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

Editors
PHILIP W. WEST *(Baton Rouge, La., U.S.A.)*
A. M. G. MACDONALD *(Birmingham, Great Britain)*

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 32, No. 4, 301–404, April 1965

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. (U.S.A.)

or to

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

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

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

▼ ▽ ■ □ ● ◎ ■ ◘ ⊖ ▣ ▪ □ + ×

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

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta has six issues to the volume, approx. 600 pages per volume, two volumes per year.

Subscription prices (post free): \$ 17.50 or £ 6.6.— or Dfl. 63.—per volume; \$ 35.— or £ 12.12.—or Dfl. 126.—per year. Additional cost for copies by airmail available on request.

For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

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

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 32, No. 4, April 1965

A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF THORIUM WITH ACID ALIZARIN BLACK SN

Acid alizarin black SN reacts with thorium at pH 4.2 to give a highly sensitive colour reaction with thorium, $\varepsilon_{600\,m\mu} = 28{,}000$. There is no interference from Ba, Ca, Cd, Ce(III), Gd, Hg, La, Mg, Mn, Pb, Pr, Sm, Sr, Zn, Zr, Cl^-, CN^-, I^-, NO_3^-, SO_4^{2-}. The interferences of Al, Bi, Co, Cu, Fe, Ni, Mo, Sb, Sn, Ti and W may be overcome by addition of masking agents. Only U(VI) and V(V) still interfere and these can be determined sequentially with the thorium. The nature of the complex is studied and the mode of its formation.

P. Kusakul and T. S. West,
Anal. Chim. Acta, 32 (1965) 301–308

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 2-DIETHYLAMINOETHANETHIOL HYDROCHLORIDE AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

2-Diethylaminoethanethiol hydrochloride is proposed for spectrophotometric determination of palladium(II). The sensitivity of the reaction is 0.0085 $\mu g/cm^2$ and the yellow colored complex shows absorption maxima at 258 mμ and 303 mμ. Color development is slow in the cold but complete after heating for 10–15 min. The optimum pH range is 3.5 to 5.5 and the system adheres to Beer's law between 0.2 and 16.8 p.p.m. of palladium. The average and maximum relative standard deviations were 0.60% and 1.40% respectively. Interferences due to other platinum metals were studied and a procedure is suggested for the simultaneous determination of rhodium and palladium.

S. C. Srivastava and M. L. Good,
Anal. Chim. Acta, 32 (1965) 309–316

FLUORIMETRIC DETERMINATION OF ZINC WITH DIBENZOTHIAZOLYLMETHANE

Dibenzothiazolylmethane produces a specific fluorescence with zinc in ethanol–water solutions. Zinc is determined quantitatively in solutions containing 0.05 to 50 mg of zinc/l. One part of zinc can be detected in the presence of 20,000 parts of cadmium and quantitative determinations of zinc in cadmium salts are readily done. The method can be applied to the analysis of non-ferrous alloys such as Dowmetals.

R. R. Trenholm and D. E. Ryan,
Anal. Chim. Acta, 32 (1965) 317–322

THE RELATIVE CONDUCTOMETRIC DETERMINATION OF SULPHUR IN PETROLEUM PRODUCTS

(in German)

The relative conductometric method for the determination of sulphur, which has already been used for microelementary analysis, is applied to various petroleum products. The results obtained show that the method is not only very suitable for the rapid determination of the total sulphur content but also gives information on the nature of the combustion processes for sulphur-containing compounds.

H. Malissa, L. Machherndl and E. Pell,
Anal. Chim. Acta, 32 (1965) 323–331

VOLTAMMETRY AND CONTROLLED-POTENTIAL COULOMETRY WITH BORON CARBIDE ELECTRODES

With the boron carbide electrode, $E_{p/2}$ values were determined for the reduction of the following ions: Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II), Ru(IV), Sb(V), and U(VI). The linear dependence of peak current on concentration is demonstrated for the U(VI) → U(IV) and Fe(III) → Fe(II) reductions at the boron carbide electrode. The suitability of the electrode for the controlled-potential coulometric titrations of Fe(II) → Fe(III), Fe(III) → Fe(II), and U(VI) → U(IV) was studied; the results were inconclusive because of the small surface area that could be used conveniently and the possibility of oxygen leaks in the cell.

W. R. Mountcastle, Jr.,
Anal. Chim. Acta, 32 (1965) 332–338

A COMPARISON OF CATHODE AND ANODE EXCITATION IN THE D.C. ARC

Cathode excitation as distinct from cathode-layer excitation was compared with anode excitation under the same experimental conditions. Data on 33 elements and 35 line pairs were used to study relative self-absorption effects, absolute sensitivities, reproducibilities, volatilisation curves, times of complete volatilisation and background effects. Cathode excitation affords greater precision for a number of the more volatile elements in a carbon matrix.

R. R. Brooks and C. R. Boswell,
Anal. Chim. Acta, 32 (1965) 339–345

THE DETERMINATION OF SELENIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

The problems involved in the determination of selenium by atomic absorption spectrophotometry are discussed. A practical method is described for which the sensitivity is approximately 1 p.p.m. Such concentrations can be determined in organic samples, but with mineral samples the preliminary treatment renders the procedure unsuitable for concentrations lower than 50 p.p.m. in a sulphide ore.

C. S. Rann and A. N. Hambly,
Anal. Chim. Acta, 32 (1965) 346–354

DETERMINATION OF SURFACE OXYGEN ON METALS BY NEUTRON ACTIVATION

(in German)

Surface oxygen on metal foils was determined by activation analysis on the basis of the reaction sequence $^6Li(n,\alpha)t$, $^{16}O(t,n)^{18}F$. The metal foils were placed between foils consisting of lithium fluoride and polystyrene, sealed in evacuated ampoules, and irradiated in the reactor. The produced ^{18}F was radiochemically separated, and measured by its annihilation radiation at 0.51 MeV. The overall cross-sections of such foil arrangements were computed by simple formulas and compared with experimental data. Instructions are given for the chemical treatment of irradiated foils of Au, Pt, Ni, Cu, Al, Fe and Zr. The following values of oxygen coverage were found on rolled foils: Pt 1.4, Ni 1.4, Cu 2.9, Al 4.9 and Fe 7.5 μg O/cm^2 of geometrical surface. Other oxygen values refer to Au, Zr and to different pretreatments of the metal surfaces. The lower limit of determination is about 0.1 μg O/cm^2.

W. LEONHARDT,
Anal. Chim. Acta, 32 (1965) 355–369

SEPARATION OF SELENITE, SULFATE AND IRON BY CATION-EXCHANGE RESIN

Selenite, sulfate and iron(III) are separated by cation-exchange resin. Microgram amounts of selenite in iron(III) sulfate solution at pH 2 are completely adsorbed on the resin together with the large excess of iron(III), while sulfate passes through. Selenite is eluted with 0.5 *N* hydrochloric acid, leaving iron(III) in the resin. The procedure is applied to the determination of these elements in natural iron sulfides.

M. YAMAMOTO AND H. SAKAI,
Anal. Chim. Acta, 32 (1965) 370–375

STUDIES IN THE TETRAARYLBORATES

PART I. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-CHLOROPHENYL)BORATE

Sodium tetrakis(*p*-chlorophenyl)borate was synthesized. It formed precipitates with K^+, Rb^+, Ca^+, quarternary ammonium and protonated basic nitrogen compounds. The potassium salt was more soluble than potassium tetraphenylborate but flocculated more readily and filtered more easily. The salts formed with nitrogen compounds offer possibilities as derivatives suitable for qualitative analysis.

F. P. CASSARETTO, J. J. McLAFFERTY AND C. E. MOORE,
Anal. Chim. Acta, 32 (1965) 376–380

THE COMPOSITION OF TETRAPHENYLARSONIUM THIOCYANATOTUNGSTATE IN CHLOROFORM

The variation of extraction efficiency as a function of thiocyanate concentration and of tetraphenylarsonium concentration has established part of the composition of the extracted species which is involved in the determination of tungsten by extraction as the tetraphenylarsonium tungsten–thiocyanate ion-pair. The thiocyanate: tungsten ratio is 2:1, and the tetraphenylarsonium:tungsten ratio is 1:1, indicating an anionic charge of one for a mononuclear complex.

H. E. Affsprung and J. W. Murphy,
Anal. Chim. Acta, 32 (1965) 381–385

THE THERMAL DECOMPOSITION OF METAL ETHYLENEDIAMINE OXALATE COMPLEXES

The thermal dehydration and deamination of some ethylenediamine complexes of Zn, Cd, Cu, Ni and Co oxalate were studied by TGA, DTA, DSC, reflectance spectroscopy, and by GE. The tris(amine) complexes deaminated to mono(amine) compounds which then decomposed directly to the metal oxide. The kinetics and heats of dehydration and deamination of several of the complexes were determined.

J. M. Haschke and W. W. Wendlandt,
Anal. Chim. Acta, 32 (1965) 386–393

THE DETERMINATION OF TRACE AMOUNTS OF SILICON IN COPPER AND COPPER-BASE ALLOYS

(Short Communication)

J. M. Sturton,
Anal. Chim. Acta, 32 (1965) 394–397

FLUORIMETRIC MOLE RATIO STUDIES OF ALUMINUM AND GALLIUM CHELATES OF *o,o'*-DIHYDROXYAZOBENZENE

(Short Communication)

J. H. Saylor and J. W. Ledbetter,
Anal. Chim. Acta, 32 (1965) 398–400.

GRAVIMETRIC DETERMINATION OF PALLADIUM WITH SALICYLOYLHYDRAZIDE

(Short Communication)

S. C. Shome and H. R. Das,
Anal. Chim. Acta, 32 (1965) 400–403

ANTON A. BENEDETTI-PICHLER

1894-1964

It is with great regret that we note the death of Professor A. A. BENEDETTI-PICHLER on December 10th, 1964. Professor BENEDETTI-PICHLER was born and educated in Austria and graduated at the Technische Hochschule in Graz, where he was a pupil of EMICH. He moved to the United States in 1929 and joined the faculty of New York University, where he remained until his retirement in 1963.

His work on the development of inorganic microchemistry and microanalysis, and particularly his pioneer work on ultramicroanalysis, are of international repute. His services to microchemistry have been recognized by many Awards from Austrian and American societies. His influence will be greatly missed, especially by the American Microchemical Society, which he helped to found nearly 30 years ago.

P.W.W.
A.M.G.M.

A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF THORIUM WITH ACID ALIZARIN BLACK SN

PRAPHAN KUSAKUL[*,**] AND T. S. WEST[**]
Chemistry Department, The University, Birmingham (Great Britain)
(Received June 26th, 1964)

The colour reaction between thorium and the trihydroxybisazo dyestuff, Acid alizarin black SN (C.I. mordant black 25), was first observed during an examination of the metallochromic indicator properties of this reagent in titrations with ethylenediaminetetraacetic acid[1]. Subsequently the indicator properties of this metallochrome were utilised for the titration of calcium[2] in dilute solution and in the determination of calcium in blood sera[3]. Preliminary work on the constitution of the calcium complexes of the indicator led to an erroneous assignment of formulae which was subsequently corrected by others[4] in a more detailed examination. However, no work has previously been reported on analytical utilisation of the sensitive and selective reaction between thorium and this reagent.

EXPERIMENTAL

Reagents

Acid alizarin black SN, 10^{-3} M. The commercially available dye usually contains a high proportion of indifferent inorganic salt as a by-product of its isolation from the reaction medium. Samples were analysed by titration of the azo groups with titanium(III) chloride. The purity of the product usually lay in the range 80–50% (with 20–50% of sodium chloride as impurity). Assay by spectrophotometric titration against a standard calcium solution confirmed the azo-group analysis and chromatography substantiated the absence of measurable amounts of other organic matter. The solution was prepared on the basis of the molecular weight of the reagent, 594.56, and its assay.

Acetate buffer pH 4.2. Dissolve 136 g of sodium acetate trihydrate in 400 ml of distilled water and add glacial acetic acid (*ca.* 240 ml) to give a pH of 4.2 (pH meter); then dilute to 1 l.

Masking agents. (*a*) Aqueous 1% potassium cyanide; (*b*) aqueous 1% thioglycollic acid; (*c*) freshly prepared aqueous 0.5% potassium iodide; (*d*) aqueous 1% triethanolamine; (*e*) sulphosalicylic acid, solid, (*f*) Tiron (catechol-3,6-disulphonic acid), solid; (*g*) ascorbic acid.

Standard thorium solution, 10^{-4} M. Prepare by dilution of a 10^{-3} *M* stock solution prepared from pure thorium nitrate and previously standardised against EDTA with xylenol orange indicator[5]. 1 ml of 10^{-4} *M* Th^{4+} soln. $\equiv$ 23.2 μg of Th.

---

[*] On study leave from the Department of Mineral Resources, Thailand.
[**] Present address: Chemistry Department, Imperial College, London, S.W.7.

Apparatus

Unicam S.P. 600 spectrophotometer with 1- and 4-cm cuvettes.

Procedure

Calibration. Into 100-ml standard flasks, pipette 2.0–12.0 ml aliquots of 10^{-4} *M* thorium nitrate solution and 10 ml of 10^{-3} *M* Acid alizarin black SN followed by 3 ml of pH 4.2 buffer. Dilute the contents of the flasks to 100 ml and set aside for 30 min. Measure the absorbance of the thorium-containing solutions against a similarly prepared solution containing all the other reagents except thorium at 600 mμ in a 1-cm cuvette.

When masking agents are employed, these should be added *before* the metallochrome. The calibration curve is a straight line over the range 58–290 μg of thorium. A more precise calibration curve from 18–46 μg may readily be obtained by using 4-cm cuvettes. It should be noted that, while the projection of the curve passes through the origin, Beer's law does not hold for amounts of thorium less than 18 μg by the recommended procedure.

Determination

Proceed as above, taking a suitable portion of test solution to give an amount of thorium in the range 20–290 μg. Add masking agents as necessary for interfering ions present in the solution, *cf.* Table I.

TABLE I

MASKING OF INTERFERENCES

(5 ml of 10^{-4} *M* Th + 1 ml of 10^{-2} *M* (or 1 ml of 10^{-3} *M*)^{a} ion. Measured in 1-cm cell against distilled water)

Ion added	*Absorbance of mixture*	*Masking agent*	*Absorbance following masking*
—	0.255	—	0.255
Al^{3+}	0.305	0.1 g sulphosalicylic acid	0.260
Bi^{3+}	0.710	1 ml 1% thioglycollic acid	0.250
Ce^{4+a}	0.265	Ascorbic acid	0.260
Co^{2+}	0.434	1 ml 1% KCN	0.255
Cu^{2+}	0.460	1 ml 1% KCN	0.250
Fe^{3+a}	0.485	Ascorbic acid + KCN	0.260
Ni^{2+}	0.350	1 ml 1% KCN	0.255
Sb(III)	0.290	1 ml 0.5% KI	0.255
Sn(IV)	0.205	1 ml 0.5% KI	0.250
Ti^{4+a}	0.310	1 ml 1% triethanolamine	0.250
W(VI)	0.141	0.1 g Tiron	0.260
Mo(VI)	0.550	0.1 g Tiron	0.275–0.015(0.260)

RESULTS AND DISCUSSION

Nature of colour reaction

Preliminary experiments confirmed the findings of earlier authors[1,2] that, whilst Acid alizarin black SN (AABSN) forms coloured chelates with several ions in alkaline media, it forms a coloured product only with thorium and a few other ions in an acetate-buffered solution. The crimson-coloured thorium complex shows maximum absorption at 530 mμ whilst the metal-free reagent absorbs at 500 mμ in a sodium acetate buffer of pH 4.2. It is apparent from Fig. 1 that the analytical measurements are best made at 600 mμ where the reagent has very little absorption and that due to the thorium complex is still appreciable.

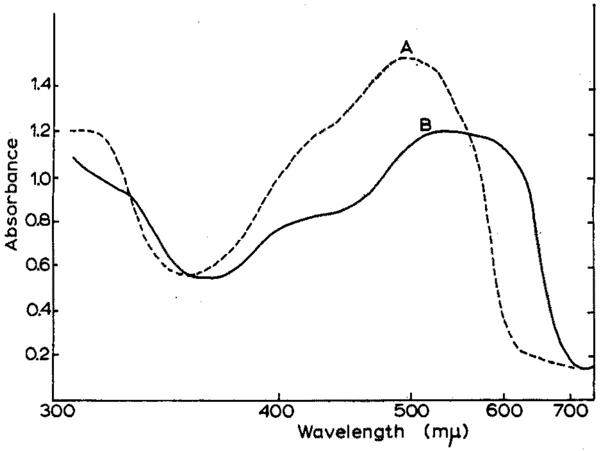


Fig. 1. Absorption spectra of AABSN (A) and Th^{4+}–AABSN complex in presence of excess of AABSN (B). (A) 20 ml 10^{-4} *M* AABSN at pH 4.2 in final volume of 100 ml. 4-cm cuvette against water. (B) As above but with 10 ml 10^{-4} *M* Th^{4+} present. Both spectra were recorded on a Hilger "Ultrascan" recording spectrophotometer.

The optimum pH for colour development was studied by lightly buffering a solution containing thorium and reagent at pH 4.2 with a sodium acetate–acetic acid buffer and varying the pH by addition of small amounts of strong acid or alkali. This study revealed that the optimum pH was in the range 4–4.3 within which range the absorbance was unchanging (Table II).

TABLE II

EFFECT OF pH ON ABSORBANCE

(10 ml of 10^{-3} *M* AABSN, 5 ml of 10^{-4} *M* Th^{4+}; final volume 100 ml; measured in 4-cm cuvettes against AABSN)

pH	*Absorbance*
3.1	0.400
3.4	0.430
3.7	0.455
4.0	0.470
4.3	0.470
4.6	0.455
4.9	0.430
5.1	0.400

Because of the well-known tendency of acetate ion to form a thorium complex, an investigation was made of the effect of buffer concentration on the absorption of the thorium–AABSN complex. It was found that with the acetate buffer solution formulated above, there was no measurable effect on the determination of *ca.* 120 μg of thorium by the recommended procedure when 5 ml or less of buffer was used. Since 3 ml of this buffer has a high enough capacity for most purposes, this probably represents an adequate safety factor. The effect of adding double the "safe" amount of buffer was almost to halve the absorption due to the thorium–AABSN chelate. It was also observed that when a 5% solution of potassium hydrogen phthalate was used at pH 4.0 there was a greater tolerance towards buffer solution. However, since thorium does not show a very pronounced tendency to undergo hydrolysis in aqueous solution it was decided to retain the sodium acetate buffer for subsequent experimentation and to use 3 ml of it in all cases.

Colour stability tests revealed that the colour system attained equilibrium within 30 min and maintained an unchanged absorbance for at least 2 h. A slight increase in sensitivity (*ca.* 10%) may be obtained by allowing the solution to stand overnight.

