

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

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Anal. Chim. Acta. Vol. 34, No 4, 381-500, April 1966
Completing Vol. 34 (1966)

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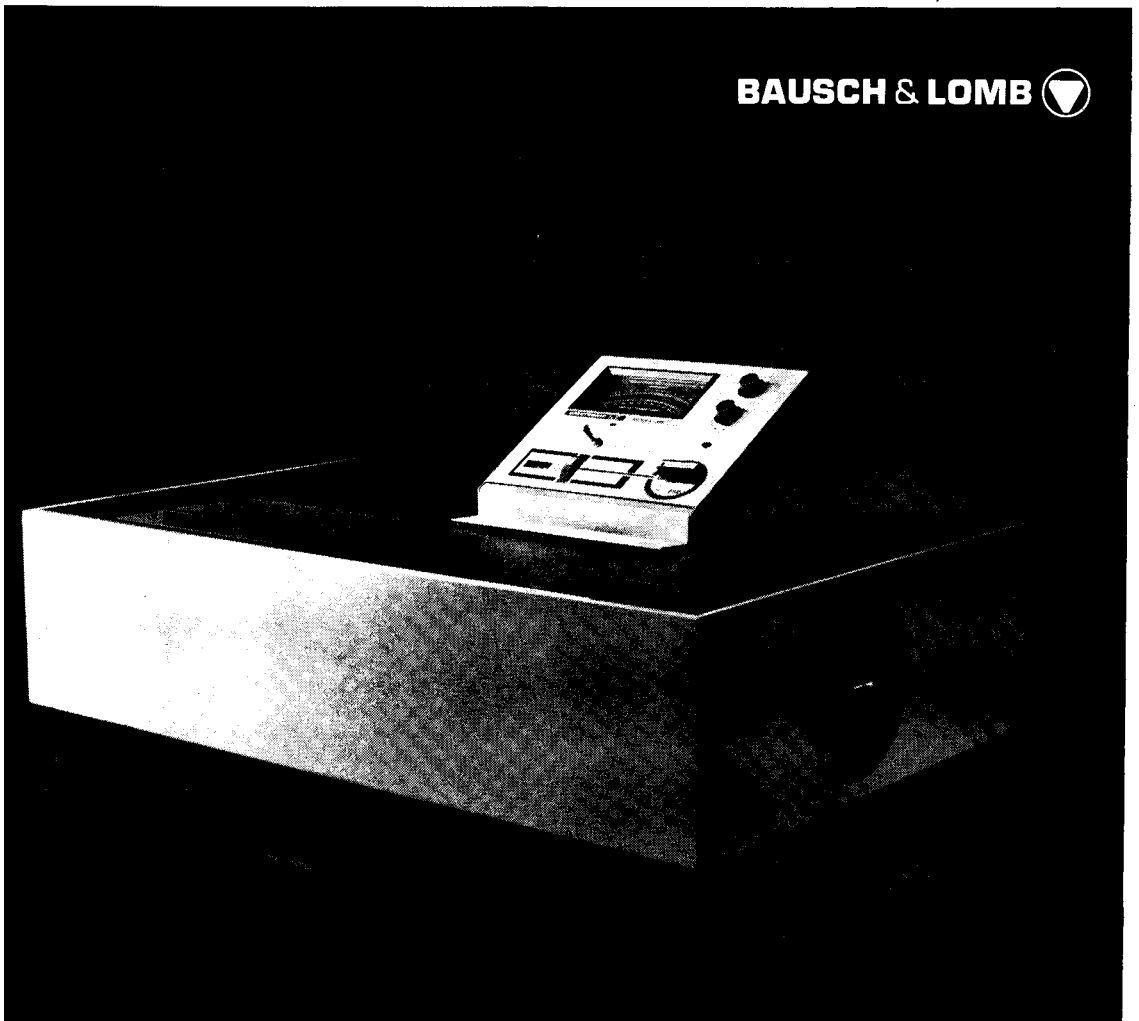
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SUMMARIES OF PAPERS PUBLISHED IN
ANALYTICA CHIMICA ACTA
Vol. 34, No. 4, April 1966

NEW COLORIMETRIC AND FLUORIMETRIC METHODS FOR
THE DETERMINATION OF 1,4-CYCLOHEXANEDIONE

1,4-Cyclohexanedione has been determined by reaction with *o*-phthalaldehyde in sulfuric acid. The determinations depend on the formation of a dicationic salt of pentacenequinone. A sensitive and highly selective fluorimetric method is recommended, but the reaction can also be used spectrophotometrically. Many organic compounds, as well as the isomers of 1,4-cyclohexanedione, give negative results. A spot test is described which can be used for quick preliminary investigations of complex mixtures for 1,4-cyclohexanedione.

E. SAWICKI AND H. JOHNSON,
Anal. Chim. Acta, 34 (1966) 381-386

SEPARATION OF TRIVALENT RARE EARTHS PLUS Sc(III)
FROM Al, Ga, In, Tl, Fe, Ti, U AND OTHER ELEMENTS BY
CATION-EXCHANGE CHROMATOGRAPHY

A method is presented for the quantitative separation of the trivalent rare earths plus Sc(III) as a group from Al(III), Ga(III), In(III), Tl(III), Fe(III), Ti(IV), U(VI), Be(II), Mn(II), Co(II), Cu(II), Ni(II), Zn(II), and Cd(II). These elements can be eluted from a cation-exchange column with 1.75 *N* HCl, while the rare earth group elements are retained. Numerous other elements not investigated have low distribution coefficients in 1.75 *N* HCl and therefore should be separated by the same procedure; Th(IV) is retained by the column when the rare earths are eluted with 3.0 *N* HCl. The only elements which partially accompany the rare earths plus Sc(III) are Zr(IV), Hf(IV), Sr(II), and Ba(II); these have to be separated by special procedures. The method is suitable for accurate reference analysis over a wide range of concentrations.

F. W. E. STRELOW,
Anal. Chim. Acta, 34 (1966) 387-393

SEPARATION OF SUGAR DERIVATIVES BY PARTITION
CHROMATOGRAPHY ON ANION-EXCHANGE RESINS

The separation of a number of sugar derivatives such as methyl, ethyl, benzyl, hydroxyethyl ethers and various glycosides has been studied. An efficient separation of most species was obtained in 94% ethanol using an anion-exchange resin in its sulfate form. The eluate concentration was determined automatically using the orcinol method.

L. I. LARSSON, O. RAMNÄS AND O. SAMUELSON,
Anal. Chim. Acta, 34 (1966) 394-400

SOME OBSERVATIONS ON MOLECULAR WEIGHT ESTIMATIONS BY MOLECULAR-SIEVE CHROMATOGRAPHY

A critical review is given of theoretical aspects of the quantitative application of molecular-sieve chromatography to the estimation of molecular weights of macromolecules. Particular reference is made to some of the inconsistencies, controversies, and sources of confusion which exist in the literature at present.

D. M. W. ANDERSON AND J. F. STODDART,
Anal. Chim. Acta, 34 (1966) 401-406

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

A new, sensitive colorimetric procedure for the determination of microgram quantities of palladium(II) with pyridine-2-aldehyde-2-quinolyldrazone is described. The reaction is practically instantaneous and not sensitive to variations in salt concentration. The platinum group metals do not interfere, and the analysis is possible with milligram amounts of these metals present.

M. L. HEIT AND D. E. RYAN,
Anal. Chim. Acta, 34 (1966) 407-411

ANALYTICAL APPLICATIONS OF β -HETEROPOLY ACIDS

PART II. THE INFLUENCE OF COMPLEXING AGENTS ON SELECTIVE FORMATION

An explanation is given of the apparently paradoxical behaviour of heteropoly acids in the presence of organic complexing agents such as tartaric acid, and methods for selective formation of particular heteropoly acids are suggested. Sensitive and rapid methods for the determination of silicate and phosphate in the presence of each other are described.

R. A. CHALMERS AND A. G. SINCLAIR,
Anal. Chim. Acta, 34 (1966) 412-418

STANDARDIZATION OF EXPERIMENTAL CONDITIONS IN THERMAL ANALYSIS

A NEW POLYPLATE SAMPLE HOLDER

Of the several variable experimental conditions in thermoanalysis, the influence of the sample layer thickness on the decomposition process can be of decisive importance. A polyplate sample holder is described on which the sample can be spread in a very thin layer. With this sample holder, TG, DTG and DTA investigations can be simultaneously carried out. The application of the polyplate holder improved the reproducibility and selectivity of thermoanalysis to a great extent.

J. PAULIK, F. PAULIK AND L. ERDEY,
Anal. Chim. Acta, 34 (1966) 419-426

THE DETERMINATION OF BORON IN SILICON AND GERMANIUM BY ACTIVATION ANALYSIS

(in German)

The determination of boron via the nuclear reaction $^{11}\text{B}(\text{p},\text{n})^{11}\text{C}$ was studied in detail; the nitrogen reaction $^{14}\text{N}(\text{p},\alpha)^{11}\text{C}$ interferes. Nitrogen also interferes deuterium activation via the nuclear reactions $^{10}\text{B}(\text{d},\text{n})^{11}\text{C}$ and $^{11}\text{B}(\text{d},\text{zn})^{11}\text{C}$; this interference must be attributed to the nuclear reaction $^{14}\text{N}(\text{d},\alpha\text{n})^{11}\text{C}$. Both interferences were investigated quantitatively. The conditions for the accurate determination of boron and for a simultaneous determination of boron and nitrogen by proton activation were established. An analytical method with chemical separation of the radioisotope ^{11}C was developed for silicon and germanium.

H. ROMMEL,
Anal. Chim. Acta, 34 (1966) 427-446

THE SZILARD-CHALMERS EFFECT APPLIED IN THE NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL SAMPLES

The Szilard-Chalmers effect has been applied in the separation of activities, originating from organically bound elements, from neutron-irradiated material. The nuclides ^{76}As , ^{198}Au , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{38}Cl , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{64}Cu , ^{59}Fe , ^{27}Mg , ^{99}Mo , ^{24}Na , ^{32}P , ^{86}Rb , ^{75}Se and ^{65}Zn were extracted from liver tissue, whole blood or muscle tissue with water or with varying strengths of hydrochloric acid. The recoveries of the alkali metal nuclides, ^{82}Br and ^{38}Cl , in the water and hydrochloric extracts were $\geq 95\%$. In the concentrated hydrochloric acid extracts, the recovery of most nuclides exceeded 90%. The enrichment of the different nuclides obtained in the Szilard-Chalmers process was investigated by reactivation of part of the extracts. The effect of dilution, which favours the yield, was investigated in the separation of ^{59}Fe from whole blood samples.

D. BRUNE,
Anal. Chim. Acta, 34 (1966) 447-455

IDENTIFICATION OF RADIONUCLIDES BY SEMIQUANTITATIVE AUTORADIOGRAPHIC DETERMINATION OF HALF-LIFE BY THE RING-OVEN METHOD

In the proposed method, a series of 9 rings is prepared from different μl -volumes of a solution of the radionuclide under test (specific activity 1.5-2.5 $\mu\text{C}/\mu\text{l}$). At a starting time $t = 0$ and at 3 later times, each series of rings is placed on X-ray film strips for a period of 1 h. After the usual development of the 4 strips, 4 density scales are obtained corresponding to 4 different times, and these can be compared by the method of weighted means. From the decrease in density of the rings, the half-life of the radionuclide can be estimated. The method is explained for the examples ^{198}Au , $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, ^{153}Sm and ^{131}I .

H. WEISZ AND D. KLOCKOW,
Anal. Chim. Acta, 34 (1966) 456-464

QUALITATIVE AND QUANTITATIVE ANALYSIS OF RARE EARTH MIXTURES BY MEANS OF MAGNETO-OPTICAL ROTATION.

(in French)

The general features of a new physical process for the qualitative and quantitative routine analysis of rare earth mixtures are given. The characteristic sharp lines in the magneto-optical rotation spectra of these elements are utilized. The recording photoelectric spectropolarimeter used is described briefly. A comparison is made with two other physical processes—absorption and X-ray fluorescence spectrometry. The proposed method appears to be best when a mixture with more than 3 or 4 elements must be analysed. The sensitivity and accuracy are given for 9 rare earths. Improvements of the process are suggested.

B. BRIAT, M. BILLARDON, J. BADOZ AND J. LORIERIS,
Anal. Chim. Acta, 34 (1966) 465-482

ION-EXCHANGE CHROMATOGRAPHY BY DISPLACEMENT DEVELOPMENT USING ELECTRICAL CONDUCTIVITY OF THE RESIN TO DETECT FRACTIONS

(Short Communication)

H. D. HARLAN,
Anal. Chim. Acta, 34 (1966) 482-484

AN EDTA METHOD FOR THE DETERMINATION OF MAGNESIUM IN ALUMINUM-BASE ALLOYS

(Short Communication)

K. E. BURKE,
Anal. Chim. Acta, 34 (1966) 485-487

DETERMINATION OF MICRO AMOUNTS OF EASILY REDUCIBLE ELEMENTS BY RING COLORIMETRY

(Short Communication)

T. J. JANJIĆ, G. JURIŠIĆ-MILOVANOVIĆ AND M. B. ČELAP,
Anal. Chim. Acta, 34 (1966) 488-491

FLUORIMETRIC DETERMINATION OF CADMIUM WITH 8-HYDROXYQUINOLINE-5-SULPHONIC ACID

(Short Communication)

D. E. RYAN, A. E. PITTS AND R. M. CASSIDY,
Anal. Chim. Acta, 34 (1966) 491-494

NEW COLORIMETRIC AND FLUORIMETRIC METHODS FOR THE DETERMINATION OF 1,4-CYCLOHEXANEDIONE

E. SAWICKI AND H. JOHNSON

Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226 (U.S.A.)

(Received September 6th, 1965)

Recently phenol, alkylated phenols and acetophenone were identified and estimated in automotive exhaust fumes by colorimetric¹, paper chromatographic², and gas chromatographic² methods. In addition, evidence was obtained for the presence of more complicated alkylated phenols, of phenols with carbonyl groups and of monocyclic carbonyl compounds. Chromatographic work is proceeding on the identification of some of these compounds. To bolster the chromatographic work some simple electronic spectral methods are being developed to help in the characterization and estimation of some of these compounds.

1,4-Cyclohexanedione is one of the compounds of interest in this project. However, specific methods of analysis for it are not available. Another difficulty lies in the method of collection which we have used in the past. The collection of automotive exhaust or other types of effluents in aqueous alkaline solution^{1,2} could alter the structure of various types of ketonic and aldehydic compounds through condensation reactions. For the analysis of some types of carbonyl compounds, effluents would have to be collected in non-alkaline media.

The present analytical work is based on the organic syntheses studies of MATTU AND MANCE³ and RIED AND ANTHOFER⁴.

In this paper new, highly selective methods for the colorimetric and spectrophotofluorimetric determination of 1,4-cyclohexanedione are described.

EXPERIMENTAL

Reagents

Reagents were obtained from commercial sources and purified where necessary. All organic solvents were distilled before use.

Apparatus

A Cary Model 11 Quartz Recording Spectrophotometer with 1-cm cells was used for all absorption spectral work. An Aminco-Bowman Spectrophotofluorimeter was used in the fluorescence studies. An R136 phototube was used in place of the 1P21 tube since it was found to be 10-18 times as sensitive for the fluorimetric measurement of the red-fluorescing chromogen.

Procedure 1

To 2 ml of the methanolic test solution is added 2 ml of 2% *o*-phthalaldehyde

in methanol followed by 1 ml of methanolic 5% sodium hydroxide solution. After 15 min, the absorbance is read at 402 m μ .

Procedure 2

(a) The procedure is the same as in 1 except that after the 15-min waiting period the mixture is evaporated to dryness and diluted to 10 ml with concentrated sulfuric acid. The absorbance is read at 618 m μ .

(b) In the fluorimetric method the same procedure is used except that readings are taken with the instrument set at an excitation wavelength of 615 m μ and an emission wavelength of 650 m μ .

Procedure 3

(a) To 1 ml of the aqueous test solution is added 0.2% *o*-phthalaldehyde in sulfuric acid to a 10-ml volume with mixing. The mixture is cooled under a tap and the absorbance is read at 622 m μ .

(b) For smaller quantities of material the fluorescence is read with the instrument set at an excitation wavelength of 625 m μ and an emission wavelength of 650 m μ .

Spot test procedure

To a piece of glass fiber paper is added 1 μ l of aqueous, alcoholic or chloroformic test solution. The spot is evaporated to dryness. A drop of 0.2% *o*-phthalaldehyde in sulfuric acid is added. The spot is exposed to the heat of a lamp, oven or hot plate (about 100°) for 1 min. Positive results are shown by a blue visible color (identification limit 0.5 μ g) and a red fluorescent color (identification limit 0.1 μ g).

DISCUSSION

Principles of the methods

1,4-Cyclohexanedione condensed with two molecules of *o*-phthalaldehyde to

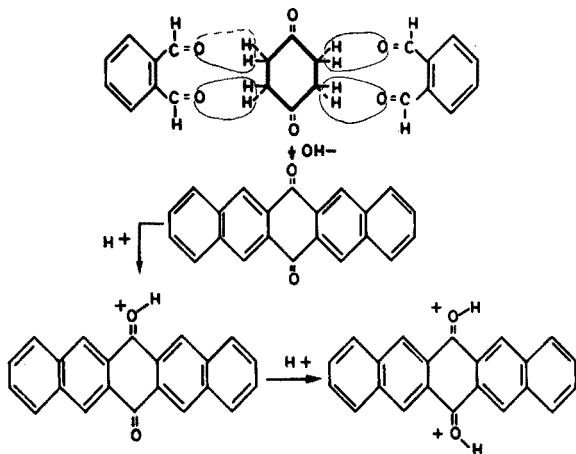


Fig. 1. Reaction of 1,4-cyclohexanedione with *o*-phthalaldehyde.

give pentacenequinone (Fig. 1). This chromogen was determined spectrophotometrically as the neutral compound and spectrophotometrically and spectrophotofluorimetrically as the dicationic salt in strong sulfuric acid solution.

The identity of the final chromogen as pentacenequinone was based on its isolation through a scaled-up analytical procedure 1 and its close spectrophotometric and spectrophotofluorimetric similarity to pentacenequinone obtained by the condensation procedure of MATTU AND MANCE³ and by the oxidation of pentacene with chromium trioxide in acetic acid. The absorption and fluorescence spectra of the pure pentacene dicationic salt are shown in Fig. 2. The dye obtained in the analytical procedure has closely similar spectra.

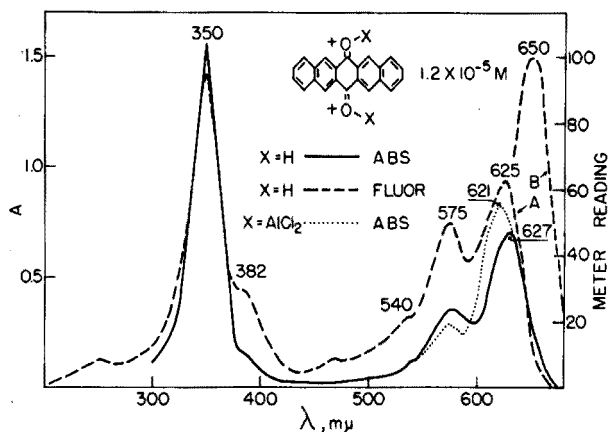


Fig. 2. Spectra of pentacenequinone ($1.2 \cdot 10^{-5} M$). Absorption spectrum in concentrated sulfuric acid (—) and in *o*-dichlorobenzene saturated with anhydrous aluminum chloride³ (.....). Fluorescence spectra in concentrated sulfuric acid at meter multiplier of 0.003 (-----); (A) excitation spectrum obtained at emission λ 650 $m\mu$, and (B) emission spectrum at excitation λ 350 $m\mu$.

On the basis of the molar absorptivity of the pure quinone in strong sulfuric acid solution a 33% yield of quinone was obtained in procedures 2a and 2b and a 51% yield in procedures 3a and 3b.

Variables

The variables in all the procedures were investigated. Variables such as percent reagent, order of addition, reaction temperature, percent alkali, percent sulfuric acid, reaction at room temperature, reaction at 100°, standing time, and type of test solvent were adjusted so that optimum intensity and reproducibility were obtained.

Comparison of methods

The various procedures are compared in Table I. The color and fluorescence intensities obtained in the sulfuric acid methods were stable for more than 24 h in procedure 2 and more than 168 h in procedure 3. Beer's law was obeyed by all methods. Procedures 3a and 3b were the simplest methods and involved the shortest procedural time. As shown by the relative standard deviation, procedure 3a was the most reproducible. Procedure 3b was the most sensitive of all the methods.

TABLE I
COMPARISON OF METHODS FOR THE DETERMINATION OF 1,4-CYCLOHEXANEDIONE

Procedure	Read at λ_{max} (m μ)	$\epsilon \cdot 10^{-3}$	Sens. ^a	Detn. limit ^b (μ g)	%S ^c	Beer's law Range (μ g) Slope ^d	Color stability (h)	Proc. time (min)
(1) Spectrophotometric	402	6.0	2.4	9.3	6	9.3-120		17
(2a) Spectrophotometric	618	18	3.6	6.2	8	6.2-80	> 24	45
(2b) Fluorimetric	615/650			2.3	10	2.3-25	> 24	45
(3a) Spectrophotometric	622	28	2.8	4	1.4	4-80	> 168	15
(3b) Fluorimetric	625/650			1	6	1-7	> 168	15

^a Sensitivity = $\frac{\epsilon \cdot 10^{-3}}{\text{Diln. factor}}$ where dilution factor = final value/test solution volume.

^b Total μ g of 1,4-cyclohexanedione in test solution or final volume giving an absorbance of 0.1 in a 1-cm cell for the spectrophotometric methods and a microphotometer reading of 10% at a meter multiplier reading of 0.01 for the spectrophotofluorimetric method. Where Beer's law is obeyed, this value is the lower limit reported.

^c Relative standard deviation.

^d Absorbance per microgram per final volume. For the fluorimetric methods the slope is the product of the meter multiplier and transmittance readings per microgram per final volume. The slope is equal to 0.1/detn. limit.

Since procedures *3a* and *3b* were superior in many respects to the other methods, interferences in these methods were investigated. Many compounds gave negative results. Examples of this type of reaction are the isomers of 1,4-cyclohexanedione (Table II). The most serious interferences are presented in this Table. In procedure *3a* the most sensitive interference was chlorogenic acid. In procedure *3b* the only interference was hydroquinone. It is believed, however, that the hydroquinone was impure and contained 1,4-cyclohexanedione or its precursor and that procedure *3b* has no obvious interferences. Because of its favorable selectivity and sensitivity, the fluorimetric procedure *3b* is recommended for the determination of 1,4-cyclohexanedione. If a fluorimeter is not available, then spectrophotometric procedure *3a* is recommended.

TABLE II

INTERFERENCES IN THE DETERMINATION OF 1,4-CYCLOHEXANEDIONE BY PROCEDURE 3

Compound	λ_{max} (m μ)	$\epsilon \cdot 10^{-3}$	<i>A</i> at 622 m μ and $3 \cdot 10^{-5}$ M	MM.T at 625/ 650 and $5 \cdot 10^{-6}$ M ^a
1,4-Cyclohexanedione	622	28	0.89	0.56
Chlorogenic acid ^b	448	5.8	0.23	0.00
	610	8.3		
Hydroquinone	562	7.2	0.15	0.015
	607	6.1		
β -Tetralone ^c	464	15.5	0.14	0.00
1,4-Dihydroxynaphthalene	458	5.8	0.05	0.00
	528	6.9		
α -Tetralone ^c	413	12.5	0.06	0.00
	436	16.0		
Succinaldehyde	381	19.0	0.07	0.00
	405	19.0		
1,2-Cyclohexanedione	382	4.9	0.00	0.00
	482	2.1		
1,3-Cyclohexanedione	428	0.5	0.00	0.00

^a Fluorimetric procedure.

^b In 50% aqueous sulfuric acid. In water solution a brown color was obtained with an absorbance value less than 0.1 at 622 m μ .

^c In methanol. Other compounds in aqueous solution.

For preliminary investigative purposes to ascertain the presence of 1,4-cyclohexanedione in complex mixtures the spot test can be quickly applied to a drop of the mixture in solution or to a drop of the chromatographic eluate.

SUMMARY

1,4-Cyclohexanedione has been determined by reaction with *o*-phthalaldehyde in sulfuric acid. The determinations depend on the formation of a dicationic salt of pentacenequinone. A sensitive and highly selective fluorimetric method is recommended, but the reaction can also be used spectrophotometrically. Many organic compounds, as well as the isomers of 1,4-cyclohexanedione, give negative results. A spot test is described which can be used for quick preliminary investigations of complex mixtures for 1,4-cyclohexanedione.

RÉSUMÉ

On propose un dosage de la 1,4-cyclohexanedione, au moyen d'*o*-phthalaldéhyde, en milieu acide sulfurique. Une méthode fluorimétrique sensible et très sélective est recommandée; ce procédé permet également un dosage spectrophotométrique. De nombreux composés organiques, de même que les isomères de la 1,4-cyclohexanedione donnent des résultats négatifs. Un essai à la touche est décrit pour une recherche préliminaire rapide.

ZUSAMMENFASSUNG

1,4-Cyclohexandion wurde durch Reaktion mit *o*-Phthalaldehyd in Schwefelsäure bestimmt. Es wird sowohl eine empfindliche und hochselektive fluorimetrische Methode als auch eine spektralphotometrische Bestimmung empfohlen. Sowohl viele organische Verbindungen als auch die Isomere des 1,4-Cyclohexandion ergeben negative Ergebnisse. Es wird ein Tüpfeltest für 1,4-Cyclohexandion beschrieben, der für schnelle vorläufige Untersuchungen komplexer Mischungen verwendet werden kann.

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Anal. Chim. Acta, 34 (1966) 381-386

SEPARATION OF TRIVALENT RARE EARTHS PLUS Sc(III) FROM Al, Ga, In, Tl, Fe, Ti, U AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY

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(Received August 2nd, 1965)

Recently a method has been described by FRITZ AND GARALDA¹ for the separation of trivalent elements like aluminium(III), yttrium(III), and the rare earths as a group from divalent elements such as calcium(II), strontium(II), magnesium(II), and nickel(II). The divalent elements are eluted by 1.5 *N* nitric acid from a column of Dowex 50-X8 resin, while the trivalent elements are retained. A separation of the rare earths plus scandium(III) from aluminium(III) and those trivalent elements which accompany them in the procedure of FRITZ would be of analytical interest, because most of these elements precipitate together with the rare earths as hydroxides in the classical silicate analysis scheme. Such a separation is not possible by cation exchange in nitric acid media because the relevant distribution coefficients are unfa-

TABLE I
DISTRIBUTION COEFFICIENTS IN 1.75 *N* ACID

	HCl	HNO ₃		HCl	HNO ₃
La(III)	70	70	Ga(III)	16.4	27.7
Ce(III)	67	65	In(III)	0.7	32.5
Sm(III)	56	42.3	Tl(III)	<0.5	—
Gd(III)	48.2	41.8			
Er(III)	41.8	52.0	Fe(III)	7.1	20.9
Y(III)	40.1	49.1	Ti(IV)	5.4	8.8
			Mn(II)	7.8	13.0
Yb(III)	39.9	56.0	Ni(II)	8.8	11.8
Sc(III)	38.8	33.1	Ca(II)	15.8	12.7
Al(III)	17.0	23.4	Sr(II)	22.5	11.8

vourable (Table I). The most selective procedures known for the separation of the rare earths from other elements very likely are those based on anion-exchange absorption of the nitrate complexes from partly organic nitric acid²⁻⁶ or nitric acid-acetic acid media⁷. However, elements such as Th(IV), U(VI), Pb(II), Bi(III), Tl(III), Ba(II), and Sr(II) accompany the rare earths and have to be separated by additional procedures. Furthermore, distribution coefficients decline with increasing atomic weights and only small amounts of the heaviest rare earths can be separated successfully from many other elements. The situation is even worse for scandium^{2,6} which cannot be separated from a large number of elements by this method at all.

EDGE AND AHRENS⁸ have separated barium(II), strontium(II), and some of the rare earths from elements more abundant in rocks by eluting the latter with 3 *N* hydrochloric acid from a cation-exchange column, but their procedure can be applied only when the rare earth group is present in trace amounts. An early breakthrough occurs for larger amounts of gadolinium(III) and erbium(III) which have distribution coefficients of 11.4 and 10.7, respectively, in 3 *N* hydrochloric acid. A systematic study of distribution coefficients^{9,10} carried out in this laboratory indicated that much more favourable conditions exist for a good separation of larger amounts of all the rare earths plus scandium from large amounts of almost all elements of the periodic table including the trivalent elements when hydrochloric acid of a considerably lower concentration is used for the chromatographic separation.

EXPERIMENTAL

Reagents and apparatus

Analytical reagent grade chemicals were used whenever possible. Rare earth oxides of 99.9% purity were supplied by L. Light and Co. Ltd., Colnbrook, England, and the xylenol orange and methyl thymol blue indicators by E. Merck, Darmstadt, Germany. The resin was the AG 50W-X8, sulphonated polystyrene of 100–200 mesh particle size manufactured by the Bio-Rad Laboratories in Richmond, California, by purification of the Dowex 50W-X8 resin. Standard solutions containing approximately 5 meq. (based on oxidation state) of the cation per 20 ml in 0.1 *N* hydrochloric acid were prepared and standardized by appropriate methods. Less concentrated solutions were prepared by dilution of the stock solutions when required. For column work borosilicate glass columns of 2 cm diameter were used as described before¹¹. A Beckman DU model spectrophotometer was employed for spectrophotometric work.

Distribution coefficients

Distribution curves were plotted for Yb(III), Sc(III), Al(III), and Ga(III) from distribution coefficients determined previously^{9,12}. These curves suggested that the most favourable conditions for the separation should be obtained by using 1.75 *N* hydrochloric acid as eluant. Distribution coefficients for a number of relevant elements were then determined in 1.75 *N* hydrochloric acid and in 1.75 *N* nitric acid using the procedure described previously⁹. The coefficients presented in Table I suggest that not only should separation of scandium(III) from Al(III), Fe(III), In(III), Ga(III) become possible by using 1.75 *N* hydrochloric acid as eluant, but also that separation from most other elements should be improved, compared with nitric acid as eluant, calcium(II) and strontium(II) being the only exceptions.

Elution of scandium

In 1.75 *N* hydrochloric acid, scandium has the lowest distribution coefficients of the rare earth group and its separation is therefore the most critical. For this reason, the elution behaviour of scandium was studied in more detail. Figure 1 shows some experimental elution curves for scandium at various concentrations and loadings using a 20-g (dry weight at 105°) resin column of 18 cm length and 2 cm diameter. The amount of scandium used was 5 meq. unless stated otherwise. A flow rate of 3.0 ± 0.2 ml/min was employed throughout. Fractions of 25 ml volume were taken

using an automatic fractionator, and, after the excess of acid had been removed by evaporation, the scandium in the fractions was determined by compleximetric titration with EDTA as described before¹¹.

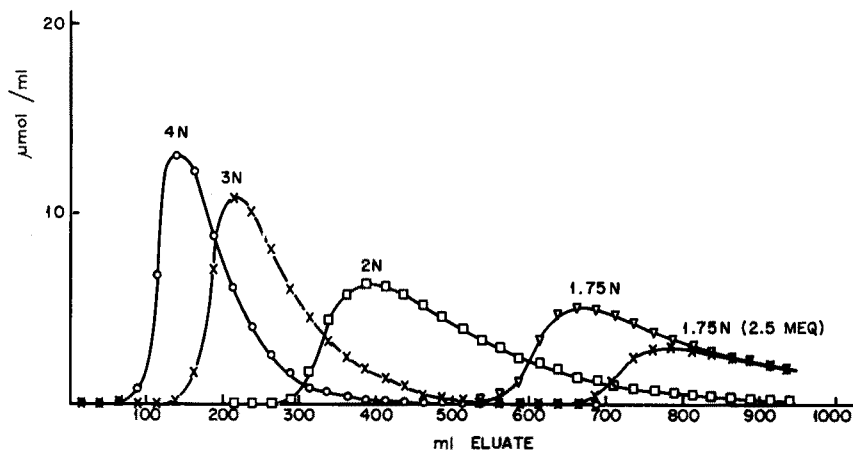


Fig. 1. Single element elution curves for scandium(III) with hydrochloric acid of various concentrations. Column of 20 g AG 50W-X8 resin; 60 ml resin volume; flow rate 3.0 ± 0.2 ml/min.

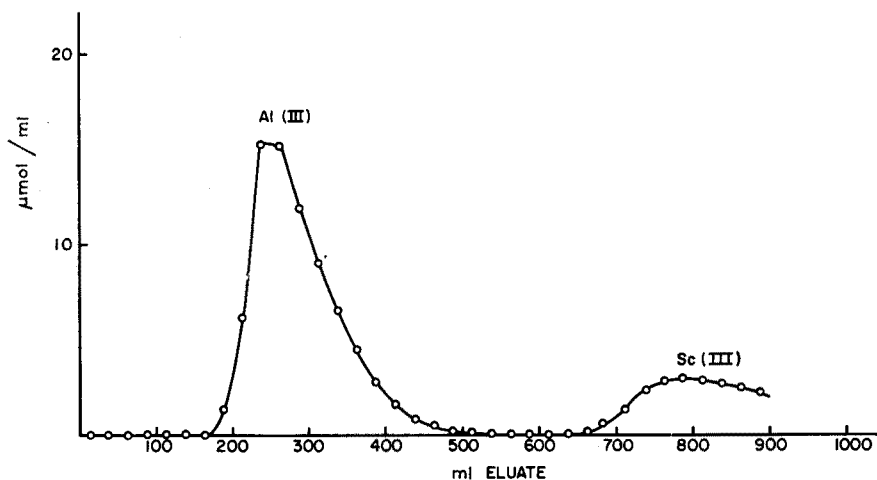


Fig. 2. Elution curve for Al(III)-Sc(III) with 1.75 N HCl. Column of 20 g AG 50W-X8 resin; flow rate 3.0 ± 0.2 ml/min.

Elution curves for ion pairs

As a next step, the elution of ion pairs was investigated using 2.5 meq. of scandium, 5 meq. of the other element and 1.75 N hydrochloric acid as eluant. The dimensions of the column and the experimental procedures were similar to those indicated above. The experimental curve for the Al(III)-Sc(III) pair is shown in Fig. 2; gallium(III) and calcium(II) have elution curves very similar to that of aluminium(III). Figure 3 shows an experimental elution curve for the Fe(III)-Sc(III) pair. Elements such as Ti(IV), U(VI), Be(II), Mg(II), Cu(II), Mn(II), Ni(II), Co(II), and

Zn(II) were found to have very similar elution curves to that of iron(III); Tl(III), In(III), Bi(III), Cd(II), and Pb(II) were found to appear in the eluate with the elution front. Other elements which, according to their distribution coefficients, should show

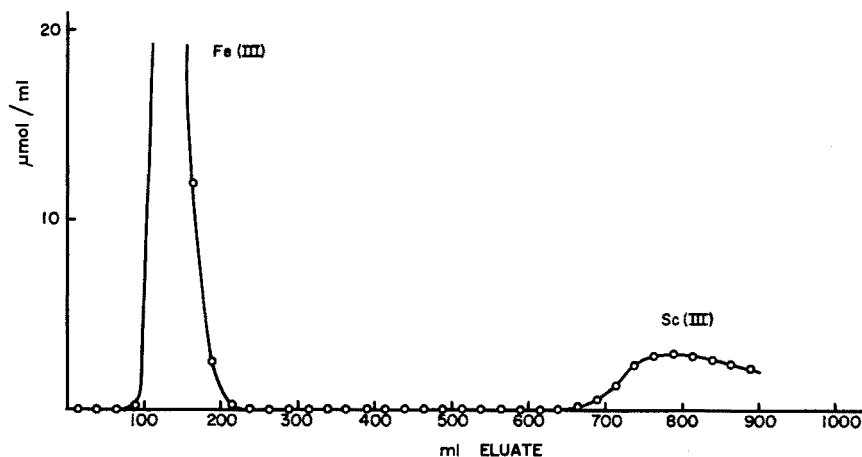


Fig. 3. Elution curve for Fe(III)-Sc(III) with 1.75 *N* HCl. Column of 20 g AG 50W-X8 resin; flow rate 3.0 ± 0.2 ml/min.

TABLE II

ANALYSIS OF SYNTHETIC MIXTURES

<i>Taken (mg)</i>		<i>Found (mg)^b</i>			
<i>Rare earth</i>	<i>Other</i>	<i>Rare earth</i>		<i>Other</i>	
Sc(III) ^a	37.42	Al(IV)	44.9	37.45 ± 0.04	44.8 ± 0.1
Sc(III) ^a	0.374	Al(III)	89.8	0.376 ± 0.003	89.8 ± 0.2
Sc(III) ^a	37.42	Ga(III)	115.8	37.43 ± 0.03	115.7 ± 0.2
Sc(III)	74.8	In(III)	191.1	74.7 ± 0.1	191.0 ± 0.2
Sc(III)	74.8	Tl(III)	169.7	74.8 ± 0.1	169.6 ± 0.2
Sc(III)	74.8	Fe(III)	91.2	74.9 ± 0.1	91.3 ± 0.1
Sc(III)	0.374	Fe(III)	456.0	0.375 ± 0.003	456.2 ± 0.3
Sc(III)	74.8	Ti(IV)	114.8	74.8 ± 0.1	114.9 ± 0.2
Sc(III)	0.374	Ti(IV)	229.6	0.375 ± 0.002	229.7 ± 0.2
Sc(III)	74.8	U(VI)	614.8	74.8 ± 0.1	614.9 ± 0.2
Sc(III)	74.8	Be(II)	23.16	74.9 ± 0.1	23.14 ± 0.04
Sc(III)	74.8	Mg(II)	60.8	74.9 ± 0.1	60.8 ± 0.1
Sc(III) ^a	37.42	Ca(II)	101.1	37.39 ± 0.04	101.2 ± 0.1
Sc(III)	74.8	Cu(II)	156.9	74.7 ± 0.1	156.8 ± 0.2
Sc(III)	74.8	Mn(II)	151.4	74.8 ± 0.1	151.3 ± 0.2
Sc(III)	74.8	Ni(II)	144.5	74.7 ± 0.1	144.4 ± 0.1
Sc(III)	74.8	Co(II)	145.1	74.8 ± 0.1	145.3 ± 0.2
Sc(III)	74.8	Zn(II)	163.5	74.8 ± 0.1	163.5 ± 0.1
Sc(III)	74.8	Cd(II)	246.2	74.7 ± 0.1	246.3 ± 0.3
La(III) ^a	220.8	Al(III)	44.9	220.7 ± 0.1	44.9 ± 0.1
Sm(III) ^a	251.9	Al(III)	44.9	251.8 ± 0.2	44.9 ± 0.2
Yb(III) ^a	144.2	Al(III)	44.9	144.2 ± 0.1	44.8 ± 0.1

^a 600 ml of 1.75 *N* HCl were used for elution.

^b The results are means of triplicate determinations with calculated standard deviations.

a similar behaviour are Sn(IV), As(III), Sb(III), Hg(II), Na(I), Li(I), V(V), Mo(VI), Se(IV), Te(IV), Au(III), and the platinum metals.

Quantitative separations

From the foregoing work a method for the quantitative separation of the rare earths and scandium from other elements was elaborated and applied to synthetic mixtures containing one element of the rare earth group and one other element. Amounts of standardized solutions were measured out, mixed and absorbed on a 20-g column as described above. About 0.1 *N* hydrochloric acid was employed as a wash solution to effect quantitative transfer. Iron(III), indium(III), thallium(III), titanium(IV) and other elements were eluted with 400 ml of 1.75 *N* hydrochloric acid at a flow rate of 3.0 ± 0.2 ml/min. The eluate was taken from the beginning of the absorption step. For the elution of aluminium(III), gallium(III) and calcium(II), 600 ml of 1.75 *N* hydrochloric acid was used to elute the last traces. The rare earths and scandium(III) then were eluted with 600 ml of 4.0 *N* hydrochloric acid at the

TABLE III
ANALYTICAL PROCEDURES

<i>Element</i>	<i>Method</i>
Sc(III), Zn(II) Tl(III)	Titration with EDTA, xylenol orange indicator. Titration with EDTA in presence of tartrate at pH 10, methyl thymol blue indicator.
Ca(II) Mg(II), Cd(II)	Titration with EDTA, methyl thymol blue indicator. Titration with EDTA, Eriochrome Black T indicator.
Cu(II) Co(II)	Iodide-thiosulphate titration. Titration with EDTA, back with Ca(II), methyl thymol blue indicator.
Fe(III) La(III), Sm(III), Yb(III)	Dichromate titration after reduction to Fe(II). Gravimetrically as oxides after precipitation with oxalic acid.
Ti(IV), Ga(III), In(III), U(VI)	Gravimetrically as oxides after precipitation with ammonium hydroxide.
Al(III) Be(II) Ni(II) Mn(II)	Gravimetrically as 8-hydroxyquinolate. Gravimetrically as benzoylacetate. Gravimetrically as dimethylglyoxime complex. Gravimetrically as $Mn_2P_2O_7$.

same flow rate. The eluates were evaporated almost to dryness and the amounts of elements were determined by appropriate analytical procedures. The results of the determinations are presented in Table II and the analytical methods are summarized in Table III.

DISCUSSION

The described method provides a simple means for the quantitative separation of the rare earths plus scandium(III) as a group from other trivalent elements forming hydroxide precipitates such as Al(III), Ga(III), In(III), Tl(III), Fe(III), and also from Ti(IV), Be(II), and U(VI). The separation of the rare earth group and especially of scandium(III) from divalent heavy metals, such as Mn(II), Co(II), Cu(II), Ni(II), Zn(II) and Cd(II), is considerably sharper than by elution with nitric acid. If sepa-

ration from these elements alone is contemplated, considerably smaller columns and elution volumes can be employed. The conditions for the separation from aluminium(III) and gallium(III) are fairly critical because these two elements have relatively high distribution coefficients and show some tailing. When triplicate amounts of 44.9 mg of aluminium(III) were eluted with 400 ml of 1.75 *N* hydrochloric acid from a column of the described size, 2.18, 1.99, and 2.13 mg of aluminium(III) remained on the column. With 600 ml of the same eluant, the amount of aluminium(III) not eluted was reduced to less than 0.03 mg. The amounts of scandium(III), yttrium(III), and the heavier rare earths should not be much higher than about 2.5 meq. total, while 5 or even 10 meq. of the rare earths can be separated when only lanthanum(III) and cerium(III) are present. As little as 0.374 mg of scandium(III) can be separated quantitatively from about 90 mg of aluminium(III) or 200 mg of iron(III) or titanium(IV) and determined with an accuracy of $\pm 1\%$.

Besides the separations presented in Table II, elements such as Li(I), Na(I), K(I), Rb(I), Cs(I), As(III), Sb(III), Bi(III), Se(IV), Te(IV), Nb(V), V(IV), V(V), Mo(VI), Hg(II), Pb(II) and Fe(II) should be separated easily according to available distribution coefficients⁹; barium(II) and strontium(II) partly accompany the rare earth group, but can be separated by a hydroxide precipitation of the latter; thorium(IV), zirconium(IV), and hafnium(IV) also remain on the resin quantitatively together with the rare earth group. Elution of the rare earths plus scandium(III) with 800 ml of 3.00 *N* hydrochloric acid will separate these from thorium, which is retained quantitatively by the column. Zirconium(IV) and hafnium(IV) partially accompany the rare earths; zirconium(IV) can be separated from the rare earths plus scandium by anion exchange in sulphuric acid media, but hafnium(IV) is not separated quantitatively¹³, and a special separation step has to be used if separation is required.

