemische Untersuchungsverfahren wichtiger Inhaltsstoffe*, Walter De Gruyter & Co., Berlin, 1964, 128 S., Plastikeinband DM 24.—.

The growing demand for water in all parts of the world for domestic, industrial and agricultural purposes makes it necessary to look to all sources of potential supplies of water. In this quest for water conservation the analyst has an important part to play, as Dr. FREIER's book shows. It deals with the chemical and physico-chemical aspects of water analysis, omitting methods for the bacteriological examination of water or determinations of radioactivity. Unlike other textbooks on the subject only one method is given for the determination of each constituent. The analysis of the elements is restricted to Al, Pb, Fe, Cu, Mn, Zn; Ca, Mg, K, Na, Li, Si; F, Cl. Methods are also described for NO_2^-, NO_3^-, CO_2, (CO_3^{2-}) (HCO_3^-), H_2S, P_2O_5, (NH_3).

The descriptions of the theoretical basis of the determinations are excellent for a book of this nature.

S. H. JENKINS (Birmingham)

Treatise on Analytical Chemistry, Edité par I. M. KOLTHOFF ET P. J. ELVING avec l'assistance de E. B. SANDELL, Part I. *Theory and Practice*. Vol. 4, Interscience Publishers, New York, xxv + 1751–2705 pp., price 189 s.

La première partie de cet ouvrage s'intitule *Méthodes analytiques basées sur le champ magnétique* et comprend 4 chapitres: Les applications analytiques de la susceptibilité magnétique nucléaire (L. N. MULAY), La résonnance magnétique nucléaire (N. F. CHAMBERLAIN), La spectrométrie de masse (F. W. MELPOLDER ET R. A. BROWN) et Les méthodes "ion-scattering" (S. RUBIN).

Dans chaque cas les auteurs donnent les bases physiques sur lesquelles reposent les méthodes et les lois qui en découlent; l'appareillage, ses techniques et ses possibilités; et les applications analytiques tant qualitatives que quantitatives avec des tableaux très bien présentés des constantes fondamentales. Les auteurs de ces 4 chapitres ont réussi, ce qui n'est pas facile pour des spécialistes, à ne donner que l'essentiel, les schémas d'appareillage ont été simplifiés, la théorie est présentée de façon simple et claire, les applications ont été choisies avec discernement. Aussi des chimistes analystes peuvent ils s'initier sans difficulté à des méthodes dont l'importance ne cesse de croître.

La deuxième partie de cet ouvrage est entièrement consacrée aux méthodes d'électroanalyses et comprend: Les réactions aux électrodes (C. N. REILLEY), Une introduction aux techniques électrochimiques (C. N. REILLEY ET R. W. MURRAY), La chronoampèrométrie et la chronopotentiométrie (P. DELAHAY), La potentiométrie (N. H. FURMAN), La voltamétrie à l'électrode à gouttes de mercure (polarographie) (L. MEITES), La voltamétrie à électrodes fixes (R. N. ADAMS), L'électrodéposition (N. TANAKA), L'analyse coulométrique (D. D. DEFORD ET J. W. MILLER), La polarographie inverse (dite à goutte suspendue) (I. SHAIN), La conductimétrie et oscillométrie (W. LOVELAND) et Les mesures de capacité (B. W. THOMAS ET R. PERTEL).

Chaque sujet est traité remarquablement par des chimistes ou physiciens spécialisés avec force démonstrations, tableaux et schémas très soignés. Peut-être pourrait-on regretter qu'il n'y ait pas une plus grande homogénéité entre les divers chapitres qui font appel, en somme, aux mêmes lois fondamentales. Ainsi par exemple en ce qui concerne la chronopotentiométrie, pas de renvoi dans ce chapitre à l'exposé général de REILLEY qui traite de la même question et avec quelle maîtrise! On constate aussi que la façon de développer les bases théoriques est différente d'un auteur à l'autre, mais on sent par contre une grande maîtrise, un soin particulier, un souci constant de l'exactitude et de la clarté qui font de cet ouvrage un remarquable recueil pour tous les analystes.

D. MONNIER (Genève)

Anal. Chim. Acta, 33 (1965) 466

A. RINGBOM, *Complexation in Analytical Chemistry*, Interscience Publishers (John Wiley & Sons), New York, London, 1963, x + 395 pp., price 113 s.