The constitution of the thorium–AABSN complex was studied by the method

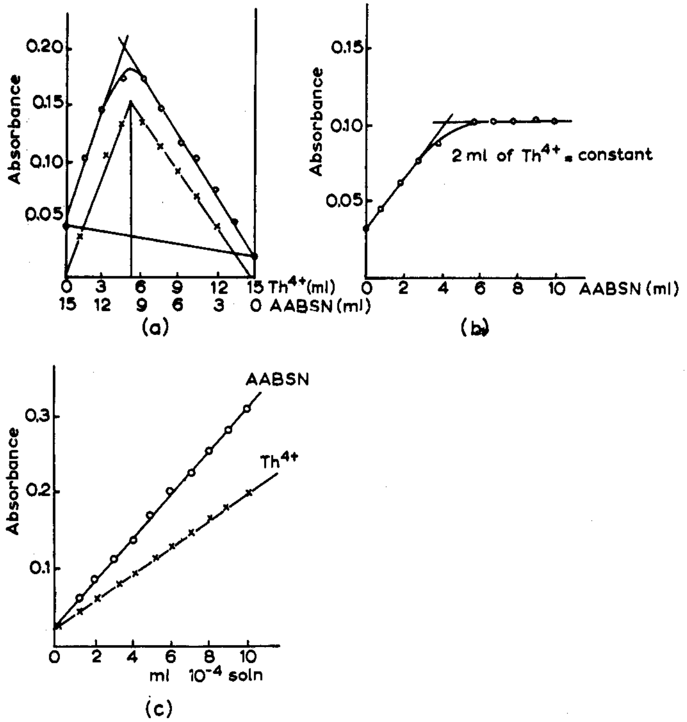


Fig. 2. (a) Job and corrected Job plots. (b) Mole-ratio plot. 2 ml of 10^{-4} *M* Th^{4+} with *x* ml of AABSN, 10^{-4} *M*. (c) Slope-ratio plot. Ml of 10^{-4} *M* Th^{4+} or AABSN with constant (10 ml. $10^{-3}M$) amount of AABSN or Th^{4+} respectively. Measured against AABSN and H_2O respectively. In all cases the pH was 4.2 and the final volume was 100 ml; measurements were made in 1-cm cuvettes at 600 mμ against water, unless otherwise specified.

of continuous variations, mole-ratio plot and slope-ratio plot. The results of these experiments are shown graphically in Fig. 2a, b and c. All clearly reveal a fairly stable 1/2 thorium–AABSN chelate. It is not possible to assign any definite structure to the complex without a substantial amount of further evidence. It is highly probable that all 6 phenolic oxygen atoms of the 2 reagent molecules are coordinated to the thorium ion. The remaining two coordination sites on the thorium ion may be taken up by water molecules, hydroxide ions or by two nitrogen atoms from the 4 azo bonds in the chelate.

There is some evidence to suggest that this is not an adsorption compound of the reagent on thorium hydroxide. The latter is well known to begin to precipitate from the majority of thorium salts at pH *ca.* 3.5. In the present instance the colour reaction between thorium and AABSN becomes apparent at much lower pH values (pH 2). This latter evidence together with the apparent firm stoichiometry of the compound (*cf.* Fig. 2) and the fact that acetate ion inhibits precipitation of thorium hydroxide suggests that we are concerned with a true soluble chelate rather than an adsorption complex. In addition we have more recently prepared a new, structurally similar reagent which shows *maximum* colour formation at pH 3 where no thorium hydroxide would be expected to be present[6]. Light-scattering experiments conducted at the isosbestic points on the absorption spectra showed no measurable increase in scattering and consequently we conclude that the chelate is not an adsorption complex of AABSN and hydrated thoria, but a true soluble complex.

Determination of thorium in presence of diverse ions

The interference of other ions was studied by adding a 20-fold molar amount of the ion under test to 5 ml of 10^{-4} *M* thorium solution and then developing the colour in the usual way. Under these circumstances no interference was observed from Ba^{2+}, Ca^{2+}, Cd^{2+}, Hg^{2+}, La^{3+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+}; in addition, no interference was observed from two-fold excesses of the rare earths Gd^{3+}, Pr^{3+}, Sm^{3+}, or from Zr^{4+}. None of the common anions was found to interfere. Interference was found from Al^{3+}, Bi^{3+}, Ce^{4+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Mo(VI), Sb(III), Sn(IV), Ti^{4+}, U(VI), V(V) and W(VI). The following complex-forming anions also interfered: fluoride, oxalate, tartrate and citrate. The interferences of all cations, except those of tin(IV) and W(VI), were positive, *i.e.* additive. The interference of tin(IV) and tungsten(VI) resembled that of the anions in that it produced a negative error.

A glance at the cationic interferences reveals that most of them should be susceptible to direct masking by addition of soluble auxiliary complexing agents. This was confirmed readily as shown in Table I. The only complications in the masking procedures were in the use of Tiron to mask tungsten and molybdenum. In both instances the absorption should be measured 15 min after developing the colour. This is necessary because of the slow attack of the masking agent on the Th–AABSN chelate. In addition, when molybdenum is involved, a strong yellow colour develops owing to the molybdenum–Tiron complex. This absorbance makes a small contribution at 600 mμ which can be corrected for by measuring the absorbance at 600 mμ on another aliquot of solution treated with Tiron and all the other reagents except AABSN. Thus the interference from all cations except vanadium and uranium can be eliminated by simple addition of masking agents.

It was not found possible to eliminate the interferences of vanadium and uranium except by measuring them and deducting their absorbances. With mixtures of vanadium and thorium, acetate ion in sufficient amount completely masks thorium, but has no effect on the absorbance of vanadium. As a result it was found possible to determine thorium in the presence of vanadium by measuring the total absorbance due to thorium and vanadium under the normal conditions and then measuring the absorbance (due to vanadium alone) in a similar aliquot of solution containing the same amount of reagents, but with 25 ml (instead of 3 ml) of the acetate buffer. The results of some determinations carried out in this way are shown in Table III. The accuracy of this method lies within ± 3% and is adequate for the determination of mixtures of vanadium and thorium when both are present in approximately equal concentrations.

TABLE III

DETERMINATION OF THORIUM IN PRESENCE OF 3.0 ml OF 10^{-4} *M* VANADIUM(V)

Th added (μg)	*Th found (μg)*
46.42	47.85
58.03	58.00
69.63	68.15
81.24	81.25
104.45	102.95
116.05	117.45
127.66	130.50
139.26	139.20

TABLE IV

DETERMINATION OF THORIUM IN PRESENCE OF 3 ml OF 10^{-4} *M* URANIUM(VI)

Th added (μg)	*Th found (μg)*
46.42	46.42
58.03	56.55
69.63	72.54
81.24	82.65
92.84	92.82
127.66	133.40
139.26	139.20

Vanadium can readily be determined simultaneously by means of this reagent by drawing up a calibration curve for vanadium under similar conditions. We have studied this procedure and will report on it at a later date.

Acetate ion masks uranium as well as thorium and this obviously provides a good route to the determination of vanadium in the presence of thorium and uranium, but the procedure cannot be used to determine thorium in the presence of uranium. This problem was overcome by using nitrilotriacetic acid (N.T.A.) as a masking agent. N.T.A. masks thorium and vanadium(IV). Thus, thorium may be determined in the presence of uranium by measuring the total absorbance of uranium and thorium on one aliquot of solution and then the absorbance (due to uranium alone) on a similar aliquot of solution treated with an excess (2 ml of 10^{-2} M) of N.T.A.

TABLE V

COMPARISON OF REAGENTS

Reagent	*pH*	*Molar absorptivity (wavelength, mμ)*
Acid alizarin black SN	4.2	28,000 (600)
Eriochrome black T	9.2	35,000 (700)
Morin	2.0	41,000 (410)
Naphthazarin	—	22,400 (620)
8-Hydroxyquinoline	3.85	8,080 (330)
Quinalizarin	—	14,000 (580)
Thoron	0.8	16,700 (545)

Results obtained in some typical experiments are shown in Table IV. These results show an accuracy somewhat less satisfactory than that for thorium in admixture with vanadium, but it is still within ± 5%. Once more it may be remarked that this reagent obviously presents a potentially sensitive and interference-free method for the determination of uranium; this will be reported on at a later date.

Finally, a combination of these procedures may be used for the sequential spectrophotometric resolution of a mixture of thorium, vanadium and uranium. Three aliquots of solution are required. In the first aliquot the normal procedure is applied to obtain the sum of absorbances due to all 3 elements (Th + U + V). In the second aliquot a normal procedure is applied save that 1 ml of 10% ascorbic acid and 2 ml of 10^{-2} M N.T.A. are added. This gives the absorbance due to uranium alone. In the third aliquot a normal procedure is applied except that 25 ml of the acetate buffer are used. This gives vanadium alone. Thus the thorium absorbance can be obtained by difference.

Assessment of AABSN as a spectrophotometric reagent for thorium

We have not attempted a direct experimental comparison between AABSN and other thorium reagents except for one of the most recently proposed hydroxyazo dyes[7], *viz.* Eriochrome black T (C.I. mordant black 11). Though the sensitivity of the latter is good, we found the stability to be considerably inferior; even after one hour there was a marked decrease in absorbance both for the reagent and its thorium complex.

The sensitivity index of the AABSN/Th complex calculated from the calibration curve data is 0.008 μg/cm² and the molar absorptivity is approximately 28,000 at 600 mμ. This compares favourably with published data for other thorium reagents (Table V). The colour system forms quickly and is stable thereafter for prolonged periods of time. Very few other metals interfere and most of those which do can be safely masked as described above. Only uranium and vanadium are not amenable to such treatment. However, their determinations singly or in combination with thorium can readily be effected by the same system using a suppressing agent for the thorium. These results clearly indicate that AABSN is a useful addition to the list of reagents available for thorium.

This work was done under an award from the International Atomic Energy Authority to one of us (P.K.).

SUMMARY

Acid alizarin black SN reacts with thorium at pH 4.2 to give a highly sensitive colour reaction with thorium, $\varepsilon_{600\ m\mu} = 28{,}000$. There is no interference from Ba, Ca, Cd, Ce(III), Gd, Hg, La, Mg, Mn, Pb, Pr, Sm, Sr, Zn, Zr, Cl^-, CN^-, I^-, NO_3^-, SO_4^{2-}. The interferences of Al, Bi, Co, Cu, Fe, Ni, Mo, Sb, Sn, Ti and W may be overcome by addition of masking agents. Only U(VI) and V(V) still interfere and these can be determined sequentially with the thorium. The nature of the complex is studied and the mode of its formation.

RÉSUMÉ

Le noir d'alizarine acide SN réagit avec le thorium à pH 4.2, pour donner une réaction colorée très sensible ($\varepsilon_{600\ m\mu} = 28{,}000$). Ba, Ca, Cd, Ce(III), Gd, Hg, La, Mg, Mn, Pb, Pr, Sm, Sr, Zn, Zr, Cl^-, CN^-, I^-, NO_3^-, SO_4^{2-} ne gênent pas; les interférences dues à Al, Bi, Co, Cu, Fe, Ni, Mo, Sb, Sn, Ti et W peuvent être empêchées par addition d'agents de masquage. Les auteurs ont examiné la nature du complexe et son mode de formation.

ZUSAMMENFASSUNG

Saures Alizarin Schwarz SN reagiert mit Thorium beim pH-Wert 4.2 und ergibt eine sehr empfindliche Farbreaktion ($\varepsilon = 28000$ bei 600 mμ). Die Reaktion wird nicht gestört durch: Ba, Ca, Cd, Ce(III), Gd, Hg, La, Mg, Mn, Pb, Pr, Sm, Sr, Zn, Zr, Cl^-, CN^-, J^-, NO_3^-, SO_4^{2-}. Störungen durch Al, Bi, Co, Cu, Fe, Ni, Mo, Sb, Sn, Ti und W können durch Zugabe maskierender Reagenzien vermieden werden. Nur U(VI) und V(V) stören und können folglich gleichzeitig mit dem Thorium bestimmt werden. Die Natur des Komplexes und die Art seiner Bildung wird untersucht.

REFERENCES

1 R. BELCHER, R. A. CLOSE AND T. S. WEST, *Chemist Analyst*, 46 (1957) 86.
2 R. A. CLOSE AND T. S. WEST, *Anal. Chim. Acta*, 23 (1960) 261.
3 R. A. CLOSE AND T. S. WEST, *Anal. Chim. Acta*, 23 (1960) 370.
4 G. ROSS, D. A. AIKENS AND C. N. REILLEY, *Anal. Chem.*, 34 (1962) 1766.
5 J. KÖRBL AND R. PŘIBIL, *Chemist Analyst*, 45 (1956) 162.
6 M. HOSAIN AND T. S. WEST, unpublished work.
7 P. F. LOTT, K. L. CHENG AND B. C. H. KWAN, *Anal. Chem.*, 32 (1960) 1702.

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 2-DIETHYLAMINOETHANETHIOL HYDROCHLORIDE AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

SURESH C. SRIVASTAVA AND MARY L. GOOD
Department of Chemistry, Louisiana State University in New Orleans, Lake Front, New Orleans, La. 70122 (U.S.A.)

(Received June 17th, 1964)

In an earlier publication[1], the use of 2-diethylaminoethanethiol hydrochloride for the spectrophotometric determination of rhodium was described. The method has several advantages over existing colorimetric procedures and is now utilized for the determination of palladium as well as for the simultaneous determination of rhodium and palladium.

BEAMISH AND MCBRYDE[2] have critically evaluated the existing colorimetric methods for the platinum metals. The conditions for color formation in most cases have to be closely controlled and the reagents themselves and their complexes are usually insoluble in water.

Compounds containing the sulfhydryl (-SH) group have received comparatively little attention for the analysis of platinum metals, though a few reagents of this class have been used for the determination of palladium[3-8]. The present reagent, 2-diethylaminoethanethiol hydrochloride, is fairly sensitive compared to the other colorimetric procedures, and the conditions do not have to be rigorously controlled. Also, the reagent as well as the complex are completely soluble in aqueous media.

In a recent publication, BURKE AND YOE[9] have described 5 analogous thioorganic compounds including 2-diethylaminoethanethiol hydrochloride as possible reagents for the spectrophotometric determination of palladium. They made detailed studies with 1-thioglycerol as representative of all the 5 compounds. No data were presented on the other reagents. In view of our earlier interest[1] in 2-diethylaminoethanethiol hydrochloride, it was thought desirable to obtain specific and detailed information on the use of this compound for determination of palladium. The information on this compound is similar in many respects to that on 1-thioglycerol; however, the effects of certain experimental variables on the two systems are different. The sensitivity of this reagent for palladium is also slightly higher than that of 1-thioglycerol. In addition, a method has been worked out for the simultaneous determination of rhodium and palladium.

EXPERIMENTAL

Instruments

A Beckman DK-1 recording spectrophotometer was employed to obtain the absorption spectra of various solutions. All other absorbance measurements were performed with a Beckman DU spectrophotometer. Matched far-UV silica cells of 10-mm path length were used for the measurements.

A Beckman Zeromatic pH meter equipped with micro glass and calomel electrodes was used for pH measurements.

Reagents

Standard palladium solution. A stock solution was prepared by dissolving analytical grade palladium chloride in distilled water, made 0.5 *M* in hydrochloric acid. The palladium content was determined gravimetrically by the dimethylglyoxime method. The stock solution contained 7.97 mg/ml of palladium.

Standard rhodium solution. A standard solution of rhodium nitrate was obtained from J. Bishop and Co. The stock solution was diluted suitably to give a concentration of 1.00 mg Rh/ml. The rhodium content was determined as described earlier[1].

Reagent solution. 2.5 g of reagent-grade 2-diethylaminoethanethiol hydrochloride (K and K Laboratories) were dissolved in 500 ml of distilled water to give a stock solution containing 5 mg/ml. The solution was standardized by determining its sulfur content. It was fairly stable when stored in an inert atmosphere.

Buffer solution. 2 *M* solutions of sodium acetate and hydrochloric acid were prepared with analytical grade reagents. A stock solution of buffer of pH 4.0 was prepared by mixing 80 ml of the acid and 100 ml of the acetate solution and diluting to 500 ml with water. 2 ml of this solution when diluted to 25 ml gave a fairly stabilized pH of 4.00 ±0.05. More concentrated solutions of the buffer may be employed in case of samples requiring greater buffering capacity.

Diverse ions. Stock solutions containing 1 mg/ml of the various ions were prepared from nitrates or chlorides of the metals. Analytical-grade reagents were employed

Recommended procedure for palladium

Introduce a suitable aliquot of the sample containing palladium into a 25-ml volumetric flask. Add 2 ml of the pH 4.0 buffer and then 5 ml of the freshly prepared reagent solution. Dilute the contents to 10 ml with water and heat the flask for 15 min over a boiling water bath. Cool the sample immediately to room temperature and dilute to the mark with distilled water. Measure the absorbance at 303 mμ against a reagent blank prepared in a similar manner. Determine the concentration of palladium using a standard calibration curve.

RESULTS AND DISCUSSION

Absorbance curves of the complex

Palladium(II) forms a yellow colored complex with 2-diethylaminoethanethiol hydrochloride in aqueous solution. The absorbance curves of two different solutions containing 4.26 and 8.51 p.p.m. of palladium respectively against a reagent blank and of the reagent against a water blank are shown in Fig. 1. The complex shows absorption maxima at 258 mμ and 303 mμ. Most of the studies described were carried out at 303 mμ. The color is stable for more than 72 h after full development and is not affected significantly by the order of addition of the reactants.

Effect of time of heating

The development of color at room temperature is slow. The peak at 258 mμ attains its full intensity after 30–60 min but the peak at 303 mμ reaches a maximum value only after more than 2 h. Color formation is very rapid when the solutions are heated on a boiling water bath, the maximum intensity being reached within 10–15 min. The color remains constant up to 45 min of heating after which it fades slightly.

To find the optimum time for heating, a series of solutions containing 1 ml of 10^{-3} *M* palladium solution, 2 ml of buffer and 5 ml reagent, made up to 10 ml with water was prepared and heated on a boiling water bath for varying lengths of time

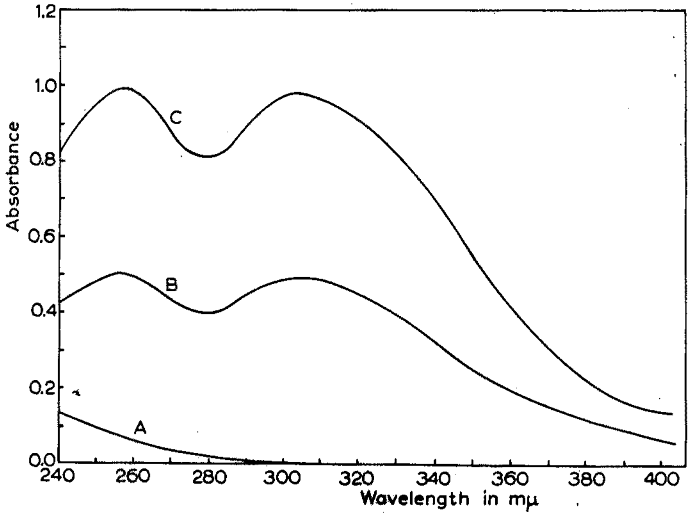


Fig. 1. Absorbance curves of palladium complex and DAT; concn. of DAT $5.9 \cdot 10^{-3}$ *M*. Curve A, reagent alone; curve B, 4.26 p.p.m. Pd(II); curve C, 8.51 p.p.m. Pd(II).

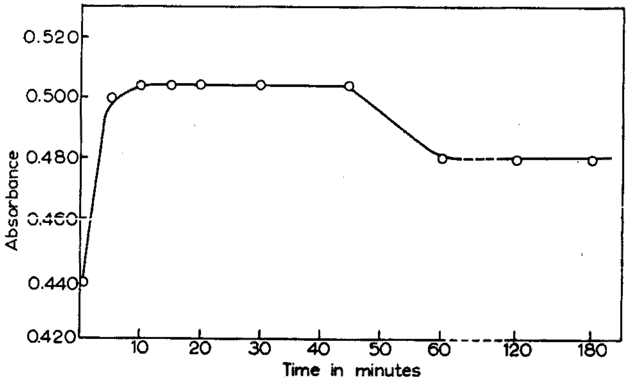


Fig. 2. Effect of heating time on solution absorbance at 303 mμ. Concn. of palladium, 4.26 p.p.m.; concn. of DAT, $5.9 \cdot 10^{-3}$ *M*.

The solutions were cooled immediately to room temperature and diluted to 25 ml with water. The absorbances were measured at 258 and 303 mμ. Some typical results are shown in Fig. 2. A 10-ml total volume of the heating solution is recommended for the satisfactory development of color.

Effect of reagent concentration

Maximum color formation is attained only when there is a large molar excess of the reagent over palladium. A series of solutions containing 1 ml of a 10^{-3} *M* palladium solution were taken through the recommended procedure except that varying amounts of the reagent solution were added. With 15 mg of reagent, the absorbance reached a plateau which continued to at least 40 mg. A total of 15–25 mg of the reagent was found to be sufficient for samples containing 0.8 to 8.5 p.p.m. of palladium, the range for the most accurate spectrophotometric measurements.