The above method thus provides separation of the rare earths plus scandium(III) as a group from almost all elements of the periodic table. Not separated quantitatively are only Sr(II), Ba(II), Zr(IV), and Hf(IV), which need special attention when present, and a few elements such as silver(I), which form insoluble precipitates in hydrochloric acid. The method has the advantage that it does not introduce large amounts of organic complexing reagents into the sample solution which complicate later separations and determinations. The relatively large elution volumes are no serious disadvantage, because considerably faster flow rates can be used than with partly organic eluting agents. The eluting agent hydrochloric acid can quite easily be removed by evaporation. The total rare earths plus scandium(III) can then be determined by precipitation with oxalic acid from a small volume of 0.05 *N* hydrochloric acid and ignition of the precipitate to the oxides, or by titration with EDTA at pH 5.8 using xylenol orange or methyl thymol blue as indicator. The method is well suited to accurate reference analysis work.

SUMMARY

A method is presented for the quantitative separation of the trivalent rare earths plus Sc(III) as a group from Al(III), Ga(III), In(III), Tl(III), Fe(III), Ti(IV), U(VI), Be(II), Mn(II), Co(II), Cu(II), Ni(II), Zn(II), and Cd(II). These elements can be eluted from a cation-exchange column with 1.75 *N* HCl, while the rare earth group

elements are retained. Numerous other elements not investigated have low distribution coefficients in 1.75 *N* HCl and therefore should be separated by the same procedure; Th(IV) is retained by the column when the rare earths are eluted with 3.0 *N* HCl. The only elements which partially accompany the rare earths plus Sc(III) are Zr(IV), Hf(IV), Sr(II), and Ba(II); these have to be separated by special procedures. The method is suitable for accurate reference analysis over a wide range of concentrations.

RÉSUMÉ

Une méthode est proposée pour la séparation quantitative de terres rares trivalentes et du scandium d'avec Al(III), Ga(III), In(III), Tl(III), Fe(III), Ti(IV), U(VI), Be(II), Mn(II), Co(II), Cu(II), Ni(II), Zn(II) et Cd(II). Ces éléments sont élués d'une colonne échangeuse de cations, par HCl 1.75 *N*, tandis que les terres rares sont retenues. De nombreux autres éléments ayant des coefficients de partage bas, dans ces conditions, pourraient être séparés par ce procédé. Th(IV) est retenu sur la colonne lorsque les terres rares sont éluées par HCl 3.0 *N*. Zr, Hf, Sr et Ba doivent être séparés par des procédés spéciaux.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen zur quantitativen Trennung der dreiwertigen Seltenen Erden und Sc(III) von Al(III), Ga(III), In(III), Tl(III), Fe(III), Ti(IV), U(VI), Be(II), Mn(II), Co(II), Cu(II), Ni(II), Zn(II) und Cd(II). Diese Elemente können von einem Kationenaustauscher mit 1.75 *N* Salzsäure eluiert werden, während die Elemente der Seltenen Erden zurückgehalten werden. Zahlreiche Elemente, die nicht untersucht wurden, besitzen niedrige Verteilungskoeffizienten in 1.75 *N* HCl und sollten deshalb durch das gleiche Verfahren abgetrennt werden. Th(IV) wird zurückgehalten, wenn die Seltenen Erden mit 3.0 *N* HCl eluiert werden. Die einzigen Elemente, welche teilweise die Seltenen Erden und Sc(III) begleiten, sind Zr(IV), Hf(IV), Sr(II) und Ba(II). Diese müssen durch besondere Verfahren abgetrennt werden.

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SEPARATION OF SUGAR DERIVATIVES BY PARTITION CHROMATOGRAPHY ON ANION-EXCHANGE RESINS

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(Received August 2nd, 1965)

Chromatographic separation of various sugar derivatives is a valuable tool in modern carbohydrate chemistry. Several comprehensive reviews have been published in recent years¹.

Partition chromatography on ion-exchange resins² with automatic determination of the eluate concentration³ is an efficient method for the separation and quantitative determination of monosaccharides. In many systems this method seems to be superior to earlier known methods. The aim of this work is to study the application of this technique to the separation and determination of sugar derivatives such as methylated sugars and glycosides.

EXPERIMENTAL

Two batches of strongly basic anion-exchange resins were used. Both consisted of macroporous beads and were converted to their sulfate form. One of the resins (T4) had the particle size 10–35 $m\mu$ and the exchange capacity 3.7 meq. per g of Cl^- resin. The other resin (T5B) consisted of smaller resin particles, 3–17 $m\mu$, and had a higher exchange capacity, 4.2 meq./g.

The elution was carried out at 75° with mixtures of ethanol and water. The equipment was the usual type with jacketed glass columns and piston-type pumps of stainless steel for feeding in the eluant (*cf.* ref. 4). Constant temperature was maintained in all parts of the column by inserting a preheater between the pump and the column. The eluate was analyzed continuously by means of a Technicon Auto-Analyzer using the orcinol method described previously⁵. This method gives a higher absorbance with pentoses than with hexoses and can also be used with substituted sugars. The absorbance is lower with methylated sugars than with unsubstituted sugars and decreases markedly with an increased degree of substitution. The amounts of individual sugar derivatives and sugars passed through the monitor varied between 6 and 70 μg . The total amount added to the chromatographic column was about 3 times as great. The abbreviations on the elution bands given in the figures refer to the substances in Table I.

RESULTS AND DISCUSSION

In agreement with the results observed in separations of monosaccharides it was observed that an increased ethanol concentration resulted in larger distribution

coefficients of various sugar derivatives, such as methylated sugars and methyl glycosides. Similarly, the separation factors (*i.e.* the ratios between the distribution coefficients of various solutes) were more favorable at high concentration. On the other hand a broadening of the elution curves occurred at excessively high ethanol concentration. These observations, which are illustrated by the chromatograms reproduced in Fig. 1, are in agreement with the results from studies of equilibria and kinetics reported earlier with sugars and polyalcohols^{6,7}. Under the conditions used in this work the optimum concentration was found to be 94% ethanol (by weight).

A chromatogram illustrating the separation of a mixture of 8 sugar derivatives and 4 monosaccharides by means of the medium capacity resin is reproduced in Fig. 2. It is seen that the separation is good enough to permit determination of all

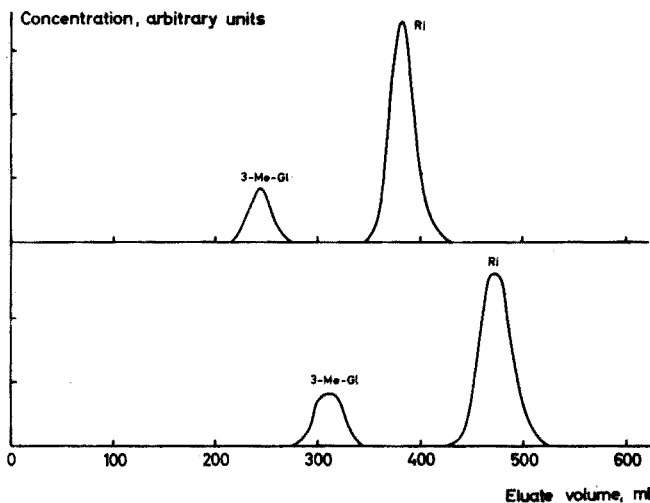


Fig. 1. Separation of 3-O-methyl-D-glucose and ribose in 94% ethanol (upper chromatogram) and in 95% ethanol (lower chromatogram). Resin bed 6×695 mm, T₄; flow rate 3.5 ml/cm²/min.

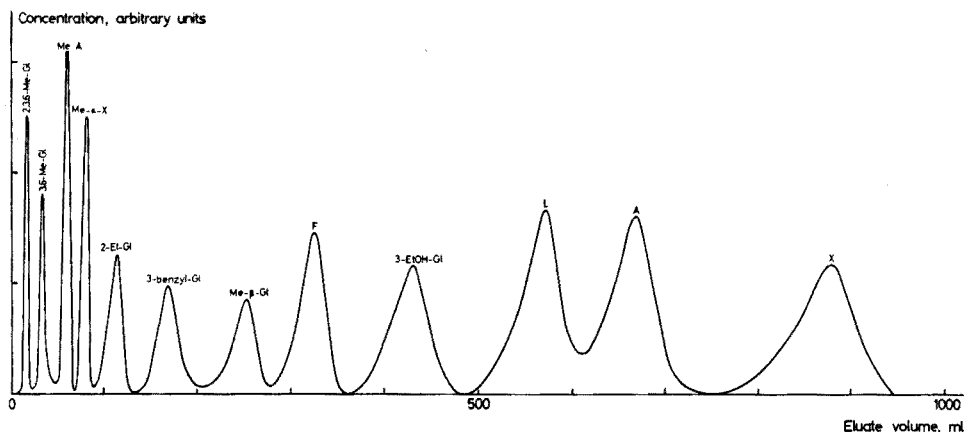


Fig. 2. Separation of various monosaccharides and sugar derivatives in 94% ethanol. Resin bed 6×695 mm, T₄; flow rate 3.5 ml/cm²/min.

substances. With more complicated mixtures containing very similar derivatives, some of the elution bands showed serious overlapping.

With such mixtures the application of the high capacity resin under the same conditions gave significant improvements. The results from a run with a somewhat longer bed of this resin are given in Fig. 3. In this run 12 sugar derivatives, 3 pentoses,

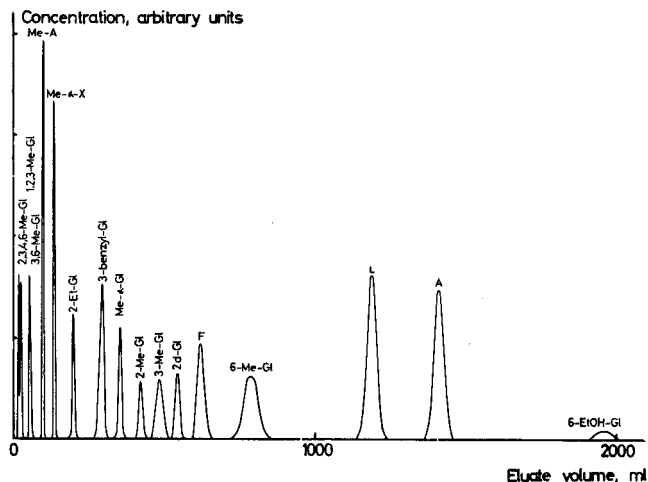


Fig. 3. Separation of various monosaccharides and sugar derivatives in 94% ethanol. Resin bed 6×950 mm, T5B; flow rate $3.5 \text{ ml/cm}^2/\text{min}$.

and 1 deoxysugar were separated from each other. Only the 2 solutes which appeared first in the eluate exhibited any overlapping. The results show that both the mutual separation of sugar derivatives and the separation of the monosaccharides from each other is much more effective in this run. This is explained by the greater selectivity of this resin as shown by the more favorable separation factors (Table I). Non-equilibrium factors, especially lower particle size and more uniform packing of the column, are also more favorable with this resin. The influence of these factors is reflected in the sharpness of the elution curves.

From the peak elution volumes determined in all experiments carried out with sugar derivatives the distribution coefficients were calculated in the usual manner⁴. In order to compensate for small variations observed in individual runs, fucose was included as a standard in each run. The variations were found to be greater with the resin of the lowest particle size and can be ascribed chiefly to small irregularities in flow rate at the high pressure drop ($30\text{--}37 \text{ kp/cm}^2$ at a flow rate of $3.5 \text{ ml/cm}^2/\text{min}$). The determinations of the distribution coefficients were, therefore, less accurate with this resin than with the coarser resin which gave a pressure drop of $5\text{--}10 \text{ kp/cm}^2$ at the same flow rate. Table I shows the separation factors relative to fucose for all the sugar derivatives studied. As usual the separation factor is defined as the ratio between the distribution coefficient of a given solute and that of the reference substance. For comparison the values obtained with some monosaccharides and deoxysugars are included in the Table.

The distribution coefficient (D_v) of fucose was 17.6 and 23.6 on the medium and high capacity resin, respectively. This indicates that greater eluant volumes are

required to elute a given solute from a column with the high capacity resin. The separation factors of most sugar derivatives are, however, more favorable with resins of high capacity. Similar observations about the influence of the exchange capacity upon the distribution coefficients⁶ and the selectivity³ were made in earlier work with monosaccharides.

TABLE I

SEPARATION FACTORS RELATIVE TO FUCOSE AT 94% ETHANOL (% BY WEIGHT)

	<i>Resin T4</i>	<i>Resin T5B</i>
2,3,4,6-Tetra-O-methyl-D-glucose (2,3,4,6-Me-Gl)	0.02	0.01
2,3,6-Tri-O-methyl-D-glucose (2,3,6-Me-Gl)	0.03	—
Methyl 2,3-di-O-methyl- β -D-glucopyranoside (1,2,3-Me-Gl)	0.04	0.02
2,3-di-O-ethyl-D-glucose	0.05	—
2,3-Di-O-methyl-D-glucose	0.07	—
3,6-Di-O-methyl-D-glucose (3,6-Me-Gl)	0.08	0.07
Methyl 4-O-methyl- β -D-glucopyranoside	0.08	—
D-Digitoxose	0.11	0.10
Methyl β -L-arabinopyranoside (Me-A)	0.17	0.14
Methyl β -D-arabinopyranoside	0.17	—
Methyl α -D-xylopyranoside (Me- α -X)	0.23	0.24
2-Deoxy-D-ribose	0.23	0.22
Methyl β -D-xylopyranoside	0.30	—
2-O-Ethyl-D-glucose (2-Et-Gl)	0.33	0.31
Ethyl β -D-glucopyranoside	0.40	—
Methyl α -D-galactopyranoside	0.46	—
3-O-Benzyl-D-glucose (3-benzyl-Gl)	0.50	0.46
Methyl α -D-mannopyranoside	0.57	—
Methyl α -D-glucopyranoside (Me- α -Gl)	0.58	0.57
2-Deoxy-D-galactose	0.63	0.63
2-O-Methyl-D-glucose (2-Me-Gl)	0.70	0.68
3-O-Methyl-D-glucose (3-Me-Gl)	0.77	0.77
Methyl β -D-glucopyranoside (Me- β -Gl)	0.77	—
4-O-Methyl-D-glucose	0.78	—
L-Rhamnose	0.82	0.82
2-Deoxy-D-glucose (2d-Gl)	0.86	0.87
L-Fucose (F)	1.00	1.00
D-Ribose	1.22	—
6-O-Methyl-D-glucose (6-Me-Gl)	1.26	1.28
3-O-Hydroxyethyl-D-glucose (3-EtOH-Gl)	1.33	—
D-Lyxose (L)	1.78	1.93
D-Arabinose (A)	2.09	2.30
D-Xylose (X)	2.74	3.04
6-O-Hydroxyethyl-D-glucose (6-EtOH-Gl)	2.87	3.19

As a first approximation, the sorption of polar solutes, such as polyhydroxy compounds, is explained by their higher solubility in the water-rich resin phase than in the less polar external solution⁸. The distribution coefficient should, therefore, be expected to decrease with an increased number of non-polar substituents in the sugars. This is confirmed by the results given in the Table. All derivatives appear earlier in the eluate than the sugar from which they are derived. Among the methylglucoses the distribution coefficient increases with a decreased number of substituents. The posi-

tion of the substituent has, however, a very great influence. With both methylglucoses and hydroxyethylglucoses an etherification of the primary hydroxyl group (6-position) has less effect than a substitution in other positions studied. The number of derivatives available to us was, however, too small to permit any generalizations about the influence of the various positions. Expectedly the methyl ethers exhibit higher distribution coefficients than the less polar ethyl ethers. Hydroxyethyl derivatives follow the ethylated and methylated sugars because no hydroxyl groups disappear during this substitution.

The comparatively high distribution coefficient of benzylglucose may seem puzzling. Strong attraction forces exist, however, between non-polar solutes and the non-polar matrix of an anion-exchange resin⁴. It is probable that interactions of this type contribute to the uptake and that this contribution is more marked between the benzene ring and the aromatic matrix than with the other sugar derivatives. In aqueous solution these forces would have a greater influence upon the order of elution than in ethanol-water. Experiments were therefore carried out in aqueous solution under otherwise unchanged conditions. The solutes studied were eluted in the following order:

trimethylglucose > fucose > xylose > benzylglucose (water)

trimethylglucose > benzylglucose > fucose > xylose (94% ethanol)

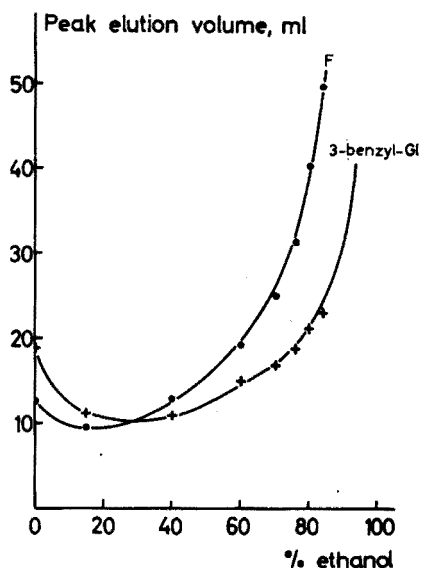


Fig. 4. Influence of the ethanol concentration upon the peak elution volume of 3-O-benzyl-D-glucose, and fucose. Resin bed 6×410 mm, T4; flow rate 2.0–3.5 ml/cm²/min.

A comparison between the elution of benzylglucose and fucose at various ethanol concentrations is given in Fig. 4. These results lend support to the hypothesis that non-polar attraction forces have an influence upon the position of the sugar derivatives on the chromatogram.

From the results given in the Table it is seen that not only etherification of the sugars, but also a conversion to glycosides, results in a lowering of the distribution

coefficient. An ethylglycoside appears ahead of the corresponding methylglycoside, which is in agreement with the rule that larger non-polar substituents have a greater influence than smaller substituents. The glycosides with α -configuration differ significantly from those with β -configuration. Expectedly, those derived from pentoses exhibit lower distribution coefficients than those from hexoses. Methylglycosides of arabinose and xylose appear in the same order as the sugars, whereas the α -derivatives of galactose and mannose appear in the opposite order compared to the unsubstituted monosaccharides.

Chromatographic separations were carried out at varying flow rates using the medium capacity resin. At high flow rate the overlapping of the elution curves corresponding to very similar solutes increased to such an extent that a valid evaluation of the chromatograms for quantitative purposes was impossible. With solutions containing only solutes with high separation factors the broadening of the elution curves (Fig. 5) did not interfere with the determination. Satisfactory separations were

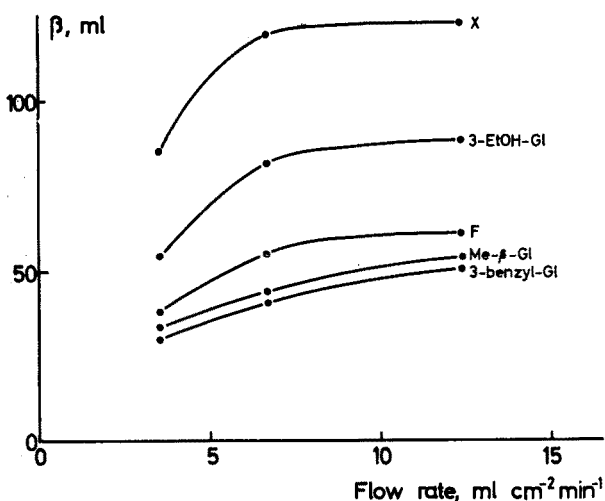


Fig. 5. Influence of the flow rate upon the width of the elution curves at the concentration C_{max}/e . Resin bed 6×695 mm, T₄.

achieved even at a flow rate of $12.5 \text{ ml/cm}^2/\text{min}$. At this flow rate the pressure drop in the column was about 35 kp/cm^2 . The high capacity resin, which consisted of smaller particles, could not be used at high flow rates because of the high pressure drop. Experience gained with other solutes shows that a very uniform particle size makes it possible to obtain good separations at high flow rates even with solutes whose distribution factors differ by only 10%. For an efficient separation at high flow rate the eluant must be preheated to the column temperature before it enters the column.

The results presented show that this method is very useful for separating sugar derivatives from sugars and that a mutual separation of a great number of sugar derivatives can be achieved under the same conditions as in the separations of monosaccharides. For a great number of these sugar derivatives, determinations can be made with the same accuracy as obtained in determinations of simple sugars⁹. In general, the conditions for a quantitative separation are better with less substituted

derivatives than with those containing several substituents. This is, of course, a serious limitation. We believe that the method will be a valuable complement to the existing methods for chromatography of sugar derivatives.

The financial support of the Swedish Technical Research Council is gratefully acknowledged. Thanks are also due to Dr. H. W. HOLY, Technicon Instruments Co., Chertsey, Great Britain, for gifts of specially prepared ion-exchange resins and to Drs. INGEMAR CROON (Örnsköldsvik), BENGT LINDBERG, OLOF THEANDER (Stockholm) and JOHN WILLARD (Princeton, N. J.) for gifts of sugar derivatives.

SUMMARY

The separation of a number of sugar derivatives such as methyl, ethyl, benzyl, hydroxyethyl ethers and various glycosides has been studied. An efficient separation of most species was obtained in 94% ethanol using an anion-exchange resin in its sulfate form. The eluate concentration was determined automatically using the orcinol method.

RÉSUMÉ

On a effectué une étude sur la séparation d'un certain nombre de dérivés de sucre, tels que méthyl, éthyl, benzyl, hydroxyethyl éthers et de divers glucosides. On propose une séparation dans l'éthanol à 94% avec résine échangeuse d'anions sous sa forme sulfate. La concentration dans l'éluat est déterminée automatiquement à l'aide de la méthode à l'orcinol.

ZUSAMMENFASSUNG

Es wurde die Trennung einer Anzahl von Zuckerderivaten wie Methyl-, Äthyl-, Benzyl-, Hydroxyäthyl-Äthern und verschiedener Glykoside untersucht. Eine wirk-same Trennung der meisten Spezies wurde in 94%igem Äthanol und einem Anionen-austauscher in seiner Sulfatform erhalten. Die Eluatkonzentration wurde automatisch mit der Orcinmethode bestimmt.

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SOME OBSERVATIONS ON MOLECULAR WEIGHT ESTIMATIONS BY MOLECULAR-SIEVE CHROMATOGRAPHY

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(Received July 19th, 1965)

Use of the so-called "gel filtration" technique for separating substances on a molecular size basis is increasing rapidly. "Gel filtration" columns can also be calibrated for direct molecular weight estimations of polystyrenes¹, proteins²⁻⁶, peptides⁷, and polysaccharides⁸ if suitable molecular-sieves and valid standards of known molecular weight are available.

Unfortunately, several sources of confusion exist in the literature. Many of the papers concerned have been published in either remote or applied biological journals; we choose to draw attention to these in an international analytical journal in the hope that increased fundamental interest in some of the present sources of difficulty will result.

The validity of PORATH AND FLODIN's term⁹ "gel filtration" as a suitable description of the essential process(es) involved has been questioned legitimately¹⁰⁻¹⁴. The discussion regarding the relative merits of the alternatives "exclusion chromatography", "restricted diffusion chromatography", and "gel permeation chromatography" has been reviewed by DETERMANN¹⁵, who proposed a differentiation between "gel filtration" and "gel chromatography". The term "molecular-sieve filtration" has also been used¹⁶.

ACKERS¹⁷ suggested that "molecular exclusion" and "restricted diffusion" are distinguishable primary molecular-sieving effects, the relative importance of which varies with the type of molecular-sieve used. Almost simultaneously, and in direct contrast, LAURENT AND KILLANDER¹⁰ concluded that the "decreased diffusion rate" was not a contributory process on the basis of the insensitivity of elution position to rate of flow. Until this disagreement is resolved—and, moreover, since gel-formers are not the only type of bed materials that can give the essential molecular-sieving effect^{11,18,19}—it appears that none of the terms referred to above is generally acceptable. Although TISELIUS, PORATH AND ALBERTSSON²⁰ stated (*cf.* ref. 15) that the technique "differs basically from common chromatography", some of their supplementary remarks support the view that the essential process is described more appropriately as "chromatography" than as "filtration". Assuming, however, that the term "molecular-sieve" is accepted to have the physico-chemical significance required to describe those porous column-packing materials which allow large molecules to be eluted faster than small molecules, the name "molecular-sieve chromatography" (M-SC)²¹ appears to be the most appropriate of those suggested to date. Perhaps it is not yet too late for the adoption of this term in preference to "gel filtration".

Confusion also arises at present from the lack of agreement regarding the best method of relating elution volumes to molecular weights. IWATSUBO AND CURDEL²² plotted elution volumes directly against molecular weight, and obtained a smooth curve. In order to obtain linear relationships, several authors^{2,3,5,23,24} have each elected to plot some different function of the elution volume against the logarithm of the molecular weight, whilst others have related the cube root of the "distribution coefficient", K_d , linearly to the square root of the molecular weight²⁶. In contrast, SANFELIPPO AND SURAK²⁷ observed a linear relationship between K_d and the *reciprocal* of the logarithm of the molecular weight for hormonally-active proteins and peptides on cross-linked dextran gels.

Defining K_d as the fraction of the internal volume, V_i , that is accessible to the solute, then

$$K_d = \frac{V_e - V_0}{V_i} \quad (1)$$

where V_0 is the void volume of the column and V_e is the elution volume²⁸. ACKERS¹⁷ has interpreted "molecular-sieve" processes in terms of a restricted diffusion mechanism in which he relates K_d to the Stokes' radius, a , of a macromolecule that is diffusing within a restrictive barrier of effective pore radius, r , by the RENKIN²⁹ equation

$$K_d = (1 - a/r)^2 [1 - 2.104 a/r + 2.09 (a/r)^3 - 0.95 (a/r)^5] \quad (2)$$

From this, ACKERS computed theoretical values for K_d for known values of a/r ; plotting these values of K_d *directly* against a/r gave good agreement with the experimental values. By plotting all ACKERS' computed values of K_d against the logarithm of a/r , we obtain curve A in Fig. 1.

An alternative approach follows from PORATH's theory²⁶; on the assumption

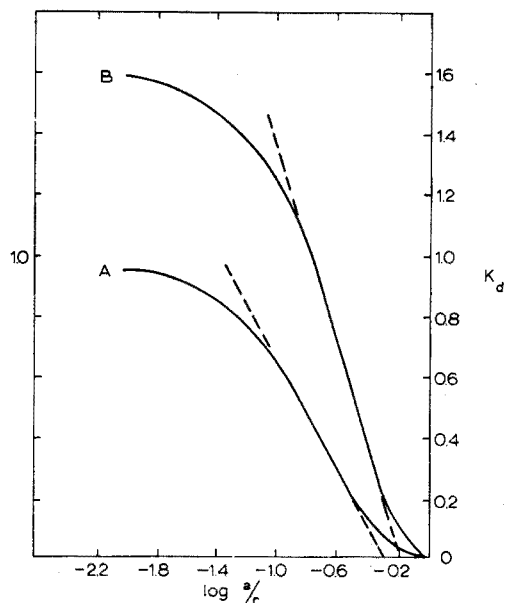


Fig. 1. Plot of K_d versus $\log a/r$. Curve A: from ACKERS' theory; curve B: from PORATH's theory.

that gel pores are conical in shape, PORATH derived, for the exclusion process, a theoretical formula which, in terms of the symbols already introduced here, is equivalent to

$$K_d = k(1 - a/r)^3 \quad (3)$$

where k is a constant, equal to 1.64 for dextran fractions on "Sephadex" gels. For this value of k , we have calculated values of K_d for known values of a/r ; a plot of K_d against $\log a/r$ gives curve B in Fig. 1.

These theoretical treatments can be used in a qualitative way to account for the empirical correlations of other investigators. For either curve A or B in Fig. 1, any restricted central portion that can be considered essentially linear is of the general form

$$K_d = -k_1 \log a/r - k_2 \quad (4)$$

where k_1 and k_2 are constants. Since a is proportional to some fractional power of the molecular weight M , eqn. (4) can be expressed as

$$K_d = -b \log M + c \quad (5)$$

where b and c are constants. A plot of K_d against $\log M$ is therefore linear²⁴ over a restricted range which is dependent on the nature of the solute molecules and on the type of molecular-sieve. Departures from linearity^{2,5} for solutes which can penetrate the molecular-sieve pores to only a very small extent are predicted by either curve A or B in Fig. 1.

Since V_0 and V_1 are constants for a particular column, eqn. (1) can be re-written as

$$V_e = -b' \log M + c' \quad (6)$$

where b' and c' are constants. This form of plot, used by ANDREWS², is the simplest possible correlation between the elution volume and $\log M$; we have found it the most convenient and reliable plot for routine use. The introduction of other constants, such as V_0 ⁵, may facilitate comparison of solute behaviour on dimensionally different columns of the same gel-former, but this is not necessary for calibration purposes.

Almost all the other logarithmic forms of plot to which reference has been made^{2,3,5,23,30} may be regarded as variants (merely involving changes in the associated constants) of eqn. (5). The equation

$$\log M = -a(V_e/V_0 - 1) + b \quad (7)$$

published (with an incorrect sign) by WHITAKER⁵, and subsequently used correctly by LEACH AND O'SHEA³, appears to be needlessly complex. The relationship of SANFELIPPO AND SURAK²⁷ is exceptional in that it does not follow directly from eqn. (5).

Values of K_d , as defined by eqn. (1), are dependent on the values found for V_1 , and there is disagreement regarding how this can best be determined experimentally. Values for V_1 have been determined (*a*) from expressions using the water regain of the gel^{1,6,23-25}, and (*b*) from the difference between the elution volumes of tritiated water and some substance that is completely excluded from the molecular-sieve¹⁷. Such determinations of V_1 include, with the internal volume, the water of hydration which is associated with the gel and is generally inaccessible to polymer solute molecules²⁸.

In addition to the poor theoretical justification for determining V_1 from an expression using the water regain, there are experimental difficulties; the internal volume of a gel packed in a column may differ from that determined experimentally under centrifugal force²⁴.

It is therefore suggested that K_d be defined according to the practice introduced by ANDREWS²; V_1 is defined as the difference between the elution volume at which molecular-sieving ceases to be operative for small molecules (of the polymer system under test) and the void volume, V_0 , of the column. This point becomes more important in the light of a recent theoretical treatment of "Sephadex gel filtration" by SQUIRE³¹, who claims that his equations might apply throughout the entire range of molecular weights, even for very small molecules. The molecular-sieve process breaks down for relatively small molecules; on a "Bio-Gel P300" column, capable of molecular weight estimations of polysaccharides⁸ in the range 5,000–125,000, the elution volumes of glucose and sucrose are identical. On ANDREWS' basis² this elution volume equals $V_0 + V_1$, and K_d is therefore unity for both glucose and sucrose. The introduction of constant k into eqn. (3) is necessary to account for the experimental observation^{1,2,26} that, in a linear plot of $K_d^{\frac{1}{a}}$ against $M^{\frac{1}{a}}$, the *intercept* on the $K_d^{\frac{1}{a}}$ axis is greater than unity. This fact was not realised, apparently, in earlier papers^{6,15} in which the straight line drawn through a number of observations would have represented the experimental data better had it not been made to pass through unit value for $K_d^{\frac{1}{a}}$ at $M^{\frac{1}{a}} = 0$.

LAURENT AND KILLANDER¹⁰ have pointed out that PORATH's assumption²⁶ that a is directly proportional to $M^{\frac{1}{a}}$ is true for flexible macromolecules only³². In contrast, SQUIRE³¹ assumed a to be directly proportional to $M^{\frac{1}{a}}$, and he deduced a linear relationship between $(V_e/V_0)^{\frac{1}{a}}$ and $M^{\frac{1}{a}}$ for proteins and dextran fractions. Both PORATH and SQUIRE claim good agreement with the experimental data, although CARNEGIE has found that SQUIRE's relationship is not as satisfactory as PORATH's for peptides on columns of "Sephadex G25" with phenol-acetic acid-water (1:1:1; w/v/v) as solvent. At present, however, practical tests of such theories are not very sensitive (*cf. ref. 10*). In contrast, the relationship between K_d and $\log M$ has the merit of holding regardless of the value of the fractional power to which M has to be raised so as to be proportional to a , provided that the fractional power is constant for the polymer series under investigation.

ALBERTSSON³³ has shown that the BRÖNSTED relationship³⁴ between the partition coefficient and the molecular weight of globular proteins applies to their distribution in certain two-phase aqueous systems. If such a relationship holds in molecular-sieve chromatography, $\log K_d$ would be expected to be proportional to $M^{\frac{1}{a}}$ (*cf. ref. 21*) if the temperature is constant.

Thin-layer chromatography of proteins on "Sephadex" has also been used for molecular weight estimations^{2,35}, and this technique has some features in common with molecular-sieve chromatography. Thus eqn. (1) can be written

$$K_d = \frac{V_e - V_0}{V_1' - V_0} \quad (8)$$

where

$$V_1' = V_0 + V_1 \quad (9)$$

Now the elution volume for a solute molecule is inversely proportional to the distance

moved by that molecule down a column in a given time. Comparing the migration distances on a thin-layer chromatogram with those on a column, eqn. (8) may be re-written in the form

$$K_d = \frac{(d_0 - d_e)d_1'}{(d_0 - d_1')d_e} \quad (10)$$

where d_0 , d_e and d_1' are the migration distances corresponding to the elution volumes V_0 , V_e and V_1' respectively. This relationship is similar to that used by CARNEGIE⁷ in his peptide mapping technique. Since $d_1'/(d_0 - d_1')$ is a constant, it follows from eqn. (10) that

$$K_d = c_1(d_0/d_e - 1) \quad (11)$$

where c_1 is a constant. If the R_0 value be defined by d_e/d_0 , then

$$K_d = c_1(1/R_0 - 1) \quad (12)$$

so that a plot of K_d against the reciprocal of R_0 should be linear. In contrast, MORRIS³⁵ has found that a plot of K_d against R_{HB} (which corresponds directly to R_0) is linear for proteins on "Sephadex" G100 and G200, and CARNEGIE⁷ found an approximately linear relationship between d_e and $\log M$ for peptides on "Sephadex" G25.

These comparatively new analytical techniques for estimating molecular weights are clearly in their infancy. The potential applications are so wide that it is important for the fundamental difficulties referred to here to be resolved, if progress is to be made on other than an empirical basis.

We thank Professor Sir EDMUND HIRST for his interest in this work, Dr. J. H. KNOX for helpful discussion on some aspects of chromatography, and the Science Research Council for a maintenance grant (to J.F.S.).

SUMMARY

A critical review is given of theoretical aspects of the quantitative application of molecular-sieve chromatography to the estimation of molecular weights of macromolecules. Particular reference is made to some of the inconsistencies, controversies, and sources of confusion which exist in the literature at present.

RÉSUMÉ

Une revue critique est présentée sur les aspects théoriques de l'application quantitative de la chromatographie sur colonne avec remplissage de tamis moléculaire, en vue d'une estimation de poids moléculaires. Les auteurs se sont référés spécialement à quelques controverses et sources de confusion existant actuellement dans la littérature.

ZUSAMMENFASSUNG

Es wird ein kritischer Überblick gegeben über theoretische Aspekte der quantitativen Anwendung der Molekularsieb-Chromatographie auf die Abschätzung von Molekulargewichten von Makromolekülen. Besonders werden einige kontroversen und Unstimmigkeiten in der gegenwärtigen Literatur berücksichtigt.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE*

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(Received July 21st, 1965)

Many reagents for the colorimetric determination of palladium have been proposed which exhibit greater or less selectivity and sensitivity. Critical review articles by BEAMISH AND MCBRYDE^{1,2} discuss a variety of these methods up to March, 1957. Of the reagents reported since 1957 for determining trace amounts of palladium, the substituted dithio-oxamides suggested by JACOBS *et al.*³⁻⁵ seem to be the most useful. Reagents containing the nitrosophenylamino group (*e.g.* *p*-nitrosodiphenylaniline) are the most sensitive for palladium, and have been successfully used for direct determination of small amounts of the metal^{6,7}; however, the deleterious effect of salt concentration and the interference of small amounts of the platinum metals limit the effectiveness of this high sensitivity.

Many of the procedures reported in the literature deal with palladium chloride solutions only; tests for interferences are often made by simply adding constituents to the chloride solution. The reactivity of platinum metal solutions is dependent on aging, ions present, solution treatment, etc.² and to be useful the solutions should be capable of reproducibility regardless of the nature of the platinum metal source.

In a recent paper⁸, the results of an investigation of the metal chelates of new tridentate chelating agents were reported; the compounds are readily prepared from commercially available chemicals. The reagents form complexes of high stability and high molecular extinction coefficients with a few metal ions; in addition the chelates are extractable and separations from masking interferences and concentration of trace amounts should be possible. These considerations prompted an investigation into the use of pyridine-2-aldehyde-2-quinolylhydrazone ($C_9H_8N-NH-N=CH-C_5H_4N$) for the determination of small amounts of palladium. A procedure has been devised to work with solutions that have been fumed with sulphuric acid and lends itself readily to the preparation of reproducible solutions for analysis.

EXPERIMENTAL

Apparatus, reagents and solutions

A Bausch and Lomb Spectronic 505 recording spectrophotometer and a Beckman DU spectrophotometer were used for absorbance measurements.

* This paper is abstracted from the Ph.D. thesis of M. L. HEIT, Dalhousie University, 1965 and was presented, in part, at the 48th Annual Conference of the Chemical Institute of Canada, Montreal, June 1965.

Palladium(II) standard solutions were prepared by dissolving Johnson & Matthey "specpure" ammonium chloropalladite in a known volume of water.

A 0.01% chloroform solution of the reagent was used for the spectral studies.

General procedure

An aliquot of the palladium solution (20–140 μg Pd) was placed in a 30-ml beaker and 1 ml of concentrated sulphuric acid added. The solution was concentrated on a steam bath, fumed, and 5–10 ml of distilled water added (procedure A). For larger amounts of palladium 5 ml of concentrated sulphuric acid were added, the solution was diluted to 50 ml with distilled water after fuming, and a 10-ml aliquot taken for analysis (procedure B). The solution was adjusted to the appropriate pH (1.5–2.3) with 5 *N* sodium hydroxide and transferred to a separatory funnel. Ten ml of the reagent solution were added and the mixture shaken for a few minutes; the reagent passes into the water layer (protonated form of the reagent) and the purple palladium complex is extracted by the chloroform. The chloroform layer was withdrawn and the aqueous layer again extracted with a further 10 ml of the reagent solution. The combined extracts were diluted to 25 ml with chloroform and the optical density of the solution measured at the wavelength of maximum absorption, 594 $m\mu$ ($E = 1.2 \cdot 10^4$).

RESULTS AND DISCUSSION

Typical results are shown in Table I.

Direct determination of palladium in aqueous solution was possible with a 0.01% solution of reagent in water (pH 1.8). However, the sensitivity of the reaction is only 60% (λ_{max} 508 $m\mu$, $\epsilon_{508} = 7.4 \cdot 10^3$) of that obtained by the extraction procedure and the problem of masking interferences is present.

TABLE I

DETERMINATION OF PALLADIUM WITH PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

Experiment	Pd taken total (μg)	Optical density	Remarks
1	5	0.024	1 ml acid (procedure A)
2	50	0.228	1 ml acid (procedure A)
3	100	0.459	1 ml acid (procedure A)
4	200	0.183	5 ml acid (procedure B)
5	400	0.367	5 ml acid (procedure B)
6	700	0.644	5 ml acid (procedure B)

Effect of acidity

A pH-absorbance study showed that quantitative extraction occurred between pH 1.5–2.3. A solution containing 50 μg of palladium gave an optical density of 0.228 ± 0.005 between these limits; the optical densities obtained at pH 1.2 and 2.6 were 0.161 and 0.137 respectively. Solutions initially containing 1 ml of concentrated sulphuric acid were successfully analyzed for palladium; low results were obtained with 1.5 ml of acid present (procedure A). Analysis of palladium solutions

(> 100 μg) in which 4–5 ml of concentrated sulphuric acid were present, were readily performed using procedure B (Table I).

Effect of time and reagent

The complex is stable indefinitely when kept in the dark, but in light the colour faded slowly; a sample containing 1.3 p.p.m. palladium gave a constant optical density of 0.148 for 3 h, falling to 0.139 after 4 h and to 0.133 in 5 h. The reagent does not absorb at 594 $m\mu$; the small quantity of reagent extracted has no effect on the determination (Fig. 1).

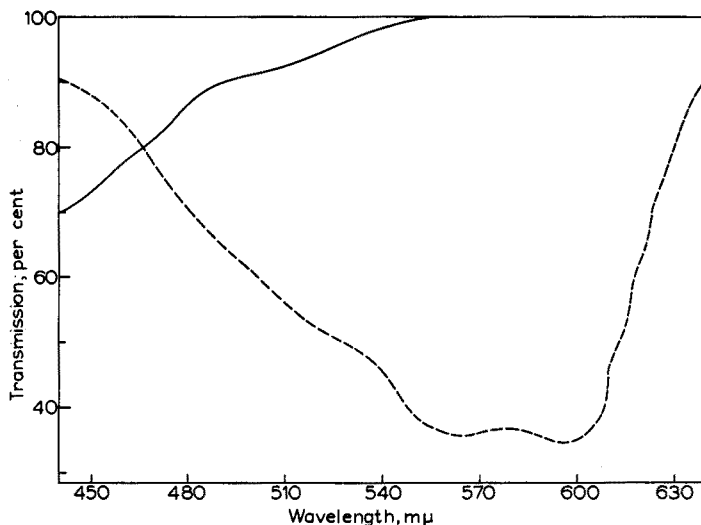


Fig. 1. Transmittance curves of: (A) $2 \cdot 10^{-4}$ M solution of reagent in chloroform; (B) palladium chelate in chloroform, 4.2 p.p.m.

Beer's law and optimum range

Many authors report sensitivity as the number of $\mu\text{g}/\text{cm}^2$ required to give an absorbance of 0.001; the sensitivity of the reaction reported as such is 0.009 μg Pd/ cm^2 . Beer's law is obeyed from 0.2 to 6 p.p.m. and the optimum range evaluated by RINGBOM's method⁹ is 1.5–7 p.p.m.

Composition of the complex

The solid palladium complex was isolated from chloroform and dried in a vacuum oven. The average palladium content was 24.1% (dimethylglyoxime precipitation) and tests for sulphate ion were positive. The palladium chelate $\text{Pd}(\text{C}_{15}\text{H}_{12}\text{N}_4)\text{SO}_4$, contains 24.2% palladium.

Effect of various ions

No interference was noted when 100-fold quantities of the sodium or potassium salts of the following ions were present during the usual colorimetric procedure: F^- , Cl^- , Br^- , NO_2^- , NO_3^- , ClO_3^- , SO_3^{2-} , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$. A 2000-fold excess of sulphate ion in addition to that obtained from sulphuric acid neutralization

did not interfere in the determination. Cyanide and iodide must be absent as they inhibit the reaction.