Subtitled *A guide for the critical selection of analytical methods based on complexation reactions*, this book might conceivably be accepted as a practical manual of methods and procedures of compleximetric analysis. However, readers of this journal familiar with Dr. RINGBOM's work on the analytical applications of equilibria involving complex ions, will recognise the book as an elaboration of this general thesis. Divided into 9 main chapters, the book deals in the first 3 with the basic concepts of ionic equilibria as applied to complex ions, and with the masking of reactions. This is followed by sections on complexímetric titrations and acid–base titrations (dealt with from the standpoint of H^+ and OH^- complexes). The remaining chapters treat complexation in ion exchange, metal extraction, electrochemical analysis and photometric analysis. An extensive appendix (some 80 pages) contains tables of equilibrium constants of importance in the interpretation of the many complexation reactions used in analytical processes.

The text abounds with examples which obviously concern actual analytical solutions and in this respect it differs greatly from the usual run of book in which the theory of ionic equilibrium is explained in more abstruse and (to the analytical chemist) impractical terms. Extensive use is made of the concept of the conditional equilibrium constant; the necessary mathematics is kept to quite simple proportions. The use of graphical methods for the presentation of data leads to an easier understanding of the problems associated with mixtures of complex ions, particularly those arising from the many unwanted yet significant side reactions which plague the development of so many complexímetric methods. The present book does not set out to be a comprehensive account of the physical chemistry of analytical processes involving complexation. It does, however, illustrate the necessity for an understanding of the practical implications of the basic theory, without losing sight of the objective — the development of theoretically sound, yet highly practical methods of chemical analysis. Any book which aims at the elimination of empiricism in analytical chemistry is to be welcomed; the authoritative nature of the present text must ensure its success.

It is paradoxical that EDTA — the most practically useful reagent ever developed for analytical purposes — should have been instrumental in opening the eyes of the analyst to a wider theoretical appreciation of analytical chemistry. Dr. RINGBOM's book shows how much further this elucidation can go.

W. I. STEPHEN (Birmingham)

Anal. Chim. Acta, 33 (1965) 466–467

Edelmetall-Analyse Probierkunde und nassanalytische Verfahren, herausgegeben vom CHEMIKERAUSSCHUSS DER GESELLSCHAFT DEUTSCHER METALLHÜTTEN- UND BERGLEUTE E.V., Springer-Verlag, Berlin–Göttingen–Heidelberg, 1964, xii + 200 S., Ganzleinen DM 39.—.

La Commission des Chimistes de la Société Allemande des Fondeurs et Mineurs a édité un nouveau livre traitant de l'analyse quantitative des métaux précieux. Cet ouvrage peut se diviser en deux parties.

La première a trait aux méthodes classiques d'analyses et donne tout d'abord une description détaillée du matériel spécial utilisé pour les essais dits préliminaires ou par voie sèche. Les divers types de fours, creusets, coupelles, fondants et instruments de manipulation sont passés en revue. Suit une description du processus proprement dit de l'analyse. C'est dans cette partie du livre qu'il faut rechercher son originalité. En effet, non seulement le côté pratique y est décrit avec minutie, mais égale-

Anal. Chim. Acta, 33 (1965) 467–468

ment la théorie moderne qui s'y rattache. Le côté historique n'est pour autant pas négligé puisqu'on y trouve même une ancienne règle toujours valable: "Kalt getrieben, heiss geblickt ist der Probieren Meisterstück!".

Diverses méthodes d'analyses par voie humide des éléments suivants sont décrites: Ag, Au, Pt, Pd, Rh, Ir, Ru et Os. Les unes sont basées sur des opérations classiques telles que la gravimétrie et la volumétrie, les autres sont empruntées aux méthodes physico-chimiques d'analyses telles que la spectrophotométrie et la potentiométrie. Pour chacune des méthodes les auteurs indiquent le principe, la sélectivité, la précision, la durée, la marche à suivre et les causes d'erreurs. Des essais spéciaux comme par exemple ceux à la pierre de touche terminent cette première partie.

La deuxième partie de cet ouvrage, tout aussi claire et bien présenté est consacrée à la séparation et à la détermination des métaux précieux dans les minerais, les produits intermédiaires du raffinage, les déchets ainsi que dans les alliages de métaux précieux et les métaux en général. Une mention est faite sur l'analyse des métaux précieux, dans certains catalyseurs, par fluorescence de rayons X.