Effect of pH

The effect of change in pH on the λ_{max} of the complex, and also on the absorbance values at 303 mμ is shown in Figs. 3 and 4. The color intensity remains unchanged

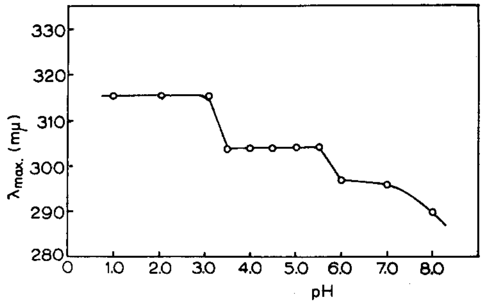


Fig. 3. Variation in the region of maximum absorbance with change in pH. Concn. of palladium, 4.26 p.p.m.; concn. of DAT, $5.9 \cdot 10^{-3}$ *M*.

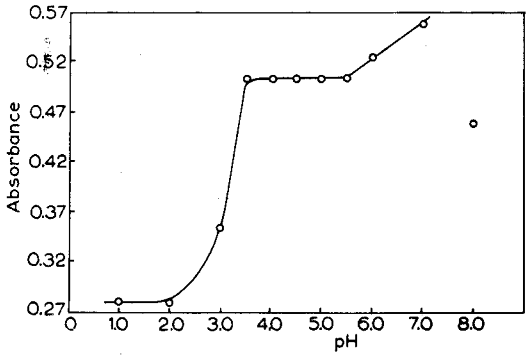


Fig. 4. Variation in color intensity with change in pH at 303 mμ. Concn. of palladium, 4.26 p.p.m.; concn. of DAT, $5.9 \cdot 10^{-3}$ *M*.

between pH 3.5 and 5.5, where the wavelength of maximum absorption remains 303 mμ; a pH of 4.0 was found to be optimal for all the studies. Buffer systems other than that specified affected the nature of the complex.

Validity of Beer's law

Solutions containing varying amounts of palladium were carried through the recommended procedure. The system was found to obey Beer's law over the concentration range 0.2–16.8 p.p.m. of palladium.

Sensitivity and precision

Expressed by SANDELL's notation[10], the sensitivity of the color reaction is 0.0085 μg/cm^2. Based on an absorbance of 0.010 units the practical sensitivity is 0.085 μg/cm^2. The optimum concentration range for the most accurate spectrophotometric measurements as determined by a RINGBOM plot[11] is between 0.8 and 8.5 p.p.m. of palladium.

The average and maximum relative standard deviations, respectively, are ±0.60% and ±1.40% at 303 mμ as shown by the absorbance values of 10 different solutions containing 4.26 p.p.m. of palladium, which were treated according to the optimum conditions.

Interferences due to diverse ions

The effect of a number of diverse ions including the other platinum metals on the system was studied. The ions were added in different amounts to solutions containing 4.26 p.p.m. of palladium and their interferences observed. The concentration of the foreign ion that produces a change in the absorbance of the complex solution of ±2% is taken as the tolerance limit. Table I shows the results.

SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

A method has been worked out for the simultaneous determination of rhodium and palladium. The method, however, does not give very precise determinations, as the error lies in the region of ±5–8%, and a close control over the conditions is necessary. The ratio of rhodium to palladium in the sample should not be greater than 0.5 and the optimum concentration ranges for the metal ions in a mixture for determination are 1.0–4.2 p.p.m. palladium and 0.8–2.5 p.p.m. rhodium.

When a solution of the reagent is added to rhodium, the color development in cold is very slow and practically no color development occurs up to about 30 min. For palladium, however, the color forms instantly at room temperature but reaches a maximum only after 2 h. If the solution is heated on a boiling water bath, color development is hastened and reaches a maximum within 10–15 min for palladium and in 30 min for rhodium.

The palladium complex shows 2 absorption maxima at 258 mμ and 303 mμ respectively. The color intensity of the peak at 258 mμ reaches a maximum value within 30–60 min in the cold, whereas the peak at 303 mμ requires more than 2 h. Due to these practical difficulties, an indirect procedure is used for the simultaneous determination of both metal ions.

Three sets of standard calibration curves are required for the determination,

TABLE I

INTERFERENCES DUE TO DIVERSE IONS

(Final concn. of Pd(II), 4.26 p.p.m.; final concn. of DAT, 1.0 mg/ml)

Foreign ions	*Added as*	*Concn. for ±2% relative error (p.p.m.)*	*Direction of change*	*Per cent relative to palladium*
Fe(III)	$Fe(NO_3)_3 \cdot 9H_2O$	430.23	+	5.4
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	50.9	+	$1.2 \cdot 10^3$
Ni(II)	$Ni(NO_3)_2 \cdot 6H_2O$	49.1	+	$1.5 \cdot 10^3$
Ru(III)	$RuCl_3$	0.29	+	6.8
Rh(III)	$RhCl_3$	0.09	+	2.1
Os(VIII)	OsO_4	1.33	+	31.3
Ir(IV)	$(NH_4)_2IrCl_6$	3.84	+	90.2
Pt(IV)	$H_2PtCl_6 \cdot 6H_2O$	1.55	+	36.4
Cu(II)	$Cu(NO_3)_2 \cdot 3H_2O$	0.48	−	11.3
Ag(I)	$AgNO_3$	7.63	−	179.3
Au(III)	$HAuCl_4$	19.2	−	451.8
Chloride	KCl	$> 10^3$	+	$> 2.3 \cdot 10^4$
Bromide	KBr	$> 10^3$	+	$> 2.3 \cdot 10^4$
Iodide	KI	257.0	−	$6.0 \cdot 10^3$
Sulphate	K_2SO_4	114.9	+	$2.7 \cdot 10^3$
Nitrate	KNO_3	688.9	−	$> 10^4$

two for palladium and one for rhodium. The rhodium curve (I) is obtained at 303 mμ at pH 4.0 by the method described earlier[1]. A calibration curve for palladium at 258 mμ (II) is prepared by plotting the absorbance of a series of solutions containing varying amounts of the palladium complex against a reagent blank. All the solutions are kept at room temperature for 30 min for the attainment of maximum absorbance. Another curve (III) is obtained by taking a similar series but heating it for 15 min on a boiling water bath and measuring the absorbances at 303 mμ against a reagent blank. It was verified that Beer's law is obeyed by both the complexes at the wavelengths of these calibration curves and that absorbances at 303 mμ for both the complexes are quantitatively additive.

A suitable sample of the mixture is taken and the color is developed in the cold. After 30 min, the absorbance is measured at 258 mμ against a reagent blank. The amount of palladium is then found from the standard curve (II). Another aliquot of the mixture is taken and the color is developed by heating for 30 min, the absorbance being measured at 303 mμ. This gives the total amount of rhodium and palladium. The absorbance due to palladium under these conditions can be obtained from the calibration curve (III), as the palladium concentration is already known. This absorbance when subtracted from the total absorbance gives the value for rhodium from the calibration curve (I).

The results for some synthetic samples are given in Table II. The method presents some limitations and may not be employed for very accurate determinations. However, it may prove useful for routine determinations in cases where an error of up to ±5–8% can be tolerated.

TABLE II

SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

Rh(III) taken (p.p.m.)	*Pd(II) taken (p.p.m.)*	*Rh(III) found (p.p.m.)*	*Pd(II) found (p.p.m.)*
4.0	4.0	3.82	4.18
4.0	4.0	3.74	4.26
3.5	4.0	3.61	3.89
3.0	4.0	3.20	3.80
2.5	4.0	2.45	4.05
2.0	4.0	2.04	3.96
1.0	4.0	1.03	3.97
0.8	4.0	0.84	3.96
0.5	4.0	0.52	3.98

Recommended procedure

Transfer an aliquot of the sample containing suitable amounts of rhodium and palladium into a 25-ml volumetric flask. Add 2 ml of a sodium acetate–hydrochloric acid buffer of pH 4.0, followed by addition of 5 ml of the reagent solution. Dilute to 10 ml with water and allow to stand for 30 min. Measure the absorbance at 258 mμ against a similarly prepared reagent blank and calculate the concentration of palladium from curve (I).

Treat another aliquot of the sample similarly but heat on a boiling water bath for 30 min, cool immediately to room temperature, dilute to 25 ml and measure the absorbance at 303 mμ against a reagent blank. This gives the total absorbance due to rhodium and palladium. Determine the concentration of rhodium as discussed above. To obtain reproducible results, care should be observed in the time of heating and in the volume of buffer and solution to be heated.

Financial support by the U.S. Atomic Energy Commission under Contract No. AT-(40-1)-2576 is gratefully acknowledged.

SUMMARY

2-Diethylaminoethanethiol hydrochloride is proposed for spectrophotometric determination of palladium(II). The sensitivity of the reaction is 0.0085 μg/cm^2 and the yellow colored complex shows absorption maxima at 258 mμ and 303 mμ. Color development is slow in the cold but complete after heating for 10–15 min. The optimum pH range is 3.5 to 5.5 and the system adheres to Beer's law between 0.2 and 16.8 p.p.m. of palladium. The average and maximum relative standard deviations were 0.60% and 1.40% respectively. Interferences due to other platinum metals were studied and a procedure is suggested for the simultaneous determination of rhodium and palladium.

RÉSUMÉ

Le chlorhydrate de 2-diéthylaminoéthanethiol est proposé pour le dosage spectrophotométrique du palladium(II). Sensibilité de la réaction: 0.0085 μg/cm^2;

maximum d'absorption à 258 et 303 mμ. La loi de Beer's applique entre 0.2 et 16.8 p.p.m. de palladium. Les auteurs ont examiné l'influence d'autres métaux du groupe du platine et ils proposent un procédé pour le dosage simultané du rhodium et du palladium.

ZUSAMMENFASSUNG

2-Diäthylaminoäthanäthiolhydrochlorid wird für die spektralphotometrische Bestimmung von Palladium(II) vorgeschlagen. Die Empfindlichkeit der Reaktion beträgt 0.0085 $\mu g/cm^2$, und der gelbgefärbte Komplex zeigt ein Absorptionsmaximum bei 258 und 303 mμ. Die Farbentwicklung erfolgt in der Kälte langsam, ist jedoch vollständig nach 10–15 Minuten Erhitzen auf dem Wasserbad. Der optimale pH-Bereich liegt zwischen 3.5 und 5.5. Das Beersche Gesetz wird zwischen 0.2 und 16.8 p.p.m. Palladium befolgt. Die durchschnittlichen und maximalen relativen Standardabweichungen betrugen 0.60% bzw. 1.40%. Störungen durch andere Platinmetalle wurden untersucht und ein Verfahren für die gleichzeitige Bestimmung von Rhodium und Palladium ausgearbeitet.

REFERENCES

1 S. C. Srivastava, *Anal. Chem.*, 35 (1963) 1165.
2 F. E. Beamish and W. A. E. McBryde, *Anal. Chim. Acta*, 9 (1953) 349; 18 (1958) 551.
3 V. L. Wagner, Jr. and J. H. Yoe, *Talanta*, 2 (1959) 223, 239.
4 W. D. Jacobs, C. M. Wheeler and W. H. Waggoner, *Talanta*, 9 (1962) 243.
5 J. T. Pyle and W. D. Jacobs, *Talanta*, 9 (1962) 761.
6 A. Goemiune, M. Herman and Z. Eeckhaut, *Anal. Chim. Acta*, 28 (1963) 512.
7 J. G. Sen Gupta, *Talanta*, 8 (1961) 785.
8 I. Dema and V. Voicu, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, 8 (1960) 173.
9 R. W. Burke and J. H. Yoe, *Talanta*, 10 (1963) 1267.
10 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959.
11 A. Ringbom, *Z. Anal. Chem.*, 115 (1939) 322.

FLUORIMETRIC DETERMINATION OF ZINC WITH DIBENZOTHIAZOLYLMETHANE

R. R. TRENHOLM AND D. E. RYAN
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia (Canada)

(Received July 15th, 1964)

Dibenzothiazolylmethane, $(C_7H_4NS)_2CH_2$, one of a number of substituted benzothiazoles under examination as analytical reagents, produces a specific fluorescence with zinc in ethanol–water solutions. This paper records the results of an investigation of the use of this reaction for the detection and determination of zinc.

EXPERIMENTAL

Apparatus

A 230-W mercury ultraviolet lamp, Hanovia type 16106, was employed for the qualitative detection of fluorescence. Quantitative measurements were made with a Turner Fluorimeter Model 110; the general purpose filters supplied with the fluorimeter were used (primary filter, wavelength 365 mμ, Corning #7–60; secondary filter passes wavelengths longer than 415 mμ, color specification #2A). In addition, a range extension filter was needed when decreased sensitivity was required (color specification ND 1%, Kodak #96).

Preparation of dibenzothiazolylmethane

Dibenzothiazolylmethane (DBM) was prepared by the method of RAI AND BRAUNWARTH[1]. The method involves a condensation of *o*-aminothiophenol (25 g, 0.2 mole) with malonic acid (10 g, 0.1 mole) in the presence of polyphosphoric acid (125 ml). The reaction mixture is kept at 150° for 2 h and, after cooling to room temperature, is poured into ice-cold distilled water. The bright yellow crystals which separate are treated in a 1-l beaker with 10% sodium bicarbonate solution until removal of phosphoric acid from the salt is complete; complete removal of phosphoric acid is indicated by a color change from the bright yellow acid salt to the nearly colorless DBM. The melting point is 96–97° (RAI AND BRAUNWARTH reported 95°). The analytical results found were: C 63.4%, H 3.3%, N 9.7%, S 22.0%; calculated for $C_{15}H_{10}N_2S_2$: C 63.8%, H. 3.6%, N 9.9%, S 22.7%.

Characteristics and reactions of DBM

Dibenzothiazolylmethane is soluble in a variety of organic solvents but is not water-soluble. In 95% ethanol, the solubility was found to be $4.5 \cdot 10^{-2}M$ at room temperature (about 20°). Thirty per cent of water by volume could be added to

$10^{-3}M$ DBM in 95% ethanol without DBM precipitating from solution; the alcohol–water ratio was kept near 7 : 3 therefore in most of the experimental work.

Dibenzothiazolylmethane reacts with aqueous solutions of H_3PO_4, HCl, HNO_3, H_2SO_4 and $HClO_4$ to give insoluble yellow compounds; no precipitate forms in acetic acid solution. When alcoholic DBM solutions are treated with strong alkali, a yellow color develops which fades on standing; the production of this yellow color occurs simultaneously with an increase in the paramagnetic susceptibility of the solution.

Dibenzothiazolylmethane dissolved in ethanol or dioxane is fluorescent when observed under ultraviolet radiation. Qualitative investigation of its reaction with metals was done by mixing 6 drops of $10^{-2}M$ DBM in dioxane with one drop of 10 mg/ml metal ion solution (both with and without one drop of 3 N potassium hydroxide present) and observing under ultraviolet radiation. Only zinc, magnesium, and lithium of 30 cations tested caused a noticeable increase in fluorescence over that due to the reagent alone; those due to lithium and zinc were particularly brilliant. In ethanol–water solutions, the fluorescence due to lithium and magnesium disappeared; similarly, the addition of water to the lithium–dioxane–DBM mixture caused a complete quenching of the fluorescence. Some quenching of the fluorescence of the reagent occurred in the presence of Cu^{2+}, Cd^{2+}, Ag^{+} and Hg^{+}.

Determination of zinc

Maximum sensitivity was obtained in alkaline solution and, in the absence of metals forming insoluble hydroxides, such solutions could be used to determine zinc in the concentration range of 0.05–2.5 mg of zinc/l. It was possible, by changing the fluorimeter range setting, to determine zinc in each of 3 concentration ranges, namely 0–0.5 μg/ml, 0–1.0 μg/ml and 0–2.5 μg/ml.

Decreased sensitivity resulted in solutions buffered with acetate–acetic acid (to give a final measured pH of 6 in 70% ethanol) but the concentration range was extended to 50 mg/l. The acetate buffer was prepared by mixing 50 g of sodium acetate trihydrate with 21 ml of glacial acetic acid and diluting to 100 ml with water.

Procedure. To determine zinc in solutions containing 0.05–2.5 mg of zinc/l, transfer a 2.0-ml aliquot to a 10-ml volumetric flask. Add 1 ml of 0.3 N potassium hydroxide, 7.0 ml of an alcoholic $10^{-4}M$ solution of DBM and mix well. Prepare standards and unknowns together and measure their fluorescence consecutively.

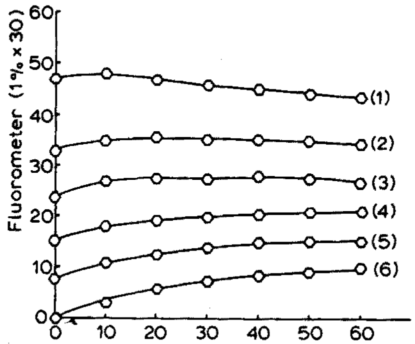
The procedure for determining zinc in solutions containing up to 50 mg of zinc/l was similar except that 1 ml of acetate buffer was substituted for the potassium hydroxide and a more concentrated ($10^{-3}M$) DBM solution was used.

RESULTS AND DISCUSSION

Results, which are typical of those obtained in all concentration ranges, are shown graphically in Figs. 1 and 2. Figure 1 shows that the fluorescence of the blank increased with time but that a linear relationship could be expected for concurrent fluorescence readings; in any single set of measurements the instrument was usually adjusted to give zero reading for the blank. Figure 2 shows that the fluorescence varied linearly with the concentration of zinc present.

Factors affecting the determination

An increase in the fluorescence of the reagent blank with time was accompanied by a decrease in the fluorescence of the zinc species. At low zinc concentrations the former effect predominated (Fig. 1) but with increased zinc concentration the latter effect became prominent (Fig. 3). For quantitative zinc determinations, it was therefore necessary to prepare standards and samples simultaneously; fluorescence readings could be made at any time provided that both standard and sample were measured after the same time interval.



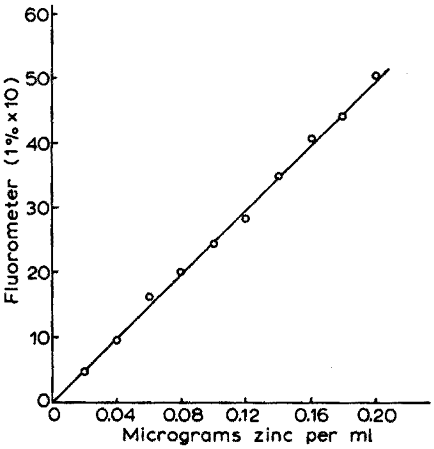


Fig. 1. Variation of fluorescence with time. The amount of zinc present varies from 1 μg (curve 1) to 0 μg (curve 6) in 0.2-μg steps.

Fig. 2. Zinc concentration *vs.* fluorimeter readings for 0–2 μg zinc (10-ml final volume of solution).

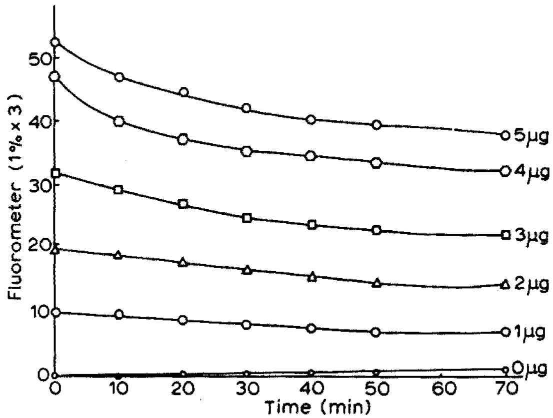


Fig. 3. Fluorescence readings *vs.* time for 0–5 μg zinc in 10-ml final volume of solution.

Maximum fluorescence per microgram of zinc resulted when the concentration of hydroxide ion was kept within the range 0.06–0.30 mmoles of base in the final 10-ml volume of solution; if the hydroxide ion content was outside this range, there was a decrease in sensitivity. Water acted as a fluorescence quencher and the ratio of ethanol to water should remain constant for any given series of samples and standards. Freshly prepared DBM solutions should be used as the background fluorescence of reagent solution increased with ageing; for a linear relationship a 10–100-fold excess of DBM over the theoretical amount for zinc was desirable. A prolonged exposure of the reaction mixture to ultraviolet light increased the rate of fluorescence decay.