The reagent reacts with cobalt, copper, iron, zinc, cadmium, lead, nickel and manganese⁸, but these cations did not interfere in the determination when 200 μg per

TABLE II

PALLADIUM DETERMINATION IN THE PRESENCE OF THE PLATINUM GROUP METALS

(Results I, 3, 6, 7, 10 and 11 were obtained by procedure A. For the remainder, procedure B was used)

<i>Experiment</i>	<i>Palladium taken</i> ($\mu\text{g}/\text{ml}$) ^a	<i>Palladium found</i> ($\mu\text{g}/\text{ml}$)	<i>Platinum group</i> <i>metal</i> ($\mu\text{g}/\text{ml}$)
I	3.1	3.1	—
2	3.1	3.0	30 Ir as IrCl_6^{2-}
3	2.2	2.2	200 Ir
4	4.4	4.3	40 Pt as PtCl_6^{2-}
5	4.0 ^b	4.0	80 Pt
6	2.3	2.3	200 Pt
7	4.4	4.4	40 Rh as RhCl_6^{3-}
8	4.0 ^b	4.0	40 Rh
9	4.4	4.4	20 Au as AuCl_4^-
10	2.2	2.1	30 Au
11	4.8	4.8	50 Rh + 50 Pt + 50 Ir
12	2.4 ^b	2.2	50 Ir + 50 Pt
13	4.0	3.9	—

^a The amounts of metal ion recorded in the Table are $\mu\text{g}/\text{ml}$ of solution taken for analysis.

^b These results were determined independently, on "unknown" samples, by R. M. CASSIDY.

ml were added to a solution containing 2 $\mu\text{g}/\text{ml}$ of palladium. Successful analyses were performed in the presence of silver and lead despite sulphate precipitation. Palladium is the only platinum group metal that reacts with the reagent; some results obtained in the presence of these metals are given in Table II.

This work was supported by the National Research Council of Canada.

SUMMARY

A new, sensitive colorimetric procedure for the determination of microgram quantities of palladium(II) with pyridine-2-aldehyde-2-quinolylylhydrazone is described. The reaction is practically instantaneous and not sensitive to variations in salt concentration. The platinum group metals do not interfere, and the analysis is possible with milligram amounts of these metals present.

RÉSUMÉ

Un nouveau procédé est décrit pour le dosage colorimétrique de microquantités de palladium, au moyen de pyridine-2-aldéhyde-2-quinolylylhydrazone. La réaction est pratiquement instantanée et non sensible aux variations de concentrations de sels. Les métaux du groupe du platine ne gênent pas.

ZUSAMMENFASSUNG

Es wird ein neues empfindliches kolorimetrisches Verfahren zur Bestimmung von Mikrogrammen Palladium(II) mit Pyridin-2-aldehyd-2-chinolyldhydrazon beschrieben. Die Reaktion erfolgt praktisch sofort und ist auf Schwankungen der Salzkonzentration nicht empfindlich. Die Metalle der Platingruppe stören nicht, auch nicht, wenn sie in Milligrammengen anwesend sind.

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Anal. Chim. Acta, 34 (1966) 407-411

ANALYTICAL APPLICATIONS OF β -HETEROPOLY ACIDS

PART II. THE INFLUENCE OF COMPLEXING AGENTS ON SELECTIVE FORMATION

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(Received July 30th, 1965)

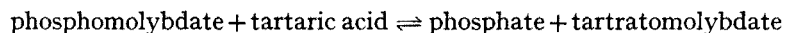
In the first part of this investigation¹ it was shown that β -heteropoly acids could be stabilised, and analytical methods based on these β -acids were described. The drawback was that from a mixture of hetero-species (*e.g.* phosphate, silicate, arsenate, germanate) a mixture of heteropoly acids would be produced, and determination of the individual species would not be possible unless some means of separation or selective formation could be found. Attention was therefore turned to the well-known paradox that certain organic acids (such as tartaric and oxalic) could be used to permit the determination of silicate in the presence of phosphate and *vice versa*, depending on whether the organic acid was added before or after the formation of the heteropoly acid. If a solution of tartaric acid and ammonium molybdate is added to a solution of silicate and phosphate, only phosphomolybdenum blue will be formed on addition of a reductant. On the other hand, if the two heteropoly acids are formed first and then a large amount of tartaric acid is added, only the silicomolybdate is left. Our work shows that the explanation lies in the kinetics and thermodynamics of the formation of the two heteropoly acids. Phosphomolybdate is formed very much more quickly than silicomolybdate, but is much more dissociated in solution. In the presence of the tartratomoxybdate complex a small amount of phosphomolybdate is formed and is quickly reduced, so that the equilibrium is shifted towards complete formation of phosphomolybdenum blue, whereas the silicomolybdate is formed so slowly that it does not interfere in the determination of the phosphate. If a large excess of tartaric acid is added to the mixture of phosphomolybdate and silicomolybdate, the phosphomolybdate is rapidly converted into phosphate and tartratomoxybdate, whereas the silicomolybdate is virtually unattacked and can be quantitatively reduced.

By a combination of the effect of organic complexing agents with that of acetone it is possible to develop methods for the determination of silicate and phosphate in the presence of each other, and a sensitive method for the determination of silicate.

EXPERIMENTAL

Two series of solutions were prepared, one for phosphate and one for silicate, each solution containing 10 ml of 4% sodium molybdate solution, 6 ml of 2 *N* sulphuric acid, a fixed amount of phosphate or silicate and amounts of 5% tartaric acid solution ranging from 0 to 20 ml, the total volume being made up to 50 ml with water. The phosphate and silicate were added last. The optical densities were measured in

1-cm cells at 420 $m\mu$ for the phosphate and 440 $m\mu$ for the silicate solutions. Figure 1 shows the results. It is evident that over a fairly wide range of tartaric acid concentrations where no silicomolybdate is formed, at least part of the phosphate is present as phosphomolybdate. The phosphomolybdate was formed very quickly (in less than 10 sec) and the amount produced was independent of the order of mixing of the reagents. This suggests that there is a rapidly established equilibrium of the type



which can be shifted to the right by increasing the concentration of tartaric acid and to the left by removing phosphomolybdate by reduction. If the ratio of tartaric acid to molybdate is too low, silicate interferes, but if it is too high the phosphate itself fails to react. This hypothesis was tested by converting the phosphomolybdate into its much more stable acetone complex² and so shifting the equilibrium.

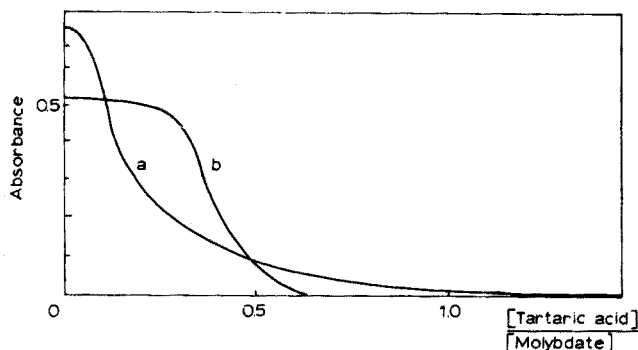


Fig. 1. Effect of tartaric acid on heteropolyacid formation. (a) phosphomolybdic acid, (b) silicomolybdic acid.

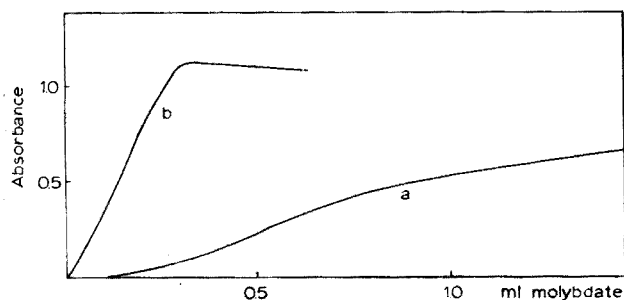


Fig. 2. Effect of acetone on formation of phosphomolybdic acid. (a) acetone absent, (b) acetone present.

Figure 2 shows the effect of adding molybdate to solutions containing (a) 0.1 mg of phosphorus as phosphate, 1 ml of 2 *N* sulphuric acid, and 5 ml of water, (b) the same amounts of phosphate and acid, 4 ml of water, and 1 ml of acetone. The acetone complex was formed completely as soon as enough molybdate was present to give a molybdate to phosphate ratio of 12:1, whereas in the absence of acetone a very large excess of molybdate was needed to push the reaction to completion. The effect of tartaric acid on the acetone complex was then tested, and it was found that, as

expected, there was none. It was also found that the effect of citric acid, which forms a more stable molybdate complex than tartaric acid does, was also largely nullified by the addition of acetone.

When the effect of complexing agents on silicomolybdate and phosphomolybdate was examined it was found that β -silicomolybdic acid was slowly attacked by various compounds as shown in Fig. 3. A series of solutions of β -silicomolybdic acid was prepared in 50-ml volumetric flasks from 5 ml of 0.01 *M* silicate, 10 ml of 4% ammonium molybdate solution, and 5 ml of 2 *N* hydrochloric acid. The solutions were

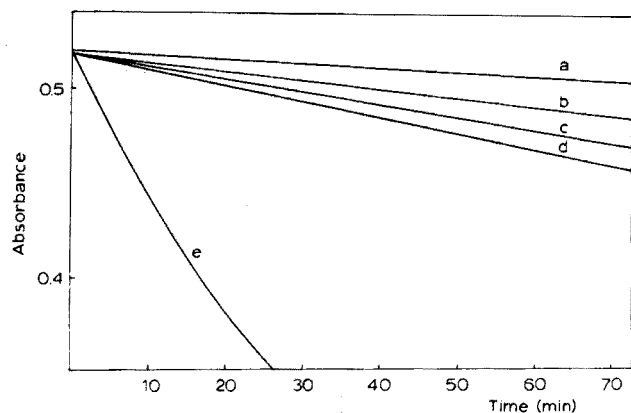


Fig. 3. Effect of complexing agents on silicomolybdic acid. (a) no complexing agent, (b) tartaric acid, (c) mannitol, (d) citric acid, (e) oxalic acid.

allowed to stand for 10 min to form the heteropoly acid completely and then to each flask enough complexing agent was added to give a 1:1 ratio of molybdate to complexing agent. The solutions were diluted to 50 ml and mixed and their optical densities measured at 440 $m\mu$ at intervals of a few minutes for a period of an hour. The experiments were repeated for phosphomolybdic acid, which was completely decomposed by this treatment. The curves in Fig. 3 show that oxalic acid is not a very suitable reagent for the destruction of phosphomolybdate if silicomolybdate is to be determined, but the other reagents tried would be suitable if measurements were made at a specified time after addition of the reagent. Mannitol is the best for covering a wide range of phosphate concentrations while having least effect on the silicomolybdate.

If, however, the silicomolybdate is to be reduced to molybdenum blue, it is permissible to use oxalic acid as recommended by MULLIN AND RILEY³, provided that the reduction is rapid and a strict time schedule is kept.

It was concluded that phosphate could be determined in the presence of silicate by forming the stable acetone complex of phosphomolybdic acid in the presence of enough tartaric acid to prevent formation of silicomolybdic acid. Systematic variation of the conditions showed that in a total volume of 50 ml the amount of composite 0.33 *M* tartaric acid/0.25 *M* sodium molybdate solution could vary from 10 to 20 ml, and the amount of acid could vary from 4 to 10 ml of 2 *N* hydrochloric without affecting the optical density obtained from a fixed amount of phosphate, but the amount of acetone was rather critical. The acetone appeared to affect

both the position of the equilibrium and the rate at which it was attained. The optimum amount was 52% (v/v): if less was added the colour faded and the maximum absorbance was proportional to the amount of acetone present, whereas if more was added the reaction was rapid at first but then continued more slowly for a long time. If too much acetone was added the reaction was inhibited. An important consequence of this behaviour was that if the acetone was added last there was a considerable variation in the resulting optical density, probably because of local variations in the acetone concentration. It was found best to mix the reagents first and to add the sample last. As much as 15 mg of orthosilicate could be added without effect. Although the method can be used for the determination of phosphate in the presence of silicate, it is much easier to eliminate silicate interference by raising the acidity of the solution to more than $0.7 N^4$. The new method, however, would be useful in situations where a high acidity is not permissible, as in the determination of the hydrolysis rates of acid-labile phosphate esters or polyphosphates.

A sensitive method for the determination of silicate in the presence of phosphate was considered worth looking for if it was free from the disadvantages of the reduction methods. The reduction methods are so sensitive that for many purposes considerable dilution of the original sample solution is necessary, with the attendant risk of dilution errors. These methods also require frequent preparation of the somewhat unstable reductant solutions, and sometimes have high and poorly reproducible blanks. Many are slow, and the complexing agent added to destroy phosphomolybdate may have time to attack silicomolybdate as well. A method based on the unreduced heteropoly acid would be better if it were sufficiently sensitive.

Isopolymolybdate species absorb light of wavelengths shorter than about $400 m\mu$, which is why the measurements on unreduced heteropoly acids are made at longer wavelengths. The absorption by both species increases rapidly as the wavelength becomes shorter as shown in Table I.

TABLE I
ABSORPTION SPECTRA FOR POLYMOLYBDATE SPECIES

Wavelength ($m\mu$)	400	390	380	370	360
Optical density of isopolymolybdate	0.011	0.035	0.098	0.277	0.709
Optical density of heteropolymolybdate	0.097	0.124	0.153	0.200	0.263

If a wavelength of $370 m\mu$ could be used the sensitivity of the heteropoly method would be increased though still only to about a quarter of the sensitivity of the reduction methods. Use of such a wavelength could be achieved in two ways: either by adding an exactly reproducible amount of molybdate each time and constructing a calibration curve, or better, by eliminating the absorbance of the excess of isopolymolybdate.

It had been observed that the mannitol complex of isopolymolybdate had a much lower absorbance in the near U.V. than the isopolymolybdate alone. Since mannitol also destroys phosphomolybdate it could serve as a dual-purpose reagent. Investigation showed that the concentrations of mannitol and acid could be varied quite widely without effect on the optical density of a silicomolybdate solution, the

only critical variable being the concentration of molybdate, but as the optical density of a 0.8% molybdate solution in 1 N sulphuric acid containing 2% of mannitol was only 0.020 in a 1-cm cell at 370 m μ no appreciable error should arise from this source if a carefully measured large excess of molybdate was used.

Certain other factors had to be taken into account. The first was the fact that mannitol destroys silicomolybdate at the rate of 0.2–0.3% per min. This can be prevented by adding acetone as stabiliser; there is no effect by acetone on the isopolymolybdate–mannitol complex. Next, the mannitol must be added after the silicomolybdate has completely formed or it will prevent further formation. Formation of silicomolybdate is usually complete in 10 min but a safety margin can be allowed, and the mannitol added after 15 min. Third, the wavelength used (370 m μ) lies on a steep slope of the absorption spectrum of the silicomolybdate and accurate wavelength setting is important. The performance of the spectrophotometer used (Unicam SP 600) was checked by determining the standard deviation of the optical density measurements when the wavelength was reset each time. The standard deviation was 0.0008 (11 measurements) at an optical density of 0.350; this was not significantly different from the value found for the same solution measured repeatedly without resetting the wavelength, and implies a precision of ± 5 parts per 1000 (95% confidence limits). Last, there may be interference by three types of other substances. There are those which absorb at 370 m μ , those which react with the reagents to form compounds which absorb at 370 m μ , and those which interfere with the formation of the silicomolybdate. The first kind can be compensated for by running a blank in which the molybdate and mannitol have been mixed before the sample is added, so that no silicomolybdate forms. The most common interference of the second kind is by phosphate; a correction can be applied or the solution can be left long enough for the mannitol to destroy the phosphomolybdate. A period of 20 min standing is enough to reduce the optical density of the phosphomolybdate to 0.010 in a 1-cm cell. Substances of the third kind must be dealt with as they are in any other method for determination of silicate as silicomolybdic acid.

METHODS

Reagents

Ammonium molybdate/sulphuric acid solution. Dissolve 40 g of ammonium paramolybdate heptahydrate in 500 ml of water in a polythene beaker, and add 500 ml of 2 N sulphuric acid. Mix and store in polythene.

Sodium molybdate/tartaric acid/hydrochloric acid solution. Dissolve 12 g of sodium molybdate dihydrate and 10 g of tartaric acid in water, add 37 ml of concentrated hydrochloric acid and dilute to 400 ml. A brown colour develops in the reagent after a few days. The reagent should not be used if it is more than 2 or 3 days old.

Procedure for phosphate

Place 26 ml of acetone and 10 ml of the molybdate/tartaric acid/hydrochloric acid reagent in a 50-ml standard flask, add the sample, dilute at once to the mark and mix. During the next 30 min measure the optical density against a reagent blank, and read off the phosphate concentration from a calibration curve. For 0–160 μ g of phosphorus measure in 4-cm cells at 400 m μ , and for 0–1 mg of phosphorus

measure in 1-cm cells at 410 $m\mu$. Beer's law is obeyed over both ranges of concentration.

Procedure for silicate

Place 10 ml of the molybdate/sulphuric acid reagent and 5 ml of acetone in a 50-ml standard flask. Add the sample solution which should contain not more than 500 μg of silica. Rinse down the inside of the neck of the flask, mix the solution, and let it stand for 15 min. Add 10 ml of 10% mannitol solution, dilute to the mark, and mix. After 15 min measure the optical density in a 1-cm cell at 370 $m\mu$ against a reagent blank. Beer's law is obeyed.

RESULTS

Various mixtures of phosphate and silicate were analysed by the procedures given, and the results are shown in Table II. The rather wider spread of results for phosphate arises mainly from the use of a measuring cylinder for adding the acetone, the volumes taken ranging from 25.5 to 26.5 ml.

TABLE II
ANALYSIS OF MIXTURES OF PHOSPHATE AND SILICATE

<i>Taken</i>		<i>Found</i>		<i>Taken</i>		<i>Found</i>	
<i>P</i>	<i>SiO₂</i>	<i>P</i>	<i>SiO₂</i>	<i>P</i>	<i>SiO₂</i>	<i>P</i>	<i>SiO₂</i>
(μg)	(μg)	(μg)	(μg)	(μg)	(μg)	(μg)	(μg)
0	100	—	101	200	100	—	104
600	100	—	104	1000	100	—	102
0	300	—	302	200	300	—	298
600	300	—	302	1000	300	—	302
0	500	—	501	200	500	—	499
600	500	—	503	1000	500	—	500
300	0	302	—	300	200	306	—
300	400	295	—	300	600	307	—
300	800	304	—	300	1000	300	—
500	0	495	—	500	200	493	—
500	400	496	—	500	600	503	—
500	800	500	—	500	1000	498	—

SUMMARY

An explanation is given of the apparently paradoxical behaviour of heteropoly acids in the presence of organic complexing agents such as tartaric acid, and methods for selective formation of particular heteropoly acids are suggested. Sensitive and rapid methods for the determination of silicate and phosphate in the presence of each other are described.

RÉSUMÉ

Les auteurs donnent une explication du comportement apparemment paradoxal d'hétéropolyacides en présence d'agents complexants organiques, tel que l'acide

tartrique. On décrit des méthodes sensibles et rapides pour le dosage de silicate et de phosphate, en présence l'un de l'autre.

ZUSAMMENFASSUNG

Das scheinbar paradoxe Verhalten von Heteropolysäuren in Gegenwart von organischen komplexbildenden Reagenzien, wie Weinsäure wird erklärt und es werden Methoden für die selektive Bildung besonderer Heteropolysäuren vorgeschlagen. Empfindliche und schnelle Methoden für die Bestimmung von Silikat und Phosphat in Gegenwart anderer Elemente werden beschrieben.

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Anal. Chim. Acta, 34 (1966) 412-418

STANDARDIZATION OF EXPERIMENTAL CONDITIONS IN THERMAL ANALYSIS

A NEW POLYPLATE SAMPLE HOLDER*

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(Received July 15th, 1965)

In thermal analysis the exact determination of characteristic temperatures is of fundamental importance. Though these temperatures must in principle be constant, data differing from one another are given in the literature for the dissociation temperatures of the same compound, depending on the nature of the thermoanalytical method and on the experimental conditions applied in the investigation. Like other authors, we have investigated this problem for various materials¹⁻⁹. These errors must be ascribed to rather complicated interactions of the experimental conditions and of the kinetics of thermal decomposition reactions; these problems are illustrated in Fig. 1.

Most thermal decomposition reactions are known to be processes which tend to attain an equilibrium. In closed systems the dissociation pressure of compounds increases exponentially with temperature. As indicated by curve 1 in Fig. 1, atmospheric pressure is generally attained at temperatures higher by 100-400° than that prevailing at the beginning of the decomposition. Curve 1 in Fig. 1 shows the dissociation pressure of calcium carbonate plotted against temperature, while curves 2 to 7 show the course of the decomposition process of calcite actually investigated by various methods of thermal analysis. From Fig. 1 it appears that under the experimental conditions of thermal analysis, the course of the dissociation of calcite does not correspond at all to the correlation of dissociation pressure and temperature. This can be explained as follows.

The investigated solid sample and the gas atmosphere formed inside the sample among the grains, must be considered as an equilibrium system. When, for example, the decomposition of calcite begins at a given temperature, some air is gradually expelled from the intergranular area of the sample by the evolving carbon dioxide. If the partial pressure of carbon dioxide inside the sample approaches the value of the dissociation pressure corresponding to a given temperature, the decomposition process will be slower and it will even be interrupted when the dissociation pressure is attained. However, the mixture of carbon dioxide and air will steadily diffuse outward from the sample. The air of the furnace in turn, steadily diffuses towards the centre of the sample. In the atmosphere of the furnace greater or smaller amounts of carbon dioxide would accumulate. Consequently, when the concentrations of carbon dioxide leaving the sample and retransported by the furnace atmosphere are commensurable, the reaction rate will decrease in proportion to these concentrations.

* Presented at the International Symposium on Thermal Analysis, London, April 1965.

Consequently we can state that within the limits defined by the correlation of dissociation pressure and temperature, the thermal decomposition processes of compounds will be determined by the double gas diffusion equilibrium which exists between the interior of the sample, the furnace atmosphere and the environment—in other words, by experimental conditions such as the shape of the sample holder, the layer thickness and packing of the sample, the dimensions and ventilation of the furnace, etc. It therefore follows that the standardization of test conditions is at present the most important problem in thermal analysis.

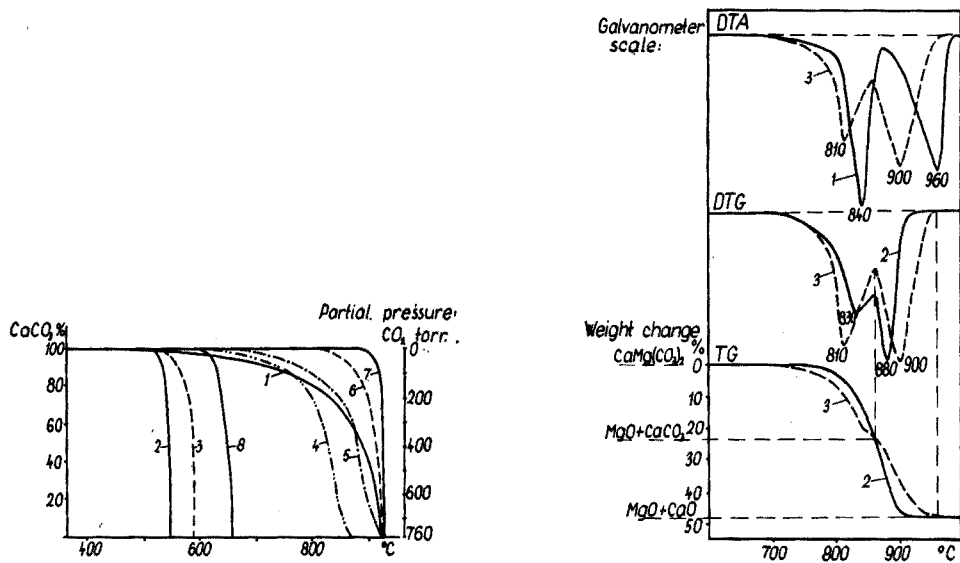


Fig. 1. Thermal decomposition of calcium carbonate plotted on the basis of different thermo-analytical methods. (1) Relation: partial pressure—temperature; (2) TG in vacuum; (3) TG by isothermal heating; (4) TG; (5) DTA and D-graph; (6) Dilatometry; (7) TG in CO₂ atm.; (8) D-graph, on polyplate sample holder.

Fig. 2. Thermal decomposition of dolomite, recorded by various methods. (1) DTA (temperature measured in the inert substance); (2) Derivative thermobalance (temperature of the furnace); (3) D-graph (temperature of the sample).

As regards the 3 thermal analytical methods of major importance, the problem of standardization has been solved to a satisfactory extent by the Derivatograph—in short D-graph¹⁰. This thermoanalytical instrument simultaneously measures the weight change (TG), the rate of weight change (DTG), the temperature and the enthalpy change (DTA) of the same sample. Consequently as regards these 4 variables, the experimental conditions are exactly the same. This can be proved by the thermal decomposition curves of dolomite in Fig. 2, which were obtained partly by means of the classical DTA apparatus (curve 1), our derivative thermobalance¹¹ (curves 2) and the D-graph (curves 3). When the curves are compared, it can be seen that those recorded with the D-graph are strictly parallel, whereas in the case of curves obtained by 3 different apparatuses, a considerable phase displacement and even discrepancy in the shape can be observed. The experimental conditions of the three tests were the same (*i.e.* weight of sample, rate of heating, etc.), but there were differences in the

shape of the sample holder (Fig. 3), as well as in the layer thickness of the sample and the type of temperature measurement (Fig. 3). Experience has shown that the method of temperature measurement causes only a slight error (*ca.* $\pm 10^\circ$), so that the discrepancies in the course of the curves in Fig. 2 must be ascribed mainly to differences in the gas diffusion conditions of the samples.

Our results proved that even experimental conditions which are seemingly quite unimportant, such as packing of the sample, may have a considerable influence on the course of thermal decomposition reactions.

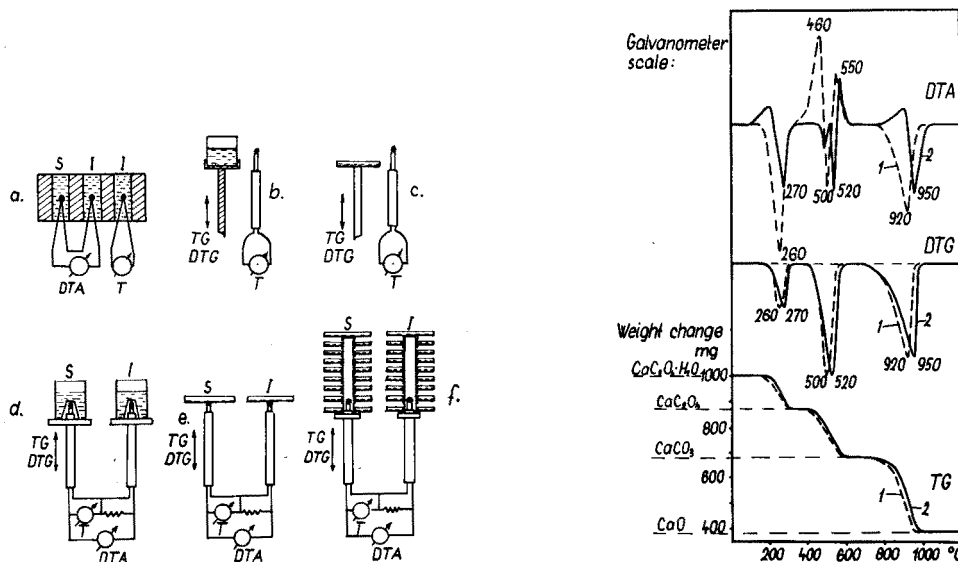


Fig. 3. Sample holders. (a) Sample holder of DTA apparatus; (b) crucible of derivative thermobalance; (c) monoplate sample holder of the derivative thermobalance; (d) crucible of the D-graph; (e) monoplate holder of the D-graph; (f) polyplate holder of the D-graph.

Fig. 4. Thermal decomposition of calcium oxalate. (1) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} - \text{Al}_2\text{O}_3$; (2) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (packed) — $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (not packed).

When the thermal decomposition curves of calcium oxalate monohydrate were recorded with the D-graph in the usual way, by using 2 crucibles, one for the sample and the other for the aluminium oxide, curves 1 of Fig. 4 were obtained. The experiment was repeated by putting equal amounts of calcium oxalate monohydrate into both the crucibles but packing one more tightly than the other; the DTA galvanometer should then have recorded a horizontal line, provided that the thermal decomposition proceeded in the same way in the two differently packed samples. However, instead of a horizontal line, curve 2 was obtained which corresponds to the difference curve of the 2 DTA curves. By observing the course of curve 2, the extent of the discrepancies in the thermal decomposition process can be estimated. On the other hand this value is given numerically in the difference of the DTG maxima, which was in the case of calcium carbonate 30° .

Consequently the problem of standardization cannot be solved even by means of complex thermoanalytical devices which examine thermal effects, weight change,

dilation or evolution of gas, although exactly the same furnace is used, but 2 or even more samples are taken. There is inevitably a risk that thermal transformations will be shifted in one direction or another by the simple fact that the samples were not packed in exactly the same way.

The results of D-graph investigations can only be reproduced if constancy of the experimental conditions is ensured. This is proved by the series of DTG curves in Fig. 5. These curves were obtained with calcite samples when the rate of heating and the weight of sample were varied, and the sample was diluted with alumina to various extents. As the curves indicate, the variation of experimental conditions resulted in fluctuations of about 170° in peak temperatures as well as in the protraction of the reactions over a wide temperature range ($250\text{--}350^\circ$).

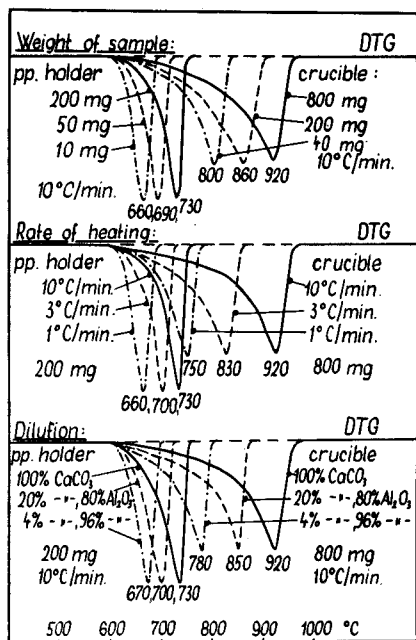


Fig. 5. Thermal decomposition curves of calcite under various experimental conditions.

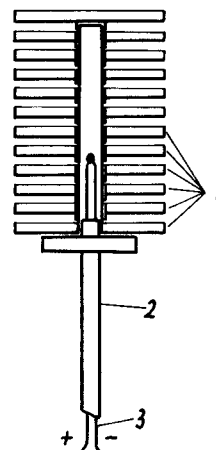


Fig. 6. Polyplate sample holder. (1) Platinum plates, (2) porcelain rod, (3) thermocouple.

This observation led us years ago to construct an open-type monoplate holder (Fig. 3c) first for the derivative thermobalance^{2,4} and later for the D-graph³ (Fig. 3e) and finally to develop a polyplate holder¹² (Fig. 3f). Meanwhile several other authors made efforts toward the solution of the problem¹³⁻¹⁵.

The polyplate sample holder shown in cross section in Fig. 6 consists of about 10 small platinum plates, fitting together in the center and thus forming a tube-like closed space in the middle. The thermocouple of the D-graph is placed into this space. In this way the thermocouple measures accurately the temperature of the sample. A solid sample of 20-1000 mg can be spread on the surface area of this multiplate sample holder in very thin layers. The application of thin layers of the sample was expected to facilitate the escape of the gaseous decomposition products, and thus to

make possible a course of decomposition which would be independent of variations in the experimental conditions.

The first experiments with this polyplate holder gave quite surprising results. Curve 8 of Fig. 1 was recorded in this way. It was found that the decomposition process of calcite spread in a thin layer took place in almost the same way as by examination in vacuum or by the method of isothermal stepwise heating.

The curves on the left of Fig. 5 prove in fact that on applying thin layers of the substance, the experimental results became much more independent of any changes in experimental conditions. It was found that, even in this case, the decomposition of calcite began at temperatures of about 600° , whereas the temperature range of the actual conversion process decreased to nearly a third of the original value.

The use of the polyplate holder also proved to be advantageous in several other respects too. Under given conditions, the selectivity of D-graph investigations was increased. The course of dehydration of copper sulphate pentahydrate is shown in Fig. 7, where the curves designated by 1 were recorded when the crucible was used, while curves 2 were obtained with the aid of the new sample holder. The shape of these curves indicates the existence of 3 steps in the dehydration process. The release of water occurs in steps of 2 moles, then 2 moles and finally 1 mole. It is of interest that the 2 first processes, which overlap each other considerably, could only be clearly distinguished from one another when the substance was investigated on the polyplate holder.

Consequently, it appears that when thin layers of the sample are applied, the

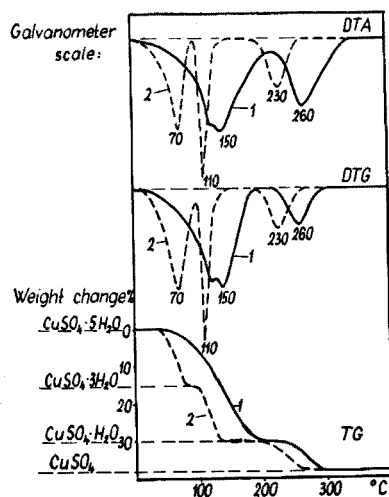


Fig. 7. Thermal decomposition curves of copper sulphate pentahydrate. (1) in crucible; (2) on polyplate sample holder.

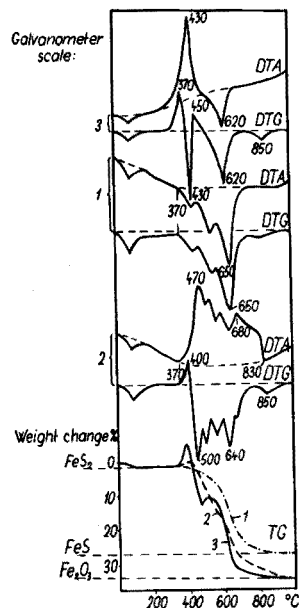


Fig. 8. Decomposition of pyrite. (1) in crucible in N_2 atmosphere; (2) in crucible in the presence of air; (3) on polyplate holder in the presence of air.

partial pressure of the gaseous products appreciably decreases in the interior of the sample; this means that the concentration of the air or oxygen increases. This is of particular importance in the case when the decomposition process leads to the formation of a compound capable of undergoing oxidation by air.

An example of this type is given in Fig. 8, which shows the decomposition of pyrite in the presence of nitrogen and air, respectively. Curves 1 and 2 were recorded when the crucible was used. Then the experiment in air was repeated with the polyplate holder (curves 3). As the curves indicate, pyrite in nitrogen simply decomposed, but in the presence of air, the conversion proceeded and iron sulphide was converted to iron(III) oxide. It follows that the concentrations of oxygen and of other gaseous decomposition products accumulated in the interior of the sample, will determine whether this oxidation reaction takes place directly, or in an intermediate way involving initial formation of iron(III) sulphate and later decomposition at a higher temperature. The shape of the curves appears to indicate that a direct conversion of pyrite took place in the crucible, whereas on the polyplate holder the intermediate decomposition steps occurred.

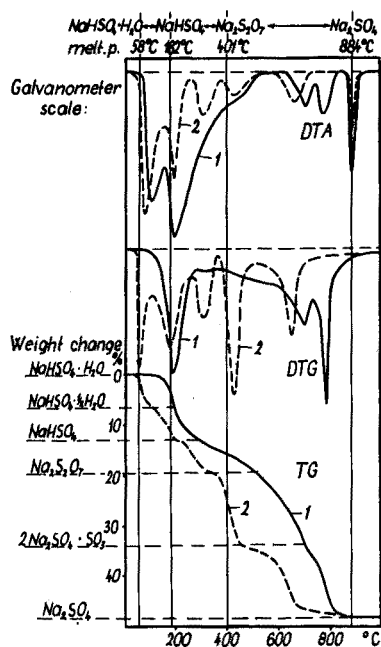


Fig. 9. Decomposition of sodium hydrogen sulphate monohydrate. (1) in crucible; (2) on polyplate sample holder.

Very many compounds melt before their thermal decomposition. The progress of decomposition cannot be indifferent to whether the liberated gaseous products are forced to pass through a thick viscous molten layer, or can escape easily through a very thin film of melt. This is proved by Fig. 9 where the decomposition curves of sodium hydrogen sulphate monohydrate are presented. The curves marked 2 were recorded with the aid of the new sample holder; it can be seen that first the compound

melts, and then the water of crystallization is liberated in two steps, after which the anhydride melts. This is followed by the liberation of constitutional water, and lastly after the melting, sulphur trioxide leaves the system in two steps as well. In the curves denoted by 1, which were established with the conventional crucible, the single steps of these processes cannot be distinguished, because the prolonged processes strongly overlap each other.

In the investigation of a number of thermal processes it is indispensable to spread the test sample over a large surface area of known size. Processes of this type are the drying of drying oils, associated with the uptake of oxygen; the drying process of lacquer films, associated with the evaporation of the solvent; the combustion process of coke, which is of importance from the aspect of metallurgy; and the various adsorption and chemisorption processes in hydrothermal reactions. As regards the application of the new sample holder, our experience is equally favorable in these fields.

SUMMARY

Of the several variable experimental conditions in thermoanalysis, the influence of the sample layer thickness on the decomposition process can be of decisive importance. A polyplate sample holder is described on which the sample can be spread in a very thin layer. With this sample holder, TG, DTG and DTA investigations can be simultaneously carried out. The application of the polyplate holder improved the reproducibility and selectivity of thermoanalysis to a great extent.

RÉSUMÉ

Des nombreuses conditions expérimentales en thermoanalyse, l'influence de l'épaisseur de la couche d'échantillon sur le processus de décomposition peut être de grande importance. Un dispositif est décrit, sur lequel l'échantillon peut être étalé en une couche très mince. Il permet d'effectuer simultanément des mesures de variation de poids, de vitesse de variation de poids, de changements de température et d'enthalpie. Cette application améliore la reproductibilité et la sélectivité de la thermoanalyse.

ZUSAMMENFASSUNG

Bei der Thermoanalyse kann der Einfluss der Probenschichtdicke auf den Zersetzungsprozess sehr wichtig sein. Es wird ein viel beschichteter Probenhalter beschrieben, auf den die Probe in sehr dünner Schicht aufgesprüht werden kann. Mit diesem Probenhalter können TG-, DTG- und DTA-Untersuchungen gleichzeitig ausgeführt werden. Die Anwendung dieses Halters fördert die Reproduzierbarkeit und Selektivität der Thermoanalyse in sehr starkem Masse.

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ZUR BORBESTIMMUNG IN SILIZIUM UND GERMANIUM DURCH AKTIVIERUNG MIT PROTONEN UND DEUTERONEN

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(Eingegangen den 12. Juli, 1965)

I. UNTERSUCHUNGEN ZUR STÖRUNG DURCH STICKSTOFF

Die Neutronenreaktionen des Bors bieten keine Möglichkeit für eine empfindliche klassisch-aktivierungsanalytische Spurenbestimmung über die Messung eines radioaktiven Produktkernes von geeigneter Lebensdauer. Der (n,γ) Produktkern ^{12}B hat nur eine Halbwertszeit von 18 millisek bei einem geringen Wirkungsquerschnitt von < 50 mb. Die $^{10}\text{B}(n,\alpha)^7\text{Li}$ -Reaktion mit einem Wirkungsquerschnitt von ~ 3800 b führt zum stabilen Kern ^7Li . Beide Reaktionen haben Anwendung gefunden für Borbestimmungen im konventionellen Empfindlichkeitsbereich durch Registrierung der prompten α - und γ -Strahlung bzw. Messung der Neutronenschwächung bei Bestrahlung mit Isotopenneutronenquellen. Die empfindlichsten Methoden^{1,2} gestatten den Nachweis von 10^{-3} bis 10^{-4} % Bor durch Autoradiographie bzw. Messung der prompten α -Strahlung. Eine spezielle Methode zur Borbestimmung in Silizium beruht auf der Verwendung des zu untersuchenden Siliziums als Halbleiterdetektor für die Registrierung der Produkte der Kernreaktion $^{10}\text{B}(n,\alpha)^7\text{Li}$ bei Bestrahlung dieses Siliziums mit Neutronen; es wurde eine Nachweisgrenze von 10^{14} bis 10^{15} B-Atome/cm³ = 10^{-7} – 10^{-6} % Bor erreicht³.

TABELLE I

KERNREAKTIONEN FÜR DIE BORBESTIMMUNG MIT PROTONEN UND DEUTERONEN

Kernreaktion	$Q_{0, \text{ber}}$ (MeV)	$E_{s, \text{ber}}$ (MeV)	$E_{s, \text{exp}}$ (MeV)	Literatur
I $^{11}\text{B}(p,n)^{11}\text{C}$	– 2.76	3.02	3.019	5–10
II $^{10}\text{B}(d,n)^{11}\text{C}$	+ 6.50	0	0	11
III $^{11}\text{B}(d,2n)^{11}\text{C}$	– 5.0	5.9	—	11.
IV $^{14}\text{N}(p,\alpha)^{11}\text{C}$	– 2.92	3.13	4.2	12, 13
V $^{14}\text{N}(d,\alpha n)^{11}\text{C}$	– 5.14	5.87	—	—

Eine Reihe von Autoren berichten über Borbestimmungen in Mineralien, Lösungen und biologischem Material durch Messung der bei Bestrahlung mit α -Teilchen aus ^{210}Po -Quellen emittierten Neutronen und γ -Quanten im Konzentrationsbereich von 0.5–10% Bor bzw. B_2O_3^4 .

Eine empfindliche aktivierungsanalytische Bestimmung des Bors ist mit den in Tabelle I angegebenen Kernreaktionen I–III durch Protonen- und Deuteronenakti-

vierung möglich; die berechneten Q_0 -Werte und Schwellenenergien sowie die experimentellen Schwellenenergien sind in Tabelle I ebenfalls angegeben.

Das nach allen 3 Kernreaktionen gebildete Analysenisotop ^{11}C ist ein reiner Positronenstrahler ($E_{\beta^+} = 968 \text{ keV}$) mit einer Halbwertszeit von 20.5 min, die seine radiochemische Abtrennung aus dem aktivierten Analysenmaterial gestattet. In einer früheren Mitteilung¹⁴ wurde bereits auf die Analysenstörung bei Protonenaktivierung durch die Stickstoffreaktion IV (Tabelle I) hingewiesen und über orientierende Versuche zum Umfang dieser Störung und die Möglichkeit ihrer Unterdrückung berichtet. Diese Messungen haben wir in weiteren Untersuchungen präzisiert und die Möglichkeit einer störungsfreien Borbestimmung durch Deuteronenaktivierung geprüft. Über die energetisch mögliche Stickstoffstörreaktion V (Tabelle I) finden sich in der Literatur keine Angaben. Störungen durch andere mit Protonen und Deuteronen zu ^{11}C führende Kernreaktionen sind bei den Endenergien von respektive 6.75 und 13.5 MeV am Rossendorfer Zyklotron nicht möglich.