En annexe, 107 références viennent compléter cet ouvrage qui peut être recommandé à tout chimiste, aussi bien chercheur qu'industriel, s'intéressant aux méthodes de dosages des métaux précieux.

W. HAERDI (Genève)

Anal. Chim. Acta, 33 (1965) 467–468

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. LÁNG, Vol. V, Akademiai Kiado, Budapest, 1965, 416 pp., price (with Index) $18.00.

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. LÁNG, Cumulative Index (I–V), Akademiai Kiado, Budapest, 1965, 112 pp.

Il s'agit de la publication du volume V de la collection de spectres d'absorptions visibles et ultraviolets dont la parution remonte à quelques années.

La présentation est analogue à celle des volumes précédents et ce tome V contient les spectres et les données numériques d'environ 200 substances organiques, aromatiques et hétérocycliques.

Les auteurs annoncent également un index cumulatif qui rendra l'utilisation de cette documentation plus aisée.

G. DUYCKAERTS (Liège)

Anal. Chim. Acta, 33 (1965) 468

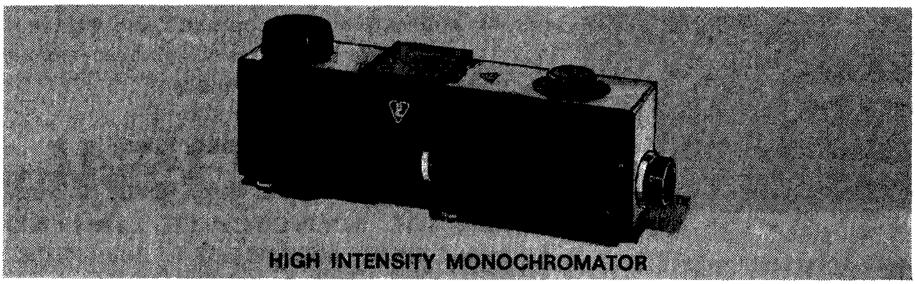
ERRATUM

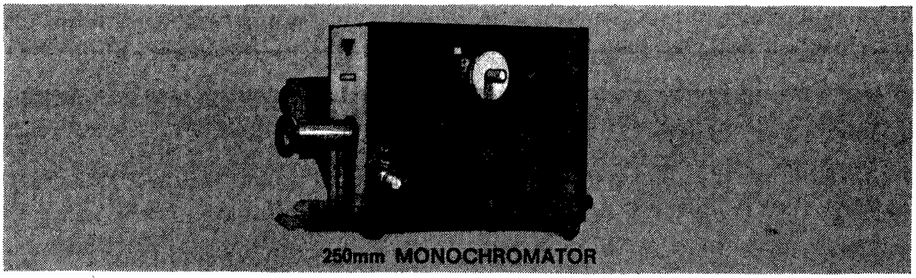
A separation scheme for gallium, indium, thallium, germanium, tin and lead by solvent extraction with N-benzoyl-N-phenylhydroxylamine; S. J. LYLE AND A. D. SHENDRIKAR, *Anal. Chim. Acta*, 32 (1965) 575.

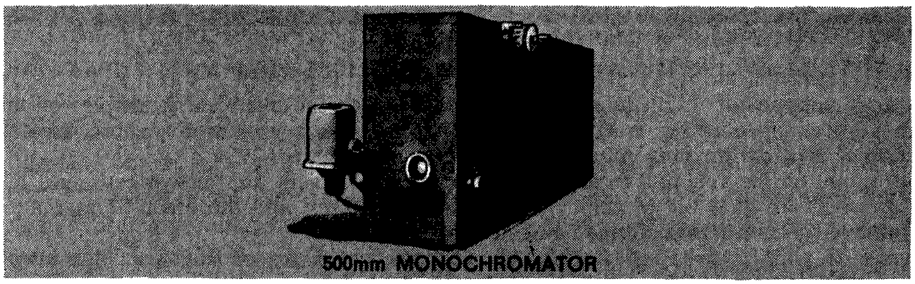
Footnote (a) to Table IV (p. 580) should read as follows:

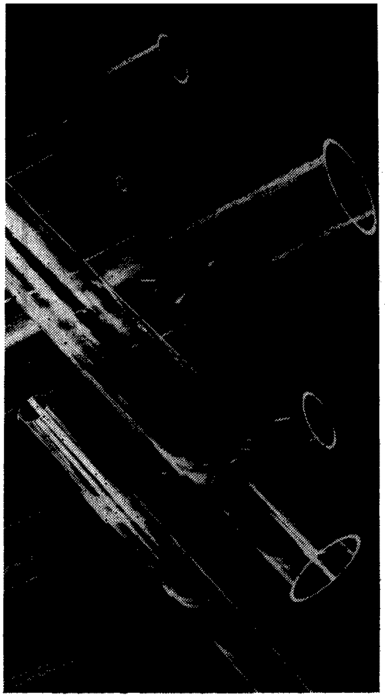
The ratio of the initial amount of impurity (B) present in the mixture (A + B) to the final amount present in the separated sample (A).

Anal. Chim. Acta, 33 (1965) 468









VITREOSIL®

pure vitreous silica tubing

Vitreosil transparent tubing can be used up to 1050°C. and with some reservations at higher temperatures, is inert to all acids except hydrofluoric and has high transmittance in the U.V. and I.R. spectral regions.

It is supplied in a wide range of diameters and wall thicknesses. Transparent tubing can be machined or fabricated to specification for special applications.

VITREOSIL

pure fused quartz and silica

is used throughout industry for research, analytical work and for manufacturing processes at high temperatures, requiring absolute standards of purity.

Full details on request.

VITREOSIL®

THERMAL SYNDICATE LIMITED

P.O. Box No. 6, WALLSEND, NORTHUMBERLAND. Tel. Wallsend 623242/3
9, BERKELEY STREET, LONDON, W.1. Tel. HYDe Park 1711

SILICA INDUSTRIAL WARE • LABORATORY WARE • OPTICAL COMPONENTS ● HIGH TEMPERATURE OXIDE CERAMICS

TEXTILE CHEMISTRY
Volume 1 - The Chemistry of Fibres

by R. H. PETERS

xiii + 477 pages 42 tables 164 figures 1083 references 1963 75s.

This first volume of a scheduled 3-volume account of the chemical principles of textile technology and processing is concerned with the origin, preparation and chemical constitution of the fibre-forming polymers and of the natural fibres.

Descriptions of the fine and molecular structure of polymers, the biosynthesis and histology of wool, silk and the principal vegetable staple fibres, and the mode of manufacture of synthetic fibres are all accorded detailed treatment.

Volumes II and III will deal respectively with the chemistry of scouring, bleaching and surface-active agents and the chemistry of dyeing and finishing agents.

The work is designed as an introduction to students and as a guide to advanced work in the field of textile chemistry.

contents

1. Introduction. 2. Condensation polymers. 3. Addition polymers. 4. Co-polymers. 5. Molecular weight determination. 6. Cotton and flax. 7. Chemistry of cellulose. 8. Amino acids and proteins. 9. Synthetic polypeptides. 10. Wool. 11. Silk. 12. Crystalline structures of polymers. 13. Melting and crystallization. 14. Fine structure. 15. Production of fibres. References. Index.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM - LONDON - NEW YORK

549 E

progress in purity 1915 to 1965

Fifty years ago a 'List of Reagents for Analytical Purposes' was published in Great Britain by the Institute of Chemistry and the Society of Public Analysts. It contained 'notes indicating the standards of purity regarded as necessary for analytical work' relating to 89 chemicals. Chemicals meeting these standards were designated by the letters 'A.R.'

Thirty years ago 'AnalaR' specifications were introduced, describing more precise methods of testing and interpreting the tests in terms of maximum permitted limits of impurities. The first (1934) edition established standards for some 240 reagents. Four more editions have been published since—a sixth edition is in preparation—extending the range of 'AnalaR' reagents to 289, and successively incorporating, with advances in analytical methods, more rigorous procedures and more exacting standards.

Against the demands of specialised and instrumental methods of analysis still more highly purified reagents have been made available, as for spectroscopy and for micro-analysis, and for a number of specific individual applications.

The most recent introductions of very highly purified chemicals however, have been concerned not directly with analysis but with radar and electronics, in the BDH 'Electronic Grade' acids, for example, impurities are measured in terms of one or two parts per thousand million. These materials are available for analytical purposes. As other substances of comparable purity are needed, in the laboratory or out of it, BDH will apply itself to the job of supplying them.