In basic solution, cyanide could be used for complexing traces of metals that interfered because of the formation of insoluble hydroxides; the concentration *versus* fluorescence relationship was linear on adding 0.5 ml of 1% potassium cyanide to an adjusted volume of 1.5 ml of zinc solution followed by 7 ml of $10^{-4}M$ DBM and 1 ml of 3 *N* potassium hydroxide. No fluorescence was developed in the presence of large amounts of cyanide, ethylenediaminetetraacetic acid or in an ammonia–ammonium chloride buffer.

In acetate buffer the fluorescence was enhanced in the presence of chloride ion but addition of 0.2 g of sodium chloride to each sample obviated the effect of variation in the concentration of chloride ion present. Nitrate ions depressed the fluorescence but, in the presence of 0.2 g of sodium chloride, as much as 40 mg of nitrate ion could be tolerated. More than 3 mg of sulphate ion should be excluded because of precipitation of metal sulphate in the alcohol–water solution; below this amount, sulphate ions enhanced the fluorescence and samples and standards had to contain the same amount of sulphate for satisfactory results. Up to 5 μg of iron(III) could be tolerated in the sample taken for analysis but larger amounts gave a turbid solution and a resulting decrease in the fluorescence; although no extensive tests were done it is probable that fluoride could be used to complex iron(III), as fluoride ion itself had little effect on the fluorescence.

Applications

The practical lower limit for the qualitative detection of zinc, using an ultraviolet lamp, was 0.1 p.p.m. in basic solution. Zinc (1 mg) in the presence of 2.0 g of cadmium produced a fairly strong fluorescence when 15 ml of $10^{-3}M$ DBM were added to 5 ml of aqueous sample (0.1 ml of 3 *N* potassium hydroxide was added after mixing); a slight fluorescence was observed when only 0.1 mg of zinc was present. It was not possible, however, to detect qualitatively trace amounts of zinc (1 μg) in the presence of large amounts of cadmium in alkaline solution because of precipitation of either cadmium hydroxide or the cadmium–DBM complex. However, quantitative determination of traces of zinc in the presence of cadmium were possible in an acetic acid–acetate buffer solution.

Zinc was determined in reagent-grade cadmium chloride and cadmium nitrate without difficulty. The regular procedure was followed (2 ml of sample, 7 ml of $10^{-3}M$ DBM and 1 ml of acetate buffer) but 200 mg of sodium chloride were added to each sample or standard. The fluorimeter readings for regular increments of zinc added to 100 mg of cadmium (from the chloride or nitrate salt) were the same as those obtained in the absence of cadmium. The percentage of zinc so found in a sample of Baker's analyzed cadmium chloride dihydrate was 0.006%; 0.007% zinc was found in a sample of Merck reagent cadmium nitrate tetrahydrate.

The value of DBM for the determination of zinc was tested further by analysis of some Dowmetals. These metals were analyzed alloys obtained from Thorn Smith (Royal Oak, Michigan, U.S.A.) and contained 0.5–1% zinc in the presence of 90–95% magnesium, 3–9% aluminium and 0.3 to 0.5% manganese. Approximately 0.35 g of each sample was dissolved in 5 ml of concentrated hydrochloric acid. The samples were evaporated to dryness on a steam bath, the residues dissolved in water and then diluted to 100 ml in volumetric flasks; 1-ml aliquots were taken for analysis, 0.2 g of sodium chloride in 1 ml of solution was added, and the regular procedure using acetate buffer was followed. A reagent blank, samples, and standard zinc chloride solutions were run simultaneously. The results shown in Table I indicate the excellent reproducibility obtained with DBM; these results are 7–10% higher than the analyzed values reported.

TABLE I

DETERMINATION OF ZINC IN DOWMETALS

Sample	*Fluorimeter reading(× 1)*	*% Zn found*	*% Zn reported (Thorn Smith analyzed values)*
0 μg Zn	0	—	—
10 μg Zn	27	—	—
20 μg Zn	50	—	—
30 μg Zn	77	—	—
Dowmetal #4	45	0.67	0.61
Dowmetal #4	45	0.67	0.61
Dowmetal #4	44	0.66	0.61
Dowmetal #5	46	0.60	0.55
Dowmetal #5	45	0.58	0.55
Dowmetal #6	88	1.11	1.03
Dowmetal #6	87	1.10	1.03
Reagent blank	0	—	—

Nature of reaction

A yellow solid is formed on adding DBM to alkaline solutions whose concentration of zinc is greater than $10^{-4}M$; the solid, after recrystallizing from dioxane–water, has a melting point of > 350°. The mole ratio of zinc to DBM was found to be 1 : 1 in this solid by photometric precipitation titration. Microanalytical results, for the compound prepared by mixing DBM and zinc in a 1 : 1 mole ratio, were: C 47.3; H 2.5; N 7.6; S 16.7; Ash 19.8. The calculated values for $[(C_{15}H_{10}N_2S_2)Zn(OH)_2]$ are: C 47.4; H 3.2; N 7.4; S 16.8; Ash 20.9.

It is possible that a free radical mechanism is involved in the formation of the fluorescent zinc species. One ml of a saturated solution of DBM in ethanol showed a 1.5-mg pull into a magnetic field of *ca.* 5500 gauss (compared to 1 ml of ethanol) and this was increased to 3 mg on adding 0.1 ml of 3 *N* potassium hydroxide (compared to 1 ml ethanol + 0.1 ml 3 *N* KOH). The solution became diamagnetic on adding 0.1 ml of zinc solution (1 mg Zn) and a yellow precipitate formed. The yellow zinc–BDM solid was non-fluorescent in the solid form but strongly fluorescent when dissolved in dioxane. It is hoped to investigate further the phenomenon of free radical formation with DBM and related compounds.

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

SUMMARY

Dibenzothiazolylmethane produces a specific fluorescence with zinc in ethanol–water solutions. Zinc is determined quantitatively in solutions containing 0.05 to 50 mg of zinc/l. One part of zinc can be detected in the presence of 20,000 parts of cadmium and quantitative determinations of zinc in cadmium salts are readily done. The method can be applied to the analysis of non-ferrous alloys such as Dowmetals.

RÉSUMÉ

Le dibenzothiazolylméthane donne une fluorescence spécifique avec le zinc, en solutions éthanol–eau. Cette réaction permet un dosage quantitatif du zinc dans des solutions renfermant 0.05 à 50 mg Zn par litre. Il est possible de doser ainsi le zinc dans des sels de cadmium; une partie de zinc peut être décelée en présence de 20,000 parties de cadmium. Cette méthode peut également s'appliquer à l'analyse d'alliages non-ferreux.

ZUSAMMENFASSUNG

In Äthanol–Wasser-Lösungen ergibt Dibenzothiazolylmethan mit Zink, eine spezifische Fluoreszenz, die eine quantitative Bestimmung des Zinks im Bereich von 0.05–50 mg Zn/Ltr ermöglicht. 1 Teil Zink kann neben 20000 Teilen Cadmium nachgewiesen und damit die quantitative Bestimmung des Zinks im Cadmium leicht durchgeführt werden. Die Methode eignet sich für die Analyse von Nicht-eisenlegierungen.

REFERENCES

1 C. Rai and J. B. Braunwarth, *J. Org. Chem.*, 26 (1961) 3434.

ZUR RELATIVKONDUKTOMETRISCHER BESTIMMUNG DES SCHWEFELS IN ERDÖLPRODUKTEN

H. MALISSA, L. MACHHERNDL UND E. PELL
Institut für Analytische Chemie und Mikrochemie, Technische Hochschule Wien (Österreich)
(Eingegangen den 21. Oktober, 1964)

Das heute am häufigsten verwendete Verfahren zur Schwefelbestimmung in Erdölprodukten ist die Verbrennung im Quarzrohr nach GROTE–KREKELER[1] und die anschliessende Erfassung der in den Absorptionsgefässen gebildeten Schwefelsäure. Sind diesem Verfahren bezüglich der Grösse der Einwaage Grenzen gesetzt, so kann dieser Nachteil bei leicht flüchtigen Proben durch die Heranziehung der Lampenmethode[2], die auf einem ähnlichen Prinzip beruht, wettgemacht werden. Für die Bestimmung von Schwefel in der Grössenordnung von 1 bis 10 mg pro kg wurde in letzter Zeit von der "International Conference of Benzole Producers" ein Verfahren[3] ausgearbeitet, das ebenfalls eine grössere Probenmenge anzuwenden gestattet. Hierbei wird eine spezielle Brennerkonstruktion angewandt und als Endbestimmung die konduktometrische Titration des gebildeten Sulfates durchgeführt. Weiters ist das Verfahren von WICKBOLD[4], die Verbrennung in der Knallgasflamme, anzuführen, das sehr zeitsparend ist und besonders zur Bestimmung kleinster Schwefelgehalte herangezogen werden kann. Die im letzten Jahrzehnt entwickelte Kolbenmethode nach SCHÖNIGER[5], die, als Halbmikromethode angewandt, bereits eine merkliche Verkürzung der Aufschlussdauer gewährleistet, darf in diesem Zusammenhang nicht unerwähnt bleiben. Auch die Röntgenstrahlenabsorption[6,7] wird bereits zur Schwefelbestimmung herangezogen und WIESNER[8] beschreibt ein ähnliches Verfahren, wobei er als Strahlendetektor ein Methandurchflusszählrohr verwendet. Letztere Analysenmethoden sind genau und rasch, doch von geringer Spezifität und verlangen grossen apparativen Aufwand.

Von den genannten Verfahren sind weiters jene, die mit einem langsamen Verbrennungsprozess verbunden sind und mit einer gravimetrischen Endbestimmung ausgeführt werden, umständlich und langwierig.

Die relativkonduktometrische Bestimmung des Schwefels

Um die Nachteile einiger der angeführten Verfahren zu vermeiden, wurde von uns das in der Mikroelementaranalyse bereits mit sehr gutem Erfolg angewandte Verfahren der Verbrennung im leeren Rohr und der relativkonduktometrischen Endbestimmung der Verbrennungsprodukte[9] auch zur Schwefelbestimmung in Erdölprodukten benützt. Es handelt sich hierbei um ein mikroanalytisches Verfahren, bei welchem — infolge der sehr empfindlichen Messmethodik — mit Einwaagen zwischen 1–15 mg das Auslangen gefunden werden kann. Bei vorsichtiger Verbrennungsführung können aber auch weitaus grössere Probenmengen eingesetzt werden, allerdings auf Kosten des Zeitvorteiles.

Prinzip und Entwicklung der Methode. Das Prinzip der Methode besteht darin, dass die organische Substanz bei Temperaturen zwischen 1200–1400° im Sauerstoffstrom in einem leeren, einseitig offenen Keramikrohr verbrannt wird. Die Verbrennungsprodukte werden mit Hilfe eines Pumpensystems durch eine aus verdünnter Schwefelsäure und Wasserstoffperoxid bestehende Absorptionslösung, in welcher das Schwefeldioxid in Schwefelsäure übergeführt wird, gesaugt. Der Verlauf der dadurch verursachten Leitfähigkeitsänderung der Absorptionslösung gegenüber einer nicht begasten Absorptionslösung oder einem geeigneten Festwiderstand wird kontinuierlich aufgezeichnet und der erreichte Endwert als Mass für den Schwefelgehalt der organischen Substanz herangezogen. Das Zusammenwirken von relativ hoher Verbrennungstemperatur mit rascher Absaugung der Verbrennungsgase und vollständiger Absorption, verbunden mit der automatischen Registrierung ergibt ein ausserordentlich präzises und rasches Analysenverfahren, bei welchem somit alle Wägevorgänge mit Ausnahme der Einwaage ausgeschaltet sind und die Erfassung und Registrierung der Verbrennungsprodukte nahezu verzögerungsfrei und selbsttätig erfolgt.

Die ersten Arbeiten zur relativkonduktometrischen Schwefelbestimmung gehen auf KOCH, ECKHARD UND MALISSA[10] zurück und beschäftigen sich in erster Linie mit der Überprüfung verschiedener Absorptionsmittel. Auch wurden Studien über die entstehenden Verbrennungsprodukte gemacht und dabei die Gewissheit erlangt,

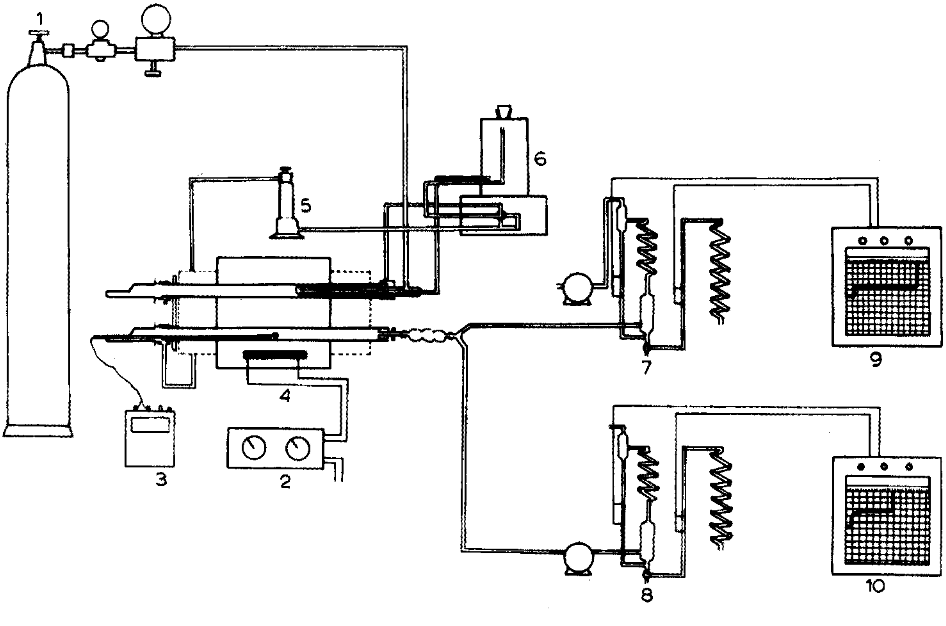


Fig. 1. Apparatur zur gleichzeitigen Schwefel- und Kohlenstoffbestimmung. 1, Sauerstoffbombe mit Reduzierventil; 2, Transformator; 3, Millivoltmeter mit Temperatureichung; 4, Verbrennungsofen; 5, Trockenvorlage; 6, Vorlage mit Natronkalk; 7, Messwertgeberapparatur für Schwefel; 8, Messwertgeberapparatur für Kohlenstoff; 9, Recorder für die Schwefelmesswertgeberapparatur; 10, Recorder für die Kohlenstoffmesswertgeberapparatur.

dass es bei den vorliegenden Temperaturen praktisch nur zur Bildung von Kohlendioxid, Wasser und Schwefeldioxid kommt[11,12]. PELL, MACHHERNDL UND MALISSA[13] entwickelten die Methode weiter zu einem genauen, schnellen und betriebssicheren Analysenverfahren, das durch systematische Reihenuntersuchungen organischer Verbindungen, die den Schwefel in den verschiedensten Bindungsformen enthalten, überprüft wurde.

Beschreibung der Apparatur. Zur Durchführung der relativkonduktometrischen Analysenverfahren dient der in Fig. 1 skizzierte Apparat*.

Er besteht im wesentlichen aus folgenden Teilen:

(*1*) Sauerstoffreinigung und Verbrennungsofen.
(*2*) Messwertgeberapparatur mit Messzelle und Pumpensystem.
(*3*) Registriereinrichtung.

ad (*1*) Als Verbrennungsofen dient ein handelsüblicher Doppelrohrsilitstabofen mit einer 200-mm langen Heizzone. Bei einer Leistungsaufnahme von 1.6 kW kann man kurzfristig eine maximale Temperatur von etwa 1450° erreichen. Temperaturen zwischen 1200–1300° können über Monate gehalten werden.

Die Vorreinigung des einer Stahlflasche entnommenen Sauerstoffes erfolgt in einer Quarzhülse, die in eines der beiden Verbrennungsrohre hineinragt. Dabei werden die im Sauerstoff enthaltenen brennbaren Verunreinigungen zu Kohlendioxid und Wasser oxydiert und in den nachfolgenden Reinigungstürmen (mit Natronkalk- und Kalziumchlorid-Füllung) zusammen mit eventuellen anderen Verunreinigungen aus dem Gasstrom entfernt. Besonderer Wert muss auf die Entfernung des bei der Verbrennung entstehenden Wassers gelegt werden.

Die Verbrennung der Analysensubstanz erfolgt in Keramikrohren von 17 mm lichter Weite und 500 mm Länge, die eine nutzbare Heizfläche von etwa 100 cm^2 ergeben.

ad (*2*) Der Hauptbestandteil der Messwertgeberapparatur ist die Messzelle. Sie besteht aus einer Mischkammer und einem Gasabscheider zur intensiven Durchmischung und nachherigen Trennung von Verbrennungsgas und Absorptionsflüssigkeit. Die gasbeladene Absorptionslösung fliesst unmittelbar danach durch eine Kapillare, in welcher mehrere Platindrahtelektroden eingeschmolzen sind. Parallel dazu befindet sich eine gleich aufgebaute Kapillare, welche von der unbegasten Absorptionslösung durchflossen wird. Die ganze Messzelle taucht in ein Ölbad, womit die beiden Elektroden-Messstrecken auf gleicher Temperatur gehalten werden.

Mittels des Pumpensystems werden die Verbrennungsgase aus dem Verbrennungsrohr gesaugt und durch die Messzelle gedrückt. Die Saugleistung ist konstant und beträgt derzeit 273 ml/min. Ein Vorratsbehälter für die Absorptionslösung ist so an das Pumpensystem angeschlossen, dass dieses die Lösung mit Druck automatisch in die Messpipette und anschliessend in die Messzelle befördert. Als Absorptionslösung dient eine $N/500$ Schwefelsäurelösung mit einem Zusatz von 0.5 ml 30 Gew.%-iger Wasserstoffperoxidlösung pro Liter.

ad (*3*) Die zwischen den beiden Elektrodenmessstrecken auftretende Spannungsdifferenz speist über ein Verstärkersystem ein Nullmotormesswerk, an das ein Zeiger mit Schreibfeder angebracht ist. Der Recorder ist ein integrierender Bestandteil der gesamten Einrichtung, denn nur mit seiner Hilfe ist es möglich, den gesamten oft

---

* Herstellungsfirma: H. Wösthoff, OHG, Hagenstrasse 30, Bochum, D.B.R.

sehr charakteristischen Verbrennungsablauf sowie sein Ende zu verfolgen, ohne Zwischenmessungen durchführen zu müssen. Fig. 2 zeigt einige typische Kurvenzüge.

Durchführung der Bestimmung. Der einer Stahlflasche entnommene Sauerstoff wird durch ein Feinreduzierventil auf einen Druck von 500 mm Wassersäule reduziert.

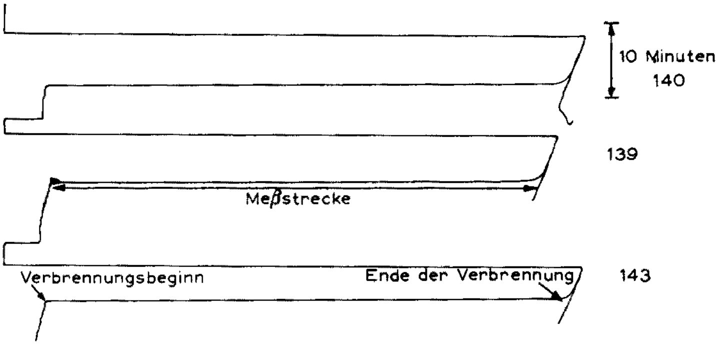


Fig. 2. Typische Kurvenzüge von Schwefelbestimmungen.

Dieser Druck ist so bemessen, dass nach Deckung des Sauerstoffbedarfes der Saugleitung am Eintrittsende des Verbrennungsrohres noch Sauerstoff austritt. Dieser "Sauerstoffvorhang" verhindert das Eindringen von Luft und erübrigt einen Verschluss.