Abschätzung der Bornachweisempfindlichkeiten der Reaktionen I–III und des Einflusses der Störreaktion IV

Wegen des Energieverlustes bei Wechselwirkung mit Materie haben schnelle Ionen nur eine begrenzte Reichweite im Targetmaterial. Dementsprechend erfolgt auch keine Durchaktivierung desselben, und die in der Schicht von der maximalen

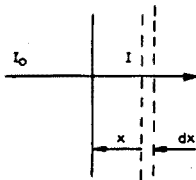


Fig. 1. Zur Ableitung der Aktivierungsgleichung.

Dicke der Ionenreichweite erzeugte Aktivität ist über die Schichtdicke wegen der Energieabhängigkeit des Wirkungsquerschnittes nicht konstant. Die Aktivität einer differentiellen Targetschicht dx nach einem Bremsweg x (Fig. 1) der schnellen Ionen berechnet sich zu

$$dA_x = {}^1N^* \cdot I_x \cdot \sigma_x \cdot dx (1 - e^{-\lambda t}) \quad (1)$$

${}^1N^*$ = Zahl der Targetkerne/cm³, σ_x = Wirkungsquerschnitt (cm²), I_x = Ionenintensität (/s), $(1 - e^{-\lambda t}) = W$ = Wachstumsfaktor einer Aktivität der Zerfallskonstanten λ mit der Bestrahlungszeit t .

Durch Integration der Gl. (1) über x von der Targetoberfläche $x=0$ bis zum Bremsweg $x=x_s$, bei dem die Ionenenergie E die Energieschwelle der Kernreaktion E_s unterschreitet und nach Substitution der Integrationsvariablen mit Hilfe der Reichweite-Energiebeziehung $E = E(x)$ sowie mit ${}^1N^* = h \cdot {}^1N$ (h = rel. Häufigkeit des Targetkerns im nat. Isotopengemisch; 1N = Zahl der Atome des Elements/cm³) folgt für die Gesamtaktivität in einem „dicken Target“

$$A = {}^1N \cdot I \cdot W \cdot h \int_{E-E_s}^{E-E_0} \frac{\sigma(E)}{-dE/dx} dE \quad (2)$$

RODD'S CHEMISTRY OF CARBON COMPOUNDS

SECOND EDITION

Editor: S. COFFEY

M. Sc. (London), D.Sc. (Leyden), F.R.I.C. Formerly of I.C.I. Dyestuffs Division, Blackley, Manchester. Assisted by an Advisory Board of prominent scientists.

The first part of CHEMISTRY OF CARBON COMPOUNDS appeared in 1951. In all, its 5 volumes and 7500 pages took some 11 years to produce. On completion it was hailed as "*the most comprehensive general textbook of organic chemistry ever to appear in the English language*" (*Endeavour*, vol. 23, no. 54, 1964)

The early volumes were written shortly after the Second World War when the upsurge in the publication of scientific information was becoming apparent. This phenomenon has since become one of the major features of contemporary science, contributing greatly to progress in all disciplines. Consequently parts of some of the earlier volumes became somewhat dated.

Accordingly **Elsevier** undertook publication of a second edition, entitled (in honour of the editor of the first edition) **RODD'S CHEMISTRY OF CARBON COMPOUNDS**.

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$$A = {}^1N \cdot I \cdot W \cdot B(E_0) \quad (3)$$

Die Ionenintensität I ist bei den geringen Wirkungsquerschnitten (< 1 b) für Kernreaktionen mit schnellen Ionen unabhängig von der Energie und darf als Konstante vor das Integral gesetzt werden. Ein Selbstabschirmeffekt, wie er bei vielen Elementen für thermische Neutronen beobachtet wird, tritt also nicht auf.

Mit den aus der Literatur bekannten Anregungsfunktionen $\sigma(E)^{6,8,9,11,13}$ und den nach der BETHE-Bremsformel¹⁵ berechneten Bremsfunktionen $-dE/dx$ ergeben sich durch graphische Auswertung des Integrals in Gl. (2) die Aktivierungsausbeuten $B(E_0)$ für Bor und Stickstoff nach den Kernreaktionen I–IV, die in Fig. 2 für Silizium als Analysenmaterial dargestellt sind. Die obere Grenze des Energiebereiches entspricht den am Rossendorfer Zyklotron verfügbaren maximalen Protonen- und Deuteronenenergien von $E_p = 6.75$ MeV und $E_d = 13.5$ MeV.

Bei der Abschätzung der Nachweisgrenzen mit Gl. (3) und Vergleich der Reaktionen I und (II + III) ist zu berücksichtigen, dass *in Praxi* die Wärmebelastbarkeit des Targets der die Empfindlichkeit begrenzende Faktor bei der Aktivierungsanalyse mit schnellen Ionen ist. Ein Deuteronenstrahl von 13.5 MeV hat eine Leistung von 13.5 W/ μ A bei einem Brennfleckdurchmesser von ca. 10 mm. Da am Rossendorfer Zyklotron Protonen primär als Wasserstoffmolekülonen (H_2^+) auf die gleiche Endenergie wie Deuteronen und damit gleiche Leistung von 13.5 W/ μ A beschleunigt werden, die erst auf der Targetoberfläche gemäss $H_2^+ + 2.65$ eV $\rightarrow 2$ p + e in Protonen der halben Energie dissoziieren, bezieht man die Nachweisgrenze zweckmässig auf

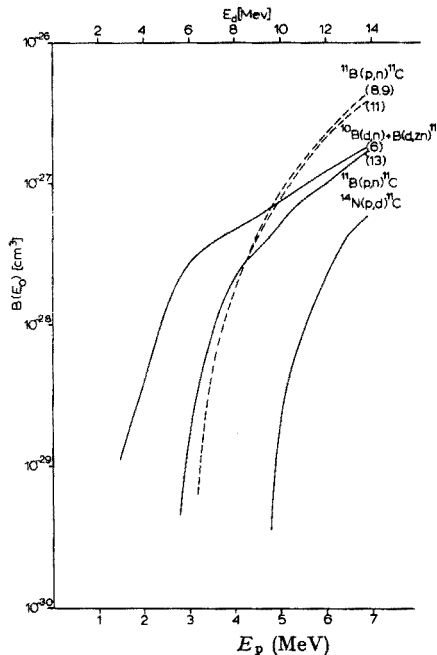


Fig. 2. Die Aktivierungsausbeute für die Kernreaktionen ${}^{11}\text{B}(p,n){}^{11}\text{C}$, ${}^{10}\text{B}(d,n) + {}^{11}\text{B}(d,2n){}^{11}\text{C}$ und ${}^{14}\text{N}(p,\alpha){}^{11}\text{C}$ in Silizium.

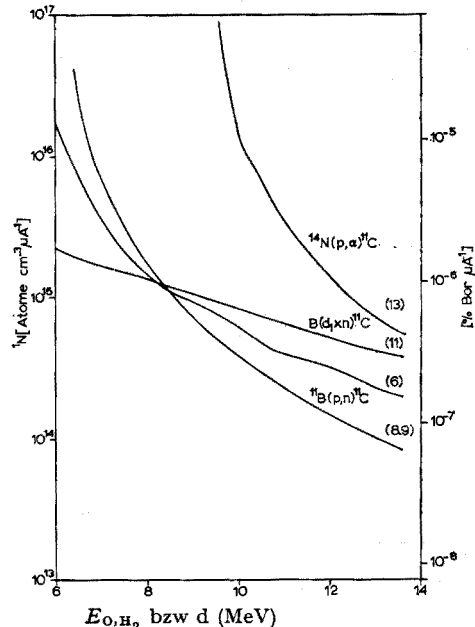


Fig. 3. Abhängigkeit der theoretischen Nachweisgrenze für Stickstoff und Bor in Silizium von der Ionenanfangsenergie.

den Deuteronen- bzw. Wasserstoffmoleküllionenstrom; die Aktivierungsausbeute für Wasserstoffmoleküllionen ist dementsprechend doppelt so gross wie die für Protonen in Fig. 2 angegebene.

Bei einer Bestrahlungszeit von 20 min — entsprechend $W=0.5$ — und einer Mindestimpulsrate von 0.5 I/s (bei gleichem Nulleffekt) nach einer Abklingzeit von $2 T_{\frac{1}{2}}$ und einer Zählhausbeute der Messanordnung von 100% ergeben sich die in Fig. 3 als Funktion der Ionenanfangsenergie (E_{0,H_2^+} bzw. $E_{0,d}$) angegebenen Nachweisgrenzen pro $1 \mu A H_2^+$ bzw. d für die Reaktionen I, (II+III) und auch für eine Stickstoffbestimmung nach der Reaktion IV. Bei etwa 8 MeV ist die Empfindlichkeit des Bornachweises für Protonen- und Deuteronenaktivierung praktisch gleich, bei Maximalenergie ist sie nach den neueren Literaturangaben für die Anregungsfunktion bei Protonenaktivierung um eine knappe Zehnerpotenz besser. Unterhalb 8 MeV ist die Deuteronenaktivierung wegen des im Gegensatz zur Reaktion I positiven Q -wertes der Reaktion II günstiger. Wie schon Fig. 2 zu entnehmen, ist die Empfindlichkeit für Stickstoff nach der Reaktion IV mit der für Bor nach I etwa vergleichbar und eine Störung durch Stickstoff bei einem Gehalt in der Grössenordnung des Borgehaltes wahrscheinlich, was sich auch in unseren Voruntersuchungen bestätigt hatte.

Als Mass für den Umfang der Stickstoffstörung kann das Verhältnis der Nachweisgrenzen (in Gew.%) von Stickstoff und Bor angesehen werden, das wir als relatives Boräquivalent des Stickstoffes a_{rel} bezeichnen.

Aus Gl. (3) folgt mit Gl. (4) für die Nachweisgrenze x_1^* (%)

$${}^1N_1 = \frac{\rho \cdot N_L \cdot x_1(\%) }{100 \cdot M_1} \quad (4)$$

ρ = Dichte des Analysenmaterials; N_L = LOSCHMIDT'sche Zahl; x_1 = Gehalt der zu bestimmenden Spurenkompente in Gew. %; M_1 = Atomgewicht der Spurenkompente.

$$x_1^* = \frac{100 \cdot A \cdot M_1}{W \cdot I \cdot B_1 \cdot \rho \cdot N_L} \quad (5)$$

Für a_{rel} folgt aus Gl. (5)

$$a_{rel} = \frac{x_N^*}{x_B^*} = \frac{M_N \cdot B_B}{M_B \cdot B_N} = 1.295 \frac{B_B}{B_N} \quad (6)$$

Das relative Boräquivalent des Stickstoffes gibt an, wievielmals der Stickstoffgehalt bei gleicher ^{11}C -Aktivität A grösser sein muss als der Borgehalt. In Tabelle II, Spalten

TABELLE II

RELATIVES BORÄQUIVALENT DES STICKSTOFFES ALS FUNKTION DER ENERGIE

E_p (MeV)	$a_{rel}(ber.)$		$a_{rel}(exp.)$	E_d (MeV)	$a_{rel}(exp.)$
	6	8,9			
6.35	4.3	10	6	12.8	3.3
4.98	31	49	15	11.1	6
4.00	∞	∞	$> 10^3$	8.9	74
3.70	∞	∞	$> 10^3$	6.5	$> 10^3$

2 und 3, sind die aus den Aktivierungsausbeuten von Fig. 2 berechneten Werte für a_{rel} als Funktion der Ionenanfangsenergie angegeben. Bei ≤ 4 MeV Protonenenergie geht a_{rel} nach ∞ , die Störung verschwindet.

EXPERIMENTELLE UNTERSUCHUNGEN

Prinzip des Verfahrens

Zur experimentellen Prüfung der voranstehenden theoretischen Abschätzungen über den Umfang der Stickstoffstörung und zur exakten Festlegung der experimentellen Arbeitsbedingungen für eine störungsfreie Borbestimmung bei Protonenaktivierung sowie zur Prüfung auf eine etwaige Stickstoffstörung bei Deuteronenaktivierung wurde, wie bereits in unserer ersten Mitteilung¹⁴ kurz beschrieben, verfahren.

Herstellung der Testproben

Körniges Silizium unbekannter Qualität (technisches Produkt) wurde durch Mahlen in einer Stahlkugelmühle homogenisiert und auf Staubfeinheit gebracht. Die Hälfte der gesamten Pulvermenge wurde durch weiteres Vermahlen mit Aluminiumnitrid in der Stahlkugelmühle auf $\sim 1\%$ Stickstoff dotiert. Eine genaue Bestimmung des Stickstoffes nach KJELDAHL ergab 0.84% N_2 . Der Borgehalt des Ausgangssiliziums und des zur Dotierung verwendeten AlN war näherungsweise gleich, wie durch Aktivierung und Vergleich der beiden Materialien bei $E_p < 4$ MeV festgestellt werden konnte. Auf Grund der Probenherstellung kann man deshalb annehmen, dass der Borgehalt im Ausgangssilizium (Si I) und im stickstoffdotierten Silizium (SiNO I) ebenfalls wenigstens näherungsweise gleich ist. In beiden Probenmaterialien wurde der Borgehalt halbquantitativ spektralanalytisch zu $1-2 \cdot 10^{-3}\%$ bestimmt. Als Aktivierungsstandard wurde ein Gemisch des gleichen Ausgangssiliziums (Si I) mit amorphem Bor verwendet (SiBO). Der Borgehalt wurde halbquantitativ spektralanalytisch zu 1% und kolorimetrisch zu 0.86% bestimmt.

Bestrahlungstechnik

Für die Bestrahlungen am Zyklotron wurde die in Fig. 4 skizzierte Bestrahlungskammer mit wassergekühltem Targethalter verwendet; für Ionenströme $\geq 1 \mu A$ hat sich Wasserkühlung als notwendig erwiesen. Das Target wurde durch Einpressen der Pulverproben in einen Kupferteller hergestellt und nach Abdeckung mit einem Cu-Folienpaket mit einer Al-Blende verschraubt (s. Fig. 4). Die Cu-Folie diente als Bremsfolie zur Variierung der Ionenenergie und zugleich auch als Monitor für den Ionenstrom. Das Folienpaket bestand aus diesem Grunde immer aus einer dem Ionenstrahl zugekehrten Cu-Folie konstante Dicke ($\sim 10 m\mu$) und einer auf die gewünschte Gesamtdicke ergänzenden zweiten Cu-Folie. Die in der ersten Folie nach $^{65}Cu(p,n)$ bzw. $(d,2n)^{65}Zn$ gebildete ^{65}Zn -Aktivität diente als Monitor für den Ionenstrom. Gegenüber einer genauen Strom- bzw. Ladungsmessung, wozu eine aufwendige elektronische Einrichtung gehört, ist diese Methode sehr einfach zu realisieren und wenig störanfällig. Sie ist darüber hinaus im Gegensatz zur Verwendung einer Kernreaktion mit dem Analysengrundmaterial als Monitor¹⁶ unabhängig von der zur Aktivierung gewählten Ionenanfangsenergie, da die Monitorfolie immer vom ungebremsten Ionenstrahl aktiviert wird. Die Verwendung des Analysengrundmaterials als Monitor hat noch weitere Nachteile gegenüber der angewandten Folienmethode. Für

Si und Ge kämen bei Protonenaktivierung die Kernreaktionen $^{28}\text{Si}(p,\gamma)^{30}\text{P}$; $T_{1/2} = 2.56$ min und $^{72/74/76}\text{Ge}(p,n)^{72/74/76}\text{As} + ^{73}\text{Ge}(p,\gamma)^{74}\text{As}$; $T_{1/2} = 26$ h, 17.5 d, 26.8 h in Frage. Im Falle des Siliziums müsste vor Abtrennung des ^{11}C die ^{30}P -Aktivität zerstörungsfrei über mehrere Halbwertszeiten gemessen werden, was sich bei einer Halbwertszeit des ^{11}C von 20.5 min nachteilig auf die Nachweisempfindlichkeit auswirkt. Beim Germanium wäre eine mit beträchtlichem Arbeitsaufwand verbundene radiochemische Abtrennung von As aus dem Aufschlussrückstand der ^{11}C -Abtrennung erforderlich.

Zur Steuerung des Zyklotrons während der Bestrahlung konnte zusätzlich der Ionenstrom am Target mit einem Galvanometer grob gemessen werden. Die kurzzei-

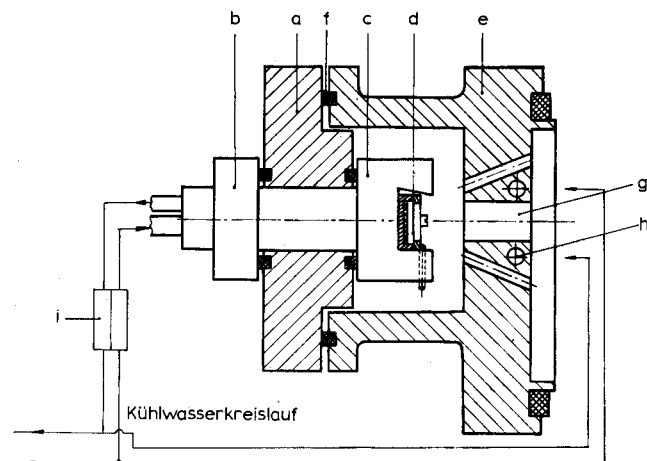


Fig. 4. Bestrahlungskammer. (a) Isolatorscheibe aus Piacryl, (b) Kühlfinger, (c) Targethalter, (d) Target, (e) Bestrahlungskammer, (f) Gummidichtungen, (g) Kollimator, (h) Kollimatorkühlung, (i) Wasserwiderstand.

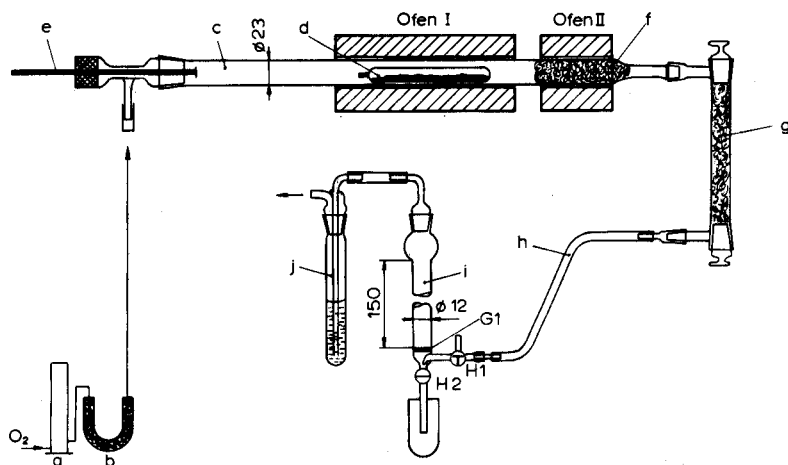


Fig. 5. Aufschlussapparatur. (a) Strömungsmesser, (b) Absorptionsrohr für H_2O und CO_2 , (c) Verbrennungrohr aus Quarz, (d) Quarzschiffchen, (e) Glasstab, (f) CuO -Katalysator, (g) Trockenröhrchen mit P_2O_5 , (h) PVC-Schlauchverbindung, (i) CO_2 -Absorptionsrohr, (j) Barytflasche, (G1) Fritte G 1, (H1, H2) Glashähne.

tigen Abweichungen des Ionenstroms vom Sollwert waren $\leq \pm 10\%$. Die Bestrahlung erfolgte im äusseren Ionenstrahl des Zyklotrons. Der Ionenstrom war ungefähr $1\ \mu\text{A}$, die Bestrahlungszeit immer 20 min.

Radiochemische Abtrennung des ^{11}C

Die besten Möglichkeiten für eine schnelle, vollständige und radiochemisch reine Abtrennung des ^{11}C aus den aktivierten Proben in einem Schritt bietet ein Schmelzaufschluss, bei dem ^{11}C in $^{11}\text{CO}_2$ überführt und aus der Schmelze in die Gasphase ausgetrieben wird. Eine solche Methode wird von GILL¹⁶ beschrieben. Als Kohlenstoffträger wird SiC zugesetzt. In Anlehnung an WIEBKE UND BRAUN¹⁷ haben wir zum Aufschluss eine Mischung aus Mennige, Bleioxid und Bortrioxid benutzt, die folgendermassen hergestellt wurde. Pb_2O_3 und B_2O_3 im Verhältnis 10:1 werden in feinpulverisiertem Zustand gemischt und bei $\sim 1000^\circ$ unter Umrühren möglichst schnell zu einer schwarzen Schmelze homogenisiert, die nach Ausgiessen auf ein Blech und Erkalten von kräftig roter Farbe sein muss. Der Schmelzkuchen wird in einer Schlagmühle fein pulverisiert — Mischung I. Etwa 40% dieser Mischung I vermischt man im Verhältnis 4:1 mit PbO_2 — Mischung II. Mit je 5 g der Mischungen I und II können 0.5 g pulverisiertes Silizium und 20 mg SiC im O_2 -Strom bei $900\text{--}1000^\circ$ in weniger als 10 min ohne Verpuffungserscheinungen aufgeschlossen werden.

Das Target wurde unmittelbar nach Bestrahlungsende (ungefähr 3–4 min) in einer Glove-Box demontiert, das Probenmaterial in einem glasierten Porzellanmörser überführt, mit 10 mg SiC und 5 g der Aufschlussmischung I vermischt, gleichmässig über die Länge eines Quarzschiffchens verteilt (s. Fig. 5) und mit 5 g der Aufschlussmischung II überschichtet. Die Aufschlussapparatur zeigt Fig. 5.

Das Schiffchen mit dem Aufschlussgut wird in den ersten Abschnitt des Quarzrohres eingesetzt und nach Einschaltung des vorgetrockneten, CO_2 -freien Sauerstoffstroms mit dem Glasstab in den Ofen I geschoben, wo bei $\sim 1000^\circ$ der Aufschluss stattfindet. Der Gasstrom passiert im Ofen II bei $\sim 350^\circ$ einen CuO-Katalysator (CuO auf Quarzbruch), dann ein P_2O_5 -Trockenröhrchen und gelangt in das mit 2.5 ml einer Lösung von 120 ml Aethanolamin in Methylglykol zu 1 l besichzte Absorptionsrohr, in dem das CO_2 quantitativ absorbiert wird. Die chemische Ausbeute beträgt 100%.

Aktivitätsmessung und Auswertung

Die Aktivität der 510 keV-Vernichtungsstrahlung des ^{11}C von 2 ml bzw. von mit Wasser im Messröhrchen zu 2 ml ergänzten Aliquoten der Absorptionslösung wurde mit einem Szintillationszähler in Bohrlochgeometrie gemessen. Die Messanordnung hatte eine Zählausebeute von ca. 70% und einen Nulleffekt von 550–600 I/min. Von allen Messproben wurden Zerfallskurven aufgenommen. Die Messzeit betrug 1 bis 5 Minuten. Die ermittelten Halbwertszeiten lagen zwischen 20 und 22 min. Eine radiochemische Verunreinigung konnte nicht festgestellt werden. Die gemessenen Aktivitäten wurden bezüglich der Messzeit korrigiert und auf das Gesamtvolumen von 2.5 ml umgerechnet. Mit Hilfe der ^{65}Zn -Monitoraktivität, die mit einem Szintillationszähler im Abstand von 2 mm zwischen Polystyrolplatten gemessen wurde, erfolgte die Normierung der ^{11}C -Aktivitäten auf gleichen Ionenstrom durch Bildung des Verhältnisses $y = A\ (\text{I/min})/Z\ (\text{I/min (mg/cm}^2))$ aus ^{11}C -Aktivität A und der auf die Dickeneinheit der Cu-Folie normierten ^{65}Zn -Monitoraktivität Z . Bei Normierung der

Monitoraktivität auf die Dickeneinheit der Folie werden geringe Dickenunterschiede zwischen den Monitorfolien eliminiert. Durch Vergleich mit dem Aktivierungsstandard wurde in bekannter Weise der Borgehalt für die Probenmaterialien Si I und SiNO I berechnet.

Ergebnisse

Beim Auftreten einer Stickstoffstörung muss man auf Grund der unterschiedlichen Energieabhängigkeiten der Aktivierungsausbeuten von Analysen- und Störreaktion (für den Fall der Reaktionen I und IV vergl. Fig. 2) einen Gang des ermittelten Borgehaltes mit der Ionenanfangsenergie beobachten. Tritt keine Störung auf, oder ist der Gehalt des störenden Stickstoffes genügend klein gegen den Borgehalt, so muss der ermittelte Borgehalt, unabhängig von der Ionenanfangsenergie, konstant sein. In Fig. 6 sind die Ergebnisse für den Borgehalt in den Probenmaterialien Si I und

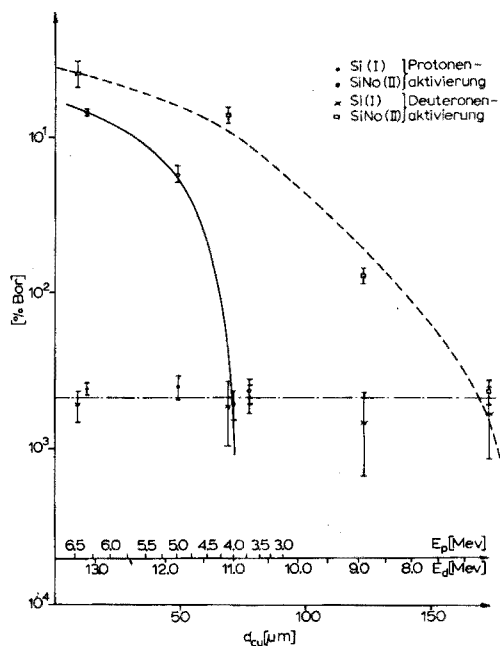


Fig. 6. Der Borgehalt in SiNO (I) und Si (I) in Abhängigkeit von der Ionenenergie.

SiNO I gegen die Ionenanfangsenergien $E_{0,p}$ bzw. $E_{0,d}$ grafisch dargestellt (Durchschnittswerte mit Vertrauensbereich des Durchschnitts für $p=0.05$). Wie zu ersehen, tritt nicht nur die bei Protonenaktivierung zu erwartende und bekannte Störung durch die Stickstoffreaktion IV auf, sondern auch eine Stickstoffstörung bei Deuteronenaktivierung. Die letztere ist sogar noch stärker ausgeprägt. Eine Auswertung dieser Ergebnisse mit statistischen Methoden ergab, dass der durch Protonen- und Deuteronenaktivierung in Si I bestimmte Borgehalt unabhängig von der Ionenenergie und der Ionenart „gleich“ ist. Mit diesem Wert in „Übereinstimmung“ sind auch die in SiNO I mit $E_p=4$ MeV und $E_d=6.5$ MeV bestimmten Borgehalte¹⁸. Der Gesamtdurchschnitt aller gemäss statistischer Prüfung „gleichen“ Werte ergibt für den Borgehalt des Ausgangsiliziums Si I $(2.14 \pm 0.11) \cdot 10^{-3} \%$.

Die Tabelle III enthält die entsprechenden Zahlenwerte. Da jede Bestrahlung, ob Probe oder Aktivierungsstandard, einen völlig unabhängigen Einzelwert liefert, und deshalb eine Probe-Standard-Zuordnung nicht möglich ist, wurden zur Berechnung des Borgehaltes alle Probe-Standard-Kombinationen berücksichtigt. Dies erwies sich auch für die hier nicht wiedergegebene Behandlung dieses Zahlenmaterials mit statistischen Prüfverfahren als notwendig¹⁸.

Diskussion

Störgrenze des Stickstoffes. Am S. 430 hatten wir als Mass für den Umfang der Störung das als rel. Boräquivalent des Stickstoffes bezeichnete Verhältnis aus Stickstoff- und Bornachweisgrenze betrachtet und den theoretischen Verlauf dieser energieabhängigen Grösse in Tabelle II angegeben. Aus den normierten ¹¹C-Aktivitäten der Tabelle III lässt sich a_{rel} nach der Beziehung

$$a_{\text{rel}} = \frac{\bar{y}_{\text{SiBO}}}{\bar{y}_{\text{SiNOI}} - \bar{y}_{\text{SiI}}} \cdot \frac{x_{\text{N}}}{x_{\text{B}}} \quad (7)$$

berechnen.

Diese experimentellen Werte sind für Protonen- und Deuteronenaktivierung bereits in Tabelle II eingetragen. Sie stimmen bei Protonenaktivierung qualitativ mit den berechneten überein. In eine exakte Berechnung der Stickstoffstörgrenze aus dem rel. Boräquivalent des Stickstoffes müssen selbstverständlich die experimentellen Fehler — die Reproduzierbarkeit der Methode — eingehen. Wir betrachten zu diesem Zweck zwei hypothetische Analysenmaterialien, deren Borgehalt exakt gleich sein soll. Der Stickstoffgehalt des einen Materials soll garantiert unter der Störgrenze liegen, der des anderen sei unbekannt. In beiden Materialien wird bei einer Ionenenergie, oberhalb der Energieschwelle der Störung der Borgehalt zu \bar{x}'_{B} und \bar{x}''_{B} bestimmt. Die Störgrenze ergibt sich dann aus dem statistischen Unterschiedskriterium für 2 fehlerhafte Durchschnitte, dem t -Test. Es gilt

$$t = \frac{|\bar{x}'_{\text{B}} - \bar{x}''_{\text{B}}|}{s} \sqrt{\frac{N' \cdot N''}{N' + N''}} = t \quad (p=0.05; n=N'+N''-2) \quad (8)$$

Wenn diese Bedingung erfüllt wird, sind die beiden Durchschnitte gerade nicht mehr nur zufällig voneinander verschieden. Die Störung beginnt sich auszuwirken. Durch Umformung von Gl. (8) ergibt sich:

$$\Delta x = |\bar{x}'_{\text{B}} - \bar{x}''_{\text{B}}| = t(0.05; n) \cdot s \cdot \sqrt{\frac{N' + N''}{N' \cdot N''}} \quad (9)$$

$$s^2 = \frac{s'^2(N'-1) + s''^2(N''-1)}{N' + N'' - 2} \quad (10)$$

Mit der Bedingung $N' = N'' = N$ gilt für kleine Differenzen Δx , wegen

$$\bar{x}_{\text{B}} = \frac{\bar{x}'_{\text{B}} + \bar{x}''_{\text{B}}}{2} \approx \bar{x}'_{\text{B}} \approx \bar{x}''_{\text{B}}, \text{ näherungsweise}$$

$$s_{\text{rel}}^2 = \frac{s^2}{\bar{x}_{\text{B}}^2} = \frac{s'^2_{\text{rel}} + s''^2_{\text{rel}}}{2} \quad (11)$$

TABELLE III

STICKSTOFFSTÖRUNG

$(\gamma = \frac{A^{11}\text{C}}{A^{65}\text{Zn}} \text{ (I/min)})$; $\bar{x}_B =$ durchschnittl. Borgehalt (Gew. %);
 $N =$ Anzahl der Einzelwerte; $s =$ Standardabweichung des Einzelwertes)

$E_{p,d}$ (MeV)	γ		\bar{x}_B				N				s	
	SiBO	Si I	SiNO I	Si I	Si I	SiNO I	Si I	SiNO I	Si I	SiNO I	Si I	SiNO I
6.35	$1.88 \cdot 10^5$	$4.69 \cdot 10^5$	$2.73 \cdot 10^4$	$2.433 \cdot 10^{-3}$	$1.438 \cdot 10^{-1}$	48	16	48	$0.468 \cdot 10^{-3}$		$0.218 \cdot 10^{-1}$	
	1.99	6.81	3.92									
	1.79	4.67	2.62									
	1.74	4.60	2.69									
			2.28									
			3.39									
			3.13									
			3.57									
			3.05									
			3.17									
			2.98									
			3.35									
4.98	$8.23 \cdot 10^4$	$2.49 \cdot 10^2$	$5.45 \cdot 10^3$	$2.509 \cdot 10^{-3}$	$5.779 \cdot 10^{-2}$	4	4	4	$0.239 \cdot 10^{-3}$		$0.481 \cdot 10^{-2}$	
	7.38	2.12	4.96									
4.00	$4.27 \cdot 10^4$	$8.26 \cdot 10^1$	$8.95 \cdot 10^1$	$1.940 \cdot 10^{-3}$	$1.964 \cdot 10^{-3}$	4	4	4	$0.136 \cdot 10^{-3}$		$0.131 \cdot 10^{-3}$	
	3.87	8.96	9.51									
3.70	$2.89 \cdot 10^4$	$9.52 \cdot 10^1$	$9.03 \cdot 10^1$	$2.130 \cdot 10^{-3}$	$2.360 \cdot 10^{-3}$	4	4	4	$0.570 \cdot 10^{-3}$		$0.324 \cdot 10^{-3}$	
	3.65	6.35	8.59									
12.8	$6.27 \cdot 10^4$	$1.35 \cdot 10^2$	$1.61 \cdot 10^4$	$1.909 \cdot 10^{-3}$	$2.568 \cdot 10^{-1}$	4	4	4	$0.254 \cdot 10^{-3}$		$0.207 \cdot 10^{-3}$	
	5.23	1.17	1.78									
11.1	$3.58 \cdot 10^4$	$7.49 \cdot 10^1$	$5.38 \cdot 10^3$	$1.862 \cdot 10^{-3}$	$1.393 \cdot 10^{-1}$	4	4	4	$0.091 \cdot 10^{-3}$		$0.098 \cdot 10^{-1}$	
	3.30	7.31	5.75									
8.9	$2.72 \cdot 10^4$	$4.55 \cdot 10^1$	$3.71 \cdot 10^2$	$1.483 \cdot 10^{-3}$	$1.288 \cdot 10^{-2}$	4	4	4	$0.069 \cdot 10^{-3}$		$0.092 \cdot 10^{-2}$	
	2.52	4.43	4.09									
6.5	$1.64 \cdot 10^4$	$3.34 \cdot 10^1$	$4.03 \cdot 10^1$	$1.680 \cdot 10^{-3}$	$2.333 \cdot 10^{-3}$	4	4	4	$0.064 \cdot 10^{-3}$		$0.310 \cdot 10^{-3}$	
	1.72	3.19	5.07									

Daraus folgt

$$\frac{\Delta x}{\bar{x}_B} = t(0.05; n=2N-2) \sqrt{\frac{s'^2_{\text{rel}} + s''^2_{\text{rel}}}{N}} \quad (12)$$

Die durch den unbekanntem Stickstoffgehalt hervorgerufene Differenz der Borgehalte beträgt also an der Störgrenze den Bruchteil $\Delta x/\bar{x}_B$ des Borgehalts. Mit dem relativen Boräquivalent ergibt sich die rel. Störgrenze des Stickstoffes daraus zu

$$a_{s,\text{rel}} = a_{\text{rel}} \cdot \Delta x/\bar{x}_B = a_{\text{rel}} \cdot t(0.05; n=2N-2) \sqrt{\frac{s'^2_{\text{rel}} + s''^2_{\text{rel}}}{N}} \quad (13)$$

In Tabelle IV sind die aus den experimentellen Werten von a_{rel} für rel. Standardabweichungen $s_{\text{rel}} \approx 0.1$, wie sie sich aus unserem experimentellen Material als charakteristisch für die Methode ergeben, berechneten Werte der rel. Störgrenze des Stickstoffes zusammengestellt.

TABELLE IV

DIE RELATIVE STÖRGRENZE DES STICKSTOFFES BEI PROTONEN- UND DEUTERONENAKTIVIERUNG

N	E_p (MeV)	$a_{s,\text{rel}}$	E_d (MeV)	$a_{s,\text{rel}}$
3	6.35	1.36	12.8	0.75
	4.98	3.4	11.1	1.36
				8.9
5	6.35	0.87	12.8	0.48
	4.98	2.17	11.1	0.87
				8.9

TABELLE V

EMPFFINDLICHKEITSVERGLEICH ZWISCHEN PROTONEN- UND DEUTERONENAKTIVIERUNG

E_p (MeV)	\bar{y}_{SiBO}	E_d (MeV)	\bar{y}_{SiBO}
6.35	$1.85 \cdot 10^5$	12.8	$5.75 \cdot 10^4$
4.98	$7.81 \cdot 10^4$	11.1	$3.44 \cdot 10^4$
4.00	$4.07 \cdot 10^4$	8.9	$2.62 \cdot 10^4$
3.70	$3.27 \cdot 10^4$	6.5	$1.68 \cdot 10^4$

Bei einem Stickstoffgehalt von $\leq 50\%$ des Borgehaltes ist die Stickstoffstörung bei max. Ionenenergien mit Sicherheit vernachlässigbar. Mit Ionenenergien $E_p \leq 4$ MeV und $E_d \leq 6.5$ MeV ist auch bei 500fachem Stickstoffüberschuss keine Störung mehr vorhanden, wie die Ergebnisse dieser Untersuchung zeigen.

Vergleich der Nachweisesmpfindlichkeiten für Bor bei Protonen- und Deuteronenaktivierung. Wie ein Vergleich der nach $^{65}\text{Cu}(p,n)$ bzw. $(d,2n)$ gebildeten ^{65}Zn -Monitoraktivität mit genaueren Strommessungen ergab, ist die Aktivitätsausbeute der Monitorreaktionen bei gleichem Wasserstoffmolekülonen- und Deuteronenstrom näherungsweise gleich, sodass die Durchschnitte der normierten ^{11}C -Aktivitäten des Aktivierungsstandards SiBO ein Mass für die Empfindlichkeit darstellen.

Wie die in Tabelle V nochmals gesondert gegenübergestellten Werte zeigen, ist

bei gleicher Wärmeleistung die Protonenaktivierung im betrachteten Energiebereich etwa um den Faktor 2 empfindlicher.

Die Kernreaktion $^{14}\text{N}(d,\alpha n)^{11}\text{C}$. Wie schon eingangs erwähnt, ist diese Reaktion in der Literatur bisher nicht beschrieben worden. Mit einer Schwellenenergie von $E_s = 5.87$ MeV ist sie unter unseren experimentellen Bedingungen jedoch energetisch möglich. Die Ergebnisse dieser Untersuchungen lassen sich nur durch die Existenz dieser Reaktion verstehen, da Sekundärprozesse wie Reaktionen mit Rückstossprotonen, die aus im Targetmaterial enthaltenem Wasserstoff oder seinen Verbindungen (Feuchtigkeit) entstehen könnten, und der Strippingprozess wegen der Grösse des Effekts mit Sicherheit ausscheiden. Auch ein geringer Anteil an H_2^+ -Ionen, der im Deuteronenstrahl des Rossendorfer Zyklotrons meist noch vorhanden ist, könnte prinzipiell nur bei Bremsfoliendicken $< 70 \mu\mu$, das entspricht einer Protonenenergie von > 4 MeV und einer Deuteronenenergie > 11 MeV (s. Fig. 6), eine Störung hervorrufen, die aber unmöglich grösser als für reine H_2^+ -Ionen sein kann. Aus den normierten ^{11}C -Aktivitäten der hier verwendeten „dicken“ Targets lassen sich relative Aktivierungsausbeuten für diese Kernreaktionen, bezogen auf die Summe der Reaktionen $^{10}\text{B}(d,n) + ^{11}\text{B}(d,2n)^{11}\text{C}$, abschätzen. Aus Gl. (3) folgt mit $^1N = \rho \cdot x_1 \cdot N_L / 100 \cdot M_1$

$$\frac{B_N}{B_B} = \frac{A_N \cdot I_B \cdot ^1N_B}{A_B \cdot I_N \cdot ^1N_N} = 1.33 \frac{y_{\text{SiNO}} - y_{\text{SiI}}}{y_{\text{SiBO}}} \quad (14)$$

Diese relativen Aktivierungsausbeuten sind in Fig. 7 über der Deuteronenenergie aufgetragen. Bei $E_d = 12.8$ MeV erreicht die Aktivierungsausbeute der Stickstoffreaktion etwa 40% der Summe der Borreaktionen.

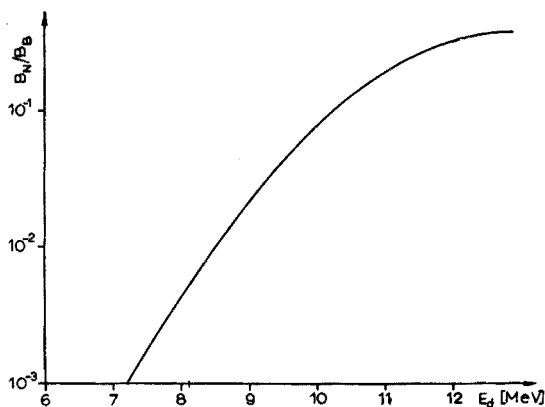


Fig. 7. Die relative Aktivierungsausbeute der Reaktion $^{14}\text{N}(d,\alpha n)^{11}\text{C}$.

II. BORBESTIMMUNG IN SILIZIUM UND GERMANIUM DURCH AKTIVIERUNG MIT PROTONEN

Auf Grund der Ergebnisse der unter I beschriebenen Untersuchungen wurde eine Methode zur Borbestimmung in Silizium und Germanium durch Protonenaktivierung ausgearbeitet. Mit Hilfe von Aktivierungsstandards, deren Herstellung und Kontrolle weiter unten noch näher beschrieben wird, wurde eine Eichung gegen die dem Ionenstrom proportionale ^{65}Zn -Monitoraktivität bei Protonenenergien von 6.35

MeV und 4.0 MeV vorgenommen. Die Bestrahlung und die radiochemische Abtrennung des ^{11}C erfolgte wie schon auf S. 431–433 beschrieben.

Aktivierungsstandards — Herstellung und Kontrolle

Zur Herstellung der zur Eichung erforderlichen Boraktivierungsstandards für Silizium und Germanium wurden 2 Wege beschritten. Leider liess sich der idealere, die Erschmelzung von Standardlegierungen aus den Elementen, nicht in der gewünschten Weise verwirklichen, da hierzu Kristallziehapparaturen erforderlich sind. Einfaches Erstarren der Schmelzen führt wegen der beim Erstarren des Siliziums und Germaniums auftretenden Volumenzunahme von resp. ca. 11% und 6% zur Zersprengung der Reguli; es können auf diese Weise keine kompakten Proben erhalten werden. Das Schmelzverfahren wurde in einigen Fällen zur Homogenisierung von Modellproben benutzt und die zersprungenen Reguli anschliessend in Stahlmörser und Kugelmühle pulverisiert. Diese Modellproben sind mit SiBS und GeBS bezeichnet. Die Standards wurden direkt durch Vermahlen der pulverförmigen Komponenten (Si und amorphes B)

TABELLE VI

BORGEHALT DER AKTIVIERUNGSSTANDARDS

<i>Standard</i>	<i>B-Mischungs- gehalt (%)</i>	<i>B-Gehalt, kolori- metrisch (%)</i>
SiBO	$9.01 \cdot 10^{-1}$	$8.64 \cdot 10^{-1}$
SiB1	$9.03 \cdot 10^{-2}$	$8.73 \cdot 10^{-2}$
SiB2	$9.03 \cdot 10^{-3}$	$9.88 \cdot 10^{-3}$
GeBo	$8.94 \cdot 10^{-1}$	$8.60 \cdot 10^{-1}$
GeB1	$8.67 \cdot 10^{-2}$	$8.10 \cdot 10^{-2}$
GeB2	$8.67 \cdot 10^{-3}$	$7.80 \cdot 10^{-3}$

in der Stahlkugelmühle und sukzessive Verdünnung mit dem Grundmaterial in Anlehnung an das in der Spektroskopie zur Testbereitung übliche Verfahren hergestellt; Bezeichnung im Text mit SiB bzw. GeB. Die Eichung wurde also nur mit Pulverstandards ausgeführt. Der durch die Mischungsverhältnisse grob eingestellte Borgehalt wurde kolorimetrisch nach der Carminsäuremethode bestimmt¹⁸ und darauf die Eichung bezogen. Die verwendeten Aktivierungsstandards und ihre Borgehalte sind in Tabelle VI zusammengestellt. Die relative Standardabweichung des kolorimetrischen Verfahrens war $\pm 12.8\%$ für Silizium und $\pm 5.2\%$ für Germanium.