BDH

POOLE · LONDON · BRISTOL · LIVERPOOL · MIDDLESBROUGH
BOMBAY · TORONTO · JOHANNESBURG · SYDNEY · AUCKLAND

LC/P2b

IMMUNO-ELECTROPHORETIC ANALYSIS

edited by **P. GRABAR**

Directeur de l'Institut de Recherches Scientifiques sur le Cancer, Villejuif (Seine), France

and **P. BURTIN**

Chef du Laboratoire d'Immunologie à l'Institut de Recherches Scientifiques sur le Cancer, Villejuif (Seine), France

Applications to Human Biological Fluids

Immuno-electrophoretic analysis, first described in 1953 by Grabar and Williams as a method for the study of antigenic substances, is currently finding application in a wide variety of research and clinical problems. The process combines the principles of zone electrophoresis with those of immunochemical analysis, thus allowing the simultaneous definition of electrophoretic mobility and immunochemical specificity of biological fluid. In addition, staining and enzymatic reactions may be carried out in the same gelified medium, thereby adding a third dimension to the analysis. This method is at present enjoying general use and this volume comprises almost all the data currently available which is relevant to the study of human material.

CONTENTS

PART I METHODS

1. The immuno-electrophoretic method of analysis. 2. The characterization reactions of the protein constituents following electrophoresis or immuno-electrophoresis in agar. 3. Quantitative interpretation of results after electrophoresis and immuno-electrophoresis in agar. 4. The immune sera and their utilization.

PART II APPLICATIONS TO HUMAN PLASMA

5. The proteins of normal human plasma. 6. Immuno-electrophoretic analyses of umbilical cord blood and of the blood of infants. 7. Immuno-electrophoretic control of the fractionation of plasma. 8. Introduction to the study of pathological sera. 9. The agammaglobulinemias. 10. The immuno-electrophoretic study of myeloma proteins. 11. Immuno-electrophoretic analysis of the macroglobulins in Waldenström's disease. 12. The cryoglobulinemias. 13. The hepatic diseases. 14. Immuno-electrophoretic studies of serum from rheumatics. 15. Immuno-electrophoretic analysis of the serum in leukemias and sarcomas. 16. Immuno-electrophoretic study of the serum during the course of systemic lupus erythematosus. 17 Various diseases. 18. Conclusions from studies of pathological sera by immuno-electrophoresis.

PART III STUDIES ON OTHER HUMAN MEDIA

19. Studies on other human media. 20. Immuno-electrophoretic study of proteinurias. 21. The proteins of the cerebro-spinal fluid. 22. Perilymphatic liquid. 23. The nature of the synovial fluid proteins. 24. Immuno-electrophoretic studies of the proteins of human milk and colostrum. 25. Immuno-electrophoretic studies of human amniotic fluid, meconium and infant stool. 26. The seminal fluid. 27. Applications of immuno-electrophoretic analysis to the study of the formed elements of the blood.

6 × 9″
xii + 302 pages
21 tables
99 illus.
663 references
1964
80s.

German edition available

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

305 E

Eastman Organic Chemicals around the world

Workers in the countries served by these distributors of Eastman Organic Chemicals can avoid the paperwork involved in importing. Some of these distributors maintain their own rather substantial stocks from which they can fill orders immediately. All can give you the benefit of the consolidated orders they place.

Among the 4000 Eastman Organic Chemicals these firms distribute are uncommon ones as well as uncommonly pure ones—organics that are often more economical to purchase than to make. These firms make it easier to purchase them. Get in touch with the one best located to serve you.

Distillation Products Industries
Eastman Organic Chemicals Department
Rochester 3, N. Y., U.S.A.