Über dieses Eintrittsende lässt sich das Verbrennungsgut rasch bis in die Verbrennungszone einführen. Die Analysensubstanz wird in einem Mikro-Platintiegel, der in einen entsprechenden Einschiebestab aus Quarz eingehängt werden kann, eingebracht. Die Grösse der Einwaage bewegt sich je nach dem zu erwartenden Schwefelgehalt zwischen 1–15 mg. Die Temperaturkontrolle erfolgt mittels eines Thermoelementes, das ebenfalls im Einschiebestab eingebaut ist. Die Verbrennungsgase gelangen nach Verlassen des Verbrennungsrohres in eine mit Kalziumchlorid gefüllte Vorlage, wo der Wasserdampf, bevor er kondensieren kann, absorbiert wird und von da in die Messwertgeber-Apparatur. Durch eine Glasdüse werden die Verbrennungsgase in die Messzelle geleitet, in welcher die Absorptionslösung während der ganzen Messdauer durch Mischkammer, Gasabscheider und Elektroden-Messstrecke im Kreislauf geführt wird. Hier erfolgt die Oxydation des Schwefeldioxides zu Schwefeltrioxid und die Bildung von Schwefelsäure. Das so von Schwefeloxiden befreite und von der Absorptionsflüssigkeit getrennte Gas gelangt schliesslich in die Atmosphäre. Nach dem Ende der Messung wird die Absorptionslösung abgelassen und Mischkammer, Gasabscheider und Elektroden-Messstrecke mit frischer Lösung gespült; schliesslich werden mit Hilfe einer in den Flüssigkeitsweg eingeschalteten Pipette derzeit genau 18 ml neue Absorptionslösung aus dem Vorratsbehälter in die Zelle gebracht. Dieser Vorgang der Spülung und Füllung mit neuer Absorptionslösung, der *ca.* 2–3 Minuten in Anspruch nimmt, erfolgt nach jeder einzelnen Bestimmung.

Die Durchführung einer gesamten Bestimmung von Einwaage bis Auswertung dauert 8–10 Minuten.

Auswertung der Messergebnisse. Da die Gesamtmethode nicht nur aus der Absorption des Schwefeldioxides besteht, sondern — wie jede andere — auch die Verbrennungseigenschaften der Probe, usw. mitenthält, ist zur Erzielung genauer Analysenresultate ein Eichen der Apparatur mit definierten Testsubstanzen notwendig. Dies hat auch den Vorteil, dass die Absorptionslösung nicht auf eine bestimmte Konzentration eingestellt werden muss. Aus einer Serie von mindestens 5 Bestimmungen dieser Testsubstanz errechnet man sich den Faktor, der mit der Konzentration des Absorptionsmittels, dem eingestellten Messbereich des Gerätes, der Verbrennungsart und anderen Versuchsbedingungen etwas schwankt und der die einem Zeigerausschlag von 1 mm entsprechende Menge Schwefel in μg angibt.

Zur Berechnung des Schwefelgehaltes unbekannter Proben wird der gemessene Endwert des Zeigerausschlages mit dem unter gleichen Versuchsbedingungen erhaltenen Faktor multipliziert und auf die Einwaage bezogen.

$$\%\text{ S in der Probe} = \frac{\text{Zeigerausschlag} \cdot \text{F} \cdot 100}{\text{Einwaage}}$$

Die Leistungsfähigkeit dieser Methode wurde mit der Kolbenmethode[5] verglichen und dieser zumindestens hinsichtlich der Analysengenauigkeit gleichwertig befunden.

Als Streumass für die möglichen Abweichungen vom arithmethischen Mittelwert einer Bestimmungsserie verwenden wir die Standardabweichung (mittlere quadratische Abweichung), errechnet nach:

$$s = \pm \sqrt{\frac{\sum\limits_{i=1}^{i=n} (x_i - \bar{x})^2}{n - 1}}$$

n = Anzahl der Messwerte
x_i = einzelner Messwert
$\bar{x}$ = Mittelwert

Im Regelfall einer Zufallsverteilung (Gauss'schen Normalverteilung) liegen 68.3% aller möglichen Messwerte innerhalb des Bereiches $\pm$ s um den wahren Mittelwert. Wegen der geringen Sicherheit von nur 68.3% wird die Grösse s selten als Mass des Prüffehlers benützt, sondern dieser Bereich auf die Breite $\pm$ 3 s erweitert. In diesen Bereich, Streubereich genannt, fallen 99.73 % aller Messwerte.

Anwendung auf Erdölprodukte

Analysenergebnisse. Rasche Verbrennung. Die relativkonduktometrische Bestimmung des Schwefels wurde auf eine Reihe schwerer flüchtiger Mineralölprodukte angewandt (siehe Tabelle I). Die erste Rubrik enthält die Schwefelgehalte dieser Produkte, die nach dem Verfahren von GROTE–KREKELER, Ö-Norm C 1140 erhalten wurden. Die $\bar{x}$-Werte hingegen sind die Mittelwerte aus je 10 bzw. 11 relativkonduktometrischen Bestimmungen, $\pm$ s in % ist die einfache Standardabweichung.

Als Beispiel für die Übereinstimmung der Parallel-Werte eines Produktes seien die Ergebnisse des Heizöl schwer, Probe Nr. 6, mit dem angegebenen Wert von 0.79% S in Tabelle II angeführt.

Aus diesen Untersuchungsreihen kann man ersehen, dass sich die Bestimmungsmethode auf jeden Fall für Produkte, deren Flüchtigkeit ein Einwägen ohne

TABELLE I

Nr.	*Material*	*Werte nach Grote–Krekeler (% S)*	*Anzahl der Bestimmungen*	$\bar{x}$ *(%)*	± *s* *(%)*
1	Heizöl schwer	3.8	10	3.74	0.038
2	Heizöl schwer	3.6	11	3.61	0.087
3	Heizöl mittel	3.1	10	3.08	0.098
4	Maschinenöl	1.61	11	1.61	0.031
5	Maschinenöl	0.93	11	0.91	0.035
6	Heizöl schwer	0.79	11	0.79	0.027
7	Heizöl schwer	0.38	11	0.39	0.027
8	Dieselöl	0.16–0.17	3	0.16	—

TABELLE II

Analysennummer	*Einwaage (mg)*	*Zeigerausschlag (mm)*	*Schwefelgehalt (%)*
1149	6.964	34.4	0.74
1150	5.578	30.9	0.83
1151	5.190	27.9	0.81
1152	5.639	29.7	0.79
1153	4.943	26.9	0.81
1154	5.034	27.4	0.82
1155	6.508	32.0	0.74
1156	4.824	25.3	0.79
1157	4.624	24.8	0.80
1158	5.540	28.4	0.77
1159	5.956	30.7	0.77
1160	5.618	29.0	0.77
	$\bar{x} = 0.79\%$	$s = \pm 0.027$	

merkliche Verluste im offenen Platintiegel ermöglicht, gut eignet. Für Produkte mit leichter flüchtigen Anteilen ist ein Einwägen in Kapillaren erforderlich.

Da man mit der Grösse der Einwaage wegen des damit verbundenen grossen Sauerstoffbedarfes pro Zeiteinheit nicht beliebig hinaufgehen kann (Einwaagengrösse max. 20 mg) ergibt sich zumindest unter normalen Versuchsbedingungen — d.h. rasches Einbringen, damit explosionsartige Verbrennung des Analysengutes — 0.1% S als untere Grenze des Schwefelgehaltes der Probe. Bei langsamen Verbrennungen — siehe Versuchsführung weiterunten — können auch kleinere Schwefelgehalte bestimmt werden. Nach oben hin ist jeder Schwefelgehalt der Probe bestimmbar.

Das Einwägen der Proben erfolgte in den meisten Fällen auf handelsüblichen Mikrobalkenwaagen. Aber auch Torsionswaagen, bei denen die Proben in Platin- oder Glasösen zur Einwaage gelangten, wurden mit gutem Erfolg angewandt.

Langsame Verbrennung. Die relativkonduktometrische Bestimmungsmethode eröffnet neben den bisher behandelten raschen Analysenverfahren noch eine zweite Möglichkeit, nämlich die der langsamen Verbrennung, die eine Zeitdauer von 0.5 Minuten bis zu einer Stunde und mehr in Anspruch nehmen kann. Damit ist einerseits infolge des wesentlich höheren Sauerstoffangebotes die Verbrennung grösserer Probenmengen — bis zu 1 g — und damit die Bestimmung niedriger Schwefelgehalte möglich, andererseits besteht der grosse Vorteil dieser Verbrennungstechnik darin, dass man — ohne Rücksicht auf die Zeitfrage — bei sogen. "gelenkten" Verbrennungen fraktionierte und temperaturkontrollierte Verbrennungsabläufe mit sehr geringen Substanzmengen ausführen kann. Wird nämlich die zu verbrennende Probe nicht plötzlich von 20° auf 1400° gebracht, sondern durch langsames Einschieben mittels eines geeigneten motorischen Vortriebes dieser Temperaturbereich in 1, 2, 10, 20 Minuten oder beliebig längerer Zeit durchlaufen, so erhält man an Stelle der fast waagrechten Linie eine in mehreren Stufen bzw. Kurven aufsteigende Aufzeichnung auf dem Registrierstreifen, die bei Einhaltung der gleichen Versuchsbedingungen für die einzelnen Substanzen reproduzierbar ist und deren Endwert stets dem zu ermittelnden Schwefelgehalt entspricht[14]. Es handelt sich dabei nicht um eine Aufteilung in Siedebereiche, einer Destillation entsprechend, sondern um ein Abdunsten im Sauerstoffstrom mit anschliessender Verbrennung dieser abgetriebenen Anteile bzw. des Crackrückstandes.

An Hand von einigen Beispielen von Verbrennungen und ihren Aufzeichnungen durch den Schreiber möge diese Versuchsführung veranschaulicht werden. Siehe dazu Fig. 3: Registrierung von Schwefel-Bestimmungen in einigen Einwaagen eines Heizöl schwer, Probe Nr. 2, Schwefelgehalt 3.6%.

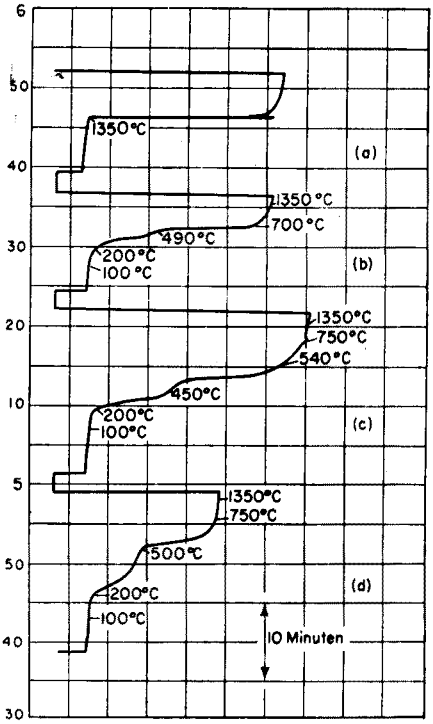


Fig. 3. Registrierung von Schwefelbestimmungen in einigen Einwaagen eines schweren Heizöles (3.6% S).

Die Aufzeichnungen a und b (Einschieben einer Einwaage im Verlauf von 1 bzw. 5 Minuten) zeigen noch keine Differenzierung in verschieden flüchtige Anteile. Erst bei einer Einschiebedauer von 10 bzw. 20 Minuten (Aufzeichnung c und d) treten stufenweise Registrierungen auf. Zwischen Raumtemperatur und 200° scheinen dabei keine wesentlichen Anteile an flüchtigen Schwefelverbindungen zu verbrennen. Im Temperaturbereich von 200–500° vergasen bzw. verbrennen Produkte, die etwas mehr als 35% des Gesamtschwefels enthalten, während der Rest zwischen 500–750° in SO_2 übergeführt wird. Über dieser Temperatur waren keine schwefelhaltigen Verbindungen mehr zu erfassen.

Bei einem anderen Heizöl schwer, Probe Nr. 1, Schwefelgehalt 3.8%, ergaben mehrere Analysen übereinstimmend die nachstehenden Werte:

Temperaturbereich (°)	*% des Gesamtschwefelgehaltes*
bis 200	15
200–250	13
250–300	4
300–400	62
400–480	6

Daraus ist ersichtlich, dass fast 70 % des Gesamtschwefelgehaltes im Temperaturbereich von 300–400° abgetrieben wird. Die Anteile zwischen 250–300° und 400–480° sind die schwefelärmsten.

Bei den Maschinenölen (Probe 4 und 5) wurde eine zweistufige Registrierung des Schwefelgehaltes in folgender Aufteilung erhalten:

Maschinenöl (Probe 4), Gesamtschwefelgehalt 1.61%.

Temperaturbereich (°)	*% des Gesamtschwefelgehaltes*
140–210	63
210–400	37

Maschinenöl (Probe 5), Gesamtschwefelgehalt 0.91 %.

Temperaturbereich (°)	*% des Gesamtschwefelgehaltes*
180–200	78.5
200–400	21.5

In beiden Fällen wird hiernach die Hauptmenge des Schwefels bis etwa 200° angezeigt.

Ein Versuch, in zwei Rohölproben (angegebener Gesamtschwefel in Probe A $\sim$0.4 bzw. in Probe B $\sim$0.6% S) auf diese Weise die Aufteilung des Schwefels auf die einzelnen Temperaturbereiche zu erfassen, ergab folgendes Bild (die Flüchtigkeit der niedrigsiedenden Anteile wurde hierbei ausser Acht gelassen):

Temperaturbereich (°)	*% des Gesamtschwefelgehaltes*	
	Rohöl A	*Rohöl B*
50– 200	47.5	40.0
200– 300	20.0	25.0
300– 400	15.0	20.0
400–1000	10.0	10.0
über 1000	7.5	5.0

Die hier angeführten Beispiele sollen zeigen, dass mit Hilfe des relativkonduktometrischen Bestimmungsverfahrens Kurven erhalten werden, die für diese Methode typisch sind und den zeitlichen und quantitativen Ablauf der Verbrennung der in der jeweiligen Substanz enthaltenen schwefelhaltigen Komponenten wiedergeben.

ZUSAMMENFASSUNG

Die Methode der relativkonduktometrischen Bestimmung des Schwefels, die bereits mit gutem Erfolg in der Mikroelementaranalyse durchgeführt wird, wurde auf die Bestimmung des Schwefels in einigen Erdölprodukten angewandt. Die angegebenen Analysenergebnisse zeigen einerseits die sehr gute Brauchbarkeit der Methode zur raschen Erfassung des Gesamtschwefelgehaltes, andererseits gibt die modifizierte Methode eine Aussage über die zeitliche Abfolge der Verbrennung schwefelhaltiger Verbindungen.

SUMMARY

The relative conductometric method for the determination of sulphur, which has already been used for microelemental analysis, is applied to various petroleum products. The results obtained show that the method is not only very suitable for the rapid determination of the total sulphur content but also gives information on the nature of the combustion processes for sulphur-containing compounds.

RÉSUMÉ

On a appliqué la méthode conductométrique relative pour le dosage du soufre dans divers dérivés du pétrole (méthode déjà utilisée en microanalyse élémentaire). Les résultats obtenus montrent que la méthode n'est pas seulement très avantageuse pour le dosage rapide du soufre total, mais qu'elle renseigne également sur la nature des procédés de combustion de composés sulfurés.

LITERATUR

1 W. Grote und H. Krekeler, *Angew. Chem.*, 46 (1937) 106.
2 *Lampenmethode ASTM D 90; D 1266; DIN 51771.*
3 I.C.B.P., *Anal. Chem.*, 36 (1964) 339.
4 R. Wickbold, *Angew. Chem.*, 64 (1952) 133; 66 (1954) 173; 69 (1957) 530.
5 W. Schöniger, *Mikrochim. Acta*, (1955) 123; (1956) 869.
6 A. Y. Mottlau und C. E. Driesens, *Anal. Chem.*, 24 (1952) 1852.
7 I. S. Wiberley, *Mikrochem. J.*, 2 (1958) 219.
8 L. Wiesner, *Atomwirtschaft*, 6 (1961) 278.
9 H. Malissa, *Mikrochim. Acta*, (1957) 553.
10 W. Koch, S. Eckhard und H. Malissa, *Arch. Eisenhuettenw.*, 29 (1958) 543.
11 H. Malissa, *Mikrochim. Acta*, (1960) 127.
12 H. Malissa, *Z. Anal. Chem.*, 181 (1961) 39.
13 E. Pell, L. Machherndl und H. Malissa, *Mikrochim. Acta*, (1963) 615.
14 E. Pell und H. Malissa, *Talanta*, 9 (1962) 1056.

VOLTAMMETRY AND CONTROLLED-POTENTIAL COULOMETRY WITH BORON CARBIDE ELECTRODES*

W. R. MOUNTCASTLE, JR.**
Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)

(Received July 22nd, 1964)

At the Oak Ridge National Laboratory easily reducible or oxidizable ions are determined routinely by controlled-potential coulometric titration. The method is well-suited to the remotely controlled analysis of highly radioactive fission products. In certain electroanalytical methods, solid electrodes can be used. However, in a large number of coulometric reduction titrations made in acid solutions, a stirred mercury pool must be used because the hydrogen ion is reduced at a noble metal electrode.

MUELLER AND ADAMS[1,2] have reported that the reduction potential for hydrogen ion at a boron carbide electrode is very high. This observation indicates that the electrode might be very useful in electrochemical methods. Accordingly, it was evaluated for such use; the results of this study are presented below.

EXPERIMENTAL

Instruments

Polarograph. An ORNL Model Q-1673[3] was used to obtain all current–voltage curves. The auxiliary apparatus (*i.e.*, cell and gas train) was conventional except that the dropping-mercury electrode was replaced by the boron carbide electrode.

Coulometric titrator. An ORNL Model Q-2005, controlled-potential[4], was used for all coulometry. The calibration, use and care of this instrument have been described[5]. A mechanical stirrer and a saturated calomel reference electrode (S.C.E.) were used in a conventional cell[6]. The Teflon cap covering the cell was modified by drilling a hole to accommodate the boron carbide electrode, which replaced the stirred mercury pool.

Reagents

Standard solutions of iron(III) were prepared from 99.95% pure electrolytic iron wire.

Standard solutions of uranium(VI) were prepared and standardized according to instructions given in the potentiometric ferric sulfate method[7].

All reagents were prepared from analytical grade chemicals.

---

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

** Present address: Birmingham-Southern College, Birmingham, Ala.

Procedures

Voltammetry. Current–voltage curves for the ions studied were determined by single-sweep voltammetric procedures. The voltage scan rate was 100 mV/min. Conventional methods were used to check the dependence of the peak current on the concentration of iron(III) or uranium(VI). No corrections of $E_{p/2}$ or peak currents were made since the currents were small.

Coulometry. Controlled-potential coulometric data were obtained conventionally. An exact test portion of the sample was added to 15 ml of supporting medium. The test solution was sparged for 5 min with helium.

For iron(III) in 1.0 M hydrochloric acid as the supporting medium, the test solution was preoxidized at + 1.000 V *vs.* S.C.E. Each test solution was then reduced at a predetermined potential to a background of 50 μA. The readout voltage was taken, and the amount of iron(III) reduced to iron(II) was determined via Faraday's laws ($n = 1$). For iron(II), the test solution was prereduced at 0.000 V *vs.* S.C.E. and was then oxidized at a predetermined potential.

For uranium(VI), the test solution was prereduced at + 0.075 V *vs.* S.C.E. and was then reduced at a predetermined potential. The amount of uranium(VI) was calculated from the readout voltage via Faraday's laws ($n = 2$).

A blanket of helium was maintained over all the test solutions during the pretitrations and titrations.

Boron carbide electrodes

The techniques of MUELLER AND ADAMS[2] were used to prepare the boron carbide electrodes. Three boron carbide cylinders were used: 3/16 × 3/4 in. and 3/8 × 1.75 in. cylinders obtained directly from the Norton Company and a 1/4 × 1 in. cylinder provided by MUELLER AND ADAMS[2] and obtained originally from the Norton Company.