Aktivitätsmessung und Auswertung

Zur Erreichung einer maximalen Empfindlichkeit wird die Aktivität A der 968 keV-Positronenstrahlung des ^{11}C mit einem Flüssigszintillationszähler gemessen. Das Blockschaltbild dieses Zählers ist in Fig. 8 angegeben. Die Messsonde steckt in einer 20 cm Stahlabschirmung. Eine Umlaufkühlung hält die Temperatur der Fotovervielfacher bei $+5^\circ$ konstant. Die 2.5 ml Adsorptionslösung, die die gesamte ^{11}C -Aktivität enthalten, werden nach Beendigung des Aufschlusses mit 7.5 ml einer Toluol–Methylglykolmischung im Volumenverhältnis 4:1 aus dem Absorptionsrohr in die Messküvette gespült und mit 10 ml einer Lösung von 10 g DPO, 0.4 g POPOP und 100 g Naphthalin in Toluol (zu 1 l) versetzt. Mit dieser Szintillatorzusammensetzung kann die ^{11}C -Aktivität bei einem Nulleffekt von 25–35 I/min mit einer Zählhausbeute von

100% gemessen werden. Bei dem genügend grossen Borgehalt und dementsprechend grosser ^{11}C -Aktivität der Aktivierungsstandards misst man bequemer die γ -Aktivität in Bohrlochgeometrie mit 70% Zählausbeute und rechnet auf die absolute Aktivität (100% Zählausbeute) um. Der Umrechnungsfaktor für unsere Messanordnungen war 1.43. Die Monitorfolien wurden wie auf S. 433 beschrieben gemessen.

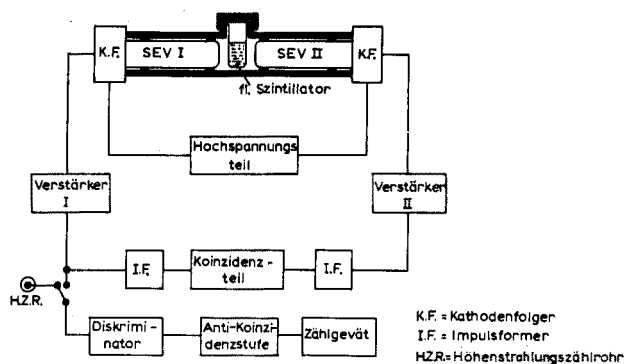


Fig. 8. Blockschaltbild des β -Flüssigszintillationszählers.

Aus Gl. (3) folgt für den Vergleich einer Analysenprobe mit einer Standardprobe des gleichen Materials

$$\frac{A_p}{A_s} = \frac{{}^1N_p \cdot W_p \cdot I_p}{{}^1N_s \cdot W_s \cdot I_s} \quad (15)$$

Da die Zahl der Targetatome je cm^3 dem Gehalt x des betreffenden Elements und der Ionenstrom der ^{65}Zn -Monitoraktivität Z proportional sind, folgt aus Gl. (15) bei konstanter Bestrahlungszeit

$$x_p(\text{Gew.}\%) = x_s(\text{Gew.}\%) \cdot \frac{Z_s \cdot A_p}{A_s \cdot Z_p} = \frac{x_s}{y_s} \cdot y_p = k \cdot y_p \quad (16)$$

Die Eichkonstante k wird durch Bestrahlung von Aktivierungsstandards mit bekanntem Gehalt x_s bestimmt.

Ergebnisse

Eichung für die Borbestimmung in Si und Ge bei Protonenenergien von $E_p = 4.0$ und 6.35 MeV. Die durch Bestrahlung der Aktivierungsstandards von Tabelle VI bestimmten Werte der Eichkonstanten k sind in Tabelle VII, einschliesslich der Anzahl der Aktivierungen N und Standardabweichungen der Einzelwerte s , angegeben. Eine statistische Prüfung durch Streuungserlegung ergibt keine Unterschiede zwischen den Durchschnitten innerhalb der Si- und Ge-Gruppe bei 4 MeV¹⁸; es kann der angegebene Gesamtdurchschnitt mit Vertrauensbereich Δk ($p = 0.05$) berechnet werden. Die Eichkonstante bei 6.35 MeV wurde nur mit den Aktivierungsstandards SiBO und GeBO bestimmt.

Aus den Eichkonstanten von Tabelle VII sind die experimentellen Nachweisgrenzen von Tabelle VIII berechnet worden. Für die untere Grenze der eindeutigen Nachweisbarkeit des Analysen isotops ^{11}C wird dabei eine Aktivität in der Grösse des Nulleffekts des Flüssigszintillationszählers von 30 I/min zugrundegelegt. Die Messung

kann 40 min = 2 Halbwertszeiten nach Bestrahlungsende erfolgen. Die Stromstärke beträgt ca. $1 \mu\text{A H}_2^+ \cong 3.3 \cdot 10^3 \text{ I/min (mg cm}^{-2}\text{)}$ ^{65}Zn -Monitoraktivität bei einer Bestrahlungszeit von 20 min. Die für gleiche Bedingungen aus den Anregungsfunktionen berechneten Nachweisgrenzen (s. Fig. 3) sind zum Vergleich in Tabelle VIII enthalten. Die Übereinstimmung ist befriedigend.

Mit den in Fig. 9 und 10 skizzierten Targethaltern für Pulver bzw. feste Ana-

TABELLE VII

EICHKONSTANTEN FÜR PROTONENAKTIVIERUNG
(^{11}C -Messung in γ -Bohrlochgeometrie; 70% Zählzubeute)

E_p (MeV)	Aktivierungs- standard	K (% I/min)	N	s	Δk ($p = 0.05$)
4.0	SiBO	$2.946 \cdot 10^{-5}$	19	$0.256 \cdot 10^{-5}$	
	SiB1	$2.900 \cdot 10^{-5}$	10	$0.218 \cdot 10^{-5}$	
	SiB2	$2.824 \cdot 10^{-5}$	9	$0.210 \cdot 10^{-5}$	
Gesamtdurchschnitt		$2.905 \cdot 10^{-5}$			$0.077 \cdot 10^{-5}$
4.0	GeBO	$2.744 \cdot 10^{-5}$	12	$0.206 \cdot 10^{-5}$	
	GeB1	$2.705 \cdot 10^{-5}$	3	$0.238 \cdot 10^{-5}$	
	GeB2	$2.918 \cdot 10^{-5}$	3	$0.056 \cdot 10^{-5}$	
Gesamtdurchschnitt		$2.767 \cdot 10^{-5}$			$0.064 \cdot 10^{-5}$
6.35	SiBO	$4.573 \cdot 10^{-6}$	10	$0.238 \cdot 10^{-6}$	$0.168 \cdot 10^{-6}$
	GeBO	$4.767 \cdot 10^{-6}$	9	$0.256 \cdot 10^{-6}$	$0.193 \cdot 10^{-6}$

TABELLE VIII

NACHWEISGRENZE DER BORBESTIMMUNG IN Si UND Ge

E_p (MeV)	Silizium			Germanium		
	exp.		theor. (At/cm ³)	exp.		theor. (At/cm ³)
	(Gew. %)	(At/cm ³)		(Gew. %)	(At/cm ³)	
6.35	$1.2 \cdot 10^{-7}$	$1.5 \cdot 10^{14}$	$1.6 \cdot 10^{14}$	$1.2 \cdot 10^{-7}$	$3.6 \cdot 10^{14}$	$2.8 \cdot 10^{14}$
4.0	$7.4 \cdot 10^{-7}$	$9.4 \cdot 10^{14}$	$1.6 \cdot 10^{15}$	$7.1 \cdot 10^{-7}$	$2.1 \cdot 10^{15}$	$2.9 \cdot 10^{15}$

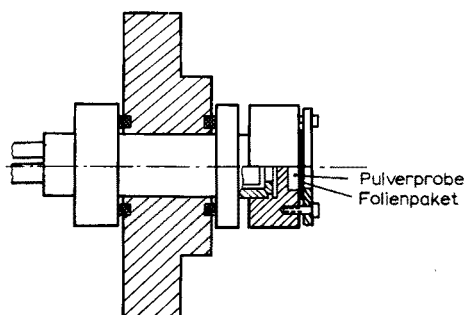


Fig. 9. Target für Pulverproben.

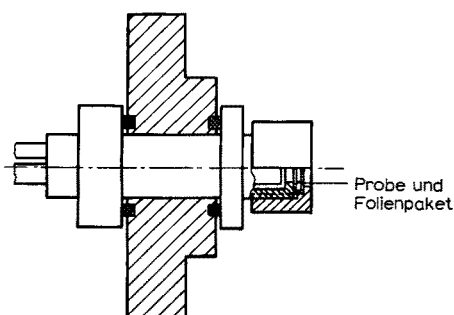


Fig. 10. Target für feste Proben.

lysenproben in Scheibenform (ca. 16 mm \varnothing ; 1–2 mm dick) lassen sich mit maximalen Stromstärken von respektive 5 und 10 μA H_2^+ um eine halbe bzw. eine ganze Zehnerpotenz niedrigere Nachweisgrenzen erreichen.

Borbestimmungen in verschiedenen Modellproben. Mit der beschriebenen Methode wurde der Borgehalt in einer Reihe von pulverförmigen Si- und Ge-Modellproben sowie in dem zu ihrer Herstellung verwendeten Ausgangsmaterial und in einigen festen Si-Proben bei $E_p=4$ MeV bestimmt. In Tabelle IX sind neben den

TABELLE IX

BORGEGHALT DER MODELLPROBEN

<i>Probe</i>	<i>B-Gehalt aktiv.- analyt. (Gew. %)</i>	<i>B-Gehalt dotiert (Gew. %)</i>	<i>B-Gehalt kolorim. (Gew. %)</i>	<i>B-Gehalt spektr. (Gew. %)</i>
<i>Pulver</i>				
SiBS I	$1.01 \cdot 10^{-1}$	$8.70 \cdot 10^{-2}$	$8.60 \cdot 10^{-2}$	$1.25 \cdot 10^{-1}$
SiBS 3	$7.88 \cdot 10^{-4}$	$8.70 \cdot 10^{-4}$	—	$1.10 \cdot 10^{-3}$
SiBS 4	$9.78 \cdot 10^{-5}$	$8.70 \cdot 10^{-5}$	—	$6.00 \cdot 10^{-5}$
Si II	$1.26 \cdot 10^{-3}$	—	—	—
SiNO II	$1.22 \cdot 10^{-3}$	—	—	$1.07(\%)N_2$
GeB 3	$7.29 \cdot 10^{-4}$	$8.76 \cdot 10^{-4}$	—	$8.0 \cdot 10^{-4}$
GeBS	$3.26 \cdot 10^{-3}$	—	$2.87 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$
Ge	$2.02 \cdot 10^{-5}$	—	—	—
Si I	$7.82 \cdot 10^{-5}$	$7.70 \cdot 10^{-5}$	—	—
<i>Fest</i>				
Si I	$7.35 \cdot 10^{-5}$	$7.70 \cdot 10^{-5}$	—	—
Si 2	$1.90 \cdot 10^{-5}$	$3.00 \cdot 10^{-5}$	—	—
Si 3	$8.90 \cdot 10^{-6}$	$6.00 \cdot 10^{-6}$	—	—

TABELLE X

DICKE DER AKTIVierten SCHICHT UND AKTIVITÄTSVERLUST BEI 1 $m\mu$ ÄTZTIEFE

E_p (MeV)	<i>Dicke der aktivierten Schicht ($m\mu$)</i>		<i>Aktivitäts- verlust (%)</i>	
	Si	Ge	Si	Ge
6.35	234	134	0.8	1.3
4.00	55	33	2.9	4.2

aktivierungsanalytischen Werten die dotierten bzw. kolorimetrisch oder spektrographisch bestimmten Gehalte angegeben; die Übereinstimmung ist gut. In Gegensatz zu den Pulverproben wurde die Oberfläche der festen Si-Proben nach der Bestrahlung durch Ätzen gereinigt. Die Proben wurden 45 sec bei 75° in einer Lösung, die je 2 N an NaOH, Na_2CO_3 und NaF war, behandelt, was einer Ätztiefe von ca. 0.5 $m\mu$ entspricht. Die Reinigung der Probenoberfläche nach der Bestrahlung ist bei Ionenaktivierungen sehr problematisch, da eine wirksame Dekontamination bei einer gut reproduzierbaren minimalen Ätztiefe erreicht werden muss. Eine zu grosse Ätztiefe bedeutet bei

den geringen Dicken der aktivierten Schicht einen merklichen Aktivitätsverlust des Analysenisotops und damit einen systematischen Fehler.

In Tabelle X sind die Werte für die Dicke der aktivierten Schicht und den Aktivitätsverlust bei $1 \text{ m}\mu$ Ätztiefe für Si und Ge angegeben. Die Erreichung der Nachweisgrenze der Methode hängt wesentlich von der Lösung des Ätzproblems ab. Die hier angewendete chemische Ätzung hat sich dazu als nicht geeignet erwiesen, da sie keine gleichmässige und gut reproduzierbare Ätzung gestattet. Als günstig erscheinen für diesen Zweck chemische und elektrochemische Polierverfahren sowie die anodische Oxidation mit anschliessender selektiver Abtragung der Oxidschicht; beim Si z.B. durch verdünnte HF.

III. SIMULTANBESTIMMUNG VON BOR UND STICKSTOFF IN SILIZIUM DURCH AKTIVIERUNG MIT PROTONEN

Auf Grund der unterschiedlichen Energieabhängigkeit der Aktivierungsausbeuten der zur Borbestimmung benutzten Kernreaktion $^{11}\text{B}(p,n)^{11}\text{C}$ und der Störreaktion $^{14}\text{N}(p,\alpha)^{11}\text{C}$ (Fig. 2) ist es möglich, Bor und Stickstoff durch Kombination von zwei Bestrahlungen bei verschiedener Energie nebeneinander zu bestimmen. Als Ionenanfangsenergien wählt man zweckmässig $E_1 = 4 \text{ MeV}$, wo Stickstoff nicht stört, und $E_2 = 6.35 \text{ MeV}$, wo sich die Aktivität des Analysenisotops ^{11}C aus einem Bor- und einem Stickstoffanteil zusammensetzt.

Der Gehalt x (%) ergibt sich aus der normierten Aktivität des Analysenisotops y und der betreffenden Eichkonstanten k zu

$$x = k \cdot y \quad (\text{vgl. II}) \quad (17)$$

Für den Borgehalt x_B bei den Ionenanfangsenergien E_1, E_2 und den Stickstoffgehalt x_N bei der Energie E_2 gilt entsprechend

$$x_B = k_{B1} \cdot y_{B1} = k_{B2} \cdot y_{B2} \quad (18)$$

$$x_N = k_{N2} \cdot y_{N2} \quad (19)$$

Der Borgehalt berechnet sich mit der ^{11}C -Aktivität y_{B1} bei der Energie E_1 aus der Gl. (18). Der Stickstoffanteil y_{N2} der ^{11}C -Gesamtaktivität y_2 ist die Differenz aus gemessener Gesamtaktivität y_2 und dem Boranteil $y_{B2} = k_{B1}/k_{B2} \cdot y_{B1}$ (aus Gl. (18)).

$$y_{N2} = y_2 - y_{B2} = y_2 - k_{B1}/k_{B2} \cdot y_{B1} \quad (20)$$

Eingesetzt in Gl. (19) folgt daraus für den Stickstoffgehalt

$$x_N = k_{N2} \cdot y_2 - k_{N2} \frac{k_{B1}}{k_{B2}} y_{B1} \quad (21)$$

Eichung

Zur Simultanbestimmung von Bor und Stickstoff unter diesen Bedingungen benötigt man also die Eichkonstanten k_{B1} und k_{B2} für Bor bei den beiden Energien E_1 und E_2 und die Eichkonstante für Stickstoff k_{N2} bei der Energie E_2 . Die Konstanten für Bor sind bereits in Tab. VII angegeben; k_{N2} erhält man in gleicher Weise aus Gl. (19). Wir können dazu die bei Aktivierung des Standards SiNO I erhaltenen Aktivitätswerte verwenden, die in Tabelle III angegeben sind. Die normierte Aktivität

$y_{\text{SiNO I}}$ ist dazu um den Aktivitätsanteil y_{SiI} des zur Herstellung des Standards SiNO I verwendeten Siliziums Si I zu korrigieren. Aus der in Tabelle III ebenfalls angegebenen Messreihe des Siliziums Si I ergibt sich ein Mittelwert von $\bar{y}_{\text{SiI}} = 5 \cdot 10^2$ für dieses Korrektionsglied. Die Konstante k_{N_2} mit Standardabweichung s und Vertrauensbereich Δk ($p = 0.05$) ist dann

$$k_{\text{N}_2} = 2.823 \cdot 10^{-5}; \quad s = 0.436 \cdot 10^{-5}; \quad \Delta k = 0.276 \cdot 10^{-5}$$

Die Gln. (18) und (21) für die Berechnung des Bor- bzw. Stickstoffgehaltes lauten damit

$$x_{\text{B}} = 2.91 \cdot 10^{-5} \cdot y_{\text{B1}} \quad (18)$$

$$x_{\text{N}} = 2.82 \cdot 10^{-5} \cdot y_2 - 1.79 \cdot 10^{-4} \cdot y_{\text{B1}} \quad (21)$$

Nachweisgrenze

Aus Gl. (19) bzw. Gl. (21) unter der Voraussetzung, dass der zweite Summand 0 wird, berechnet sich mit k_{N_2} und den angegebenen experimentellen Bedingungen (siehe II) eine Nachweisgrenze für Stickstoff von

$$x_{\text{N, min}} = 10^{-6} \text{ Gew. } \% / \mu\text{A H}_2^+ = 10^{15} \text{ At/cm}^3 \cdot \mu\text{A H}_2^+$$

was mit dem aus der Anregungsfunktion berechneten Wert von *ca.* $8 \cdot 10^{14} \text{ At/cm}^3 \cdot \mu\text{A H}_2^+$ gut übereinstimmt. Die möglichen Ionenströme betragen wie beim Bor (s. S. 442) für Pulver $5 \mu\text{A}$ und für feste Proben $10 \mu\text{A}$. Die im speziellen Fall erreichbare Stickstoffempfindlichkeit wird bei Gegenwart von nachweisbaren Mengen Bor durch dessen Gehalt festgelegt. Völlig analog zu der mit Hilfe des relativen Boräquivalentes a_{rel} und des statistischen Unterschiedskriteriums (S. 436), des *t*-Tests, berechneten Stickstoffstörgrenze lässt sich auch eine allgemeine Stickstoffnachweisgrenze mit Rücksicht auf den Borgehalt berechnen. Dazu ist lediglich zu fordern, dass der Unterschied zwischen den beiden dort eingeführten hypothetischen Analysenmaterialien

TABELLE XI

DIE RELATIVE NACHWEISGRENZE DES STICKSTOFFES

E_p (MeV)	$a_{\text{n, rel}}$	
	$N = 3$	$N = 5$
6.35	2.25	1.28
4.98	5.60	3.20

TABELLE XII

SIMULTANBESTIMMUNG VON STICKSTOFF UND BOR IN MODELLPROBEN

Nr.	Probe	\bar{y}_2	\bar{y}_{B1}	x_{B} (Gew. %)	x_{N} (Gew. %)	$t \geq t(p, n)$
1	SiB 1	$2.200 \cdot 10^4$	$3.026 \cdot 10^3$	$8.79 \cdot 10^{-2}$	$\leq 2.3 \cdot 10^{-1}$	$1.08 < 2.23$ ($p = 0.05$)
2	SiBS 1	$2.090 \cdot 10^4$	$3.476 \cdot 10^3$	$1.01 \cdot 10^{-1}$	$\leq 8.8 \cdot 10^{-2}$	$1.15 < 2.23$ ($p = 0.05$)
3	SiB 2	$2.505 \cdot 10^3$	$3.516 \cdot 10^2$	$1.02 \cdot 10^{-2}$	$\leq 1.2 \cdot 10^{-2}$	$1.88 < 2.26$ ($p = 0.05$)
4	SiBS 3	$2.025 \cdot 10^2$	$2.714 \cdot 10^1$	$7.88 \cdot 10^{-4}$	$(8.5 \pm 2.6) \cdot 10^{-4}$	$3.76 > 3.25$ ($p = 0.01$)
5	SiBS 4	$8.945 \cdot 10^1$	3.366	$9.78 \cdot 10^{-5}$	$(19.2 \pm 2.9) \cdot 10^{-4}$	$15.8 > 5.04$ ($p = 0.01$)

signifikant sein soll; d.h. $t = t(p = 0.01; n = N' + N'' - 2)$. Die analoge Gleichung für die relative Nachweisgrenze lautet dann (vgl. Gl. (13))

$$a_{n,rel} = a_{rel} \cdot \Delta x / \bar{x}_B = a_{rel} \cdot t(0.01; n) \sqrt{\frac{s'^2_{rel} + s''^2_{rel}}{N}} \quad (22)$$

Die Zahlenwerte enthält die Tabelle XI. Die Nachweisgrenze für Stickstoff ist demnach für $N = 5$, etwa gleich dem Borgehalt. Wenn der nach Gl. (21) berechnete Stickstoffgehalt in der Grössenordnung des Borgehaltes liegt, muss in jedem Falle die Differenz der beiden Summanden in Gl. (21) mit dem t -Test auf Signifikanz geprüft werden. Die Standardabweichung s ergibt sich dabei nur aus der Streuung von y_2 und y_{B1} . Die Konstanten sind in diesem Fall als fehlerfrei zu betrachten.

Simultanbestimmungen von Stickstoff und Bor in einigen Modellproben

In einer Reihe der schon im Rahmen dieser Untersuchungen verwendeten Aktivierungsstandards bzw. Modellproben wurde auf diese Weise neben Bor der Stickstoffgehalt bestimmt.

In Tabelle XII sind die Durchschnitte der normierten ^{11}C -Aktivitäten, der nach Gl. (18) berechnete Borgehalt und der nach Gl. (21) berechnete Stickstoffgehalt mit den dazugehörigen Vergleichsgrössen des t -Tests angegeben. In Übereinstimmung mit obenstehenden allgemeinen Betrachtungen ist die Nachweisgrenze für Stickstoff etwa gleich dem Borgehalt (Proben SiB 1, SiBS 1 und SiB 2) und der Stickstoffgehalt, der in allen Proben von der Grössenordnung $\sim 10^{-3} \%$ ist, lässt sich erst bestimmen, wenn der Borgehalt etwa gleich oder kleiner als dieser Wert ist (Proben SiBS 3 und SiBS 4).

Es ist mir ein Bedürfnis, meinem verehrten Lehrer, Herrn Prof. Dr. Dr. h. c. K. SCHWABE, für die Förderung und Unterstützung dieser Arbeit herzlich zu danken. Ferner gilt mein Dank der Abteilung Zyklotronbetrieb des ZfK Rossendorf für die Ausführung der Bestrahlungen.

ZUSAMMENFASSUNG

Die aktivierungsanalytische Borbestimmung über die Kernreaktion $^{11}\text{B}(p,n)^{11}\text{C}$ unterliegt einer Störung durch Stickstoff nach der Kernreaktion $^{14}\text{N}(p,\alpha)^{11}\text{C}$. Wie diese Untersuchungen gezeigt haben, tritt auch bei Deuteronenaktivierung nach $^{10}\text{B}(d,n)^{11}\text{C}$ und $^{11}\text{B}(d,2n)^{11}\text{C}$ eine Störung durch Stickstoff auf, die der Kernreaktion $^{14}\text{N}(d,\alpha n)^{11}\text{C}$ zugeschrieben werden muss. Beide Störungen werden quantitativ untersucht. Die Bedingungen für eine störungsfreie Borbestimmung sowie eine Simultanbestimmung von Bor und Stickstoff durch Protonenaktivierung werden ermittelt. Ein Analysenverfahren mit chemischer Abtrennung des Analysenisotops ^{11}C wurde für Silizium und Germanium ausgearbeitet.

SUMMARY

The determination of boron via the nuclear reaction $^{11}\text{B}(p,n)^{11}\text{C}$ was studied in detail; the nitrogen reaction $^{14}\text{N}(p,\alpha)^{11}\text{C}$ interferes. Nitrogen also interferes deuteron activation via the nuclear reactions $^{10}\text{B}(d,n)^{11}\text{C}$ and $^{11}\text{B}(d,2n)^{11}\text{C}$; this interference

must be attributed to the nuclear reaction $^{14}\text{N}(d,\alpha n)^{11}\text{C}$. Both interferences were investigated quantitatively. The conditions for the accurate determination of boron and for a simultaneous determination of boron and nitrogen by proton activation were established. An analytical method with chemical separation of the radioisotope ^{11}C was developed for silicon and germanium.

RÉSUMÉ

L'auteur a examiné en détail l'analyse par activation du bore dans le silicium et le germanium, par la réaction nucléaire $^{11}\text{B}(p,n)^{11}\text{C}$. L'azote gêne; ce qui peut être attribué à la réaction $^{14}\text{N}(d,\alpha n)^{11}\text{C}$. Les conditions de dosage précis du bore et d'un dosage simultané bore-azote, par activation au moyen de protons ont été établies. Une méthode analytique avec séparation chimique du radioisotope ^{11}C a été développée pour le silicium et le germanium.

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Anal. Chim. Acta, 34 (1966) 427-446

THE SZILARD-CHALMERS EFFECT APPLIED IN THE NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL SAMPLES

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(Received July 14th, 1965)

The Szilard-Chalmers effect is widely applied in radiochemical separations^{1,2}. The recoil energy of a nucleus formed through an (n, γ) reaction is obtained by the following expression

$$\bar{E}_R = \frac{\sum I_\gamma E_\gamma^2}{1862 M \sum I_\gamma}$$

where \bar{E}_R denotes the weighted mean value of the recoil energy, M the atomic mass of the product nucleus and E_γ the energy of the quantum emitted with intensity I_γ ³. For atoms with masses of between 20 and 200 the recoil energy would vary between about 1000 eV and 100 eV, assuming a single prompt γ -ray emission of 6 MeV, which might lead to the rupture of most of the chemical bonds, usually of energies of 1-5 eV⁴. The active nuclides produced may then exist in chemical states that can be separated from the inactive nuclides. In an ideal case the isolated active nuclides are carrier-free. The recoil atoms, "hot" atoms, resulting from the neutron-capture reactions then travel a certain distance in the material before being thermalized. Thus, in haemoglobin molecules of unit-cell dimensions $109 \times 63 \times 53 \text{ \AA}^5$ the recoil length of an ⁵⁹Fe particle might be⁶ about 30 \AA , assuming the slowing-down processes to be essentially due to elastic encounters with carbon and oxygen.

In the present investigation the Szilard-Chalmers effect was applied in the analysis of biological samples, simply through extraction of the induced activities in water or hydrochloric acid from the samples. However, the activities separated from the samples through extraction are not only to be ascribed to this effect. Different elements are present in biological systems as ions, which are easily extractable in water or hydrochloric acid. Parts of the organic material containing activities are also dissolved in the extraction process. Further, exchange reactions may participate in the processes involved in the transfer of activities. An active nuclide still bound owing to recombination might be extractable through isotopic exchange with carrier, and also through ion exchange in hydrochloric acid medium.

A common procedure in the activation analysis of biological material is to destroy the organic material with mineral acids after neutron irradiation, following this with a chemical separation, *e.g.* through precipitation or ion exchange, before the activity measurements are performed. The destruction of organic material is, however, often time-consuming, and may prevent the determination of short-lived nuclides, *e.g.* ²⁷Mg, with a half-life of 9.5 min. A simple extraction procedure would therefore in such cases be advantageous.

Fast destruction of organic materials has been performed by fusing the samples in a mixture of sodium peroxide and sodium hydroxide². In this case, however, there might be a risk of loss of activities due to volatilization^{7,8}, and the risk of explosion, too, should not be overlooked.

In the present work studies have been limited to the elements As, Au, Br, Ca, Cd, Co, Cr, Cs, Cu, Fe, Mo, Na, P, Rb, Se and Zn, which are present in liver tissue or whole blood and which have been determined in earlier work^{9,10}, and to the element magnesium in muscle tissue.

If a high degree of separation is to be attained in the Szilard–Chalmers process, a slow rate of exchange between the radioactive atoms in their new chemical state and the inactive atoms in the target compound is necessary.

In general, atoms with covalent bonds exchange very slowly. In this connection it may be mentioned that iron-haemoglobin does not exchange with iron(III), which could be expected assuming the ionic character of the bonds. However, in this case the structure of the molecule is very complex and the observed relations could be ascribed to steric hindrance¹¹.

Irradiation in diluted conditions favours the yield obtained by a Szilard–Chalmers process, in as much as the retention can be considerably lowered during dilution¹². This effect was also applied in the investigation of the yield of ⁵⁹Fe in aqueous extracts, through the irradiation of whole blood samples in the solid phase after freezing them in the presence of their extra- and intracellular fluids; the freezing was employed to prevent high pressures in the sealed ampoules due to radiolysis. Frozen conditions might, however, be advantageous as favouring a higher yield. The retention is otherwise often high in solid systems¹³. However, the frozen sample of whole blood might be considered as a heterogeneous and diluted solid system. In this system the rate of diffusion of the radioactive species formed might be low as compared to the corresponding rates in liquids. Consequently, lower retention might be expected.

The application of the Szilard–Chalmers effect in the analysis

In biological systems certain elements such as sodium and chlorine, present in about equivalent amounts in blood serum, occur in an ionic state¹⁴. Further, the metabolism of bromine in most living organisms is associated with the bromide ion¹⁴. On the other hand, iron is mainly bound to protein, such as porphyrin, or as heme compounds¹⁵. Vitamin B₁₂ contains cobalt¹⁵, molybdenum is associated with the flavoprotein enzymes¹⁵, and phosphorus occurs mainly as esterified P, as lipid P and as different nucleotides^{16–18}. In muscle tissue, about 30% of the magnesium present occurs as a free ion, while about 70% is bound in different complex forms¹⁹. It might thus be expected that the elements occurring as free ions together with the corresponding activities would be mostly extractable in a suitable medium from the irradiated sample. Further, the activities formed in the organically bound elements ought also to be extractable to some extent owing to the Szilard–Chalmers effect.

Analytical technique

The enrichment obtained in the Szilard–Chalmers process is often defined by the enrichment factor expressing the ratio between the specific activity of the separated form and the specific activity of the irradiated material¹². It is thus necessary to know the amounts of inactive material that are dissolved during the extraction. This

was investigated as follows. After extraction, the solution was divided into two parts, one of which was subjected to analysis for the different nuclides. The other part was allowed to cool, and was then submitted to reactivation under the same irradiation conditions and analysed. The specific activities in the two solutions were then compared, and the ratio, denoted as the "reactivation" factor, gave information about the amounts of the different elements dissolved. For example, a value of 0 for this factor revealed no dissolution of the element, and the activity thus extracted was ascribed to the Szilard-Chalmers process. Lower "reactivation" factors might be expected for, *e.g.*, Co, Fe, Mo and P when the extractions are performed in water. In this connection it should be mentioned that *e.g.* haemoglobin is easily soluble in water²⁰. However, the samples had been dried at 110° giving rise to denaturation, and essential molecular rearrangements occur during the irradiation in the strong gamma and neutron fluxes applied, which might considerably change the solubility conditions. "Reactivation" factors around 1, which indicate the predominance of simple dissolution, are expected for, *e.g.*, sodium, bromine and chlorine, as has been previously pointed out.

In one case the magnesium content of a muscle residue (sample after extraction of the ²⁷Mg activity) was reactivated in order to determine the amount of magnesium retained after the extraction. In this case the "reactivation" factor refers to a comparison of the ²⁷Mg activity induced in the residue and that in the initial sample.

The "reactivation" factor *R* is, moreover, the inverse value of the enrichment factor, *F*, according to the following relationships:

$$F = \frac{A_1/W_1}{A_2/W_2}; \quad R = \frac{A_3/W_1}{A_1/W_1}$$

where *A*₁ and *W*₁ express the activity and the amount of the corresponding element extracted from the irradiated material, *A*₂ denotes the activity induced in an element present in the quantity *W*₂ in the unextracted material, and *A*₃ symbolizes an activity induced in the extract in connection with reactivation.

Hence,

$$\frac{A_2}{W_2} = \frac{A_3}{W_1} \quad \text{then} \quad F \cdot R = 1$$

EXPERIMENTAL

Samples

Liver or whole blood samples (calf and pig) of about 2 g wet weight and dried at 110° were irradiated for periods of 2–3 days and 10 h respectively in thermal fluxes of $2 \cdot 10^{12}$ and $2 \cdot 10^{13}$ n/cm²/sec in the reactors R1 and R2.

Dried muscle samples (rat) of 10–100 mg wet weight were irradiated at the flux $2 \cdot 10^{13}$ n/cm²/sec for 10 min.

Whole blood samples of about 2 g wet weight were, when undried and frozen in liquid nitrogen, irradiated for periods of about 10 min also in positions of thermal flux of $2 \cdot 10^{13}$ n/cm²/sec.

Extractions

The irradiated samples were homogenized, and then extracted by shaking 3 times at 100° with 3 ml of water, or with 0.1 N, 1 N or concentrated hydrochloric

acid. The extractions were performed both with and without carriers of the elements to be determined.

Chemical separation and reactivation

The extract solution, coloured brown by dissolved organic material, was treated with hydrogen peroxide during boiling, whereupon the solution became clear. The activities in the solution were then separated into groups suitable for γ -spectrometry by means of ion-exchange and distillation techniques^{9,10,21}. The residue of the organic material was also exposed to this procedure after destruction of the organic material with sulphuric acid and hydrogen peroxide.

Analyses were made of the whole solution or of half the solution, the other half being allowed to cool, after which it was evaporated and then reactivated.

In one case the residue of muscle tissue after the hydrochloric acid extraction was reactivated.

An equal volume of extraction solution was also evaporated and activated as "blank" solution.

Zinc monitors were used for the determination of the thermal neutron dose.

Measurements

The γ -spectrometric measurements were performed with a transistorized 256-channel pulse-height analyzer attached to a 3" \times 3" NaI (Tl) crystal.

RESULTS AND DISCUSSION

Yields in the extraction procedure

The yields of the nuclides ⁷⁶As, ¹⁹⁸Au, ⁸²Br, ⁴⁷Ca, ¹¹⁵Cd, ³⁸Cl, ⁶⁰Co, ⁵¹Cr, ¹³⁴Cs, ⁶⁴Cu, ⁵⁹Fe, ²⁷Mg, ⁹⁹Mo, ²⁴Na, ³²P, ⁸⁶Rb, ⁷⁵Se and ⁶⁵Zn extracted in water or hydrochloric acid from either irradiated liver, whole blood or muscle tissue were determined. The results are given in Tables I to III.

The nuclides ⁸²Br, ³⁸Cl, ²⁴Na, ⁸⁶Rb and ¹³⁴Cs were found in the water or hydrochloric acid extracts to 95% or more. Further, the nuclides ⁴⁷Ca, ⁶⁴Cu, ⁶⁰Co, ⁵⁹Fe and ⁶⁵Zn were found to be extractable in concentrated hydrochloric acid from liver samples to 90% or more. From the muscle tissue ²⁷Mg could be extracted with the concentrated acid and determined with a recovery of 98%.

This extraction procedure might thus be advantageously applied in the quantitative analysis of biological materials for elements in trace quantities. The extraction procedure should be useful in the determination of short-lived nuclides such as ²⁷Mg and ^{60m}Co. In this connection it may be mentioned that magnesium has been determined in needle-biopsy samples of muscle tissue with extraction and fast precipitation in strong alkaline solution²².

For ⁸²Br a high yield value was obtained in concentrated hydrochloric acid even though losses of activities through evaporation had occurred. For the analysis of ⁸²Br and ³⁸Cl, water would be a more suitable extraction medium when closed systems are not used.

During the short extraction periods of about 30 sec, only a little of the organic material was dissolved in the aqueous phase. However, in the hydrochloric acid extracts considerable amounts of the material were dissolved.

TABLE I

RECOVERY OF RADIONUCLIDES EXTRACTED FROM LIVER TISSUE

Nuclide	Percentage recovery		Extn. in 1 N HCl Carrier added	Extn. in conc. HCl	
	Extn. in water Carrier not added	Extn. in 0.1 N HCl Carrier added		Carrier added*	Carrier not added
¹⁹⁸ Au	5	2	2	20 (14)	30, 15
⁸² Br	96	98	98	97 (2)	95, 95
⁴⁷ Ca	57		97	91 (7)	94
¹¹⁵ Cd	15	92	93	81 (8)	75
⁶⁰ Co	12	97	97	91 (4)	92, 95
⁵¹ Cr	70	62	65	87 (10)	90
¹³⁴ Cs	96	99	99	97 (2)	95, 96
⁶⁴ Cu	10	28	93	93 (5)	97, 90
⁵⁹ Fe	28	80	95	90 (7)	97
⁹⁹ Mo	54	14	32	41 (8)	30, 35
²⁴ Na	98	99	99	98 (1)	99, 98
³² P	53	57	75	77 (3)	70, 72
⁸⁶ Rb	98	99	99	98 (1)	99, 98
⁷⁵ Se	42	15	30	49 (20)	51
⁶⁵ Zn	3	95	95	92 (6)	97, 83

* In this case the mean value of recovery with standard deviation of a single value of 3 determinations (in bracket) is given.

TABLE II

RECOVERY OF RADIONUCLIDES EXTRACTED IN WATER FROM WHOLE BLOOD

Nuclide	Percentage recovery		Nuclide	Percentage recovery	
	Carrier not added	Carrier added		Carrier not added	Carrier added
⁷⁶ As	75, 80	72	⁵⁹ Fe	16, 20	4, 10, 19
⁸² Br	98, 96	96	²⁴ Na	99, 97	98
⁴⁷ Ca	89		³² P	46, 45	51
³⁸ Cl	97, 96	97	⁸⁶ Rb	99, 97	97
¹³⁴ Cs	98, 96	96	⁷⁵ Se	38, 31	40
⁶⁴ Cu	5, 19	6			

TABLE III

RECOVERY OF ²⁷Mg EXTRACTED FROM MUSCLE TISSUE

Nuclide	Percentage recovery			
	Extn. in conc. HCl		Extn. in water	
	Carrier added	Carrier not added	Carrier added	Carrier not added
²⁷ Mg	98, 97, 97, 98	95, 93, 95	45, 52	5, 15

When the whole blood samples were irradiated in undried and frozen conditions, considerably higher yields were obtained for ^{59}Fe than in the case of irradiation of dried samples (Tables II and VI). This was expected, but the best yields of 50–60% obtained were still too low to be applied in quantitative work.

Interpretation of the Szilard–Chalmers effect in the analysis

The "reactivation" factors and the enrichment factors for the nuclides ^{82}Br , ^{38}Cl , ^{60}Co , ^{134}Cs , ^{59}Fe , ^{27}Mg , ^{99}Mo , ^{24}Na , ^{32}P , ^{86}Rb and ^{65}Zn obtained on extraction in water or concentrated hydrochloric acid from either liver, whole blood or muscle tissue are given in Tables IV–VI.

For some of the nuclides investigated (not tabulated) the activities were considerably higher after reactivation, which must be due to contamination; for example, for ^{64}Cu "reactivation" factors exceeding 10 were obtained. This contamination could not be explained by impurities in the extractant and was probably due to the glass or filters used.

TABLE IV

THE "REACTIVATION" AND ENRICHMENT FACTORS FOR RADIONUCLIDES, OBTAINED BY EXTRACTION FROM LIVER TISSUE

Nuclide	Extraction with water		Extraction with conc. HCl	
	"Reactivation" factor	Enrichment factor	"Reactivation" factor	Enrichment factor
^{60}Co	0.1	10	0.4	2.5
^{134}Cs	1.0	1.0	1.0	1.0
			0.9	1.1
^{59}Fe	0.1	10	0.4	2.5
			0.7	1.4
^{99}Mo	0.3	3.3	0.4	2.5
		5.0	0.1	10
^{24}Na	0.9	1.1	1.0	1.0
			1.0	1.0
^{32}P	0.1	10	0.4	2.5
			0.4	2.5
^{86}Rb	0.9	1.1	1.0	1.0
			1.0	0.9
^{65}Zn			0.4	2.5
			0.8	1.3

TABLE V

THE "REACTIVATION" AND ENRICHMENT FACTORS FOR ^{27}Mg , OBTAINED BY EXTRACTION WITH CONCENTRATED HCl FROM MUSCLE TISSUE

(The "reactivation" factor is also given in the case of reactivation of the muscle residue)

Nuclide	Muscle		Muscle residue
	"Reactivation" factor	Enrichment factor	
^{27}Mg	0.7	1.4	0.3
	0.6	1.7	

On reactivation, the nuclides ^{24}Na , ^{86}Rb and ^{134}Cs were found in about the same strength as the first activation. Similar results were also obtained for ^{82}Br and ^{38}Cl .

The compounds of the alkali metals were simply dissolved in the extractant, as was to be expected. On the other hand, the nuclides ^{60}Co , ^{59}Fe , ^{99}Mo and ^{32}P were found to contribute 10–30% of the initial activities in connection with the reactivation of the water extracts, resulting in enrichment factors of 3.3 to 10.

TABLE VI

THE "REACTIVATION" AND ENRICHMENT FACTORS FOR RADIONUCLIDES, OBTAINED BY EXTRACTION OF DRIED AND UNDRIED WHOLE BLOOD SAMPLES WITH WATER

Nuclide	Dried sample		Undried, frozen sample	
	"Reactivation" factor	Enrichment factor	"Reactivation" factor (recovery)	Enrichment factor
^{82}Br	0.8	1.3		
	1.0	1.0		
^{38}Cl	0.9	1.1		
	0.9	1.1		
^{59}Fe	0.2	5.0	< 0.1 (66%)	> 10
	0.1	10.0	< 0.2 (53%)	> 5.0
^{24}Na	0.8	1.3		
	1.0	1.0		

In the hydrochloric acid extracts the "reactivation" factors were somewhat higher than in the water extracts, owing to destruction, dissolution and ion-exchange processes. Here, too, however, the Szilard-Chalmers effect may have played a fundamental role. In this case enrichment factors between 1.0 and 10 were obtained.

The relation of the ^{27}Mg activity obtained after reactivation of the residue of muscle tissue to the total ^{27}Mg activity induced in the sample when subjected to the first activation is given in Table V. In this case 95% of the ^{27}Mg activity as against 70% of the magnesium content was extracted in the concentrated hydrochloric acid; 30% of the magnesium content thus remained in the residue, which was in agreement with the "reactivation" factor of 0.3 obtained. Since considerable amounts of inactive magnesium had been dissolved during the extraction in concentrated hydrochloric acid, the enrichment factors obtained, 1.4 and 1.7, were relatively low.