DPi

Distributors

AUSTRALIA

H. B. Selby & Co. Pty. Ltd.
35 York Street
Sydney, N.S.W.

H. B. Selby & Co. Pty. Ltd.
393 Swanston Street
P. O. Box 409G
Melbourne, C.1

H. B. Selby & Co. Pty. Ltd.
Box 606J, G.P.O.
Brisbane, Queensland

AUSTRIA

Heilmittelwerke Wien
G.m.b.H.
III/40, Rennweg 12
Vienna

W. J. Rohrbecks Nachf.
Wehrgasse 18
Vienna V

BELGIUM

Analis, S. A.
14, Rue Dewez
Namur

DENMARK

H. Struers Chemiske
Laboratorium
38, Skindergade
Copenhagen K

FINLAND

G. W. Berg & Co.
Fabiansgatan 14
Helsinki

Havulinna Oy
P. O. Box 468
Helsinki

FRANCE

Touzart & Matignon
3, Rue Amyot
Paris V^{e}

Substantial stocks maintained

GERMANY

Serva-Entwicklungslabor
Romerstrasse 45
Heidelberg

GREAT BRITAIN

Kodak Limited
Kirkby
Liverpool

Substantial stocks maintained

HOLLAND

N. V. Holland Indonesia
Agenturen Mij.
HIAM
139 De Ruyterkade
Amsterdam C

INDIA

The Andhra Scientific Co., Ltd.
4, Blacker's Road,
Mount Road
Madras

Raj-Der-Kar & Co.
Sadhana Rayon House
Dr. D. Naoroji Road
Bombay

INDONESIA

N. V. Chemicalienhandel
Rathkamp and Co.
18 Djalan Madja Pahit
Djakarta

ITALY

Prodotti Gianni, s.r.l.
Via Mecenate, 30/14
Milano

JAPAN

Tokyo Tsusho Kaisha, Ltd.
New Kaijo Building
6, Marunouchi 1-chome,
Chiyoda-ku
Tokyo

NEW ZEALAND

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 1495
Wellington, C.1

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 319
Dunedin, C.1

NORWAY

Nerliens Kemisk-Tekniske
Aktieselskap
Tollbodgt. 32
Oslo

PORTUGAL

Soquimica, Sociedada de
Representacoes de
Quimica, Lda.
Rua dos Correeiros, 113-3°
Lisbon

SOUTH AFRICA

Kodak (South Africa) (Pty.)
Limited
"Kodak House"
45 Shortmarket Street
Cape Town