One end surface of the 3/16 in.-diameter cylinder was polished to a mirror-like finish. Erratic behavior was observed when the polished cylinder was used as a working electrode. It was reported[2] that anodic stripping at + 1.00 V in 1 M nitric acid was effective in reducing residual currents. Some caution must be exercised. When 3 V was applied for 64 h to an electrolysis cell consisting of the polished electrode (anode), auxiliary electrode, and 1 M nitric acid, the shape of the electrode was changed to a sharp cone. Spectrographic analysis of the remains of the cylinder of boron carbide indicated the presence of traces of Al, Cu, Ca, Fe, and Mg, but the sum of these impurities did not exceed 1% of the electrode material. Boron carbide has a higher resistance than conventional metal electrodes. It seems probable that strains or microfissures were created in the polishing procedure. Disintegration of the electrode could have resulted from high local currents originating from short-range potential differences across the fissures at the electrode–solution interface.

The 1/4 in.- and 3/8 in.-diameter electrodes were used as received. The electrodes were cleaned in carbon tetrachloride and hot concentrated nitric acid. The 3/8 in.-diameter electrode was mounted for coulometric work with about a 1/2-in. length of the cylinder exposed (effective area ≈ 0.6 in.^{2}). The working surface areas were defined by winding drafting tape tightly around the cylinders. The tape was covered with ceresin wax. The electrodes were resistant to dilute acids; however, on alternate usage in 20% (v/v) hydrochloric acid and 8 M ammonia, they eventually leaked.

DISCUSSION OF RESULTS

Voltammetry

Because the curves have somewhat broad maxima, the exact measurement of the E_p values is difficult. Table I summarizes the half-peak potential ($E_{p/2}$) values for the current–voltage curves obtained in the voltammetric studies. The curves are typical of those found in solid-electrode voltammetry. A linear dependency between peak current and concentration was found for the Fe(III) → Fe(II) and U(VI) → U(IV) reductions in 0.5 *M* sulfuric acid.

TABLE I

RESULTS OF VOLTAMMETRY OF VARIOUS CATIONS WITH BORON CARBIDE INDICATING ELECTRODE

(Determined by procedure given in text)

Cation	*Supporting medium*			$E_{p/2}$ *vs. S.C.E.*	*Observation*
	Identity	*M*	*Reaction*[a]		
Cd(II)[b]	NH_4OH	8	Cd(II) → Cd(0)	~ −1.0	
Co(III)[b]	NH_4OH	8	Co(III) → Co(II)	−0.02	Slope does not change sharply at $E_{p/2}$
			Co(II) → Co(0)	~ −0.9	
Cu(II)[b]	H_2SO_4	0.5	Cu(II) → Cu(0)	−0.10	Breaks apparent for stepwise reduction at $E_{p/2}$ = ~ −0.05 and ~ −0.15
	HNO_3	1.0	Cu(II) → Cu(I) → Cu(0)	−0.11	Distinct breaks for stepwise reduction at $E_{p/2}$ = ~ −0.06 and ~ −0.18
	HCl	1.0	Cu(II) → Cu(I)	+0.03	
			Cu(I) → Cu(0)	−0.40	
Fe(III)	H_2SO_4	0.5	Fe(III) → Fe(II)	+0.35	Concentration-i_p dependent
	HNO_3	1.0	Fe(III) → Fe(II)	+0.30	Concentration-i_p dependent
H^+	HNO_3	1.0	$2\,H^+ \rightarrow H_2\uparrow$	(−0.65)	Potential where background current = 1 μA
	HCl	1.0	$2\,H^+ \rightarrow H_2\uparrow$	(−0.75)	
	H_2SO_4	0.5	$2\,H^+ \rightarrow H_2\uparrow$	(−0.80)	
Ni(II)[b]	NH_4OH	8	Ni(II) → Ni(0)	~ −1.1	Estimate; H_2 evolution very close
Pb(II)	HNO_3	1.0	Pb(II) → Pb(0)		Current = 1 μA at *E* = −0.60 V. Increases to 10 μA at *E* = −0.68 V
Ru(IV)	H_2SO_4	0.5	Ru(IV) → ?		Current = 2 μA at *E* = −0.65 V. Increases to 10 μA at *E* = −0.75 V
Sb(V)[b]	HCl	(20 v/v%)	Sb(V) → Sb(III)	+0.06	
			Sb(III) → Sb(0)	~ −0.5	
U(VI)	H_2SO_4	0.5	U(VI) → U(IV)	−0.33	Concentration-i_p dependent

[a] The reduction products were not identified unambiguously. I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. II, 2nd Ed., Interscience, New York, 1952, was used as a reference.

[b] After deposition of monometallic layer on solid electrode, H_2 evolution follows. The degree of interference will depend on the hydrogen overvoltage on or at the metallic surface.

Coulometry

Figure 1 was obtained by carrying out the reduction or oxidation in the usual manner except that the potential was adjusted periodically to a value that caused cessation of current. The readout voltage, which is proportional to total current consumed or to extent of reaction, and electrode potential were recorded; the electrolysis was then continued. The optimum electrode potential for a controlled-potential coulometric titration can be established from a curve of this type[8]. These curves relate the extent of reaction with the electrode potential under actual titrating conditions.

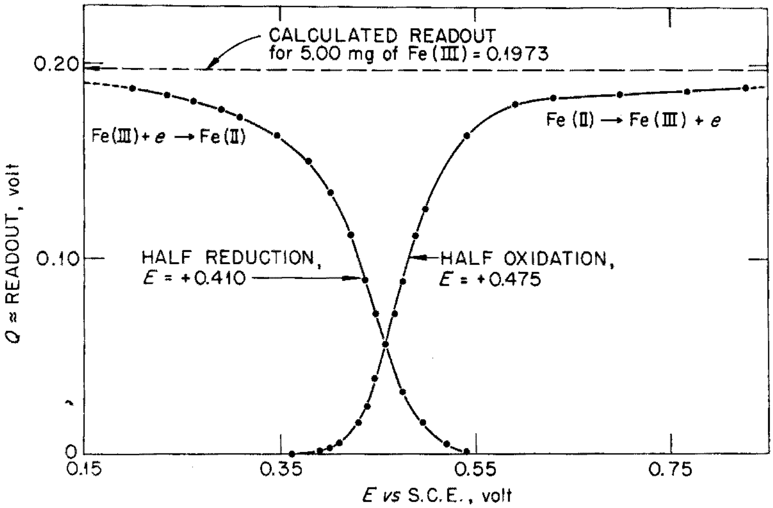


Fig. 1. Curves for the controlled-potential coulometric reduction of Fe(III) → Fe(II) and oxidation of Fe(II) → Fe(III); boron carbide electrode. 5.00 mg of Fe(III) in 15 ml of 1.0 *M* HCl.

Figure 1 indicates that the Fe(II) → Fe(III) half-oxidation potential (+0.48 V *vs.* S.C.E.) is close to the $E_{p/2}$ value reported by Mueller and Adams[2] (+0.46 V *vs.* S.C.E.). The half-reduction potential (+0.41 V *vs.* S.C.E.) is about 0.06 V more positive than the $E_{p/2}$ value reported in Table I (+0.35 V *vs.* S.C.E.). These curves indicate that approximately all the iron(III) is reduced at +0.10 to +0.15 V *vs.* S.C.E. On a platinum electrode, 100% reduction of iron(III) is obtained at +0.35 V *vs.* S.C.E.[9]. For the boron carbide electrode, these curves indicate that the coulometric titration should be performed at +0.75 to +0.85 V *vs.* S.C.E. to obtain 100% oxidation; on the platinum electrode, the titration can be performed at +0.69 V *vs.* S.C.E.[9]. In all these instances, 1 *M* hydrochloric acid is the electrolyte.

Figure 2 relates readout voltage *vs.* potential for the U(VI) → U(IV) reduction. For this reduction, the titrating current does not "come to background" at any reasonable value of controlled potential. Thus, the expected readout voltage (a measure of *Q*), predicted from the coulometric factor of the instrument and the amount of uranium(VI) added, is exceeded.

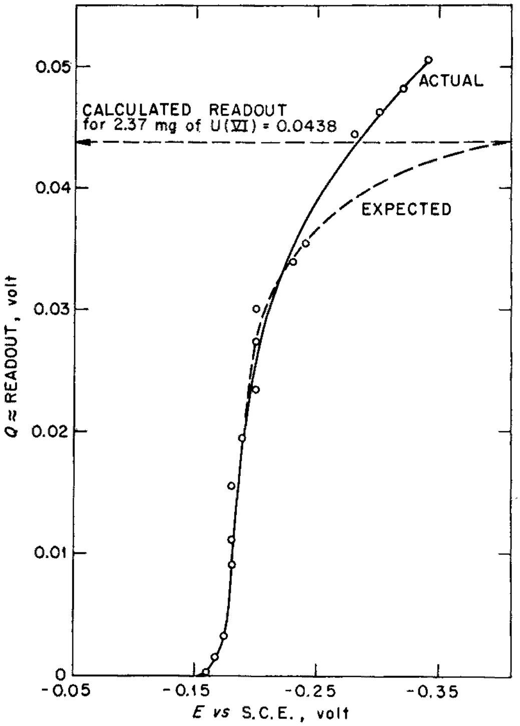


Fig. 2. Curve for the controlled-potential coulometric reduction of U(VI) → U(IV) in 0.5 *M* H_2SO_4; boron carbide electrode. 2.37 mg of U(VI) in 15 ml of 0.5 *M* H_2SO_4.

Table II shows the results of the controlled-potential studies of the Fe(III) → Fe(II) reduction, Fe(II) → Fe(III) oxidation, and U(VI) → U(IV) reduction. When one considers the length of time required for the Fe(III) → Fe(II) reduction (*i.e.*, 60 to 90 min), the results are acceptable. Much better results would be expected for an electrode having a larger surface area. Low results were obtained for the coulometric oxidation of Fe(II) → Fe(III) at the boron carbide electrode (Table II). During the long titration time, it is likely that a large amount of the Fe(II) is oxidized by oxygen introduced through leaks in the system or present in the helium used as sparge gas.

High results were obtained for the coulometric determination of known amounts of uranium(VI) (as the only reducible cation) at the boron carbide electrode (Table II). When a known amount of iron(III) was added to a known amount of uranium(VI) and the test solution reduced coulometrically at −0.45 V *vs.* S.C.E., the results (Table II) corresponded more closely to the calculated readout voltage. No attempt was made to perfect this procedure; however, its advantages in a controlled-potential coulometric titration involving a slow reaction have been pointed out by SHULTS[10].

TABLE II

RESULTS OF CONTROLLED-POTENTIAL COULOMETRIC TITRATIONS; BORON CARBIDE ELECTRODE

(Determined by procedure given in text)

Controlled potential vs. S.C.E.	*Amount of ion present (mg)*	*Readout voltage*		*Amount of ion electrolyzed (%)*[a]
		Calculated	*Found*	
Fe(III) → Fe(II); 1.0 M HCl				
+0.200	5.00	0.1975	0.1946	98.7
+0.300	5.00	0.1975	0.1973	99.9
0.000	0.75	0.0295	0.0294	99.9
0.000	0.75	0.0295	0.0280	95.0
0.000	0.50	0.0198	0.0194	98.5
Fe(II) → Fe(III); 1.0 M HCl				
+1.000	5.00	0.1975	0.1877	95.4
+0.750	0.75	0.0295	0.0257	87.0
+1.100	0.50	0.0198	0.0174	88.4
U(VI) → U(IV); 0.5 M H_2SO_4				
−0.450	2.37	0.0439	0.0541	123.6
U(VI) → U(IV); Fe(III) added, 0.5 M H_2SO_4				
−0.450	2.37	0.0439	0.0430[b]	98.0
−0.450	5.91	0.1096	0.1104[c]	101.0
−0.450	5.91	0.1096	0.1025[c]	94.0

[a] Coulometric factors: U = 54.0 mg/V, $n = 2$; Fe = 25.3 mg/V, $n = 1$.
[b] Background correction for 0.075 mg of Fe(III) added = 0.0026 V.
[c] Background correction for 1.0 mg of Fe(III) added = 0.0396 V.

The author acknowledges the advice and assistance of P. F. THOMASON, W. D. SHULTS, and T. R. MUELLER and the performance of the spectrographic analyses by C. A. PRITCHARD. All are members of the Analytical Chemistry Division of the Oak Ridge National Laboratory.

SUMMARY

With the boron carbide electrode, $E_{p/2}$ values were determined for the reduction of the following ions: Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II), Ru(IV), Sb(V), and U(VI). The linear dependence of peak current on concentration is demonstrated for the U(VI) → U(IV) and Fe(III) → Fe(II) reductions at the boron carbide electrode. The suitability of the electrode for the controlled-potential coulometric titrations of Fe(II) → Fe(III), Fe(III) → Fe(II), and U(VI) → U(IV) was studied; the results were inconclusive because of the small surface area that could be used conveniently and the possibility of oxygen leaks in the cell.

RÉSUMÉ

Les valeurs $E_{p/2}$ ont été déterminées avec l'électrode de carbure de bore, pour la réduction des ions suivants: Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II), Ru(IV), Sb(V), et U(VI). L'auteur a examiné la possibilité d'adapter cette électrode aux titrations coulométriques à potentiel contrôlé de Fe(II) → Fe(III), Fe(III) → Fe(II) et U(VI) → U(IV). Les résultats ne furent pas concluants en raison de la faible surface utilisable et de la possibilité de fuite d'oxygène dans la cellule.

ZUSAMMENFASSUNG

Mit der Bor–Karbid-Elektrode wurden $E_{p/2}$-Werte für die Reduktion folgender Ionen bestimmt: Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Po(II), Ru(IV), Sb(V) und U(VI). Die lineare Abhängigkeit des Spitzenstromes von der Konzentration wird für die U(VI) → U(IV) und die Fe(III) → Fe(II) Reduktion mit der Bor–Karbid-Elektrode gezeigt. Die Eignung der Elektrode für coulometrische Titration (mit geregeltem Potential) von Fe(II) → Fe(III), Fe(III) → Fe(II) und U(VI) → U(IV) wurde untersucht. Die Ergebnisse sind nicht schlüssig, da die bequem nutzbare Oberfläche klein war und ein Eindringen von Sauerstoff in die Zelle nicht ausgeschlossen werden konnte

REFERENCES

1 T. R. Mueller, C. Olson and R. N. Adams, in I. L. Longmuir, *Advances in Polarography*, Vol. 1, Pergamon, New York, 1960, p. 198–209.
2 T. R. Mueller and R. N. Adams, *Anal. Chim. Acta*, 23 (1960) 476.
3 M. T. Kelley and H. H. Miller, *Anal. Chem.*, 24 (1952) 1895.
4 M. T. Kelley, H. C. Jones and D. J. Fischer, *Anal. Chem.*, 31 (1959) 488, 956.
5 H. C. Jones, Automatic Coulometric Titrator, ORNL Model Q-2005, Electronic, Controlled-Potential, Method Nos. 1 003029 and 9 003029 (R. 6-7-62), *ORNL Master Analytical Manual*, U.S. At. Energy Comm. Rept. TID-7015, Supp. 5, Dec. 1963.
6 W. D. Shults, Uranium, Automatic Controlled-Potential Coulometric Method, Method Nos. 1 219225 and 9 00719225 (1-29-60), *ORNL Master Analytical Manual*, U.S. At. Energy Comm. Rept. TID-7015, Supp. 3, June 1961.
7 B. J. Ginocchio, Uranium, Automatic Potentiometric Ferric Sulfate Method, Method Nos. 1 219224 and 9 00719224 (2-24-58), *ORNL Master Analytical Manual*, U.S. At. Energy Comm. Rept. TID-7015, Sec. 1, April 1958.
8 R. W. Stromatt, Formal Redox Potentials with a Controlled-Potential Coulometer, *HW-58212*, November 12, 1958.
9 W. M. MacNevin and B. B. Baker, *Anal. Chem.*, 24 (1952) 986.
10 W. D. Shults, *Anal. Chem.*, 33 (1961) 15.

A COMPARISON OF CATHODE AND ANODE EXCITATION IN THE D.C. ARC

R. R. BROOKS AND C. R. BOSWELL

Department of Chemistry and Biochemistry, Massey University of Manawatu, Palmerston North (New Zealand)

(Received July 22nd, 1964)

Before the introduction of cathode-layer excitation in the D.C. arc[1], anode excitation was the usual technique in spectrochemical analysis. Although the use of anode excitation declined somewhat following the discovery of the cathode-layer effect, it has been more widely used in recent years and both methods would appear to be of equal interest today. Little has been published on a comparison of the 2 methods of excitation from experiments carried out under the same conditions. Cathode excitation, as distinct from cathode-layer excitation, has received an even briefer mention. AHRENS AND TAYLOR[2] have, however, used the data of a number of independent workers to compare anode and cathode-layer excitation and have concluded that the advantages of cathode-layer excitation have been overstated in the past. They appear, on balance, to favour anode excitation but stress the difficulty of making comparisons on data obtained under different experimental conditions. The merits of either of the 2 methods have been discussed by several other workers[3-8].

STRASHEIM AND CAMERER[9] have compared anode and cathode-layer excitation for the analysis of Cr, Co, Ni, Zn, Ti, V, Sn, Mo and Pb and conclude that the precisions obtainable by the two methods are similar. However, their conclusions are based solely on the slopes of working curves for the various line pairs and bear no relation to coefficients of variation of replicate arcings. SKORNYAKOV[10] has discussed the relative volatilisation of some 15 elements in anode and cathode-layer excitation.

The purpose of this paper is to examine the potentialities of cathode excitation (as distinct from cathode-layer excitation) in spectrochemical analysis and to compare it directly with anode excitation under the same experimental conditions.

In order to obtain a meaningful comparison of the 2 techniques, the following properties were studied: absolute sensitivity, times required for complete consumption of the sample, rates of volatilisation, times for complete volatilisation of each element, background intensities, self-absorption and finally, the reproducibility of intensity ratios of a number of line pairs in 3 different matrices. Although the results will only hold for the experimental conditions used in these studies, there is little reason to suppose that they will not apply to a much wider range of experimental conditions.

A study of spectral longitudinal intensity distribution was not carried out since this is already well known[2] and moreover, the optical system of the spectrograph was arranged to provide uniform illumination at the slit. No study was made of arc temperatures as these have been investigated by many other workers[11-15].

EXPERIMENTAL

The experiments were carried out on a Hilger E742 large automatic spectrograph with quartz optics. In all cases the operating conditions were as summarised in Table I.

TABLE I

SPECTROGRAPHIC OPERATING CONDITIONS

Slit length	12 mm
Slit width	0.15 mm
Wavelength range	2400–3400 Å
Photographic plates	Kodak IN
Current	7 A, d.c.
Exposure	To completion
Electrodes	Johnson-Matthey 4B graphite (1/16″ internal diameter × 6 mm deep)
Photographic processing	4 min at 20° in Kodak D. 19b
Densitometry	Hilger microphotometer with Galvoscale calibrated in B-values[16]
Optical system	Convex quartz lens placed at slit to give even illumination at this point and to provide an image of the arc at the collimator
Arc gap	4 mm

Absolute sensitivities, background intensities and volatilisation rates

Experiments on absolute sensitivities were carried out by arcing identical weights of a charge of two parts of carbon powder to one part of Johnson-Matthey R. U. powder and measuring the spectral line intensities of 33 elements. In order to avoid errors due to variation between plates, samples were arced in triplicate on the same plate for each of the 2 methods of excitation. Good agreement between the triplicates of each series was obtained by careful control of the conditions. Photometric measurements of line intensities were carried out by a Hilger microphotometer with a scale calibrated in B-values[16] to provide a linear response for the photographic emulsion

$$(B = 50\left[\log\left(\frac{d_0}{d} - 1\right) + \log\left(\frac{d_0}{d}\right) + 1.2\right]$$

where d_0 = full scale deflection of 50 on a linear scale, and d = actual deflection on a linear scale).

Table II shows line intensities, background values and the ratios of both these quantities for the 2 methods of excitation. The Table also shows the times needed for complete volatilisation of 12 elements (Pb, Tl, Sn, Ga, In, Au, Sb, Ag, Bi, Zn, As and Cu) together with the ratio of these times for cathode and anode excitation. The volatilisation experiments were carried out separately on samples containing trace amounts of the elements in a carbon matrix. The arcings were in triplicate and the plate holder was racked at 5-sec intervals to obtain volatilisation curves. The curves for lead, which typify those for the other elements, are shown in Fig. 1.