Effects of carriers in the extraction procedure

If, for example, a ^{27}Mg nuclide is still bound in an organic compound due to recombination or bound to the surface of the organic sample, this nuclide may exchange with the magnesium carrier, and thus become extractable. The addition of 10 mg of magnesium as carrier increased the recovery value from about 10 to 50% when the extraction was done with water. When concentrated hydrochloric acid was the extractant with the addition of the same amount of carrier, a recovery of 98% was obtained. However, extraction with this acid resulted in a recovery of 95% without the addition of carrier.

In the case of water extraction of nuclides from whole blood, no carrier effect

similar to that observed for magnesium, was revealed for the nuclides ^{64}Cu , ^{59}Fe , ^{32}P and ^{75}Se of low yields in this extractant. (table II)

In the separation of ^{27}Mg from the muscle tissue the effect of the hydrochloric acid seems to have been of much greater importance than the effect contributed by the carrier alone. The difference (about 3%) in the yield of ^{27}Mg when extractions were done with and without the addition of carrier, might be explained as due to isotopic exchange between ^{27}Mg bound to the muscle tissue and magnesium carrier, and also to the hold-back carrier effect.

The addition of carriers in amounts of about 0.5 mg seemed to have no essential effect on the yields when the extraction was done with concentrated hydrochloric acid from liver tissue (Table I); this was expected, assuming that different amounts of activities adsorbed on the sample were dissolved through ion-exchange processes with hydrogen ions in high concentration.

It should be borne in mind that carriers are produced during the extraction process, as the different elements present in the organic material are partly dissolved, and the system could thus not be studied in the complete absence of carriers. However, the concentration of carriers thus obtained is usually lower by several orders of magnitude than the carrier concentrations generally applied. Thus, liver tissue contains Ca and P in milligram quantities, Br, Cd, Cu, Fe, Mo, Rb, Se and Zn in microgram quantities and Au, Co, Cr and Cs in submicrogram quantities⁹; however, some of these quantities that are dissolved during extraction with concentrated acid are bound to organic material, implying the loss of the carrier function.

ACKNOWLEDGEMENT

The author is greatly indebted to Miss S. HACKBARTH for skillful technical assistance.

SUMMARY

The Szilard-Chalmers effect has been applied in the separation of activities, originating from organically bound elements, from neutron-irradiated material. The nuclides ^{76}As , ^{198}Au , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{38}Cl , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{64}Cu , ^{59}Fe , ^{27}Mg , ^{99}Mo , ^{24}Na , ^{32}P , ^{86}Rb , ^{75}Se and ^{65}Zn were extracted from liver tissue, whole blood or muscle tissue with water or with varying strengths of hydrochloric acid. The recoveries of the alkali metal nuclides, ^{82}Br and ^{38}Cl , in the water and hydrochloric extracts were $\geq 95\%$. In the concentrated hydrochloric acid extracts, the recovery of most nuclides exceeded 90%. The enrichment of the different nuclides obtained in the Szilard-Chalmers process was investigated by reactivation of part of the extracts. The effect of dilution, which favours the yield, was investigated in the separation of ^{59}Fe from whole blood samples.

RÉSUMÉ

L'effet Szilard-Chalmers a été appliqué à l'analyse d'échantillons biologiques par activation au moyen de neutrons. Les radionucléides ^{76}As , ^{198}Au , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{38}Cl , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{64}Cu , ^{59}Fe , ^{27}Mg , ^{99}Mo , ^{24}Na , ^{32}P , ^{86}Rb , ^{75}Se et ^{65}Zn ont

été extraits de foie, de sang ou de muscle, avec de l'eau ou avec de l'acide chlorhydrique à diverses concentrations. La récupération des nucléides ^{82}Br et ^{38}Cl dans les extraits d'eau et d'acide chlorhydrique est de 95% ou plus. Dans les extraits d'acide chlorhydrique concentré la récupération des nucléides est supérieure à 90%. L'enrichissement des différents nucléides obtenus par le procédé Szilard-Chalmers a été examiné par réactivation d'une partie des extraits. L'effet de dilution favorisant le rendement a été examiné aussi pour la séparation de ^{59}Fe dans des échantillons de sang.

ZUSAMMENFASSUNG

Der Szilard-Chalmers-Effekt wurde bei der Abtrennung von Aktivitäten organisch gebundener Elemente in neutronenaktiviertem Material angewendet. Die Nuklide ^{76}As , ^{198}Au , ^{82}Br , ^{47}Ca , ^{115}Cd , ^{38}Cl , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{64}Cu , ^{59}Fe , ^{27}Mg , ^{99}Mo , ^{24}Na , ^{32}P , ^{86}Rb , ^{75}Se und ^{65}Zn wurden aus Lebergewebe, Blut oder Muskelgewebe mit Wasser oder Salzsäure verschiedener Stärke extrahiert. Die Rückgewinnung der Alkalimetallnuklide des ^{82}Br und ^{38}Cl in den wässrigen und salzsauren Extrakten betrug 95% oder mehr. In den konzentrierten salzsauren Extrakten überschritt die Rückgewinnung der meisten Nuklide 90%. Die Anreicherung der verschiedenen Nuklide, die beim Szilard-Chalmers-Prozess erhalten wurden, wurde durch Reaktivierung eines Teils des Extrakts untersucht. Der Verdünnungseffekt, der die Ausbeute begünstigt, wurde bei der Abtrennung von ^{59}Fe aus den Blutproben untersucht.

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IDENTIFIZIERUNG VON RADIONUKLIDEN DURCH HALBQUANTITATIVE AUTORADIOGRAPHISCHE BESTIMMUNG IHRER HALBWERTSZEIT MIT HILFE DER RINGOFENMETHODE

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(Eingegangen den 8. August, 1965)

Die Möglichkeiten zur Anwendung der Ringofentechnik auf radiochemische Probleme, insbesondere auf den Nachweis und die halbquantitative Bestimmung geringster Mengen radioaktiver Substanzen durch Autoradiographie, wurden bereits in einer Reihe von Arbeiten¹⁻⁷ dargelegt. Eine der Bedingungen, welche bei der halbquantitativen Autoradiographie erfüllt sein müssen, ist die, dass die erforderlichen Expositionszeiten (einige Stunden bis Tage) gegenüber den Halbwertszeiten der zu untersuchenden Radionuklide vernachlässigt werden können. Würde man nun diese Expositionen in genügend grossen Zeitabständen mit jeweils den gleichen Proberingen mehrere Male wiederholen, so müsste sich aus den Schwärzungsabnahmen der erhaltenen Autoradiogramme die Halbwertszeit des vorliegenden radioaktiven Isotops ermitteln und damit das Isotop selbst identifizieren oder zumindest einer kleinen Gruppe von Isotopen ähnlicher Halbwertszeit zuordnen lassen. Auf diese Nachweismöglichkeit wurde bereits im Zusammenhang mit einem früher beschriebenen Mikro-Trennungsgang für Uranspaltprodukte mit Hilfe der Ringofenmethode² hingewiesen. Auch GEBAUHR UND MARTIN⁸ bestimmten im Rahmen aktivierungsanalytischer Untersuchungen an hochreinem Silicium halbquantitativ die Halbwertszeit aktivierter Verunreinigungszentren in der Matrix durch Autoradiographie. Als Ergänzung zu den oben zitierten Arbeiten soll nun im folgenden gezeigt werden, wie sich durch Kombination von Ringofentechnik und Autoradiographie Halbwertszeiten in einfacher Weise halbquantitativ ermitteln lassen.

GRUNDLAGEN DES VERFAHRENS

Die mathematische Grundlage des Verfahrens ist durch das Gesetz des radioaktiven Zerfalls gegeben:

$$\frac{dN}{dt} = -\lambda N \text{ bzw. } N_{(t)} = N_{(0)} \cdot e^{-\lambda t} \quad (1)$$

$N_{(t)}$ = vorhandene Kerne zur Zeit t , $N_{(0)}$ = vorhandene Kerne zur Zeit $t=0$, λ = Zerfallskonstante.

Da $\lambda = \ln 2/T_{\frac{1}{2}}$, so folgt aus (1):

$$N_{(t)} = N_{(0)} \cdot 2^{-t/T_{\frac{1}{2}}} \quad (2)$$

$T_{\frac{1}{2}}$ = Halbwertszeit.

Eine Umformung von (2) liefert die Gleichung zur Berechnung von $T_{\frac{1}{2}}$:

$$2^{t/T_{\frac{1}{2}}} = \frac{N_{(0)}}{N_{(t)}}$$

$$\frac{t}{T_{\frac{1}{2}}} \cdot \log 2 = \log \frac{N_{(0)}}{N_{(t)}}$$

$$T_{\frac{1}{2}} = t \cdot \frac{\log 2}{\log \frac{N_{(0)}}{N_{(t)}}} \quad (3)$$

Die Bestimmung von $N_{(0)}$ und $N_{(t)}$, d.h. die Messung der entsprechenden Aktivitätsraten $A_{(0)}$ und $A_{(t)}$, wird nun, wie auch sonst in der halbquantitativen Autoradiographie mit Hilfe der Ringofentechnik üblich^{6,7}, auf einen visuellen Vergleich von Probe- und Standardschwärzungen nach der Methode des "gewogenen Mittels"⁹ zurückgeführt. Eine Serie von Ringen, die man in bekannter Weise aus verschiedenen Tropfen der zu untersuchenden Radionuklidlösung anfertigt, liefert durch Exposition zum Zeitpunkt $t=0$ eine Skala von Standardschwärzungen entsprechend der Aktivitätsrate $A_{(0)}$. Die Anfangsaktivität $a_{(0)}$ eines Tropfens der Lösung muss so hoch sein, dass die Expositionszeit klein gehalten werden kann gegenüber $T_{\frac{1}{2}}$. Nach Verstreichen einer geeigneten Zeitspanne t ergeben die gleichen Ringe in der gleichen Expositionszeit eine Skala von Schwärzungen entsprechend der Aktivitätsrate $A_{(t)}$. Der visuelle Vergleich der zweiten Skala ("Probeschwärzungen") mit der ersten ("Standardschwärzungen") liefert den Quotienten $N_{(0)}/N_{(t)}$. Mit Hilfe der bekannten Zeitspanne t lässt sich dann nach Gleichung (3) $T_{\frac{1}{2}}$ berechnen.

Wie man nun praktisch eine solche Halbwertszeitbestimmung durchführt und welche Fehlerquellen man zu beachten hat, soll im folgenden Abschnitt am Beispiel des ^{198}Au ($T_{\frac{1}{2}} = 2.697$ d) ausführlich geschildert werden.

BESTIMMUNG DER HALBWERTSZEIT VON ^{198}Au

Da wir uns bei unseren Versuchen aus zeitlichen Gründen auf Radionuklide mit Halbwertszeiten in der Grössenordnung von einigen Tagen beschränken wollten, was es notwendig, die Expositionszeit auf 1 Stunde zu begrenzen, um sie bei den Berechnungen vernachlässigen zu können. Demzufolge mussten die Ausgangslösungen der Isotope eine etwa 20mal höhere spez. Aktivität aufweisen, als es sonst bei der halbquantitativen Autoradiographie mit Hilfe der Ringofentechnik erforderlich ist^{6,7}. Von ^{198}Au stand uns eine salzsaure Lösung mit einer spez. Aktivität von 2.3 $\mu\text{C/ml}$ bzw. 2.3 $\text{nC}/\mu\text{l}$ zur Verfügung (Trägermenge: 0.1 mg Au(III)/ml).

Zum Auftragen verschiedener Volumina der Radionuklidlösungen auf Rundfilter (Macherey, Nagel & Co. MN 2260) wurde nicht eine der üblichen selbstfüllenden Kapillarpipetten verwendet, sondern eine in μl geeichte Kapillarbürette⁷ (Benedetti-Pichler-Bürette; Gesamtvolumen 30 μl). Dies hat zur Folge, dass nicht mehr *Tropfenzahlen*, sondern *unganzzahlige μl* in die Berechnungen eingehen, was aber an der Auswertung nichts ändert. Die Benedetti-Pichler-Bürette erleichtert das Auftragen grösserer Flüssigkeitsmengen wesentlich. Die ^{198}Au -Ringe wurden auf dem Ringofen in der üblichen Weise mit destilliertem Wasser gewaschen, nachdem man vor und nach

dem Auftragen der aktiven Lösung mit je 1 Tropfen ($6 \mu\text{l}$) KCN-Lösung (1%ig an CN^-) angetupft hatte. Es entstand eine Skala von Ringen aus 1.00, 2.55, 4.70, 6.05, 8.90, 10.20, 12.85, 16.10, 21.70 μl der ^{198}Au -Lösung. Bei Verwendung einer selbstfüllenden Kapillarpipette hätte man eine Serie von Ringen aus 1, 2, 4, 6, 8, 10, 13, 16 und 20 Tropfen erhalten^{6,7}.

Zu einem Zeitpunkt $t=0$ wurden nun die 9 ^{198}Au -Ringe auf einen in schwarzer Supronylfolie (Hersteller: Kalle & Co. A.G., Wiesbaden) verpackten ADOX-DONEO-Röntgenfilm (Hersteller: ADOX-Fotowerke Dr. C. Schleusner GmbH., Frankfurt/Main) des Formats 3.6×24 cm gelegt und beschwert^{6,7}. Nach genau 1 Stunde wurde die Exposition unterbrochen und der Filmstreifen zum Aufbewahren in eine Tiefkühltruhe gelegt^{7,10}. Die zweite Exposition (mit den gleichen Ringen) erfolgte 24 Stunden, eine dritte 48 Stunden und eine vierte 96 Stunden nach der ersten. Die Expositionszeit betrug stets genau 1 Stunde. Die von der ersten, zweiten und dritten Exposition herrührenden latenten Autoradiogramme wurden so lange in der Tiefkühltruhe aufbewahrt, bis sie gemeinsam mit dem vierten Filmstreifen (Exposition zum Zeitpunkt $t=96$ Stunden) mitentwickelt werden konnten^{6,7}.

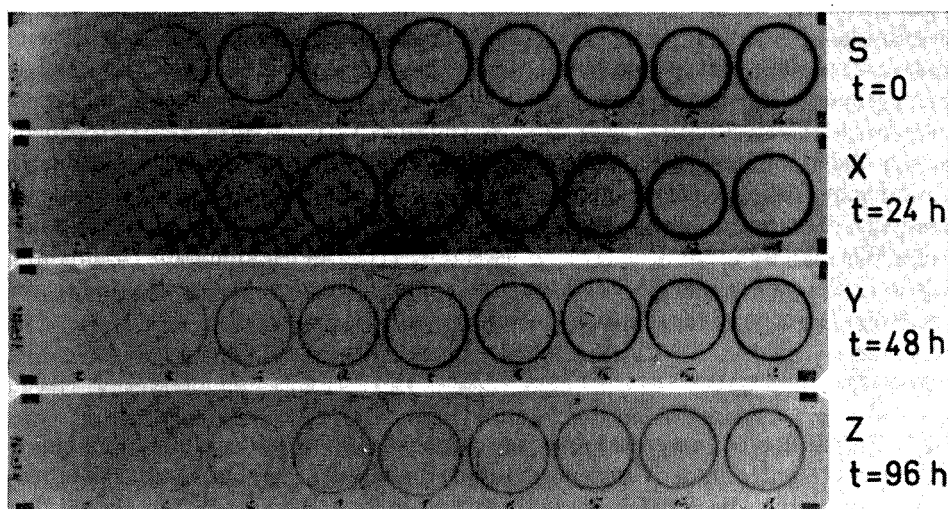


Fig. 1. ^{198}Au -Schwärzungsskalen.

Fig. 1 zeigt die 4 Filmstreifen mit den zu den Zeiten $t=0$ (S), $t=24$ Stunden (X), $t=48$ Stunden (Y) und $t=96$ Stunden (Z) gehörenden Schwärzungsskalen. Bei konstanter Expositionszeit (in diesem Fall 1 Stunde) ist nach dem BUNSEN-ROSCOESEN Reziprozitätsgesetz zu einem bestimmten Zeitpunkt t die von einem Ring erzeugte Schwärzung der gerade vorliegenden Aktivität $a(t)$ je Tropfen (μl) der Radionuklidlösung und der Anzahl z der Tropfen (μl), aus welcher der Ring hergestellt wurde, proportional^{6,7}. Es ist also

$$N_{(0)} \sim A_{(0)} \sim a_{(0)} \cdot z \text{ zum Zeitpunkt } t=0$$

und

$$N_{(t)} \sim A_{(t)} \sim a_{(t)} \cdot z \text{ zum Zeitpunkt } t.$$

Geht man nun so vor, dass man das Abklingen der Aktivität von $A_{(0)}$ bis $A_{(t)}$ auf ein scheinbares exponentielles Absinken der Tropfenzahl z zurückführt, dann wird

$$N_{(0)} \sim A_{(0)} \sim a_{(0)} \cdot z_{(0)} \quad \text{zum Zeitpunkt } t=0$$

und

$$N_{(t)} \sim A_{(t)} \sim a_{(0)} \cdot z_{(t)} \quad \text{zum Zeitpunkt } t.$$

Hiermit wird folgendes ausgesagt: Ein Ring aus $z_{(0)}$ Tropfen (μl) einer Lösung der spez. Aktivität $a_{(0)}$ bildet t Stunden nach der ersten Exposition nur noch so stark ab wie ein Ring aus $z_{(t)}$ Tropfen (μl) einer Lösung der gleichen spez. Aktivität ($z_{(0)} > z_{(t)}$).

Dieser Sachverhalt lässt sich nun zur Auswertung der 4 Schwärzungsskalen durch visuellen Vergleich nach der Methode des "gewogenen Mittels" heranziehen. Man betrachtet den zu $t=0$ gehörenden Filmstreifen (S) als Standardskala und die übrigen drei (X, Y, Z) als Serien von Probeautoradiogrammen. Versteht man unter $\Sigma z_{(0)}$ bzw. $\Sigma z_{(t)}$ ($t=24, 48$ oder 96 Stunden) die Summe der Tropfenzahlen (μl -Zahlen) der Standardringe bzw. Proberinge, deren Autoradiogramme zur Berechnung herangezogen werden^{6,7}, so lässt sich Gleichung (3) umschreiben zu

$$T_{\frac{1}{2}} = t \cdot \frac{\log 2}{\log \frac{a_{(0)} \cdot \Sigma z_{(0)}}{a_{(0)} \cdot \Sigma z_{(t)}}} = t \cdot \frac{\log 2}{\log \frac{\Sigma z_{(0)}}{\Sigma z_{(t)}}}$$

und

$$T_{\frac{1}{2}} = t \cdot n_{(t)} \quad (4)$$

mit

$$n_{(t)} = \frac{\log 2}{\log \frac{\Sigma z_{(0)}}{\Sigma z_{(t)}}} \quad (5)$$

Der visuelle Vergleich der Skalen X, Y und Z mit der Standardskala S liefert 3 Serien von geschätzten Schwärzungswerten, ausgedrückt in μl , und demzufolge auch drei verschiedene $\Sigma z_{(t)}$ -Werte, nämlich $\Sigma z_{(24)}$, $\Sigma z_{(48)}$ und $\Sigma z_{(96)}$. Für das Beispiel ¹⁹⁸Au (vgl. Fig. 1) sind diese Schätzungen in Tabelle I wiedergegeben.

$\Sigma z_{(0)}$ wird direkt aus den μl -Zahlen der Ringe errechnet. Die Summe beträgt

TABELLE I

VERGLEICH DER SKALEN X, Y UND Z MIT DER STANDARDSKALA S

Skala Ring Nr.	Standard S $t = 0$	X $t = 24 \text{ h}$	Y $t = 48 \text{ h}$	Z $t = 96 \text{ h}$
I	1.00	Ausserhalb S	Ausserhalb S	Ausserhalb S
II	2.55	2.00	1.40	Ausserhalb S
III	4.70	3.60	3.10	1.40
IV	6.05	4.20	3.60	2.20
V	8.90	6.05	4.15	3.10
VI	10.20	7.50	5.40	3.10
VII	12.85	9.55	6.75	3.60
VIII	16.10	12.15	8.90	4.70
IX	21.70	17.90	11.50	6.05
		$\Sigma z_{(24)} = 62.95$	$\Sigma z_{(48)} = 44.80$	$\Sigma z_{(96)} = 24.15$

83.05 für den Vergleich von X und Y mit S (Ring Nr. I bleibt unberücksichtigt) und 80.50 für den Vergleich von Z mit S (die Ringe Nr. I und II werden nicht mitgerechnet). Somit erhält man

$$\frac{\Sigma z_{(0)}}{\Sigma z_{(24)}} = \frac{83.05}{62.95} = 1.319; \quad \frac{\Sigma z_{(0)}}{\Sigma z_{(48)}} = \frac{83.05}{44.80} = 1.854; \quad \frac{\Sigma z_{(0)}}{\Sigma z_{(96)}} = \frac{80.50}{24.15} = 3.333$$

und mit Hilfe von Gleichung (5)

$$n_{(24)} = 2.5036 \quad n_{(48)} = 1.1228 \quad n_{(96)} = 0.5758$$

Mit diesen drei $n_{(t)}$ -Werten können nach Gleichung (4) drei Werte für die gesuchte Halbwertszeit berechnet werden, nämlich $24 \cdot 2.5036 = 60.1$ h, $48 \cdot 1.1228 = 53.9$ h und $96 \cdot 0.5758 = 55.3$ h. Das arithmetische Mittel hieraus liefert als vorläufiges Ergebnis: $T_{\frac{1}{2}}' = 56.4$ h.

Dieses Resultat wird deswegen als vorläufig bezeichnet, weil hierin noch nicht die günstigsten Möglichkeiten zur Mittelwertbildung verarbeitet sind. Verwendet man nämlich nicht nur den Filmstreifen S (X, Y, Z als "Proben"), sondern auch den Streifen X (Y, Z als "Proben") sowie den Streifen Y (Z als "Probe") als Standardskala, so lassen sich in der eben beschriebenen Weise 3 weitere $n_{(t)}$ -Werte und damit auch 3 zusätzliche Werte für die Halbwertszeit berechnen. Werden Y ($t=48$ Stunden) und Z ($t=96$ Stunden) mit X ($t=24$ Stunden) als Standardskala verglichen, dann erhält man nochmals einen $n_{(24)}$ -Wert (48-24) sowie einen $n_{(72)}$ -Wert (96-24). Wird Z mit Y als Standardskala verglichen, dann lässt sich ein zusätzlicher $n_{(48)}$ -Wert (96-48) gewinnen. Insgesamt stehen also 6 unabhängig voneinander errechnete $n_{(t)}$ -Werte zur Verfügung (2 mal $n_{(24)}$, 2 mal $n_{(48)}$, $n_{(72)}$ und $n_{(96)}$), von denen man mindestens zwei zur endgültigen Berechnung von $T_{\frac{1}{2}}$ heranziehen sollte. Wie diese Auswahl im Hinblick auf ein optimales Resultat zu treffen ist, soll die folgende Fehlerbetrachtung zeigen.

Man kann davon ausgehen, dass eine logarithmische Beziehung zwischen $T_{\frac{1}{2}}$ und dem Quotienten $\Sigma z_{(0)}/\Sigma z_{(t)}$ besteht (siehe Gleichungen (4) und (5)), und dass dieser Quotient in Abhängigkeit von t bzw. $t/T_{\frac{1}{2}}$ definierte, durch das Zerfallsgesetz gegebene Werte annehmen muss. Umgekehrt werden sich also Schätzfehler, die zu fehlerhaften $\Sigma z_{(t)}$ -Werten führen, bei der Berechnung von $T_{\frac{1}{2}}$ in exponentieller Abhängigkeit von t bzw. $t/T_{\frac{1}{2}}$ auf das Endergebnis bemerkbar machen. Es ist demnach von grosser Bedeutung für das Resultat der Halbwertszeitbestimmung, ob $\Sigma z_{(24)}$ mit einem bestimmten prozentualen Fehler behaftet ist, oder $\Sigma z_{(96)}$. Dieser Sachverhalt wird in Fig. 2 veranschaulicht. Hier sind gegen das Verhältnis $t/T_{\frac{1}{2}}$ als Abszisse diejenigen Plus- bzw. Minusfehler aufgetragen, um welche die gefundene Halbwertszeit vom Sollwert abweicht, wenn $\Sigma z_{(t)}$ 10% zu hoch bzw. 10% zu tief gefunden wird. (Derartige Schätzfehler sind in der halbquantitativen Autoradiographie mit Hilfe der Ringofenmethode durchaus vertretbar?). Die Berechnung der Ordinatenwerte erfolgte mit Hilfe der Gleichungen (4) und (5) nach geeigneter Umformung.

Aus den Kurven der Fig. 2 lässt sich leicht folgendes ablesen: Ein Schätzfehler von $\pm 10\%$ macht sich erst bei einem Verhältnis $t/T_{\frac{1}{2}} \sim 1.5$ in der gleichen Grösse im Endergebnis bemerkbar. Für $t/T_{\frac{1}{2}} < 1$ steigt der Fehler, mit welchem $T_{\frac{1}{2}}$ behaftet ist, steil auf Werte $\gg \pm 10\%$ an, während für $t/T_{\frac{1}{2}} > 1.5$ die errechnete Halbwertszeit trotz des Schätzfehlers von $\pm 10\%$ stets weniger als 10% vom Sollwert abweicht und sich diesem asymptotisch nähert.

Man wird also ganz allgemein bei der Halbwertszeitbestimmung immer mit denjenigen $\Sigma_{z(t)}$ - bzw. $n_{(t)}$ -Werten die besten Resultate erhalten, für welche t möglichst gross ist. Im gleichen Sinne macht sich auch die Tatsache bemerkbar, dass der Schätzfehler beim Vergleich zweier Schwärzungsskalen nicht—wie oben angenommen—über den gesamten $t/T_{\frac{1}{2}}$ -Bereich konstant bleibt, sondern normalerweise umso grösser sein wird, je kürzer der Zeitabstand t zwischen den Expositionen ist. Mit anderen Worten: $\Sigma_{z(24)}$ wird im allgemeinen fehlerhafter sein als $\Sigma_{z(48)}$, und dieser Wert wiederum fehlerhafter als $\Sigma_{z(96)}$. Entsprechendes gilt für die $n_{(t)}$ -Werte.

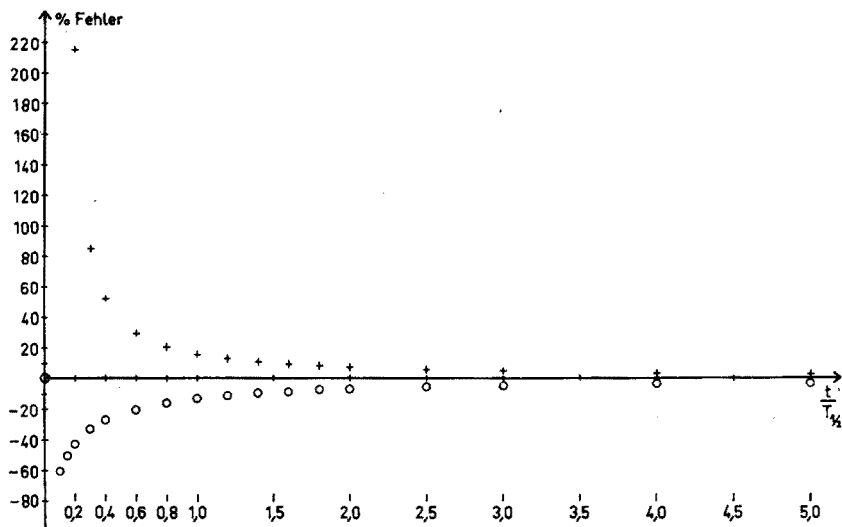


Fig. 2. Abweichung der gefundenen Halbwertszeit vom Sollwert (in %) bei einem Schätzfehler von (+) + 10%, bzw. (o) - 10%, in Abhängigkeit von $t/T_{\frac{1}{2}}$.

Auf Grund der obigen Fehlerbetrachtungen wird für die Halbwertszeitbestimmung folgendes Rechenverfahren vorgeschlagen: Man vergleiche die Autoradiogramme X, Y und Z mit dem Streifen S als Standardskala, errechne in der bereits beschriebenen Weise $n_{(24)}$, $n_{(48)}$ und $n_{(96)}$ und hieraus als vorläufiges Ergebnis $T_{\frac{1}{2}}'$. Zur endgültigen Berechnung der Halbwertszeit wähle man aus den 6 möglichen $n_{(t)}$ -Werten diejenigen aus (mindestens zwei), für welche t so gross ist, dass $t/T_{\frac{1}{2}}' \geq 1$ wird. Kann diese Forderung nicht erfüllt werden (z.B. bei $T_{\frac{1}{2}}' > 96$ Stunden), so ziehe man zur Berechnung stets die den beiden grössten Zeitspannen ($t=72$ und $t=96$ Stunden) entsprechenden Werte $n_{(72)}$ und $n_{(96)}$ heran. (Bei zu grossen Halbwertszeiten muss man—wie es später für ^{131}J beschrieben wird—unter Umständen die Zeitspannen zwischen den einzelnen Expositionen vergrössern.)

Für ^{198}Au wurde $T_{\frac{1}{2}}'$ bereits zu 56.4 h gefunden. Nach obiger Rechenvorschrift muss also der endgültige Wert für die Halbwertszeit mit Hilfe von $n_{(72)}$ und $n_{(96)}$ ermittelt werden. Hierzu ist noch ein Vergleich von Z mit X als Standardskala notwendig, der zu $n_{(72)} = 0.8355$ führt. Mit $n_{(72)}$ und $n_{(96)}$ erhält man

$$t \cdot n_{(72)} = 72 \cdot 0.8355 = 60.2 \text{ h}$$

sowie

$$t \cdot n_{(96)} = 96 \cdot 0.5758 = 55.3 \text{ h}$$

und hieraus als Mittelwert das endgültige Ergebnis

$$T_{\frac{1}{2}} = 57.8 \text{ h} = 2.41 \text{ d}$$

Die gefundene Halbwertszeit für ^{198}Au weicht vom Sollwert¹¹ 2.697 d um -10.6% ab.

WEITERE BEISPIELE

$^{99}\text{Mo}/^{99\text{m}}\text{Tc}$

Die Ringe wurden durch Waschen mit 5%iger Ammoniaklösung aus einer schwach alkalischen $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ -Lösung der spezifischen Aktivität $1.59 \mu\text{C}/\text{ml}$ bzw. $1.59 \text{ nC}/\mu\text{l}$ (Trägermenge: $1.95 \text{ mg Mo(VI)}/\text{ml}$) hergestellt. Die Expositionen (Expositionszeit wiederum 1 Stunde) von X, Y und Z erfolgten 24 Stunden, 49 Stunden bzw. 95 Stunden nach der Exposition von S ($t=0$). $T_{\frac{1}{2}}'$ wurde mit $n_{(24)}$, $n_{(49)}$ und $n_{(95)}$ zu 58.7 h berechnet. Mit $n_{(71)}$ und $n_{(95)}$ erhielten wir als Endresultat

$$T_{\frac{1}{2}} = 61.9 \text{ h} = 2.58 \text{ d}$$

Dieses Ergebnis weicht vom Sollwert¹¹ 66.0 h um -6.2% ab.

^{153}Sm

Von diesem Isotop stand uns eine salzsaure Lösung der spezifischen Aktivität $2.1 \mu\text{C}/\text{ml}$ bzw. $2.1 \text{ nC}/\mu\text{l}$ (Trägermenge: $0.06 \text{ mg Sm(III)}/\text{ml}$) zur Verfügung. Die 9 Ringe wurden durch Waschen mit 0.1 N Salzsäure angefertigt. Die Expositionen von X, Y und Z erfolgten 24 Stunden, 49 Stunden bzw. 95 Stunden nach der Exposition von S ($t=0$).

Nachdem mit Hilfe von $n_{(24)}$, $n_{(49)}$ und $n_{(95)}$ $T_{\frac{1}{2}}'$ zu 48.7 h berechnet worden war, erhielten wir mit $n_{(49)}$, $n_{(71)}$ und $n_{(95)}$ als endgültiges Ergebnis $T_{\frac{1}{2}} = 45.0 \text{ h} = 1.88 \text{ d}$. Die für ^{153}Sm gefundene Halbwertszeit weicht um -4.5% vom Sollwert¹¹ 47.1 h ab.

^{131}J

Für die Herstellung der Ringe, die mit 5%iger Ammoniaklösung gewaschen wurden, verwendeten wir eine $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}_2\text{O}_3$ -haltige ^{131}J -Lösung der spezifischen Aktivität $1.96 \mu\text{C}/\text{ml}$ bzw. $1.96 \text{ nC}/\mu\text{l}$ (Trägermenge: $0.1 \text{ mg J}^-/\text{ml}$).

Zunächst wurde mehrere Male versucht, in der gleichen Weise wie beim ^{198}Au , $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ und ^{153}Sm auch für die Halbwertszeit von ^{131}J brauchbare Ergebnisse zu erzielen. Wir erhielten jedoch stets dermassen fehlerhafte und stark streuende Einzelwerte, dass eine vernünftige Mittelwertbildung nicht mehr möglich war. Die Gründe hierfür wurden bereits bei der Fehlerbetrachtung genannt: Die Zeitspannen von $t=24$, 48 bzw. 96 Stunden für die Expositionen von X, Y bzw. Z sind gemessen an der Halbwertszeit von ^{131}J zu klein. Sie sollten nur bei solchen Radionukliden beibehalten werden, deren Halbwertszeiten maximal 100 Stunden betragen.

In einem weiteren Versuch wurden die Zeitspannen etwa verdoppelt: Die zweite Exposition (X) erfolgte 48 Stunden, die dritte (Y) 95 Stunden und die vierte (Z) 190 Stunden nach der ersten (S; $t=0$). Die Expositionszeit betrug wie bei den anderen Isotopen 1 Stunde. Mit $n_{(48)}$, $n_{(95)}$ und $n_{(190)}$ erhielten wir $T_{\frac{1}{2}}' = 156.2 \text{ h}$. Zur endgültigen Berechnung mussten also $n_{(142)}$ (durch Vergleich von Z mit X als Standardskala gewonnen) und $n_{(190)}$ herangezogen werden. Diese Werte ergaben

$$t \cdot n_{(142)} = 142 \cdot 1.3742 = 195.1 \text{ h}$$

und

$$t \cdot n_{(190)} = 190 \cdot 0.9373 = 178.1 \text{ h.}$$

Das arithmetische Mittel hiervon ist die gesuchte Halbwertszeit $T_{\frac{1}{2}} = 186.6 \text{ h} = 7.78 \text{ d}$. Durch Erhöhen der Zeitspannen t konnte also auch für die Halbwertszeit von ^{131}J ein befriedigendes Ergebnis erhalten werden, das 3.7% unter dem Sollwert¹¹ 8.08 d liegt.

Herrn Prof. Dr. W. SEELMANN-EGGEBERT, dem Direktor des Instituts für Radiochemie der Kernreaktor Bau- und Betriebsgesellschaft m.b.H., Karlsruhe, danken wir herzlich für die Überlassung von Radio-Isotopen.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Identifizierung von Radionukliden durch halbquantitative autoradiographische Bestimmung ihrer Halbwertszeit mit Hilfe der Ringofenmethode beschrieben. Hierbei wird eine Serie von 9 Ringen, die man aus verschiedenen Volumina (μl) einer Lösung des nachzuweisenden Radionuklids (spez. Aktivität 1.5–2.5 nC/ μl) anfertigt, zu einem Zeitpunkt $t=0$ und zu 3 verschiedenen Zeiten danach jeweils 1 Stunde lang auf je einen Röntgenfilmstreifen gelegt. Nach dem gemeinsamen Entwickeln der 4 Filmstreifen erhält man 4 Schwärzungsskalen (entsprechend 4 verschiedenen Zeitpunkten), die man nach der Methode des "gewogenen Mittels" gegeneinander vergleicht. Aus den gefundenen Schwärzungsabnahmen lässt sich mit Hilfe des in geeigneter Weise umgeformten Zerfallsgesetzes die Halbwertszeit des betreffenden Radionuklids ermitteln. Das Verfahren wird an den Beispielen ^{198}Au , $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, ^{153}Sm und ^{131}J erläutert.

SUMMARY

In the proposed method, a series of 9 rings is prepared from different μl -volumes of a solution of the radionuclide under test (specific activity 1.5–2.5 $\mu\text{C}/\mu\text{l}$). At a starting time $t=0$ and at 3 later times, each series of rings is placed on X-ray film strips for a period of 1 h. After the usual development of the 4 strips, 4 density scales are obtained corresponding to 4 different times, and these can be compared by the method of weighted means. From the decrease in density of the rings, the half-life of the radionuclide can be estimated. The method is explained for the examples ^{198}Au , $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, ^{153}Sm and ^{131}I .

RÉSUMÉ

Un procédé est décrit pour l'identification de radionucléides par détermination autoradiographique semiquantitative de leur période, en utilisant la méthode du four circulaire. Une série de 9 anneaux est préparée avec différents volumes (μl) d'une solution du radionucléide à examiner (activité spécifique 1.5–2.5 nC/ μl). La période du radionucléide peut être estimée en mesurant la diminution de densité de l'anneau. Exemples choisis: ^{198}Au , $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, ^{153}Sm et ^{131}I .

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ANALYSE QUALITATIVE ET QUANTITATIVE DE MELANGES COMPLEXES DE CHLORURES DE LANTHANIDES, EN UTILISANT LA DISPERSION ROTATOIRE MAGNETIQUE

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(Reçu le 9 août, 1965)

Les progrès considérables des recherches sur le groupe des lanthanides durant ces dernières années ont été conditionnés en premier lieu par la mise au point de nouvelles méthodes physiques d'analyse, beaucoup plus sensibles que les processus chimiques dans ce cas particulier.

Le problème est double: il s'agit d'une part, de déterminer les proportions relatives des différents constituants d'un mélange; il faut, d'autre part, disposer d'un procédé de dosage extrêmement sensible afin de mettre en évidence les traces éventuelles d'impuretés qu'un élément "pur" peut encore contenir.

Nous proposons une méthode physique originale, qui permet d'analyser qualitativement et quantitativement des mélanges de lanthanides en solution, et qui répond aux 2 critères ci-dessus. Elle fait appel à la technique de la dispersion rotatoire magnétique, couramment appelée "effet Faraday". Cette méthode est simple, rapide, très sélective, et ne nécessite pas l'emploi d'un matériel trop encombrant ni coûteux. Elle nous semble particulièrement bien adaptée au contrôle de la purification des lanthanides par échange d'ions. Nous avons estimé sa sensibilité et l'ordre de grandeur de l'erreur commise lors de la détermination d'une concentration.

RAPPEL DE NOTIONS UTILES

Définition du pouvoir rotatoire magnétique (effet Faraday)

Quand une vibration lumineuse monochromatique, polarisée rectilignement, tombe sur une substance placée dans un champ magnétique H parallèle aux rayons lumineux, elle tourne d'un angle α proportionnel à la différence de potentiel magnétique $H \cdot l$ entre les deux extrémités de l'échantillon:

$$\alpha_{\lambda} = A_{\lambda} \cdot H \cdot l$$

A_{λ} est la constante de Verdet de la substance pour la longueur d'onde λ ; l est son épaisseur.

En réalité, on ne dispose jamais d'une radiation purement monochromatique et le flux lumineux est réparti dans une bande passante $\Delta\lambda$. Remarquons que des

mesures sur un même échantillon au voisinage d'une longueur d'onde λ ne seront comparables que si on utilise la même bande passante.

Si nous considérons maintenant une solution de concentration c et de masse spécifique d , on peut admettre en première approximation que les contributions du soluté et du solvant à la rotation sont additives :

$$\alpha = H \cdot l \{c[A] + (d-c)[A_s]\}$$

$[A]$ et $[A_s]$ étant les pouvoirs rotatoires magnétiques spécifiques du soluté et du solvant respectivement. Cette égalité traduit la "loi d'additivité de Verdet", explicitée plus tard par d'autres auteurs^{1,2}. On a pu montrer qu'elle rendait en général bien compte des phénomènes observés, quand on dispose de solutions assez diluées et quand des associations ou des dissociations moléculaires n'interviennent pas. Dans ces conditions, $[A]$ est bien caractéristique du soluté.

Il faut souligner que, contrairement à la polarisation rotatoire naturelle, l'effet Faraday est un phénomène très général qui ne nécessite pas le choix de combinaisons chimiques privilégiées. Par contre, le fait que le solvant contribue lui-aussi à "l'activité" d'une solution complique la détermination de $[A]$.

Dispersion rotatoire magnétique

Il est particulièrement intéressant de faire des mesures de dispersion rotatoire magnétique (DRM), c'est-à-dire de connaître les variations de $[A]$ en fonction de λ . Pendant très longtemps, ces mesures ont été effectuées en dehors des régions d'absorption des solutés.

C'est COTTON³ qui eut le mérite de signaler le premier l'existence d'une dispersion "anormale" au voisinage des bandes d'absorption de certaines substances paramagnétiques. En fait, les premières mesures précises et exploitables de ce genre ont été réalisées entre 1906 et 1911 par ELIAS⁴ et concernaient des solutions aqueuses de lanthanides.

Cette technique a été relativement peu développée jusqu'à ces dernières années. Elle suscite maintenant un intérêt nouveau en raison des nombreux perfectionnements apportés aux appareils.

"Anomalies" rencontrées en région d'absorption

On a longtemps considéré 2 types d'anomalies en région d'absorption :

(1) un type diamagnétique : $[A]$ présente un minimum pour la longueur d'onde λ_0 correspondant au centre de la bande d'absorption et 2 maximums de part et d'autre du minimum. C'est le cas en particulier de certaines combinaisons organiques—transitions $\eta \rightarrow \pi^*$ de cétones aliphatiques (Fig. 1) et de composés azotés^{5,6}.

(2) un type paramagnétique : la courbe de DRM présente un point d'inflexion au voisinage immédiat de λ_0 . On rencontre ce cas lors de l'étude de nombreux ions paramagnétiques, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ et $[\text{Fe}(\text{CN})_6]^{3-}$ (Fig. 2)^{6,7}.