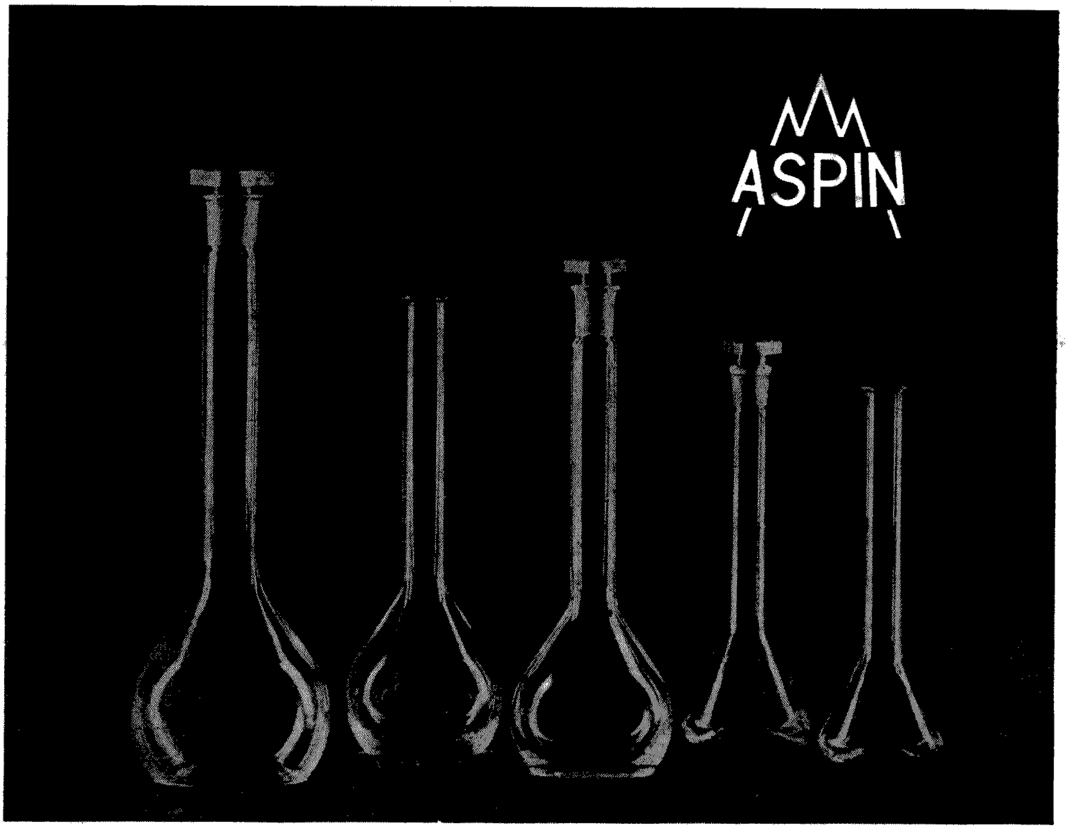
SWEDEN

Rudolph Grave A/B
Pyramidvagen 9, Fack Solna 1
Stockholm 3

SWITZERLAND

Dr. Bender & Dr. Hobein AG.
Riedtlistrasse 15a
Zurich 6

Distillation Products Industries *is a division of* **Eastman Kodak Company**



FIOLES JAUGÉES de précision ASPIN

Les nouvelles fioles jaugées ASPIN fabriquées dans les ateliers de PROLABO sont de la **classe de précision A** définie dans le projet de norme française AFNOR Pr B 35-307. Les tolérances correspondantes sont reportées dans le tableau ci-dessous; ce sont des tolérances très serrées, deux fois plus étroites que celles de la classe B, qui est la classe de précision la plus courante. La marque ASPIN, apposée sur chaque fiole, **garantit** formellement la conformité de l'instrument. La garantie est fondée sur un double contrôle individuel de chaque fiole, qui subit deux épreuves indépendantes de précision, la première en cours de fabrication, la seconde sur l'instrument terminé.

La forme et la présentation des fioles ASPIN sont soignées; elles sont moulées en verre de chimie, verre peu soluble et mouillant bien. Les parois sont épaisses et solides, le col bien calibré, de diamètre intérieur bien adapté à la précision de l'instrument. Le trait de jauge est régulier, net et fin.

Les inscriptions portées sur le corps sont absolument indélébiles, cementées dans le verre.

Ces fioles se présentent sous forme de fioles à col lisse ou de fioles à col rôdé avec bouchon de MANOLENE.

Capacité en ml	5	10	20	25	50	100	200	250
Tolerance en ml	0,02	0,02	0,03	0,03	0,05	0,08	0,15	0,15

12, Rue Pelée
PARIS 11ᵉ

PROLABO

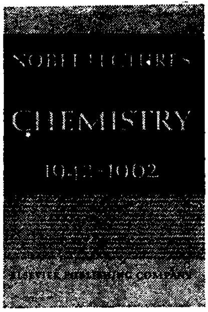
Téléphone:
797-41-59

Vol. **33** No. 4 ANALYTICA CHIMICA ACTA OCTOBER 1965

CONTENTS

Short Communications

PRINTED IN THE NETHERLANDS



NOBEL PRIZE LECTURES

CHEMISTRY

In three volumes 1901–1921
1922–1941
1942–1962

Total price: £24.0.0 or Dfl. 24,00

In the world of science, the history of research and progress during the present century is largely a history of the accomplishments of the winners of the Nobel Prize. These achievements are placed in perspective at the Nobel Prize ceremonies held each December in Stockholm. The official Nobel Lectures, delivered by the laureates on these occasions have hitherto appeared in the Nobel Foundation's annual publication "Les Prix Nobel" in the language in which they were presented. They are now being published in the English language, arranged in chronological order and according to Prize fields. They are preceded by the presentation addresses to the prize-winners and followed by a biography. For a large circle of readers, the appearance of this series will provide the first opportunity to read the Nobel Laureates' own accounts of the long years of preparation and creative effort which led up to their celebrated achievements.

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

in preparation

NOBEL LECTURES CHEMISTRY 1922–1941

Aston – Bergius – Bosch – Butenandt – Debye – H. Fischer – Harden – Haworth – Joliot – Joliot-Curie – Karrer – Kuhn – Langmuir – Pregl – Ružicka – Soddy – Svedberg – Urey – Von Euler-Chelpin – Wieland – Windaus – Zsigmondy

xvi + 499 pages + indexes, 1965

NOBEL LECTURES CHEMISTRY 1901–1921

Arrhenius – Buchner – Marie Curie – E. Fischer – Grignard – Haber – Moissan – Nernst – Ostwald – Ramsay – Richards – Rutherford – Sabatier – Van't Hoff – Von Baeyer – Wallach – Werner – Willstätter

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

272 Ea