TABLE II

RELATIVE INTENSITIES AND INTENSITY RATIOS FOR CATHODE AND ANODE EXCITATION[a]

Element	*Line (Å)*	*Cathode excitation*			*Anode excitation*					
		A	*B*	*C*	*a*	*b*	*c*	*D*	*E*	*F*
Tl	2767	27	—	4	8	—	2	—	3.4	2.0
Mn	2798	116	—	—	47	—	—	—	2.5	—
Sn	2839	7	—	24	3	—	12	—	2.3	2.0
Ga	2943	7	—	24	3	—	9	—	2.3	2.3
Fe	3020	37	—	—	18	—	—	—	2.1	—
In	3256	14	45	24	7	23	10	2.0	2.0	2.4
B	2497	321	—	—	168	—	—	—	1.9	—
Si	2514	115	—	—	60	—	—	—	1.9	—
Pb	2833	13	—	21	7	—	7	—	1.9	3.0
Mg	2942	37	—	—	21	—	—	—	1.8	—
Au	3122	18	41	24	10	15	11	2.7	1.8	2.2
P	2535	25	—	—	15	—	—	—	1.7	—
Sb	2598	20	—	22	12	—	10	—	1.7	2.2
V	3184	44	40	—	28	17	—	2.3	1.6	—
Ag	3280	57	49	24	36	23	10	2.1	1.6	2.4
Al	3082	125	26	—	81	12	—	2.2	1.5	—
Bi	3067	20	32	20	16	12	8	2.7	1.3	2.5
Na	3303	370	—	—	309	—	—	—	1.2	—
Zn	3282	777	48	15	628	23	6	2.1	1.2	2.5
As	2860	12	—	7	11	—	2	—	1.1	3.5
Be	3131	76	—	—	68	—	—	—	1.1	—
Mo	3170	16	45	—	15	20	—	2.2	1.1	—
Cr	2843	10	—	—	10	—	—	—	1.0	—
Ti	3234	100	34	—	117	19	—	—	0.9	—
Cu	3247	80	39	24	86	19	8	2.1	0.9	3.0
Eu	3930	111	—	—	119	—	—	—	0.9	—
Y	3216	14	—	—	23	—	—	—	0.6	—
Ca	3179	665	50	—	1380	17	—	2.9	0.5	—
La	3337	20	—	—	41	—	—	—	0.5	—
Zr	3273	13	—	—	39	—	—	—	0.3	—
Yb	3289	5	—	—	23	—	—	—	0.2	—

[a] A, a = Line intensities, corrected for background.
B, b = Background intensities.
C, c = No. of 5-sec time intervals to completely volatilise the element.
D = Ratio B/b.
E = Ratio A/a.
F = Ratio C/c.

Self-absorption

Samples containing from 5 p.p.m. to 50% of a single element in a carbon matrix were arced under the conditions of Table I. Intensity ratios of a high-intensity strongly-absorbing line and a weaker non-absorbing line of the same element were measured and the results plotted as a function of concentration. Where possible, a pair of lines of the same multiplet was used. The line pairs used were: In 3256/3274, Cu 3247/3274, Ag 3280/3383, Tl 2918/2921, Ag 2349/2456, Bi 3067/3025, Zn 3345/3346, Au 2676/3122, Pb 2833/2823 and Sn 2850/3175. In most cases, results of high precision were hard to obtain because of the inherently irreproducible nature of the onset of self-absorption. However, there was little difference in effect whichever method of

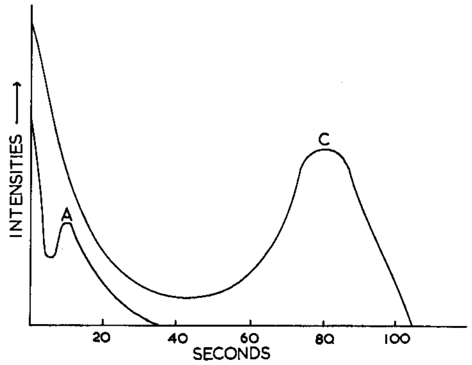


Fig. 1. Volatilisation + curves for lead. A - Anode excitation. C - Cathode excitation.

excitation was used and the pattern throughout was, in most cases, of intensity ratios rising to a limiting value at low concentrations.

Reproducibility

Reproducibility measurements for the 2 methods of excitation were carried out by arcing up to 14 replicates of trace amounts of a number of elements. Three matrices (sodium chloride, calcium chloride and carbon) were used to study the effects of different arc temperatures and matrices on reproducibilities.

The relative intensities of 35 line pairs were measured and the coefficient of variation of each of these was determined. The results are shown in Table III. During these experiments, the times for the complete combustion of the samples were recorded and are shown in Table IV.

DISCUSSION

From Table II it is clear that for most of the elements studied, cathode excitation afforded greater sensitivity in a carbon matrix. For the remainder of the elements, anode excitation provided greater sensitivity. Attempts to correlate these results with excitation potentials and ionisation potentials were not successful. However, those elements showing greater sensitivity for anode excitation were in the main refractory, whereas the remainder included a large proportion of more volatile elements.

A disadvantage of cathode excitation is the high background which in these experiments was greater by a factor of 2 or 3 than that for anode excitation. However, it is sometimes desirable to have backgrounds of sufficient intensity for them to be measured with reasonable accuracy, provided that they do not represent too large a fraction of the intensity of the analysis line.

The reproducibility experiments produced interesting and significant data for a number of volatile elements. Of the 33 line pairs measured for the sodium chloride matrix, 22 showed lower coefficients of variation with anode excitation. The reverse was the case for the carbon matrix where 23 out of 35 arcings showed lower coefficients with cathode excitation. The line pairs were selected by choosing the best for each method of excitation and for each matrix and then measuring the same line pairs under all the other conditions employed. The highest precision for cathode excitation

TABLE III

REPRODUCIBILITY TESTS ON THREE DIFFERENT MATRICES[a]

Line pair	*Coefficients of variation*					
	NaCl matrix		*$CaCl_2$ matrix*		*Carbon matrix*	
	Anode	*Cathode*	*Anode*	*Cathode*	*Anode*	*Cathode*
Ga/Cu	19.1	10.7	36.0	23.0	29.6	6.8
Ga/Pb	34.0	17.0	42.6	24.5	14.1	4.1
Ga/Sn	17.3	17.0	54.6	35.4	5.8	9.6
Bi/Pb(I)	18.3	9.2	58.3	11.2	19.0	10.3
Bi/Pb(II)	13.0	16.0	37.2	28.8	11.2	5.5
Hg/Ga					13.8	17.9
Hg/As					13.4	14.7
Cd/As	15.6	28.2	42.5	43.3	57.2	11.4
Cd/Cu	33.0	41.7	55.1	56.7	12.2	5.9
Cd/Bi	17.1	33.3	23.5	45.6	8.2	7.9
Sn/Ag	17.0	10.5	43.0	39.0	17.0	8.4
Sn/Sb	16.9	31.1	42.5	34.9	9.2	3.5
Sn/Ga	17.4	15.3	51.6	41.9	5.6	9.0
Pb(I)/Ga	14.2	17.0	28.4	25.8	11.5	4.1
As/Zn	8.2	15.3	50.0	14.1	10.3	13.3
As/Sb	8.5	18.0	18.6	21.6	8.3	6.2
As/Ga	23.1	32.4	34.9	30.4	6.3	14.0
Ag/Cu	5.0	7.9	24.9	4.3	8.4	3.5
Ag/Bi	21.1	27.7	58.0	48.7	7.8	5.7
Ag/Pb(I)	9.2	19.5	26.4	46.0	14.8	7.0
Zn/Pb(I)	11.6	12.0	27.4	35.7	11.6	14.7
Zn/As	7.3	15.2	42.0	16.3	9.7	10.4
Zn/Sb	16.9	16.9	44.8	25.5	4.9	17.0
Sb/Sn	10.5	24.1	32.4	35.9	8.8	2.5
Sb/Zn	10.9	15.6	52.3	21.1	11.5	18.0
Cu/Ag	5.0	8.2	26.0	8.4	7.0	4.5
Cu/Bi	21.9	19.0	50.3	56.0	7.3	7.1
Tl/In	10.4	20.0	20.0	22.6	9.0	3.6
Tl/Sb	7.6	21.0	57.7	47.3	45.5	11.3
In/As	17.4	12.6	49.8	34.3	35.0	13.2
In/Tl	8.3	22.7	35.0	32.2	9.4	10.4
Au/Cu	20.1	10.5	54.9	42.8	11.7	12.2
Au/Ag	21.8	14.0	75.5	38.3	20.6	11.8
Pb(I)/Bi	15.3	9.3	51.7	18.7	12.1	10.8
Pb(I)/Ga	18.9	19.3	46.9	50.5	9.3	7.5
Averages	15.5%	18.4%	41.6%	32.1%	14.2%	9.2%

[a] Lines used were: As 2860, Ag 3280, Au 2676, Bi 3067, Cd 3261, Cu 3274, Ga 2943, Hg 2536, Pb(I) 2823, Pb(II) 2833, Sb 3267, Tl 3229, Zn 3345, In 3256.

TABLE IV

TIME REQUIRED FOR COMPLETE COMBUSTION OF THE SAMPLE (sec)

Excitation	*NaCl matrix*	*$CaCl_2$ matrix*	*Carbon matrix*
Anode	68 ± 3	50 ± 10	35 ± 2
Cathode	100 ± 5	95 ± 8	80 ± 6

with a carbon matrix was 2.5% for the Sb/Sn line pair and 4.9% for the Zn/Sb pair for anode excitation. That overall precision was also better for cathode excitation was shown by a study of the average coefficients of variation of 35 line pairs which gave values of 14.2% and 9.2% for anode and cathode excitation respectively for the carbon matrix. The sodium chloride matrix gave lowest values of 9.2% for Bi/Pb with cathode excitation, 5.0% for Cu/Ag with anode excitation and average values for all line pairs of 15.5% and 18.4% respectively.

It is concluded therefore, that, at least for these 13 elements, cathode excitation with a carbon matrix would afford higher precision than anode excitation. When a sodium chloride matrix is used, there is less difference between the 2 techniques, though in this case, anode excitation would appear to offer the better results. This may be explained by the higher temperature of anode excitation enabling the depressant effect of sodium chloride on line intensities of various elements[2] to be overcome to some extent, with a consequent improvement in reproducibility. The higher precision for cathode excitation in a carbon matrix may be due in part to incomplete combustion in the anode because of the higher rate of material consumption and the physical ejection of some of the material. The slower burning cathode would tend to reduce this effect. The same conclusion would seem to apply to the calcium chloride matrix, but owing to the poor reproducibility and irregular burns with this material, the only definite conclusion that can be made is that, for reproducibility, it is far inferior to carbon or sodium chloride as a matrix.

In order to summarise the findings and conclusions of the work described in this paper, a Table (Table V) has been prepared in which the characteristics of both methods of excitation are compared. It is hoped that this work will have served to

TABLE V

A COMPARISON OF ANODE AND CATHODE EXCITATION UNDER IDENTICAL CONDITIONS

Property	*Conclusions*
Absolute sensitivity	Higher with cathode excitation for a number of volatile elements. Higher with anode excitation for some refractory elements
Time required for complete consumption of sample	Consumption occurs approximately twice as fast with anode excitation for each of the 3 matrices used in these experiments
Time for complete volatilisation of an element	Considerably higher for cathode excitation, a 2–3-fold factor being involved
Volatilisation curves	Curves are similar in shape for both methods of excitation but with considerable compression of the time axis for anode excitation
Self-absorption	Appears to be approximately the same for both excitation methods
CN emission	Greater for cathode excitation
Background emission	A 2–3-fold increase for cathode excitation
Reproducibilities	Overall, slightly better for anode excitation with a NaCl matrix but appreciably better for cathode excitation with a carbon matrix
General conclusions	Cathode excitation appears to offer advantages in sensitivity for a number of non-refractory elements and gives greater overall precision in a carbon matrix for a number of volatile elements

highlight the potentialities and limitations of the hitherto somewhat neglected cathode excitation technique.

SUMMARY

Cathode excitation as distinct from cathode-layer excitation was compared with anode excitation under the same experimental conditions. Data on 33 elements and 35 line pairs were used to study relative self-absorption effects, absolute sensitivities, reproducibilities, volatilisation curves, times of complete volatilisation and background effects. Cathode excitation affords greater precision foı a number of the more volatile elements in a carbon matrix.

RÉSUMÉ

Les auteurs ont effectué une étude de comparaison entre l'excitation cathodique et l'excitation anodique, dans les mêmes conditions expérimentales. Ils ont examiné les influences de self-absorption relative, les sensibilités absolues, les reproductibilités, les courbes de volatilisation, les durées de complète volatilisation, et les effets de "background". L'excitation cathodique donne une plus grande précision pour un certain nombre d'éléments les plus volatils.

ZUSAMMENFASSUNG

Unter denselben experimentellen Bedingungen wurde für den Gleichstrombogen die Kathodenanregung zum Unterschied von der Kathodenschichtanregung mit der Anodenanregung verglichen. Die Daten von 33 Elementen und 35 Linienpaaren wurden benutzt um relative Selbstabsorptionseffekte, absolute Empfindlichkeiten, Reproduzierbarkeiten, Flüchtigkeitskurven, Zeiten zur vollständigen Verflüchtigung und Untergrundseffekte zu untersuchen. Bei der Kathodenanregung ergibt sich eine grössere Reproduzierbarkeit für eine Anzahl von stärker flüchtigen Elementen in einer Kohlenstoffmatrix.

REFERENCES

1 R. MANNKOPFF AND CL. PETERS, *Z. Physik*, 120 (1943) 228.
2 L. H. AHRENS AND S. R. TAYLOR, *Spectrochemical Analysis*, 2nd Ed., Addison–Wesley, Reading, Mass., 1961.
3 R. E. THIERS, J. F. WILLIAMS AND J. H. YOE, *Anal. Chem.*, 27 (1955) 1725.
4 W. C. PIERCE, O. R. TORRES AND W. W. MARSHALL, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 41.
5 L. H. AHRENS AND W. R. LIEBENBERG, *Trans. Geol. Soc. S. Afr.*, 49 (1946) 133.
6 R. L. MITCHELL, *The Spectrographic Analysis of Soils, Plants and Related Materials*, Tech. Comm. No. 44 of the Commonwealth Bur. Soil Science, Harpenden, England, 1948.
7 L. W. STROCK, *Spectrum Analysis with the Carbon Arc Cathode Layer*, Adam Hilger, London, 1936.
8 L. W. STROCK, *Symposium on Spectroscopic Light Sources*, A.S.T.M. Tech. Pub. 76 (1946) 69.
9 A. STRASHEIM AND L. CAMERER, *J. S. African Chem. Inst.*, 8 (1955) 28.
10 G. P. SKORNYAKOV, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 19 (1955) 57.
11 A. VON ENGEL, *Ionised Gases*, Clarendon Press, Oxford, 1955.
12 J. A. M. DIKHOFF, *Spectrochim. Acta, Proc. Colloq. Spec. Inter. VI*, (1957) 162.
13 L. S. ORNSTEIN AND H. BRINKMAN, *Physica*, 1 (1934) 797.
14 O. P. SEMENOVA, *Compt. Rend. Acad. Sci. USSR*, 51 (1946) 683.
15 W. LOCHTE-HOLTGREVEN, *Rept. Progr. Phys.*, 21 (1959) 312.
16 C. R. BOSWELL AND R. R. BROOKS, in press.

THE DETERMINATION OF SELENIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

C. S. RANN AND A. N. HAMBLY
Chemistry Department, Australian National University, Canberra, A.C.T. (Australia)
(Received July 5th, 1964)

We became interested in the determination of selenium in the presence of large amounts of sulphur during another investigation in these laboratories[1], that dealt with compounds and solid solutions of sulphur with selenium. As the use of atomic absorption spectrophotometry for other elements was under study at the time, this method seemed attractive, despite statements in the literature[2] that it could not be used for the determination of selenium. There is considerable interest in the determination of this element in human and animal diets. Grain plants grown on seleniferous soils, concentrate the element into the seed protein; animals fed on such grain become emaciated, lose hair and hoofs, and develop other pathological symptoms of selenium toxicity[3]. Selenium poisoning affects large areas in U.S.A., particularly in Nebraska and the Dakotas, and also some areas in Northern Australia. More recently SCHWARZ AND FOLTZ[4] have shown that selenium is an essential trace element in some animal diets. Low concentrations, of the order of 0.1 p.p.m., in the diet prevent a form of oedema in chickens, muscular dystrophy in calves and lambs and necrosis of the liver in rats. Concentrations of about 20 times this value give rise to symptoms of toxicity.

It has also been suggested that the selenium content of sulphide ores, in which ionic substitution is readily possible with the anions differing by only 8% in radius, can be used to diagnose the origin of the deposit. The element is usually isolated from sulphide ores of hydrothermal origin.

Most methods for the determination of selenium are based on its separation from other materials by distillation of the bromide from mixtures containing hydrogen bromide and bromine[6] followed by precipitation of selenium with sulphur dioxide, hydroxylamine, hydrazine[7], or ascorbic acid[7a]. Selenium is then determined iodimetrically after conversion to selenious acid, colorimetrically with codeine sulphate reagent or turbidimetrically as the element. These methods can usually be employed for concentrations greater than 1 or 2 p.p.m. While our work was in progress, ALLAN[8] reported that he had been able to obtain a sensitivity of 5 p.p.m. in the analysis of simple selenium solutions by atomic absorption, with a hydrogen continuum as a light source and a monochromator set at 2040 Å. He later informed us (private communication) of considerable improvements in his method for determining this element.

EXPERIMENTAL

Apparatus

The units employed in a standard arrangement for atomic absorption spectrophotometry in a flame are shown in Fig. 1. The special features associated with these units, when used for the determination of selenium, are discussed in the following paragraphs.

(i) Spectral source. The selenium atom has a ^3P ground state and the lowest energy transitions involving this state are shown in Fig. 2. Those in which the ^5S excited state is concerned, though forbidden under strict Russell–Saunders coupling conditions, are present at moderate intensity in the emission spectrum of our sources. They did not show perceptible absorption in our experiments. The relative populations of the members of the ^3P state at the temperature of a propane–air flame (say, 1965°) and at the temperature of the acetylene–air flame (2250°) are given in Table I. If it is assumed that true equilibrium exists at the flame temperature, it is obvious that the greatest sensitivity will be given at 1960 Å.

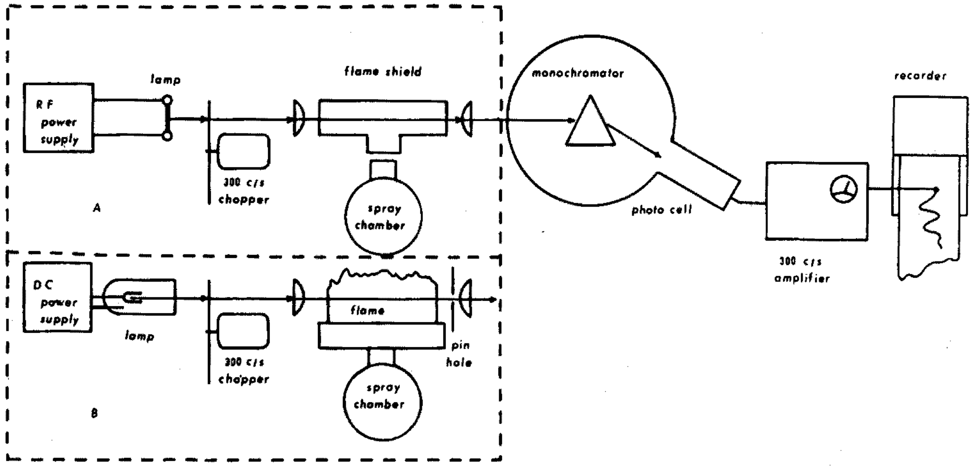


Fig. 1. Arrangement of units for atomic absorption measurements.