En fait, cette classification commode est arbitraire. Des travaux récents⁶⁻⁸ ont confirmé des observations antérieures bien résumées dans une note de COTTON⁹. Certains composés peuvent fort bien ne pas présenter d'extrémums au voisinage d'une bande d'absorption. D'autres peuvent au contraire fournir des contributions de type "diamagnétique" ou "paramagnétique" selon la région spectrale considérée. L'un de nous a souligné ce dernier point dans deux notes^{10,11} sur la DRM de tous les lantha-

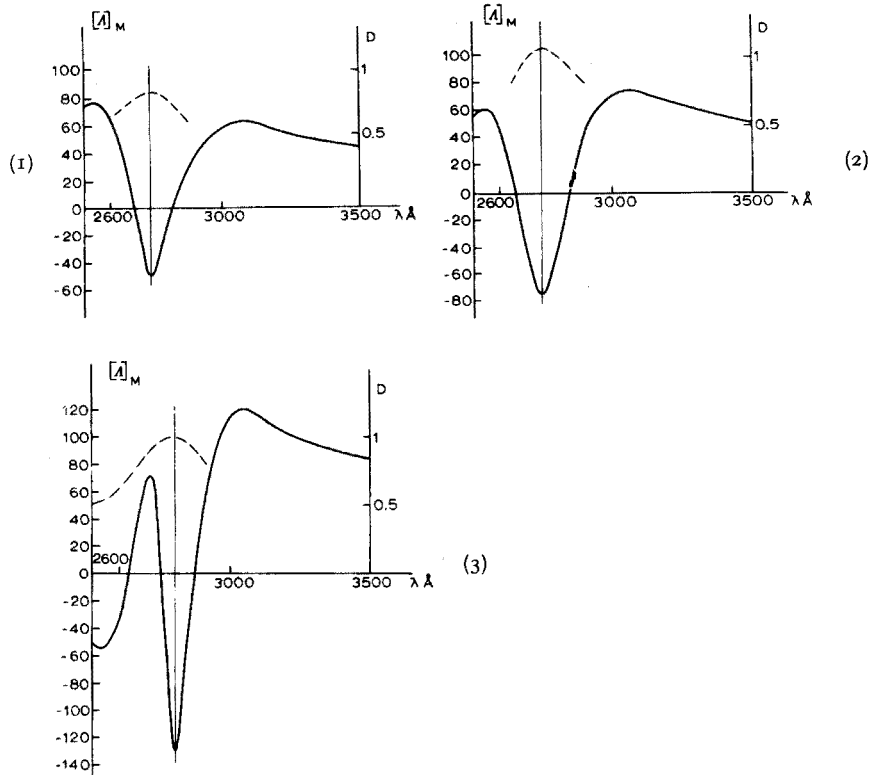


Fig. 1. DRM (—) et densité optique (---) de cétones saturées acycliques. (1) acétone; (2) méthyl-éthylcétone; (3) méthylisobutylcétone. $[A]_M$, pouvoir rotatoire magnétique moléculaire en 10^{-3} deg/g/cm/mole.

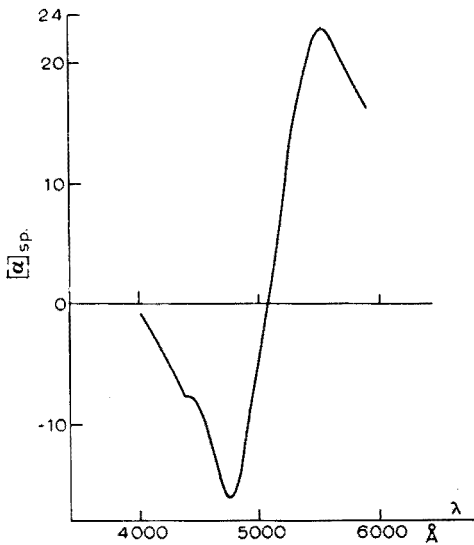


Fig. 2. DRM du cobalt acétate.

nides présentant des bandes d'absorption entre 2500 Å et 6000 Å, à la température ordinaire. A titre d'exemple, nous reproduisons (Fig. 3) le spectre du chlorure d'erbium en solution acide, à 40 g de sesquioxyde par litre. On y distingue parfaitement un type de courbe "paramagnétique" vers 2546 Å tandis qu'au voisinage des trois longueurs d'onde 3790 Å, 4873 Å et 5229 Å on observe des dispersions de type "diamagnétique".

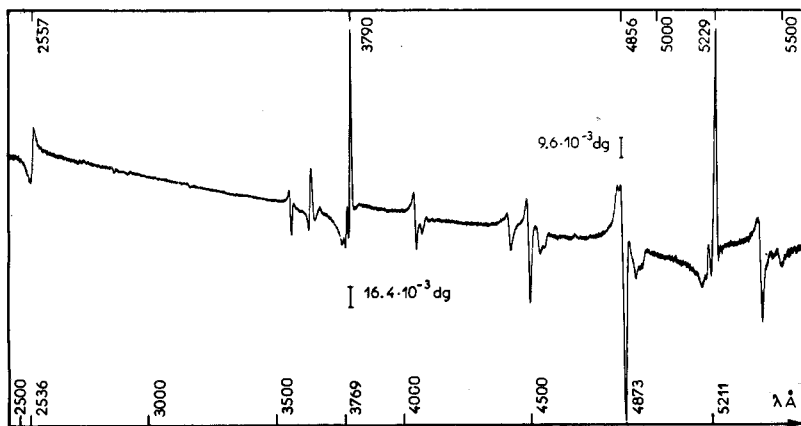


Fig. 3. Le spectre du chlorure d'erbium. 40 g/l en oxyde; pH, 1; θ , 21°; σ , 75.3.

PRINCIPE DU DOSAGE DES LANTHANIDES PAR DRM

Présentation des spectres

Le spectropolarimètre à effet Faraday dont nous disposons est particulièrement sensible; il permet de détecter des angles de rotation aussi petits que $0.4 \cdot 10^{-3}$ degré dans le domaine spectral 3000 Å–6000 Å et, à 2700 Å la sensibilité est encore de $0.7 \cdot 10^{-3}$ degré.

En outre, cet appareil est doté d'un dispositif automatique qui permet l'enregistrement en fonction de la longueur d'onde de l'angle α ou plutôt d'une grandeur i qui lui est proportionnelle ($i = \alpha / A_\lambda$). A_λ est une fonction monotone de la longueur d'onde si bien que les variations brutales de la pente de la courbe $i = f(\lambda)$ traduisent bien les anomalies de dispersion de α et par voie de conséquence, de $[A]^\circ$.

Variable choisie

Examinons les spectres présentés sur la Fig. 4. Nous avons enregistré les variations de i en fonction de λ pour 9 ions. L'un de nous a déjà signalé^{9,10} que pour chacun des éléments, il existe au moins un certain domaine $\Delta\lambda$ privilégié ($\Delta\lambda < 50$ Å) dans lequel la courbe $i = f(\lambda)$ présente un "pic", généralement très aigu. C'est évidemment ce domaine que nous avons choisi.

Nous avons songé à utiliser cette propriété pour analyser qualitativement et quantitativement des mélanges de plusieurs lanthanides. On conçoit en effet que la présence d'un élément sera décelée par l'apparition dans le spectre du mélange, d'un pic au voisinage de la longueur d'onde prévue. Par ailleurs, nous avons pu montrer expérimentalement et par le calcul que, pour un ion donné, les distances telles que

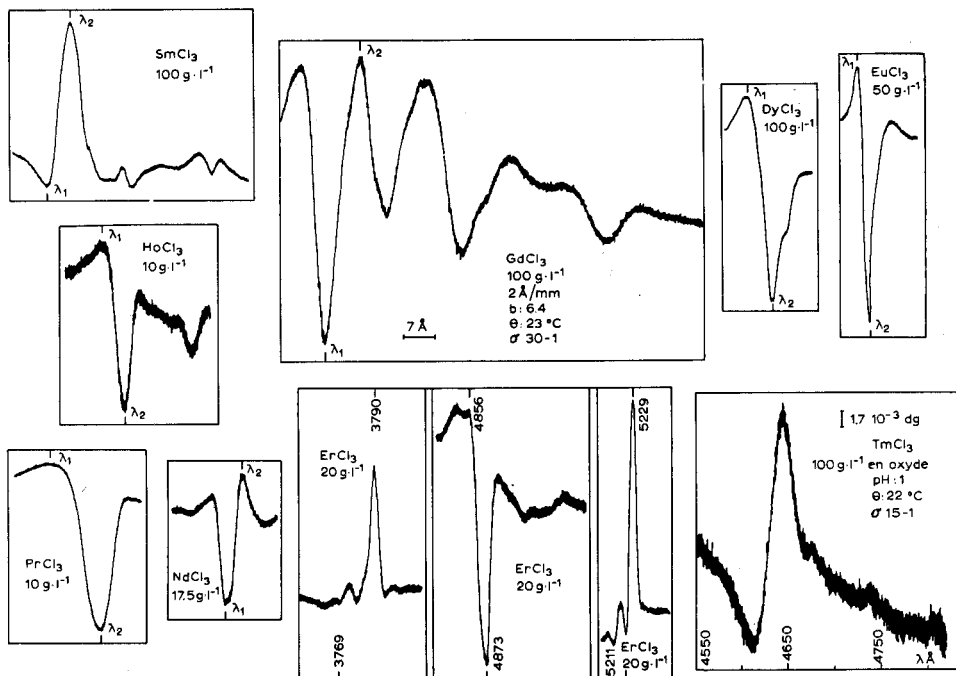


Fig. 4. Les variations de i en fonction de λ pour 9 terres rares.

$\Delta i = i_{\lambda_2} - i_{\lambda_1}$ étaient proportionnelles à la concentration de cet ion, et ceci quelle que soit la nature de la matrice cationique environnante.

Conditions opératoires

Les deux longueurs d'onde λ_1 et λ_2 sont choisies de telle façon que l'amplitude Δi du signal soit maximale. Toutefois, il est indispensable d'enregistrer la courbe $i = f(\lambda)$ au voisinage des deux extrémums choisis et non pas de faire seulement une mesure de i pour chacune des 2 longueurs d'onde λ_1 et λ_2 . Dans ce cas, une erreur de 1 Å sur le repérage de celles-ci pourrait occasionner une erreur très importante sur Δi .

DÉTAILS EXPÉRIMENTAUX

Appareillage

Nous utilisons le montage mis au point par BILLARDON¹², en remplaçant la cuve de mesure de pouvoir rotatoire naturel par une cuve de mesure de DRM. Ce montage permet une détection linéaire du signal et son enregistrement direct en fonction de la longueur d'onde λ . Nous pouvons facilement modifier l'échelle des abscisses ou des ordonnées en faisant varier la vitesse de déroulement du papier et des longueurs d'onde, ou la sensibilité du dispositif enregistreur.

Le champ magnétique (environ 5000 Oe) est produit à l'aide d'un aimant permanent. En outre, un second aimant, monté en opposition avec le premier, permet de compenser en grande partie la rotation du solvant ou de faire des mesures différentielles.

Echantillons

Les chlorures de lanthanides utilisés (à une pureté supérieure à 99,9%) ont été préparés au Laboratoire des Terres Rares du C.N.R.S. à Bellevue (S&O). Le pH des solutions est de l'ordre de 1 à 2.

Cuve de mesure

La cuve de mesure est constituée par un support en verre, les glaces de fermeture étant des disques en silice de 0,2 mm d'épaisseur, transparents dans l'ultra-violet. Ces disques sont collés sur les faces du support à l'aide d'une résine siliconée qui se polymérise rapidement à l'air.

Le volume de la cuve est voisin de 0,5 ml et ainsi, 2 ml de solution permettent son rinçage et son remplissage. Cette quantité est très faible si l'on songe que les colonnes utilisées pour la séparation des lanthanides par échange d'ions peuvent avoir une capacité de plusieurs dizaines de litres.

DOSAGE QUALITATIF DES LANTHANIDES

Éléments dosables

La DRM s'apparente par bien des points à la spectroscopie d'absorption, c'est-à-dire que les éléments qui ne présentent pas de bandes d'absorption entre 2500 Å et 6000 Å (La, Yb, Lu, Y) ne peuvent pas être décelés par la méthode proposée.

En outre, bien que le pouvoir rotatoire magnétique spécifique de l'ion Tb^{3+} varie beaucoup sur toute l'échelle spectrale, sa dispersion est assez monotone¹⁰; le spectre de cet ion ne présente pas de pic aigu qui permettrait de le mettre en évidence sans ambiguïté.

Le cas du cérium est particulier: sa présence dans un mélange peut être décelée qualitativement mais une estimation quantitative de sa concentration nous semble difficile; de plus, cet ion masque la présence éventuelle du gadolinium.

Résultats

(1) Nous avons montré que, lorsque plusieurs éléments sont présents en solution avec des concentrations voisines, on peut très facilement déceler chacun d'eux en explorant une région spectrale relativement étroite. C'est ainsi que nous avons été amenés à établir, pour 9 ions, un répertoire des domaines de longueurs d'ondes caractéristiques: c'est dans ces domaines que l'amplitude Δi du signal est la plus grande pour une concentration déterminée. Le Tableau I résume nos observations. Les valeurs de λ_1 et λ_2 sont données à titre indicatif, étant bien entendu qu'il faut enregistrer le spectre de part et d'autre de ces valeurs. Nous avons également noté le "signe" du pic observé. Un pic est positif lorsqu'il est situé au dessus du fond continu et négatif dans le cas contraire. En d'autres termes, le pic est positif lorsque la valeur de $[A]$ correspondant à l'extrémum est plus positive que celle qui correspond au fond continu dans les régions spectrales voisines. La présence dans les spectres de pics positifs et négatifs confère à la DRM un avantage incontestable sur les méthodes physiques usuelles d'analyse qualitative.

(2) La présence en solution d'éléments non identifiables ne gêne pas la détection des autres. Il faut toutefois faire une exception pour l'ion Ce^{3+} qui, comme nous l'avons signalé, masque Gd^{3+} à cause de sa forte absorption dans le proche UV.

TABLEAU I

ANALYSE QUALITATIVE DES LANTHANIDES: LONGUEURS D'ONDE DES EXTRÊMUMS ET SIGNE DES PICS OBSERVABLES

Élément	Pics intenses		Pics secondaires		Signe des pics
	λ_1^a	λ_2^a	λ_1^a	λ_2^a	
Pr	4396	4440 ^b			—
Nd	5211 ^b	5226	4811	4817 ^b	—
Sm	3987	4011 ^b	5726 ^b	5798	+
Eu	3926	3935 ^b			—
Gd	2719 ^b	2730			—
Dy	3622	3646 ^b	2700–2800		—
Ho	5338	5361 ^b	3234	3261 ^b	—
Er	3769	3790 ^b	4812	4850 ^b	+
	4856	4873 ^b			—
	5211	5229 ^b			+
Tm	4612	4642 ^b			+

^a Exprimées en angströms.^b Extrémité la plus aigüe du pic.

Afin d'illustrer ces conclusions, nous reproduisons le spectre d'un mélange de 12 constituants (Fig. 5) : les 9 ions du Tableau I, auxquels on a ajouté La^{3+} , Yb^{3+} et Tb^{3+} . La concentration de chacun d'eux est voisine de 8 g de sesquioxyde par litre (8 g/l). L'enregistrement a été effectué entre 2400 Å et 6000 Å en 72 min. Le cérium a été volontairement exclu afin de ne pas masquer le gadolinium. Huit éléments ont ainsi pu être caractérisés par la présence dans le spectre du mélange, de leurs pics intenses ainsi que de nombreux pics secondaires. Il y a seulement une ambiguïté dans le cas de l'ion Tm^{3+} qui est masqué vers 4650 Å par les pics secondaires de Ho^{3+} . Nous verrons d'ailleurs que la DRM est peu sensible pour détecter cet ion. Par contre le gadolinium est facilement décelable par la présence dans le spectre de nombreux extrémums entre 2700 Å et 2800 Å.

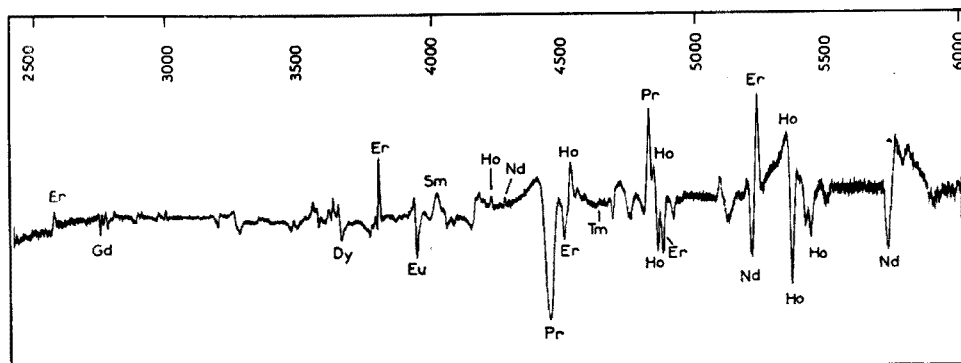


Fig. 5. Analyse qualitative d'une solution de 12 éléments: La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb. *c*, 8 g/l; σ , 30–4; θ , 22°.

Ions gênants

Les conclusions que nous avons exprimées au sujet de l'analyse qualitative d'un mélange de plusieurs éléments en concentrations sensiblement égales peuvent être en défaut si quelques éléments sont prédominants tandis que d'autres sont très dilués; il peut alors être difficile de déceler ces derniers. En effet, les pics secondaires des ions concentrés peuvent éventuellement interférer avec les pics les plus intenses des éléments minoritaires.

Nous avons pu vérifier que, dans la plupart des cas, ces interférences ne sont pas gênantes. Examinons pourtant les résultats obtenus pour des solutions ne contenant pas l'ion Ce^{3+} .

Sm^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} . Peuvent être décelés très facilement.

Pr^{3+} . Au voisinage du pic intense situé à 4440 Å, seul Er^{3+} présente un pic secondaire. Pratiquement, ces deux éléments ne se trouvent pas ensemble en solution à la sortie des colonnes échangeuses d'ions. Pourtant, si une telle éventualité se produisait, on repérerait Pr^{3+} par son pic situé vers 4817 Å.

Nd^{3+} . Seul Er^{3+} peut masquer le pic intense de cet élément. On utiliserait alors le pic situé vers 5725 Å.

Dy^{3+} . Son spectre entre 3200 Å et 3700 Å est très caractéristique. La présence simultanée de Er^{3+} ou Ho^{3+} se traduit par quelques pics très peu intenses qui ne gênent pratiquement pas l'analyse.

Er^{3+} . Il peut toujours être décelé par la présence dans le spectre du mélange, de ses 3 pics caractéristiques.

DOSAGE QUANTITATIF DES LANTHANIDES

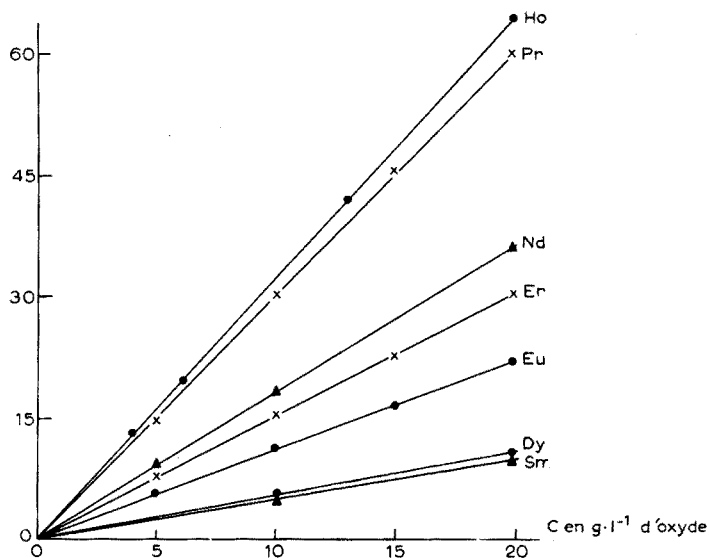
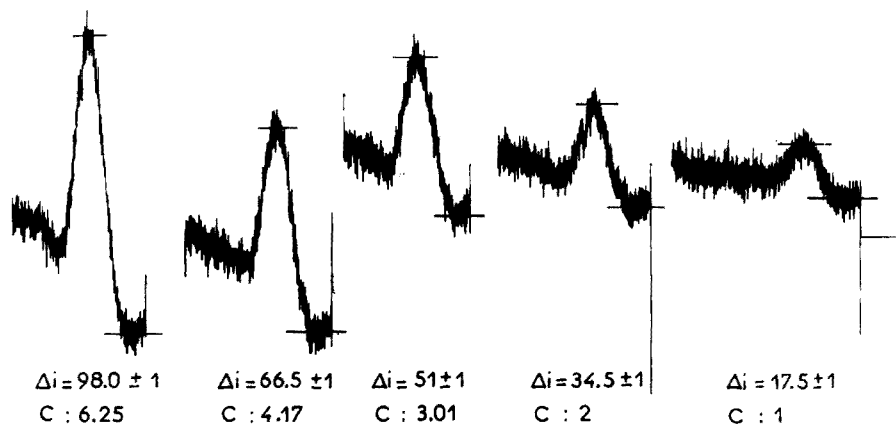
Nous avons montré pour 7 éléments (Pr, Nd, Sm, Eu, Dy, Ho, Er) que Δi entre 2 longueurs d'onde caractéristiques λ_1 et λ_2 était proportionnel à la concentration de la solution en ion M^{3+} , quelle que soit la nature en lanthanides étrangers, de la matrice environnante.

Cette étude a d'abord été effectuée pour des solutions aqueuses contenant un seul ion M^{3+} puis sur des mélanges à plusieurs constituants, rencontrés fréquemment (ions voisins dans le tableau périodique). Nous avons noté un résultat très important: la pente de la droite $\Delta i = f(c)$ pour un élément donné, ne dépend pas de la nature ni de la concentration des autres ions contenus dans la solution. Ainsi, connaissant la valeur de Δi pour une solution étalon, une concentration inconnue sera déterminée par une mesure suivie d'une règle de trois:

$$c_{\text{inconnue}} = c_{\text{étalon}} \times \frac{\Delta i_{\text{mesuré}}}{\Delta i_{\text{étalon}}}$$

Solutions M^{3+} -eau

Nous avons étudié des solutions relativement peu concentrées (généralement moins de 25 g/l à l'état de sesquioxyde). Pour chaque ion, les variations de Δi en fonction de c sont très bien représentées par une droite passant par l'origine (Fig. 6). La pente K de cette droite a été déterminée par la méthode des moindres carrés. Dans le cas particulier des ions Pr^{3+} et Ho^{3+} , nous avons effectué de nombreuses mesures pour des concentrations faibles afin de montrer que, même dans ce domaine, la loi est

Fig. 6. Δi en fonction de c pour 7 éléments.Fig. 7. Analyse quantitative de Ho^{3+} . Δi en mm; c en g/l de sesquioxyde; σ , 30-1.

bien suivie. La Fig. 7 illustre les résultats obtenus pour quelques solutions de chlorure d'holmium.

Le Tableau II résume nos observations: région spectrale explorée (valeurs approximatives de λ_1 et λ_2) et valeur numérique du coefficient K . Dans le Tableau III figurent les valeurs de Δi (unités arbitraires) en fonction de c pour les différents éléments.

Remarque. Dans le cas de Gd^{3+} et Tm^{3+} , nous n'avons pas effectué de mesures de Δi en fonction de c . Les valeurs de K qui figurent à titre indicatif dans le Tableau II, ont été extrapolées à partir de la mesure de Δi pour $c = 100$ g/l.

Mélanges de terres cériques

Nous avons étudié de nombreux mélanges binaires (La-Pr, La-Nd, Pr-Nd),

TABLEAU II

ANALYSE QUANTITATIVE DES LANTHANIDES

(λ_1 et λ_2 , longueurs d'onde de mesure exprimées en Å; ϵ , plus petite quantité décelable en g/l de sesquioxyde)

Élément	λ_1	λ_2	K	Nombre de mesures	ϵ
Pr	4396	4440	3.038	13	0.07
Nd	5211	5226	1.819	8	0.16
Sm	3987	4011	0.453	6	0.40
Eu	3926	3935	1.379	8	0.15
Gd	2719	2730	0.379	1	0.33
Dy	3622	3646	0.53	5	0.25
Ho	5338	5361	3.229	11	0.09
Er	3769	3790	1.36	8	0.09
	4856	4873	1.43	8	0.12
	5211	5229	1.52	8	0.14
Tm	4612	4642	0.146	1	1.12

TABLEAU III

VALEUR DE Δi EN FONCTION DE c

(c en g/l de sesquioxyde; Δi en unités arbitraires)

c	Pr	Nd	Sm	Eu	Dy	Ho	Er		
							5211 Å	4856 Å	3769 Å
							5229 Å	4873 Å	3790 Å
0.2	0.96								
0.5	2.04								
1	3.48					3.55			
2	6.60					7.00			
2.5	7.68	4.65					3.84	3.48	3.36
3.125						10.35			
3.33	9.96					13.50			
4.167									
5	14.64	9.30	1.95	5.73			7.80	7.32	6.84
5.208						16.40			
6.25						19.89			
7.5				8.44			11.40	10.68	10.56
10	30.10	18.23	4.10	11.46	5.5		15.30	14.40	13.40
12.5				13.67			19.00	18.23	16.75
13.125						42.40			
13.33		24.38							
15	46.06	27.77	6.65	16.68			22.47	21.20	20.40
17.5	53.81	30.95		19.10			26.50	24.80	24.20
20	59.74	36.14	9.50	22.11	10.60	64.54	30.32	28.83	27.13
25				26.93		80.30			
30					16.50				
40					21.20				
40.5			18.44						

obtenus en faisant varier notablement les proportions relatives des différents constituants. Dans tous les cas, Δi varie linéairement en fonction de c et la pente K de la droite $\Delta i = f(c)$ est la même (aux erreurs expérimentales près) que celle qui figure dans le Tableau II. Ainsi pour les mélanges La-Pr trouve-t-on 3.02 au lieu de 3.04.

L'analyse d'un mélange ternaire (La, 4 g/l; Pr, 2 g/l; Nd, 4 g/l) et de 2 mélanges quaternaires—La, Pr, Nd, Ce et Pr, Nd, Sm, Eu—a confirmé ces résultats. Dans ce der-

nier cas, nous avons pu doser Sm^{3+} et Eu^{3+} présents en quantité assez faible (2 g/l pour chacun d'eux).

Mélanges de terres yttriques

Nous avons également préparé et analysé plusieurs mélanges binaires contenant l'élément de base yttrium et des proportions variables de Dy^{3+} , Ho^{3+} , Er^{3+} .

Les solutions contenant Er^{3+} ont été étudiées pour 3 couples de longueurs d'onde. Pour toutes ces solutions ainsi que pour 2 mélanges quaternaires Y–Ho–Dy–Er nous avons retrouvé les mêmes valeurs de K que pour les ions pris séparément en solution aqueuse.

Ainsi, nous avons pu montrer expérimentalement qu'il est possible de doser un ion dans une solution lorsque les concentrations relatives des autres éléments varient dans de fortes proportions. Nous allons maintenant définir et expliciter la limite de sensibilité de la méthode proposée.

Limite de sensibilité

La limite de sensibilité de la méthode (ε en g/l de sesquioxyde) est la plus petite concentration décelable. La valeur de ε dépend de différents facteurs: reproductibilité des mesures, habileté de l'expérimentateur, etc.

Afin d'éliminer, dans la mesure du possible, le côté subjectif de son estimation, nous avons adopté la définition suivante: la limite de sensibilité (ε g/l) est la concentration pour laquelle $\Delta i = i_{\lambda_2} - i_{\lambda_1}$ (voir p. 468) est égal aux fluctuations les plus grandes.

Les valeurs de ε ont été notées dans le Tableau II. On peut constater que l'ion le plus difficile à déceler est Tm^{3+} . Toutefois, dans la plupart des cas, on peut mettre en évidence des concentrations voisines de 0,1 g/l sans aucune ambiguïté.

En fait, nous verrons dans p. 479 qu'il est possible de déceler des traces d'impuretés à une concentration très inférieure à ε . Afin de pouvoir comparer la DRM avec d'autres méthodes physiques d'analyse, nous pensons qu'il est raisonnable de diviser par 5 les valeurs du Tableau II.

Analyse différentielle

Notre appareil permet une analyse différentielle. Cette méthode est utilisée, en particulier, lorsqu'un élément difficilement décelable (Tm^{3+} ou Sm^{3+} par exemple) est à l'état de trace dans un mélange.

On détermine tout d'abord la concentration approximative des éléments les plus concentrés et l'on prépare une solution équivalente. La cuve contenant celle-ci est placée dans un champ H' antiparallèle au champ H dans lequel est placé l'échantillon à doser. Dans ces conditions, le signal détecté est proportionnel à la concentration de ce dernier et l'on ne redoute pas les interférences dues aux pics secondaires des éléments les plus concentrés. C'est ainsi que nous avons dosé Sm^{3+} (0,5 g/l) dans 2 mélanges à base de Pr^{3+} , Nd^{3+} , Ce^{3+} , La^{3+} , avec une précision meilleure que 10%.

JUSTIFICATION DE LA MÉTHODE PROPOSÉE

Hypothèses

Afin de simplifier le calcul et d'estimer l'ordre de grandeur de l'erreur commise dans la détermination d'une concentration, nous ferons les hypothèses suivantes:

(1) on mesure la différence $\Delta\alpha$ des rotations pour les 2 longueurs d'onde λ_1 et λ_2 (ceci ne poserait pas de difficulté technologique majeure avec un appareillage plus élaboré).

(2) on suppose que lors du mélange, il n'y a aucune modification du volume de chacun des composants pris séparément. Ce n'est là qu'une loi approchée, mais elle est relativement bien suivie tant que l'on demeure dans un domaine de concentrations assez faibles et qu'il n'y a pas d'associations moléculaires.

Données du problème

On désigne par c et $[A]$ la concentration (en g/ml) et le pouvoir rotatoire magnétique spécifique de l'élément à doser. c_i et $[A_i]$ représentent les mêmes données pour les autres ions contenus dans la solution. d , d_s et d_x sont les masses spécifiques respectives de la solution, du solvant et du soluté. $[A_s]$ est le pouvoir rotatoire magnétique spécifique du solvant.

Au début de la mesure, les polariseurs peuvent être décroisés d'un certain angle; soit α_0 cet angle. Sa valeur ne change pas entre les 2 longueurs d'onde λ_1 et λ_2 .

Le différence de potentiel magnétique entre les deux extrémités de la cuve de mesure est Hl . Une deuxième cuve contenant le solvant (longueur l') est disposée dans un champ H' antiparallèle à H .

Dosage d'un seul ion en solution

Pour une longueur d'onde λ , l'angle de rotation enregistré est :

$$\alpha = \alpha_0 + H \cdot l \{c[A] + (d-c)[A_s]\} - H' \cdot l' [A_s] d_s$$

En pratique, $H' \cdot l'$ est très voisin de $H \cdot l$ et l'on peut poser $H' \cdot l' = k \cdot H \cdot l$, k étant une constante peu différente de 1 (légèrement inférieure pour notre montage). Il vient :

$$\alpha = \alpha_0 + H \cdot l \{c[A] + (d-c-kd_s)[A_s]\}$$

Explicitons notre seconde hypothèse. On obtient la relation :

$$d = c + \left(1 - \frac{c}{d_x}\right) d_s$$

d'où

$$d - c - kd_s = \left(-\frac{c}{d_x} + 1 - k\right) d_s$$

$$\alpha = \alpha_0 + H \cdot l \left\{c[A] + \left(-\frac{c}{d_x} + 1 - k\right) A_s\right\}$$

A_s désigne la constante de Verdet du solvant ($A_s = [A_s] d_s$)

Calculons alors la différence $\Delta\alpha$ des rotations pour 2 longueurs d'onde voisines λ_1 et λ_2 :

$$\Delta\alpha = Hl \left\{c \cdot \Delta[A] + \left(-\frac{c}{d_x} + 1 - k\right) \Delta A_s\right\}$$

Ainsi peut-on constater que $\Delta\alpha$ est proportionnel à c quand k est égal à l'unité ou

lorsque l'on peut ajuster sa valeur pour chaque concentration et chaque soluté de telle façon que $k = 1 - c/d_x$. Ceci est techniquement réalisable.

Le montage que nous avons utilisé ne permet pas cet ajustement du coefficient k si bien que les variations de $\Delta\alpha$ en fonction de c sont représentées par une droite qui ne passe pas par l'origine. L'ordonnée à l'origine est égale à $H \cdot l(1-k)\Delta A_s$. En pratique, pour un intervalle $\Delta\lambda$ d'une vingtaine d'angströms, sa valeur est voisine de $0.2 \cdot 10^{-3}$ dg. L'appareil permettant de déceler des rotations aussi petites que $0.4 \cdot 10^{-3}$ dg, l'erreur commise à la limite de sensibilité serait de 50% si l'on ne faisait pas de correction.

Dosage d'un ion en présence de plusieurs autres

Il vient alors :

$$\Delta\alpha = H \cdot l \left\{ c\Delta[A] + \sum_i c_i \Delta[A_i] + \left(-\frac{c}{d_x} - \sum_i \frac{c_i}{d_{i_x}} + 1 - k \right) \Delta A_s \right\}$$

On constate que si l'on dilue un mélange donné, tout se passe comme si le seul élément de concentration c était dissout. En effet, tous les termes tels que c_i sont alors proportionnels à c .

Il y a un terme d'erreur supplémentaire lorsque les proportions relatives des différents constituants varient de façon notable. En pratique, le terme $\sum_i \frac{c_i}{d_{i_x}} \Delta A_s$ est petit devant le terme $\sum c_i \Delta[A_i]$. Par ailleurs, nous avons pu montrer expérimentalement et par le calcul que ce dernier était en général négligeable. De toute façon, on peut envisager d'établir une fois pour toutes une table de correction où seraient notés les d_{i_x} de tous les éléments dosables et leurs $\Delta[A_i]$ pour tous les couples de longueurs d'onde λ_1 et λ_2 . Dès lors, la connaissance approximative des c_i permettrait de corriger la valeur déterminée pour c .

Si l'on utilise la méthode différentielle, tout se passe comme si l'ion à doser était seul en solution.

Conclusion

Le calcul du terme d'erreur a été effectué en supposant que l'on mesurait une différence d'angles de rotation. En fait, avec notre appareil, nous détectons un signal Δi . Nous avons pu montrer que dans ce cas, le choix d'une formule à un seul terme ($\Delta i = k \cdot c$) était bien fondé à condition de choisir judicieusement l'angle α_0 . Bien plus, il n'est plus alors besoin de faire notre seconde hypothèse.

Quand l'angle α_0 est quelconque, le terme correctif reste faible. Ainsi, à la limite de détection de l'ion Pr^{3+} l'erreur peut être réduite à moins de 10%.

DIFFÉRENTES CAUSES D'ERREUR. PRÉCISION DU RÉSULTAT

Expérimentalement et par le calcul, nous avons montré que les distances Δi étaient proportionnelles à la concentration des solutions en un élément donné. Nous avons souligné que le terme correctif est, soit négligeable, soit calculable. Nous n'en tiendrons donc pas compte dans l'estimation des erreurs.

Pour un élément donné, le coefficient K de proportionnalité ne dépend pas de c ni de l'environnement cationique de l'ion, quand la température reste voisine de 25°. Qu'advient-il si l'on modifiait notablement cette dernière?

Influence de la température

Les mesures ont généralement été effectuées à 25° ou 26° sans utiliser un dispositif thermostaté. Les théories de la DRM laissent prévoir pour les lanthanides une augmentation de $[\Delta]$ (donc de Δi) inversement proportionnelle à la température absolue. On a donc $\Delta c/c = -\Delta T/T$ c'est-à-dire qu'une variation de température de 1° peut conduire à une erreur relative de $3 \cdot 10^{-3}$ sur la concentration.

En fait, nous avons effectué une mesure sur des échantillons de Sm^{3+} et de Nd^{3+} refroidis à 5° puis introduits dans l'entrefer; nous n'avons pas noté de variation sensible de Δi .

Dès lors, la précision d'un résultat (écart en pourcentage entre la valeur exacte et la valeur déterminée) ne dépend plus que de la reproductibilité des mesures et de l'erreur commise à la lecture du diagramme.

Reproductibilité des mesures

La Fig. 8 montre les résultats obtenus avec une solution de chlorure d'holmium à 1 g/l en sesquioxyde. On peut estimer que les mesures sont reproductibles à 1 ou 2% près. Nous avons effectué le même essai avec une concentration de 10 g/l et une sensibilité beaucoup plus faible; nous avons obtenu des écarts inférieurs à 1% par rapport à la valeur moyenne.

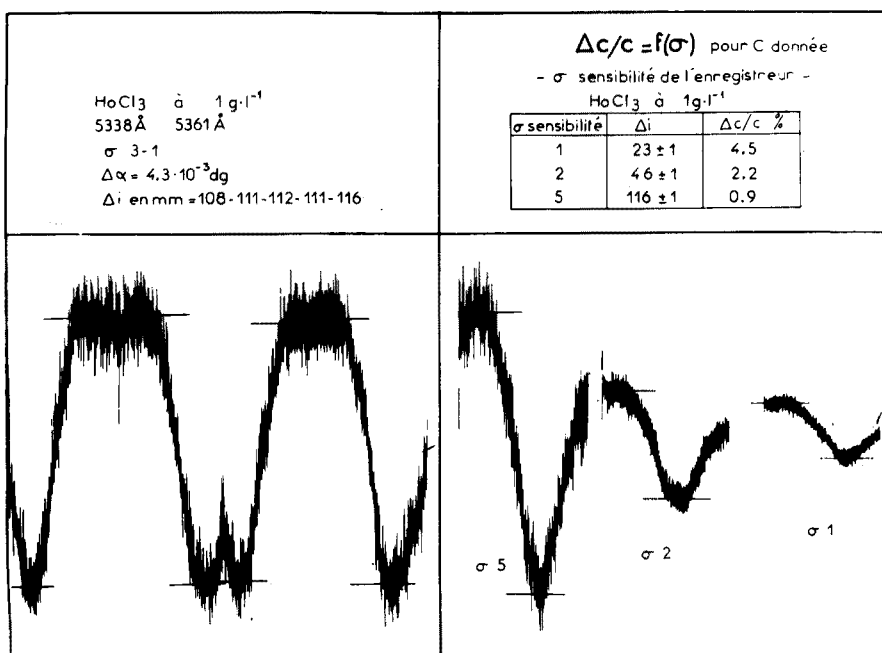


Fig. 8. Reproductibilité d'une mesure.

Erreur de lecture du diagramme

Nous avons vu que les résultats étaient reproductibles à environ 1 ou 2% près, tant que la concentration est au moins égale à 1 g/l.

Il n'en est plus de même quand c est plus faible que 1 ou 2 g/l.

Les fluctuations du signal sont importantes et il devient difficile de repérer leur centre avec une bonne approximation. Afin d'estimer l'erreur commise, nous avons effectué plusieurs essais :

(a) la Fig. 7 montre que, si l'on conserve la même sensibilité et que l'on dilue la solution, l'erreur *absolue* sur Δi est pratiquement constante.

(b) sur la Fig. 8, nous avons enregistré les variations de Δi en fonction de λ pour une solution de chlorure d'holmium à 1 g/l, en faisant varier la sensibilité du dispositif de mesure du signal. On constate, là encore, que l'erreur *absolue* sur le repérage de Δi est indépendante de la sensibilité. Ainsi, la précision est-elle d'autant plus grande que la sensibilité est plus grande. En pratique, pour les très faibles concentrations, on choisit la sensibilité de façon que la trace des fluctuations sur le papier d'enregistrement soit de l'ordre de 20 mm. Dans ces conditions, si l'on admet que l'incertitude sur Δi est de 1 mm, on constate qu'il est possible de mettre en évidence des traces aussi petites que $\varepsilon/10$. En fait, cette estimation est très difficile; afin de comparer la DRM aux autres méthodes physiques d'analyse, nous considérerons que la plus petite quantité décelable (avec une précision de 50%) est de l'ordre de $\varepsilon/5$. C'est en fait la véritable limite de sensibilité de la méthode.

CRITIQUE DE LA MÉTHODE

Rappel des performances

(1) *Sélectivité*. La méthode proposée est très sélective; elle permet de mettre en évidence sans ambiguïté la présence de 8 éléments dans une solution. En outre, la présence de pics de signes opposés dans les spectres, lui confère un grand avantage sur les méthodes usuelles d'analyse qualitative des lanthanides.

(2) *Sensibilité*. Si l'on excepte l'ion Tm^{3+} difficile à doser à l'état de trace, il est possible de mettre en évidence très facilement des quantités ε d'élément de l'ordre de 0.1 g/l (à l'état de sesquioxyde). Nous avons signalé également que l'on peut doser des traces aussi petites que $\varepsilon/5$, à condition de prendre certaines précautions.

(3) *Précision*. Elle dépend naturellement de la concentration à déterminer et elle est limitée par la reproductibilité des mesures et l'erreur commise lors de la lecture de l'enregistrement. Résumons les résultats obtenus :

$c \geq 5$ g/l: $\Delta c/c \sim 1\%$ (reproductibilité d'une mesure),

1 g/l < c < 5 g/l: $\Delta c/c \sim 1-2\%$ (reproductibilité + lecture du diagramme),

$\varepsilon/5 < c < 1$ g/l: $\Delta c/c$ varie sensiblement linéairement en fonction de $1/c$ entre les valeurs extrêmes 2% et 50% (difficulté de lecture du diagramme obtenu).

Améliorations possibles

Il est possible de diminuer notablement la limite de détection et d'augmenter la précision en apportant une modification au montage. En effet, celui-ci a été conçu pour étudier la DRM en région d'absorption intense et l'on peut montrer que, dans ce cas, le signal est proportionnel au champ H quelle que soit la longueur l . Ceci nous a conduit à l'utilisation d'aimants permanents peu encombrants.

L'ion Ce^{3+} mis à part, les lanthanides ne présentent pas dans les régions spectrales considérées, des bandes d'absorption intenses et, dans ce cas, le signal est proportionnel à $H \cdot l$. Il est possible de le multiplier par 10 en utilisant par exemple un solénoïde qui donnerait un champ de 1000 Oe sur une longueur de 10 cm. Le volume

de la cuve serait de 8 ml mais on pourrait déceler une concentration moyenne de l'ordre de 0.003 g/l. Si l'on suppose que les solutions utilisées ont une concentration de 10 g/l en élément de base, on peut alors repérer $3 \cdot 10^{-4}$ parties d'impuretés.

On peut également concentrer les solutions avant d'effectuer la mesure; dans ces conditions, on peut espérer mettre en évidence 30 p.p.m. d'impuretés.

Remarque

La méthode a été développée à partir de mesures effectuées sur des chlorures. Pour une utilisation pratique éventuelle, il serait évidemment judicieux d'effectuer des mesures semblables en modifiant l'anion ou en complexant les éléments. Il serait alors sans doute possible de généraliser nos résultats et d'analyser des solutions telles qu'elles se présentent dans une colonne échangeuse d'ions.

CONCLUSION

En conclusion, nous nous proposons de comparer la DRM avec d'autres méthodes physiques d'analyse des lanthanides.

En dehors des techniques faisant appel à des propriétés nucléaires (spectrographie de masse, analyse par activité), les principales méthodes d'analyse des éléments des terres rares sont des méthodes spectrales—spectrographie d'arc ou de flamme, spectrométrie par fluorescence de rayons X, spectrométrie d'absorption. C'est à ces 2 dernières que s'apparente la dispersion rotatoire magnétique, non pas dans son principe, mais par la similitude des modes opératoires, le même caractère non destructif, et par les possibilités qu'elle offre également en tant que méthode d'analyse quantitative.

La spectrométrie par fluorescence X présente certes l'avantage de permettre l'analyse de tous les éléments des terres rares, tandis que la DRM comme la spectrométrie d'absorption, est inapplicable dans le cas des éléments qui ne possèdent pas de bandes d'absorption dans le spectre visible ou proche ultra-violet.

Du point de vue de la sensibilité, la comparaison n'est pas défavorable à la DRM. On dose facilement 0.1 g de sesquioxyde par litre de solution, et si d'un élément à l'autre les limites de détection sont assez variables (la sensibilité est bien meilleure pour Pr, Ho et Er que pour Tm) il en est de même pour la spectrométrie X (la sensibilité est 10 fois moins grande pour les éléments cériques que pour les derniers éléments yttriques—Er, Tm, Yb, Lu) et pour la spectrométrie d'absorption.

La comparaison apparaît encore plus favorable à notre méthode quand il s'agit d'opérer sur des solutions contenant un nombre assez élevé d'éléments. En spectrométrie X, les interférences rendent le dosage simultané de 4 ou 5 ions voisins très délicat, dans presque toute la série des lanthanides; seuls La, Ce, et Pr, d'une part, Yb et Lu d'autre part, échappent à cette difficulté. En absorption, l'élargissement des bandes en fonction de la concentration interdit pratiquement, en présence d'un élément très abondant, le dosage de la plupart des autres terres rares. Les spectres de DRM restent certainement plus utilisables dans ces conditions et de plus, l'existence dans un même spectre d'extrémums de part et d'autre du fond continu lui confère un avantage supplémentaire; elle permet, dans certains cas, de lever l'obstacle des interférences.

Finalement, on peut estimer que la méthode de dosage que nous proposons

pour l'analyse des mélanges de terres rares en solution se classe très favorablement parmi les autres procédés actuellement les plus utilisés. La mise en oeuvre est simple et il faut peu de temps pour effectuer une analyse. On peut envisager de l'associer à une méthode complémentaire telle que la spectrographie de flamme, et l'on disposera ainsi d'un ensemble d'équipement analytique permettant de résoudre dans les meilleures conditions les problèmes de dosage des éléments de la série des lanthanides.

Nous tenons à remercier Mlle. CLERC (Laboratoire des Terres Rares du C.N.R.S.) qui a préparé les échantillons et contrôlé leur pureté, et M. LELIBOUX (Laboratoire d'Optique Physique, EPCI) qui a préparé de nombreux mélanges et effectué une partie des travaux expérimentaux.

RÉSUMÉ

On présente les caractéristiques essentielles d'une méthode physique d'analyse tout à fait nouvelle, qui permet le dosage qualitatif et quantitatif de mélanges complexes de lanthanides. Les auteurs utilisent le fait que les spectres de dispersion rotatoire magnétique (DRM) de ces éléments présentent des raies fines très caractéristiques. Le spectropolarimètre photoélectrique enregistreur utilisé est décrit brièvement.

La DRM est comparée avec 2 autres procédés physiques d'analyse—la spectrométrie d'absorption et la spectrométrie de rayons X. Il s'avère que son choix est particulièrement judicieux quand on désire analyser un mélange contenant plus de 3 ou 4 éléments (grande sélectivité). La plus petite quantité décelable et la précision des résultats ont été estimées pour chaque élément dosable. Enfin, des améliorations notables sont suggérées.

SUMMARY

The general features of a new physical process for the qualitative and quantitative routine analysis of rare earth mixtures are given. The characteristic sharp lines in the magneto-optical rotation spectra of these elements are utilized. The recording photoelectric spectropolarimeter used is described briefly. A comparison is made with two other physical processes—absorption and X-ray fluorescence spectrometry. The proposed method appears to be the best when a mixture with more than 3 or 4 elements must be analysed. The sensitivity and accuracy are given for 9 rare earths. Improvements of the process are suggested.

ZUSAMMENFASSUNG

Es wird eine neue physikalische Analysenmethode vorgeschlagen, die es erlaubt, Mischungen von Lanthaniden qualitativ und quantitativ zu analysieren. Sie beruht auf der Tatsache, dass magnetische Rotationsspektren sehr charakteristische feine Linien aufweisen. Ein Vergleich des Verfahrens mit der Absorptions- und der Röntgenspektroanalyse zeigt, dass es vorteilhaft für Mischungen mit 3 und mehr Elementen angewendet werden kann. Die Nachweisgrenzen und die Genauigkeit des Verfahrens werden angegeben und Verbesserungen vorgeschlagen.

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Anal. Chim. Acta, 34 (1966) 465-482

SHORT COMMUNICATIONS

Ion-exchange chromatography by displacement development using electrical conductivity of the resin to detect fractions

Measurement of electrical conductance of solutions effluent from chromatographic columns has long been used as a means of detecting fractions^{1,2}. However, conductance measurements have not proven widely useful for such application to ion-exchange chromatography.

Ion-exchange chromatography normally involves elution or displacement development with solutions of high conductance³⁻⁵. Since the concentration of an eluted ion is ordinarily relatively low, the conductivity of the effluent solution will change little upon the emergence of a fraction. For that reason other methods of analysis have been commonly used in conjunction with ion-exchange chromatography.

Because of the variation in the selectivity of a resin for different ions and the accompanying different mobilities of those ionic species within the resin, the conductance of a resin will differ depending upon the ionic species present, more so than do equivalent aqueous solutions of those ions⁶. The expectation was therefore held that measurement of electrical conductance might be used as a means of detecting bands developed in an ion-exchange column if the conductance of the resin itself at the exit end of the column were measured.

Materials

The resin used was a sulfonated polystyrene cation-exchange resin, Dowex 50W-X4, 50-100 mesh. Salts used were all reagent-grade chlorides. Water was boiler condensate which was passed through an Illco-Way Research Model de-ionizer.

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Apparatus

The columns used had a diameter of about 2.5 mm and were 400 mm long. As shown in Fig. 1, at the exit end of the column were 2 electrodes of platinized platinum wire, in intimate contact with the resin bed. The combined resistance of the resin and solution between the electrodes was measured with an Industrial Instruments, Inc. Model RC16B1 conductivity bridge.

Procedure

A solution containing known amounts of sodium, magnesium and calcium chlorides was passed through the column in the hydrogen form at a rate of 0.5 ml/min. Development of the mixture thus adsorbed was by displacement using a 0.00500 *M* solution of barium chloride. The flow rate of the displacing solution was also 0.5 ml/min.

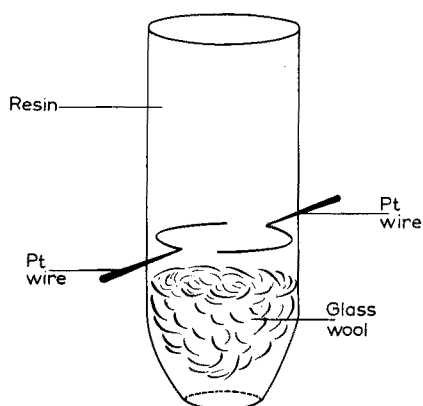


Fig. 1. Electrode-containing portion of the ion-exchange chromatographic column.

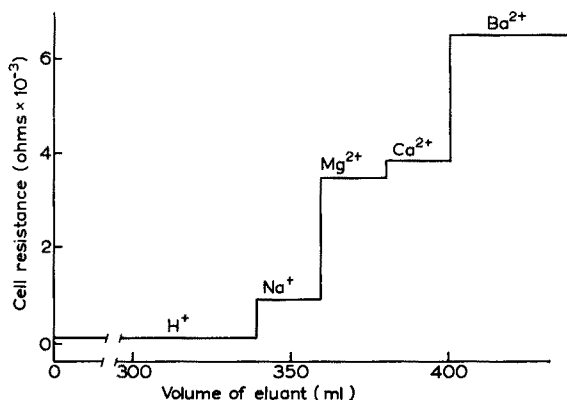


Fig. 2. Displacement analysis of a sodium, magnesium and calcium chloride mixture on a 400 mm \times 2.5 mm column of Dowex 50W-X4 at a flow rate of 0.5 ml/min. Eluant solution, 0.00500 *M* barium chloride.

Results and discussion

Figure 2 shows results obtained by displacement analysis of a mixture of sodium, magnesium and calcium chlorides.

The resistance of the resin bed is seen to be a qualitative indication of the ion emerging and a quantitative measurement is obtained in the number of equivalents

TABLE I

DETERMINATION OF SODIUM, MAGNESIUM AND CALCIUM IONS BY DISPLACEMENT ANALYSIS IN AN ION-EXCHANGE COLUMN

<i>Sodium</i>		<i>Magnesium</i>		<i>Calcium</i>	
<i>Added</i> (mg)	<i>Found</i> (mg)	<i>Added</i> (mg)	<i>Found</i> (mg)	<i>Added</i> (mg)	<i>Found</i> (mg)
4.60	4.55				
9.12	9.09				
		2.43	2.49		
		4.86	4.93		
				4.01	3.92
				8.02	9.91
4.60	4.57	2.43	2.39	4.01	4.04
9.12	9.06	4.86	4.81	8.02	8.09

of barium ion added while the front is passing (measurement is from inflection point to inflection point).

The results of development of single salts and mixtures are indicated in Table I.

Application of the method to analysis of ion mixtures which are separable by displacement development and also to mixtures involving elution development with weak electrolytes is anticipated. Analyses of natural waters, soil extracts, etc. are possible applications of the method.

This work was supported in part by state-appropriated funds for organized research at Southwest Texas State College.

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(Received July 11th, 1965)

An EDTA method for the determination of magnesium in aluminum-base alloys

The traditional gravimetric method for the determination of magnesium in aluminum-base alloys requires nearly a day per analysis because of the separation steps before the precipitation of magnesium as magnesium ammonium phosphate¹. The ASTM procedure² is somewhat similar; major amounts of aluminum are separated as sodium aluminate and iron and manganese are removed with ammonia and bromine, before titration of magnesium with EDTA. The ASTM method may be completed in half the time required by the older method but it still requires two separation steps.

In the proposed procedure for alloys containing 1–10% magnesium, the dissolution of the alloy as well as the separation and purification of the magnesium are effected in one simple step. Sodium hydroxide, in the presence of complexing agents, *i.e.* triethanolamine (TEA) and sodium cyanide, is used to dissolve aluminum and to precipitate magnesium hydroxide. Under these conditions major amounts of the interfering elements are separated from magnesium hydroxide because they form soluble complexes with cyanide or TEA, or they are subsequently converted to a soluble form by hydrogen peroxide. The magnesium hydroxide is dissolved, masking agents are added, the pH is adjusted, and the magnesium is titrated with EDTA.

Reagents

pH 10 buffer solution. Dissolve 67.5 g of ammonium chloride and 570 ml of ammonium hydroxide (s.g. 0.89) in sufficient distilled water to make 1 l.

EDTA solution. Prepare a 0.05 M solution of the disodium salt. Standardize against pure zinc (Bunker Hill 99.9985%) if high purity magnesium is not available.

Standard magnesium solution, 0.05 M. Dissolve 1.216 g of high purity magnesium (Belmont 99.8%) in 200 ml of 20% hydrochloric acid and dilute to 1 l.

Indicator. Mix eriochrome black T (J. T. Baker Chemical Co.) with sodium chloride in the ratio of 1:100. Calmagite (G. F. Smith Chemical Co.) can also be used and has a somewhat sharper end-point.

All other reagents were analyzed-reagent grade.

Procedure

Dissolution. Select a sample weight so that the aliquot finally taken will contain about 5 mg of magnesium or require about 4 ml of 0.05 M EDTA. Accurately weigh shavings of the sample into a 250-ml beaker. Add 1 g of sodium cyanide, 10–20 ml of TEA, 5–6 g of sodium hydroxide and 10–20 ml of water; cover the beaker, and swirl to dissolve the sodium hydroxide if the reaction does not begin within a few minutes. Double the amount of sodium hydroxide if it is necessary to take a sample weight of 2 g or larger. After the violent dissolution reaction subsides, heat the sample to insure complete reaction. When the dissolution is complete, add about 5 ml of 30% hydrogen peroxide dropwise. Dilute the sample with about 150 ml of water and digest for 15–20 min. Filter the sample through a Whatman No. 52 paper, or any similar paper which is compatible with sodium hydroxide. Wash this precipitate thoroughly with hot water so as to insure the removal of sodium cyanide.

Separation. Discard the filtrate (in a hood) and place the original 250-ml beaker under the funnel containing the precipitate of magnesium hydroxide. Dissolve this precipitate with about 40 ml of hot 1:1 hydrochloric acid. Rinse the paper thoroughly. Add a few drops of peroxide and boil the sample to remove the excess acid. Do not allow the sample to go to dryness. Dilute the sample to volume.

Titration. Treat an appropriate aliquot in a 150-ml beaker with 10 ml of 10% TEA solution, about 0.2 g of ascorbic acid, 20 ml of pH 10 buffer, 1 g of sodium cyanide, and about 0.5 g of the indicator. Titrate with standardized EDTA to the blue end-point and calculate the percent magnesium.

Results and discussion

The development and evaluation of the proposed method was based on the analysis of the standard NBS 85b, which is a wrought aluminum alloy with 93.1% aluminum; the other components are listed in Table I. The NBS alloy was analyzed

TABLE I
DETERMINATION OF MAGNESIUM IN ALUMINUM-BASE STANDARDS

Sample no.	Nominal chemical composition (%)	Mg%	
		Certified (\pm range)	Found ($\pm \sigma$)
NBS 85b	Cu 3.99, Mn 0.61, Fe 0.24, Si 0.18, Ni 0.08, Ti 0.02, Zn 0.03, Pb 0.02, V 0.006, Ga 0.02, Cr 0.21	1.49 \pm 0.01	1.49 \pm 0.02
Series No. 1362 ^a	Cu 1.02, Mn 0.04, Fe 0.40, Si 18.1, Ni 1.10, Ti 0.025, Zn 0.037, Pb 0.025, Bi 0.031, Sn 0.03, Cr 0.07	1.06	1.07 \pm 0.03
Series No. 1369 ^a	Cu 3.20, Mn 0.28, Fe 0.65, Si 10.62, Ni 0.10, Ti 0.09, Zn 0.85, Pb 0.045, Bi 0.03, Sn 0.04, Cr 0.04, Ca 0.0015	1.05	1.03 \pm 0.02
BCS 181/1	Cu 3.99, Mn 0.10, Fe 0.36, Si 0.38, Ni 2.04, Ti 0.14, Zn 0.02, Pb 0.02, Sn 0.02, Cr < 0.01	1.42 \pm 0.03	1.41 \pm 0.01
BCS 216/1	Cu 4.42, Mn 0.73, Fe 0.40, Si 0.74, Ni 0.06, Ti 0.10, Zn 0.11, Pb 0.05, Sn 0.05, Sb 0.05	0.74 \pm 0.01	0.75 \pm 0.03
BCS 262	Cu 0.03, Mn 0.06, Fe 0.19, Si 0.10, Ti 0.10, Zn 0.05, Cr 0.06	10.57 \pm 0.05	10.57 \pm 0.03
BCS 300	Cu 1.28, Mn 0.41, Fe 0.30, Si 0.16, Ni < 0.02, Ti 0.15, Zn 5.98, Pb 0.003, Sn 0.006, Cr 0.15	2.76 \pm 0.06	2.76 \pm 0.02

^a Aluminium Laboratory Ltd., Arvida, Que.

successfully by the ASTM method²; however, when the second precipitation step was eliminated and the titration was done in the presence of masking agents, the results were about 13% high. Iron and manganese were thought to be the major causes for the high results, but when iron was removed by extraction with tri-*n*-butylphosphate or tri-*n*-octylphosphine oxide, the results were still 9–13% high. Apparently manganese was the major cause of interference and its effect could only be eliminated by separation.

Sodium hydroxide precipitates nickel(II), iron(III) and manganese(II) hydroxides, which are thus separated with magnesium hydroxide and interfere in the subsequent EDTA titration. When TEA and sodium cyanide are added to the hydrox-

ides of nickel, iron, or manganese, soluble complexes of these ions are formed. Similarly hydrogen peroxide converts titanium and chromium to soluble species. Thus a relatively pure precipitate of magnesium hydroxide can be obtained by the use of masking agents along with the sodium hydroxide dissolution of aluminum.

Magnesium hydroxide formed by the dissolution of an aluminum-base alloy with sodium hydroxide in the presence of complexing agents is certainly not chemically pure; small amounts of aluminum and other metals are likely to be occluded and an element like iron may be present in a form which is not attacked by sodium hydroxide, thus remaining with the magnesium hydroxide. It is therefore important to add TEA to mask small amounts of aluminum, manganese or iron which are still present. Cyanide is added to the basic solution to prevent EDTA from reacting with any nickel, copper, or zinc which may still be present. Cyanide may also react with manganese, or with iron to form ferricyanide; therefore, some ascorbic acid is added to reduce the iron(III) complex to ferrocyanide, which does not oxidize the indicator. Interfering amounts of calcium are not normally present in aluminum-base alloys. If a measurable amount of calcium is present it may be removed by oxalate precipitation³ or the EDTA titration can be carried out under slightly different conditions, *e.g.* at pH 12 with calcein indicator to determine only calcium⁴; EDTA forms complexes with both magnesium and calcium at pH 10 but only with calcium at pH 12.

The precision and accuracy of the procedure was demonstrated by the analysis of NBS 85b, which is certified to contain 1.49% magnesium. Twelve determinations showed the precision to be $\pm 0.02\%$; similarly, the exact mean was in the interval $1.49 \pm 0.005\%$. Additional aluminum-base standards were analyzed by the proposed procedure. Examination of the data given in Table I shows that milligram quantities of Ni, Cu, Zn, Mn, Fe, Cr and Ti are present and do not interfere. Magnesium at the 1–10% level can be determined with an accuracy of $\pm 0.01\%$.

The proposed method is applicable only to aluminum-base alloys which are dissolved with sodium hydroxide. Most aluminum alloys consist of aluminum, solid solutions of aluminum, or intermetallic compounds of aluminum, all of which are dissolved by sodium hydroxide. The aluminum-base standards, containing 83–93% Al, analyzed by this method were readily dissolved with sodium hydroxide.

The author thanks THOMAS RUPPERT for his assistance in obtaining the technical data.

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(Received August 23rd, 1965)

Determination of micro amounts of easily reducible elements by ring colorimetry*

It is well known that elements cannot be determined by ring colorimetry (WEISZ's ring-oven method) if the test solution contains other elements which react in the same way with the reagent used. In such cases it is necessary to separate the element previously, for example by paper chromatography^{1,2}. In order to avoid this separation in determining elements which are easily reduced in mixtures with other elements, we have examined the use of different reducing agents. With suitable reductants, characteristically coloured rings of the reduced elements were obtained; these were stable and suitable for colorimetry. With mixtures containing elements which could not be conveniently reduced, but which formed coloured rings on washing out, it was possible first to carry out a reduction and then to wash the other element with a suitable solvent.

TABLE I
CONDITIONS OF ANALYSIS

Element	Solution used for determination	Washing out agent	Reducing agent	Temp. (°) and time (min) for reduction	Ring colour
Au	H ₂ AuCl ₄ in 2 N HCl	1% NaCl in 0.01 N HCl	2 N HCOONa in 2 N HCOOH	105; 10	Violet
Ag	AgNO ₃ (aqueous soln.)	5 · 10 ⁻³ N KCN in 1 · 10 ⁻³ N NaOH	3 N HCOONa in 5 · 10 ⁻⁴ N NaOH	130; 30	Brown
Pt	H ₂ PtCl ₆ (aqueous soln.)	0.05 N HCl	2 N HCOONa in 2 N HCOOH	105; 10	Brown
Pd	H ₂ PdCl ₄ in 2 N HCl	0.05 N HCl	2 N HCOONa in 2 N HCOOH	105; 10	Brown
Rh	Na ₃ RhCl ₆ (aqueous soln.)	0.05 N HCl	2 N HCOONa in 2 N HCOOH	105; 10	Brown
Os	Na ₂ [OsO ₄ (OH) ₂] in 2 N NaOH	0.4 N HCl	1.7 N HCOONH ₄ in 0.1 N NH ₄ OH	125; 1 ^a	Dark violet
Ir	(NH ₄) ₂ IrCl ₆ (aqueous soln.)	Water	2 N HCOONa in 2 N HCOOH	120; 10	Brown
Se	H ₂ SeO ₃ (aqueous soln.)	Water	NH ₂ OH · HCl (saturated soln.)	70; 10	Orange
Te	H ₂ TeO ₃ in 2 N HCl	Water	2 M H ₂ NNH ₂ · 2HCl	70; 10	Brown
Hg	HgCl ₂ (aqueous soln.)	0.01 N HCl	2 N HCOONa in 2 N HCOOH	105; 10	Brown

^a Reduction was performed on the ring oven.

* This work was supported by the Serbian Republican Fund for Scientific Research and presented at the 11th National Meeting of the Serbian Chemical Society, Belgrade, January 1965.

The method described is suitable for the determination of gold, silver, platinum, palladium, rhodium, osmium, iridium, selenium, tellurium and mercury (ruthenium could not be determined because it could not be reduced under these conditions). The principle of reduction in ring colorimetry has also been applied by other workers^{3,4} but only gold, platinum, rhodium and selenium were determined; the reducing agents were different from those used in the present work.

Procedure for individual elements

Transfer a few drops of the test solution to the centre of a filter paper (Whatman No. 1, diam. 5.5 cm) by a 1.2- μ l capillary pipette. Wash the substance out with a suitable solvent on the ring oven. Add a few drops of the appropriate reagent at the centre and continue the washing out. Finally, heat the paper in an oven in order to form coloured rings of the reduced element. Prepare the standard scale in an analogous way from 1, 2, 4, 6, 8 and 10 drops of the corresponding element solution. Compare the intensity of the coloured rings and calculate the results in the usual manner⁵. The other experimental conditions are given in Table I.

Results and discussion

The results obtained from 4 successive determinations of individual elements are presented in Table II. The average errors were as follows: gold 3.3%, silver 5.1%, platinum 1.5%, palladium 2.7%, rhodium 4.1%, osmium 3.8%, iridium 2.3%, selenium 1.6%, tellurium 4.4%, and mercury 2.5%. The amount of each element required for one determination ranged from 2 μ g (Hg) to 17 μ g (Rh).

TABLE II
DETERMINATION OF INDIVIDUAL ELEMENTS

Element	Concentration (mg/ml)		Error (%)	Element	Concentration (mg/ml)		Error (%)
	Actual	Found			Actual	Found	
Au	0.35	0.35	0.0	Os	1.17	1.14	2.3
	0.35	0.33	5.7		1.17	1.20	2.5
	0.51	0.53	3.9		2.00	2.11	5.5
	0.51	0.53	3.9		2.00	2.10	5.0
Ag	0.53	0.56	5.6	Ir	1.26	1.35	7.1
	0.53	0.57	7.5		1.26	1.29	2.3
	0.79	0.81	2.5		2.34	2.34	0.0
	0.79	0.83	5.0		2.34	2.34	0.0
Pt	0.20	0.20	0.0	Se	0.31	0.30	3.2
	0.20	0.20	0.0		0.31	0.30	3.2
	0.71	0.73	2.8		0.60	0.60	0.0
	0.71	0.72	1.4		0.60	0.60	0.0
Pd	0.26	0.27	3.8	Te	0.42	0.43	2.3
	0.26	0.27	3.8		0.42	0.43	2.3
	0.60	0.61	1.6		0.78	0.83	6.4
	0.60	0.61	1.6		0.78	0.83	6.4
Rh	1.54	1.63	5.8	Hg	0.20	0.20	0.0
	1.54	1.41	8.4		0.20	0.19	5.0
	2.10	2.15	2.3		0.60	0.57	5.0
	2.10	2.10	0.0		0.60	0.60	0.0

TABLE III
 ANALYSIS OF MIXTURES

Element	Concentration (mg/ml)		In the presence of (mg/ml)	Error (%)	Element	Concentration (mg/ml)		In the presence of (mg/ml)	Error (%)
	Actual	Found				Actual	Found		
Au	0.20	0.20	Cu, 20	0.0	Pt	0.60	0.57	Cu, 6.0 Ni, 6.0 Fe, 6.0	5.0
	0.20	0.20		0.0		0.60	0.58		3.3
	0.60	0.63	Fe, 60	5.3		0.28 0.28	0.29 0.28	Ru, 2.8	3.5
	0.60	0.57		5.3					0.0
	0.22	0.21	Zn, 44	4.1	Pd	0.25 0.25	0.26 0.24	Ru, 5.0	4.0
	0.22	0.22		0.0					4.0
	0.24	0.25	Pb, 72	4.1	Ir	1.17 1.17	1.25 1.21	Ru, 12	6.9
	0.24	0.25		4.1					3.4
	0.40	0.38	Ni, 120	5.0	Se	0.40 0.40	0.40 0.40	Te, 0.4	0.0
	0.40	0.38		5.0					0.0
	0.58	0.53	As, 58	8.2	Te	0.40 0.40	0.40 0.40	Se, 20	0.0
	0.58	0.53		8.2					0.0
	0.62	0.60	Sn, 31	3.3	Hg	0.60 0.60	0.57 0.60	Cu, 0.6 Cd, 0.6 Pb, 0.6 As, 0.6 Sn, 0.6	5.0
	0.62	0.60		3.3					0.0
	0.44	0.46	Se, 44	4.5					
	0.44	0.47		6.9					
	0.42	0.40	Te, 42	4.7					
	0.42	0.41		1.4					

 TABLE IV
 ANALYSIS OF ELECTROLYTIC COPPER SLIMES

Element	Amount of metal found (%)		Amounts of other elements present (%)
	Ring colorimetry	Standard method	
Au in slime I	6.92 7.00	6.90 ^a 6.95 ^a	Sn 16.83, Pb 16.57, Se 1.96, Te 1.40, Zn 1.25, Cu 0.41, Fe 0.23
Au in slime II	4.45 4.40	4.52 ^a 4.48 ^a	Cu 20.37, As 2.01, Se 1.80, Te 1.68, Sn 1.43, Pb 1.54, Sb 0.72, Ni 0.63, Fe 0.19
Te in slime II	1.65 1.70	1.68 ^b 1.70 ^b	Se 1.80

^a By cupellation.

^b Gravimetrically as elemental tellurium.

The results given in Table III show that easily reducible elements can be determined with almost the same precision whether they are alone or together with considerable quantities of elements which are not reduced. It can also be seen that under certain conditions, these elements can be determined even in mixtures provided that only one of them is reduced by the reagent used (*e.g.* selenium in the presence of tellurium, and gold in the presence of selenium and tellurium).

Reduction can also be utilized for the separation of micro amounts of elements on the ring oven. This can be seen from the results for the determination of tellurium in the presence of selenium. In this case selenium was reduced at the starting point by hydroxylamine, while tellurium was washed out to the ring zone and reduced by hydrazine.

In order to show the applicability of the method described for the determination of micro amounts of easily reducible elements, gold and tellurium were determined in electrolytic copper slime. Gold was determined in the hydrochloric acid solution obtained by treating the sample with aqua regia; the nitric acid was eliminated by heating the solution obtained with hydrochloric acid. For the determination of tellurium the solution was prepared in the usual manner⁶. The results obtained as well as the results of comparative analyses by standard methods are shown in Table IV. It can be seen that the results are in good agreement.

From all these results it can be concluded that the reduction principle can be efficiently applied in ring colorimetry. This offers possibilities for the determination of micro amounts of easily reducible elements without prior separation from other elements.

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(Received July 20th, 1965)

Anal. Chim. Acta, 34 (1966) 488-491

Fluorimetric determination of cadmium with 8-hydroxyquinoline-5-sulphonic acid

In a recent study of solubility of cadmium hydroxide in basic solutions¹, reliable measurements of small changes in solubility were necessary. A method based on the measurement of fluorescence developed when 8-hydroxyquinoline-5-sulphonic acid reacts with cadmium ion² proved satisfactory. The factors influencing the determination are discussed in this paper.

Apparatus

Quantitative measurements were made with a Turner Fluorimeter model # 110; the general purpose filters supplied with the fluorimeter were used (360 m μ Corning # 7-60; secondary filter passes wavelengths longer than 405 m μ , colour specification # 2A).

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Solutions

8-Hydroxyquinoline-5-sulphonic acid was recrystallized from water and a 0.003% solution prepared.

A 0.01 *M* cadmium stock solution was prepared by dissolving pure cadmium metal in a minimum amount of dilute nitric acid and excess nitric acid was eliminated by evaporation. This solution was diluted to prepare various cadmium standards.

Acetate-acetic acid buffers were prepared by dissolving 20 g of sodium acetate in 100 ml of water and adjusting to the desired pH with 6 *M* acetic acid.

Ammonia-ammonium chloride buffers were prepared by dissolving 20 g of ammonium chloride in 100 ml of water and adjusting to the desired pH with 6 *M* ammonia.

Determination of cadmium

Constant maximum sensitivity was attained when the pH was controlled between 7.1 and 8.5; one p.p.b. of cadmium, at a sensitivity setting $\cdot 10$, could be determined with an accuracy of ± 0.1 p.p.b. The sensitivity setting $\cdot 30$ could not be used to determine smaller amounts of cadmium because it was not possible to obtain a zero reading for the blank. The maximum amount of cadmium that could be determined between pH 7.1 to 8.5 was 0.25 p.p.m. (sensitivity setting $\cdot 1$).

At lower pH values, larger amounts of cadmium could be determined (~ 2 p.p.m.) because of decreased sensitivity; excellent results were obtained down to

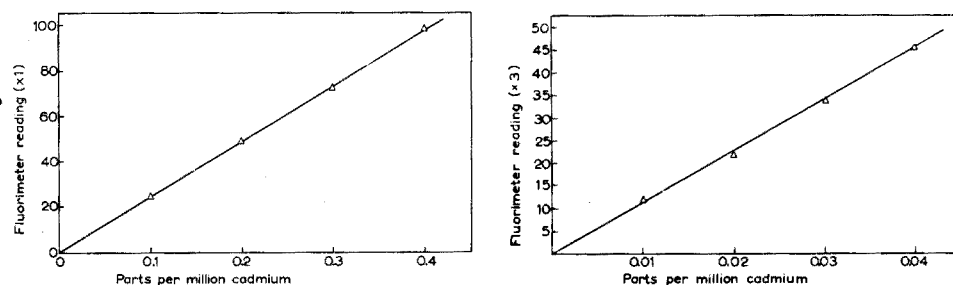


Fig. 1-2. Determination of Cd in the p.p.m. range (1), at pH 6.7; (2), at pH 7.9.

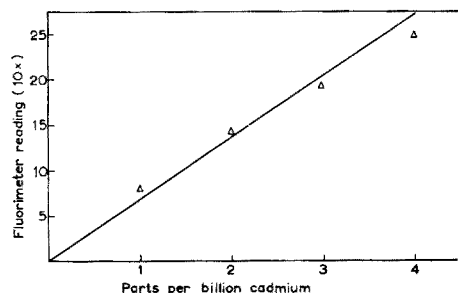


Fig. 3. Determination of Cd in the p.p.b. range at pH 7.9.

pH 5, but close control of solution pH was essential. The results shown in Fig. 1 are typical. Figures 2 and 3 illustrate the sensitivity of the method; these results were obtained with solutions buffered at pH 7.9.

Procedure. Transfer 0.01–2 μg of cadmium in solution to a 10-ml volumetric flask. Add 1 ml of ammonia–ammonium chloride buffer to adjust the pH within 7.1–8.5. Add 4 ml of 0.003% reagent for maximum sensitivity and dilute to 10 ml with doubly distilled water. Prepare the blank by the same procedure.

Factors affecting fluorescence

Although the reagent itself fluoresces, the intensity is very small relative to the cadmium species.

The fluorescence intensity of the cadmium hydroxyquinoline species varied little with time; a 0.1 p.p.m. cadmium sample varied by only 1% over a period of 5 h.

A study of the effect of pH on fluorescence (0.1 p.p.m. Cd) showed that the fluorescence was maximal and constant between pH 7.1 and 8.5. A study was also done on the effect of ionic strength on the fluorescence of the cadmium species (up to $\mu = 3.0$) using sodium perchlorate. No changes in fluorescence intensity were observed.

The fluorescence of the cadmium species is markedly affected by the quantity of excess reagent. Figure 4 shows, for 0.1 p.p.m. cadmium, that constant readings are obtained when the mole ratio of reagent to cadmium is in excess of 60 to 1.

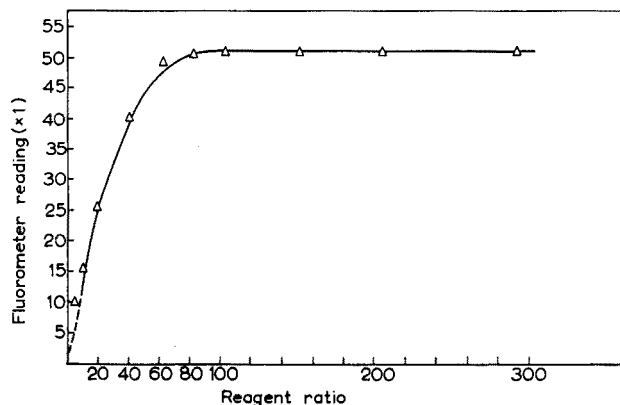


Fig. 4. Effect of excess reagent (0.1 p.p.m. Cd).

Fluorescence of other metals

BISHOP² and STEVENS³ have commented on the failure of transition metal cations to give fluorescence with 8-hydroxyquinoline-5-sulphonic acid. Using a 230-W mercury ultraviolet lamp, Hanovian type 16106, 30 cations were tested for fluorescence with the reagent. Strong fluorescence was observed between pH 7.1 to 8.5 with Cd^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , La^{3+} , Ce^{4+} , Th^{4+} and Sn^{4+} . The following ions fluoresced weakly or not at all: Li^{+} , Na^{+} , K^{+} , Ag^{+} , Ba^{2+} , Hg^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Sn^{2+} , Pd^{2+} , B^{3+} , As^{3+} , Sb^{3+} , Bi^{3+} , Cr^{3+} , Fe^{3+} , Zr^{4+} , Ta^{5+} , Nb^{5+} , W^{6+} .

The fluorescence spectra for both the cadmium and zinc species have their maxima at the same wavelength (520 $\text{m}\mu$). Zinc is therefore a positive interference

in the determination of cadmium; for example, the amount of cadmium found in the presence of 0.1 p.p.m. of zinc was 0.13 p.p.m. when 0.1 p.p.m. of cadmium was taken for analysis.

This work was supported by a grant from the Defence Research Board of Canada.

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- 1 D. E. RYAN, J. R. DEAN AND R. M. CASSIDY, *Can. J. Chem.*, 43 (1965) 999.
- 2 JOHN A. BISHOP, *Anal. Chim. Acta*, 29 (1963) 172.
- 3 H. M. STEVENS, *Anal. Chim. Acta*, 20 (1951) 5432.

(Received August 2nd, 1965)

Anal. Chim. Acta, 34 (1966) 491-494

BOOK REVIEWS

H. BENNETT AND W. G. HAWLEY, *Methods of Silicate Analysis*, 2nd Ed., Academic Press, London and New York, for the British Ceramic Research Association, 1965, x + 334 pp., price 63 s.

Analysts appreciate an authoritative source of information on those occasions when materials outside their normal field are to be analysed, and experts in the field like to keep abreast with current analytical practice. This revised and extended version of the 1958 publication meets both of these requirements and, like its predecessor, it is essentially a practical book for analysts engaged in ceramic and allied industries.

Although the title of the book refers specifically to silicate analysis, procedures are included for the analysis of materials in which the silica content is low. In many respects the presentation of both editions is the same, *e.g.*, the methods given in each chapter are self-contained, without any undue cross references. The book is certainly comprehensive, bearing in mind the prime purpose for which it is intended, but the recommended procedures are, justifiably, restricted to those that have been successfully applied in extensive laboratory trials to specified materials, with special attention to current requirements.

Whilst the approach to silicate analysis has not changed radically since the last edition of the book appeared, the authors are to be congratulated for implementing timely changes based on further instrumentation, and new techniques currently used in other analytical fields.

W. T. ELWELL (Birmingham)

Anal. Chim. Acta, 34 (1966) 494

E. RABINOWITCH AND R. LINN BELFORD, *Spectroscopy and Photochemistry of Uranyl Compounds*, International Series of Monographs on Nuclear Energy, Chemistry Division, Vol. I, Pergamon Press, Oxford, 1964, x + 370 pp., price 80 s.

This book is really a companion volume to the Nuclear Series and perhaps suffers somewhat by being published so much later. It deals with 4 main aspects of the subject: (1) the absorption spectrum in the infrared and Raman spectrum, (2) the absorption spectrum in the visible and near ultraviolet regions and fluorescence spectra, (3) the photochemistry of uranyl compounds, (4) the possible electronic structure of some typical uranyl compounds.

Work published before 1949 is critically reviewed and presented together with an adequate bibliography. Work published between 1949–1959 whilst being reasonably well covered is not nearly so well reviewed, but the bibliography is adequate. After 1960 however the subject is only sparsely covered.

The book is written in a semi-historical manner which clearly shows the magnitude of problems and how the experimental results have been utilized. It is perhaps not so easy to use this work as a reference as might be desired owing to the historical presentation. However, a very clear picture is given of most aspects of the subject which can be further augmented by reference to the bibliography.

E. W. T. RICHARDS

Anal. Chim. Acta, 34 (1966) 495

A. J. MOSES, *Nuclear Techniques in Analytical Chemistry*, International Series of Monographs on Analytical Chemistry, Vol. 20, Pergamon Press, Oxford, 1964, vii + 142 pp., price 45 s.

Nuclear Techniques in Analytical Chemistry is, according to the author, intended to acquaint the analytical chemist with nuclear techniques. The book attempts to cover a variety of tracer methods such as radiometric measurements, exchange reactions and isotope dilution, and discusses activation with neutrons, charged particles and γ -photons.

Separate chapters deal with safety and instrumentation and appendices include a chart of the nuclides and thermal neutron activation data; throughout the book outline procedures serve as examples.

This is a very short book which is concerned with a wide range of nuclear techniques, and in which it is inevitably impossible to discuss any topic in depth. However, the book does contain useful information and will therefore appeal primarily to those analytical chemists who have no knowledge of nuclear techniques and wish to obtain a general idea of the scope of the methods with relatively little reading. The inquiring reader or those intending to apply the methods will require more information than is provided by this book.

T. B. PIERCE (Harwell)

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ORGANOMETALLIC CHEMISTRY REVIEWS

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 change to a monthly publication schedule, it was not possible to publish more than original papers.

On careful consideration it was therefore decided that review papers should be published in a separate medium which would contain only review articles. The name of this new journal will be ORGANOMETALLIC CHEMISTRY REVIEWS and it will exist side by side with the Journal of Organometallic Chemistry.

One volume will be published per year to begin with. Each volume will consist of four issues and, to avoid delay in publication, these will be published as soon as sufficient material is available. If necessary, issues will be combined occasionally.

It is hoped that ORGANOMETALLIC CHEMISTRY REVIEWS will aid in making valuable literature in this field more readily available.

PUBLICATION

One volume per year in four issues. Issues will vary in size as necessary for prompt publication of material available. Size of journal is 6½ x 9½".

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The scope will be the same as that of the papers in the Journal of Organometallic Chemistry. Two types of Reviews will be published:

- (a) those of certain areas of organometallic chemistry with thorough literature coverage; these may be a complete coverage of the field in question or a coverage of recent advances only;
- (b) those by research workers active in the organometallic area, of their own contributions to a certain aspect of organometallic chemistry; this type of review will serve to summarize and to put into proper perspective personal research carried out over a period of years.

Although the Editors will, at times, solicit review article manuscripts from established authorities in organometallic chemistry, unsolicited reviews will also be welcomed.

It is however requested that subjects for such unsolicited reviews be cleared with the appropriate Editor before a manuscript is submitted, so that suitability for publication may be considered and any duplication may be avoided.

Manuscripts should be in double-spaced typing. References should be given at the end of the paper; they should be numbered consecutively and the numbers should appear in the text at appropriate places.

Line drawings should preferably be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in pencil. Photographs should be submitted as clear black-and-white prints on glossy paper. Legends to the illustrations should be typed on a separate page of the manuscript, and not underneath the drawings or on the reverse of photographs. All illustrations should be numbered consecutively throughout the paper.

Reviews will be published preferably in English, but French or German texts are also acceptable.

Authors should keep a carbon copy of their manuscripts, as the original manuscript will not be sent to them with the proofs. Since the Reviews will be reproduced by IBM-typed offset procedure, it is particularly requested that corrections should be restricted to the absolute minimum required.

ORGANOMETALLIC CHEMISTRY REVIEWS

Some manuscripts received for publication

ORGANOFUNCTIONAL BORONIC ESTERS

D. S. Matteson

GRIGNARD AND ORGANOLITHIUM REAGENTS DERIVED FROM DI- AND POLY-HALOGEN COMPOUNDS

H. Heaney

ORGANIC TIN-NITROGEN COMPOUNDS

K. Jones and M. F. Lappert

ORGANIC BORON-SULPHUR COMPOUNDS

R. H. Cragg and M. F. Lappert

SIGMA BONDED ORGANOMETALLIC CATIONS IN AQUEOUS SOLUTIONS AND CRYSTALS

R. Stuart Tobias

RECENT ADVANCES IN THE CHEMISTRY OF ORGANOMAGNESIUM COMPOUNDS

a) The nature of the Grignard reagent, b) New organomagnesium compounds

B. J. Wakefield

AZIDE DERIVATIVES OF ORGANOMETALLIC COMPOUNDS

J. S. Thayer

PENTAFLUOROPHENYL-METAL COMPOUNDS

R. D. Chambers and T. Chivers

SYNTHESIS OF ORGANOHALOBORANES

K. Niedenzu

REDISTRIBUTION REACTIONS OF ORGANOMETALLIC COMPOUNDS OF SILICON, GERMANIUM, TIN AND LEAD

K. Moedritzer

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SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. BELCHER

Professor of Analytical Chemistry,
The University of Birmingham, Great Britain

6 × 9", ix + 173 pages, 12 tables, 35 illus., 186 lit. refs., 1966, Dfl. 27.50, 55s., \$10.00

Contents: 1. Introduction. 2. The balance. 3. General apparatus. 4. The determination of nitrogen. 5. Carbon and hydrogen. 6. Chlorine. 7. Bromine and iodine. 8. Fluorine. 9. Sulphur. 10. Phosphorus and arsenic. 11. Carboxyl groups. 12. Organic bases in non-aqueous media. 13. Alkoxy and N-methyl groups. 14. Acetyl groups. 15. The carbonyl group. 16. Olefinic unsaturation. 17. Oxidation with periodate. 18. The determination of nitro and nitroso groups. 19. Thiol groups. 20. The cryoscopic determination of molecular weight. Index.

TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged

by R. KALVODA

Institute of Polarography, Czechoslovak Academy of
Sciences, Prague, Czechoslovakia

with a preface by Professor J. Heyrovský

6 × 9", 213 pages, 3 tables, 90 illus., 263 lit. refs., 1965, Dfl. 30.00, 60s., \$11.00

Contents: Preface (J. Heyrovský); Author's Preface; 1. Introduction. 2. Examples of application of the oscillographic method. 3. Practical oscillographic exercises. 4. Maintenance of apparatus and construction of auxiliary electrical circuits. Index.

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. BEYNON, R. A. SAUNDERS AND A. E. WILLIAMS

Research Department, Imperial Chemical Industries Ltd.,
Manchester, Great Britain

9½ × 6½", xix + 392 pages, 1965, Dfl. 45.00, 90s., \$16.50

These tables are intended to make it easy to determine the ionic reaction which gives rise to any meta-stable peak in a mass spectrometer, and will prove indispensable to any laboratory possessing this equipment. The introduction is given in English, German, French and Russian, to make the tables more generally useful.

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography

Group of the Czechoslovak Chemical Society, at Liblice

by K. MACEK AND I. M. HAIS

7 × 10", 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965, Dfl. 42.50, 85s., \$16.00

Contents: List of participants in the discussion. Introduction. Opening speech. I. Chromatography papers. II. Thin-layer materials. III. Stationary liquids and adsorbents in paper chromatography. IV. Stationary liquids and impregnations for thin layers. V. General problems of the stationary phase. Discussion. Closing remarks. Author index. Subject index.



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