TABLE I

RELATIVE POPULATIONS OF MEMBERS OF TRIPLET GROUND STATE OF SELENIUM ATOM

State	*Absorption wavelength (Å)*	*Population at*	
		1965°	*2250°*
$^3P_2$	1960	100	100
$^3P_1$	2040	17	20
$^3P_0$	2063	4	5

The source usually recommended for atomic absorption measurements is a large discharge tube, filled with neon or argon at low pressure, and with a hollow-cathode made of the element[9,10]. The volatility and low melting point of selenium pose special difficulties. Two types of hollow-cathode lamp were made. The first had a copper cathode into the central hollow of which was packed some copper selenide. This form gave trouble because of the volatilisation of selenium from the active positions in the cathode. The second form had as cathode a rod of spectrographic carbon with a hole drilled into the centre, and the whole was soaked in molten selenium in a vacuum. This gave a much longer life in that selenium lost by evaporation was replaced by diffusion from the surrounding graphite. There was considerable deposition of red selenium on the walls of the tube and the silica end-window of the lamp had to be cleared by careful application of a pointed flame. Both forms, particularly the second, showed a rapid "clean up" of the inert gas[10], and continuity of operation could only be obtained by periodically admitting further argon from a reservoir attached to the lamp.

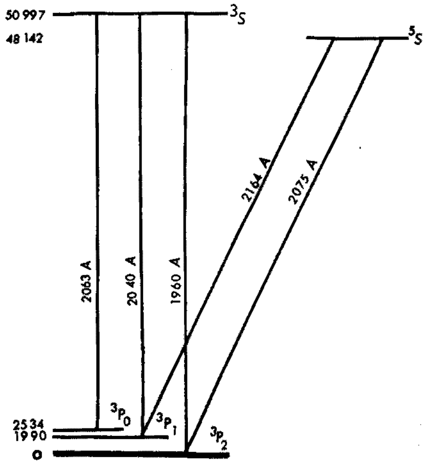


Fig. 2. Transitions between lower energy levels of Se atom.

As an alternative source, an electrode-less discharge in a vapour containing selenium was used. Small silica tubes with a central capillary about 2 cm long and end-pieces that were wider and about 1 cm long were evacuated and a small amount of selenium, or a sulphur–selenium mixture, was distilled in from a side tube. The tube was sealed and the end-pieces were held in clips to which were attached the shielded leads from a 15 Mc/s radio-frequency transmitter. On heating the tube with a burner a discharge commenced which, if the correct amount of chalcogen was present, settled down to a steady state when the burner was removed. Careful adjustment of the filling of the tube and of the power supply was necessary to maintain this discharge at a low selenium pressure so that there was not too great a self-reversal of the 1960 Å line.

(ii) Control of incident beam. The output from the hollow-cathode, or from the central part of the electrode-less discharge, was at the focus of a lens 2.5 cm in diameter so that a parallel beam passed through the flame. A similar lens focussed

the beam on to the slit of the monochromator and the lenses were chosen to have the same aperture as the collimating mirror of the monochromator. A narrow beam from the source could be isolated by inserting a diaphragm with a central hole 1 mm in diameter before the second lens. Measurements of optical densities in the flame when this narrow beam was used are referred to as "small area densities". The incident light was modulated at a frequency of 300 c/s by a rotating disc placed between the source and the first lens.

(iii) Flame. A major disadvantage in working at wavelengths as short as 1960 Å is the absorption of light by the flame gases (Table II). This absorption not only reduced the available signal to less than 20% of its initial value at the desired wavelength, but it also converted any turbulence in the flame, which has Fourier components which would be accepted by the amplifier, into "noise". The absorption varied considerably according to the operating conditions. The transmission of a fuel-rich acetylene–air flame could diminish by 20% when distilled water was sprayed into it but the effect was much less in 'lean' flames.

TABLE II

TRANSMISSION OF ACETYLENE AND ACETYLENE–AIR FLAMES AT EMISSION WAVELENGTHS OF SELENIUM SOURCE[a]

Wavelength (Å)	*Transmission (%)*	
	Acetylene[b]	*C_2H_2/air flame*
2164	100	68
2076	88	52
2062	90	50
2040	84	44
1960	34	18

[a] Determined with standard 10-cm slit burner.
[b] Air + acetylene as used for column 3, but not ignited.

Two forms of burner (Fig. 1) were employed both of which used the spray chamber of an 'EEL' flame photometer (Evans Electroselenium Ltd., London). The earlier work was carried out with a 10-cm slit burner similar to that described by WILLIS[11] (Fig. 1B). With this type of burner, operation with acetylene was more satisfactory than with propane, and absorption due to selenium atoms was stronger for fuel-rich mixtures than for those of low acetylene content. Best results were obtained when the acetylene–air flame showed a "feather", due to C_3 molecules[12], for about 5 mm above the inner, pale blue cone. The distribution of selenium atoms when a solution of selenium in mixed nitric and sulphuric acids was sprayed into this flame is shown in Figs. 3*a* and *b*. The contours of equal optical density at 1960 Å were obtained by scanning the flame horizontally and vertically past a 1-mm aperture placed in the optical path. For lean acetylene–air mixtures the sensitivity would be much higher if small area densities were used in the central region of high absorption; the advantages of small area densities were not so pronounced for the fuel-rich flames. A sensitivity of 1 p.p.m. of selenium was obtained in the acetylene flame.

The second form of burner was made by adding a T-shaped silica combustion chamber as a flame shield above the standard burner unit of the 'EEL' flame photometer (Fig. 1A). This was made from silica tubing of 2.5-cm internal diameter and had a 15-cm horizontal section centred along the optical axis, with a vertical section, 3 cm long, inserted at the mid-point. The tube was mounted with the opening of the vertical section *ca.* 1 cm above the burner of the "EEL" unit to admit some secondary air, but this was insufficient for total combustion and there were small flames at the ends of the horizontal arm. The noise due to turbulence in the flame was much less in this arrangement. Propane–air flames were used with this burner and an effective sensitivity of 1 p.p.m. was again achieved. This arrangement was employed for analysis since its adjustment was less critical.

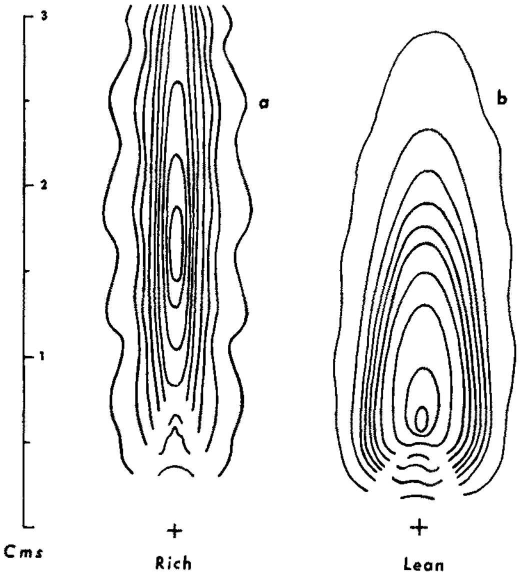


Fig. 3. Distribution of selenium atoms in acetylene–air flame using standard 10-cm burner. (*a*) Fuel-rich flame; (*b*) lean flame with no "feather". + = Position of burner port. Contours are spaced at 0.1 unit of optical density with the highest density in centre.

(iv) Monochromator and detector. A Zeiss reflecting monochromator SPM1, with an aperture of 1 : 6.7, and fitted with a sodium chloride prism, was used. The effective half-width of the 1960 Å line on the recorder chart was 1 Å. The radiation passing the exit slit of the monochromator was received by an E.M.I. 6256S photomultiplier tube, fitted with a "Spectrosil" window. This tube had a particularly low background current. The output was amplified by a Hewlett-Packard, Model 302A, wave analyser which has a selectivity of ± 3 c/s at the 3-db points and can be locked to the chopper frequency by an automatic frequency control circuit. The output of the amplifier was simultaneously presented on a meter and on a Varian Model G10 recorder.

Calibration and test solutions

Stock solutions were prepared by dissolving 1 g of grey selenium in each of the following reagents: (*i*) mixed concentrated nitric and sulphuric acids which converted the element to selenious acid; (*ii*) concentrated aqueous sodium sulphite solution with which it formed a selenosulphate; (*iii*) concentrated aqueous sodium cyanide solution which converted it into selenocyanate. These solutions were then diluted to 1 l and, from these stocks, standards containing 10 p.p.m. and 100 p.p.m. of selenium were prepared for test. The absorption due to the selenium sprayed into the flame was expressed as an optical density, log I_0/I, where I_0 is the intensity of the radiation reaching the detector when distilled water is sprayed into the flame, and I is the comparable intensity when the solution under test is sprayed. There were losses in intensity due to scattering of the incident radiation by solid particles produced from the reagents in the sprayed solution, and in some cases due to absorption at 1960 Å by other materials formed from the solution. The density of the flame for the above 3 solutions is shown in Table III; a correction, calculated to be about 0.01 could be applied to these figures for losses in intensity not due to absorption by selenium. It is apparent from these values, which each represent the mean of 3 or more determinations, that there was no significant difference for the 3 radically different methods of preparing the calibrating solution, and that there was no significant absorption from transition to the ^5S level of selenium.

TABLE III

OPTICAL DENSITY DUE TO Se ATOMS IN PROPANE–AIR FLAMES

Frequency (Å)	*Concn. of Se (p.p.m.)*	*Reagent used for stock solution*		
		Na_2SO_3	*NaCN*	*H_2SO_4/HNO_3*
1960[a]	10	0.05_9	0.06_9	0.03_7
1960[a]	100	0.25	0.24	0.24
2040	100	0.13_4	0.12_5	0.13_2
2063	100	0.03_6	0.03_5	0.05_5
2076	100	0.01_0	0.01_2	0.01_1
2164	100	0.00_9	0.01_2	0.01_0

[a] These two sets of measurements were obtained with the electrode-less discharge operating under different conditions from those applicable to the other 4 sets.

With the electrode-less discharge tube the relative sensitivity at 1960 Å was less than the calculated value. While the monochromator accepted the full radiation at 1960 Å, the selenium atoms in the flame only absorbed an extremely narrow range (about 0.01 Å) in the centre of the emission line. It is just this central region which suffers self-absorption by selenium atoms in the outer part of the discharge. In this case the sensitivity was reduced and the optical density of the flame was much less than proportional to its selenium content and varied with the operating conditions of the discharge tube. It was, therefore, necessary to obtain the absorptions due to the calibrating solution and the unknown concentration during a minimum time interval. A typical calibration curve is shown in Fig. 4. With the first form of burner one could increase the sensitivity by a factor of two by using small-area densities. This was not effective with the flame confined in the cylindrical shield (Fig. 1A), and was not employed in the analyses below. Flames must always be operated under a suitable hood because of the toxicity of selenium.

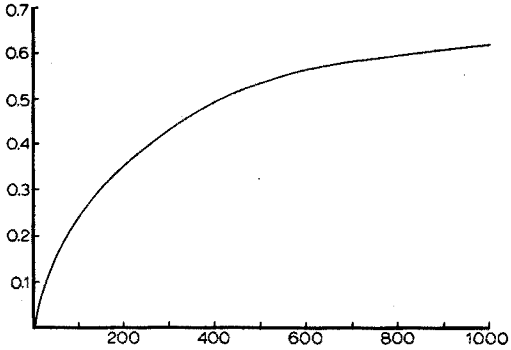


Fig. 4. A typical calibration curve with an electrode-less discharge as source and dilute solutions of Se.

RESULTS

A sample of seleniferous wheat (*Triticum* sp.) was obtained from South Dakota by courtesy of the Division of Plant Industry, C.S.I.R.O., and a specimen of galena from the Lake George Mine, Captains Flat, N.S.W. The major advantages in the use of atomic absorption methods are their speed and their freedom from interference by other elements. These advantages are only realised if the preparation of the test solution does not involve laborious separation procedures. Methods which involve the digestion of the sample followed by distillation of selenium as bromide by boiling with hydrogen bromide and bromine as recommended[5,6] for standard determinations of the element, are to be avoided if possible.

Assay of selenium in wheat

The sample of South Dakota wheat was supplied with a certificate that an analysis, by the method of KLEIN[6], of two 10-g samples had shown an average selenium content of 16.7 p.p.m. Such wheat is toxic. The solution for spraying was prepared by burning 10 g of the roughly ground wheat in the bomb of a Parr calorimeter unit. Because of the small size of the bomb, which was designed for other purposes, 5 successive 2-g lots had to be burned in oxygen at a pressure of 30 atm. Samples of Australian wheat, checked by this method to be free of selenium, were ground, and prepared as calibration standards by appropriate additions of standard selenium solutions. In the first experiments a small quantity of aqueous alkali was present in the bottom of the bomb to absorb the acidic products of combustion, including selenium dioxide. Later a test was made by bubbling the gases from the bomb slowly through water at the conclusion of the combustion, and it was shown that there was no appreciable loss of selenium from the cold bomb even when no alkali had been added. After the 5 combustion stages, the bomb was washed out with water and the extract filtered to remove small amounts of solid. These washings (*ca.* 50 ml), which were acidic with nitric and sulphuric acids formed during the combustion, were evaporated to less than 10 ml and then made up to this volume.

The lower part (to 10 p.p.m.) of the calibration curve obtained from the wheat sample sto which selenium had been added, corresponded to that obtained with the solution described on p. 351, but at higher concentrations the curve for the treated wheat samples fell below that for simple solutions. Small amounts of incompletely oxidized organic matter in the washings made these appreciably more viscous than the standard solutions, and thus modified the spraying conditions. With the calibration curve from the wheat samples a value of 16.5 p.p.m. was obtained from 4 determinations on the seleniferous wheat with a standard deviation of ± 0.75 p.p.m.

Assay of selenium in galena

A 3-g sample of finely ground galena was carefully mixed with about 20 g of dry sodium peroxide in a nickel crucible. The surface of the charge was covered with a layer of anhydrous sodium carbonate and the oxidation started by careful heating with a burner. After the first vigorous reaction had subsided the crucible was kept at a red heat for 5 min and then the soluble contents were leached out with boiling water. The total extract was evaporated to less than 100 ml, filtered to remove precipitated lead dioxide and then made up to 100 ml. This solution was sprayed directly into the flame. A 50-ml aliquot of this solution was used for determination of selenium by a gravimetric method. The aliquot was made strongly acidic with hydrochloric acid and an excess of hydroxyammonium chloride was added. The solution was heated on a water bath for 5 h and cooled overnight, and the red precipitate of selenium was collected in a sintered glass crucible (porosity 4) and weighed.

TABLE IV

ANALYSES OF GALENA, LAKE GEORGE MINE, CAPTAINS FLAT, N.S.W.

Sample	*Selenium content (%)*	
	Atomic absorption	*Gravimetric*
1	0.11_4	0.11_4
2	0.15_7	0.15_9
3	0.17_5	0.17_5
	Standard deviation ± 0.004%	

There was excellent agreement (Table IV) between the results of atomic absorption and gravimetric determinations on 3 samples which were known to contain somewhat different amounts of pyrite and chalcopyrite as impurities. Previous analyses of ore samples from this mine[5] had indicated a much lower selenium content.

With solutions containing such large quantities of inorganic materials as these mineral extracts, there was a considerable loss of signal by scattering and absorption in the flame due to constituents other than selenium. The correction for this (which could be as high as 0.08 density units) was obtained by measuring the optical density of the flame during the spraying period using a continuum at *ca.* 1950 Å which was emitted by the electrode-less discharge. This correction, together with the difficulties of spraying such concentrated solutions, would make sodium peroxide fusion unsuitable for concentrations less than 50 p.p.m. of selenium.

We gratefully acknowledge the support received by one of us (C.S.R.) from an Australian National University postgraduate scholarship.

SUMMARY

The problems involved in the determination of selenium by atomic absorption spectrophotometry are discussed. A practical method is described for which the sensitivity is approximately 1 p.p.m. Such concentrations can be determined in organic samples, but with mineral samples the preliminary treatment renders the procedure unsuitable for concentrations lower than 50 p.p.m. in a sulphide ore.

RÉSUMÉ

Les auteurs ont examiné les différents problèmes que pose le dosage du sélénium, par spectrophotométrie par absorption atomique. Ils décrivent une méthode pratique, présentant une sensibilité d'environ 1 p.p.m. De telles concentrations peuvent être déterminées dans des substances organiques; mais dans le cas de substances minérales, le traitement préliminaire ne permet pas de doser moins de 50 p.p.m. de sélénium, dans un minerai sulfuré.

ZUSAMMENFASSUNG

Probleme, die bei der Bestimmung von Selen mit der atomaren Absorptionsspektrophotometrie auftreten, werden diskutiert. Es wird eine Methode beschrieben, bei der die Empfindlichkeit in organischen Proben ungefähr 1 p.p.m. beträgt. Bei Gesteinsproben beeinflusst die vorhergehende Behandlung das Verfahren ungünstig und erlaubt z.B. die Bestimmung von nur 50 p.p.m. in Schwefelerzen.

REFERENCES

1 L. L. HAWES, *Nature*, 193 (1962) 766; 198 (1963) 1267.
2 W. T. ELWELL AND J. A. F. GIDLEY, *Atomic Absorption Spectrophotometry*, Pergamon Press, London, 1961, p. 42.
3 K. W. FRANKE AND E. P. PAINTER, *Cereal Chem.*, 13 (1935) 67.
4 K. SCHWARZ AND C. M. FOLTZ, *J. Am. Chem. Soc.*, 79 (1957) 3292.
5 A. B. EDWARDS AND G. C. CARLOS, *Proc. Australian Inst. Min. Metallurgy*, 172 (1954) 31.
6 R. A. OSBORN, *J. Assoc. Offic. Agr. Chemists*, 19 (1936) 236.
7 K. BRUCKNER, *Z. Anal. Chem.*, 94 (1933) 305.
7a Report of Assoc. British Chem. Manufr., *Analyst*, 81 (1956) 612.
8 J. E. ALLAN, *Spectrochim. Acta*, 18 (1962) 259.
9 B. J. RUSSELL, J. P. SHELDON AND A. WALSH, *Spectrochim. Acta*, 8 (1957) 317.
10 W. G. JONES AND A. WALSH, *Spectrochim. Acta*, 16 (1960) 249.
11 J. B. WILLIS, *Spectrochim. Acta*, 16 (1960) 259.
12 A. G. GAYDON, *The Spectroscopy of Flames*, Chapman and Hall, London, 1957, p. 129.

BESTIMMUNG DES OBERFLÄCHENSAUERSTOFFS AUF METALLEN DURCH AKTIVIERUNG IM REAKTOR

W. LEONHARDT*
Zentralinstitut für Kernforschung, Rossendorf (D.D.R.)

(Eingegangen den 18. Juli, 1964)

Die Dicke von Sauerstoffilmen, mit denen Metalloberflächen nach längerer Lagerung an der Luft in Form von Sauerstoff-Oxyd- bzw. Hydratschichten bedeckt sind, ist eine ausserordentlich wichtige Grösse zur Beurteilung des Korrosions- und Passivitätsverhaltens der betreffenden Metalle. Bisher verfügen wir vor allem über umfangreiches Untersuchungsmaterial zur Bildung dicker Zunderschichten auf verschiedenen Metallen bei erhöhten Temperaturen[1] bzw. über die Bildung von Chemisorptions- und primären Oxydschichten auf reinen, durch Verdampfen im Hochvakuum hergestellten Metallfilmen[2]. Aufgabe der vorliegenden Arbeit war es, in dem zwischen den beiden Extremen liegenden Bereich die Sauerstoffbelegung auf blanken Metallfolien, die einige Monate normaler Zimmerluft ausgesetzt waren, vergleichend und in Abhängigkeit von der Vorbehandlung zu bestimmen. Es handelt sich um die Bestimmung typischer Sauerstoffschichten, die auf den Metallen beim normalen Gebrauch anzutreffen sind, sofern besonders korrodierende Einflüsse fehlen.

Zur Lösung der gestellten Aufgabe ist die Aktivierungsanalyse hervorragend geeignet, nicht zuletzt zur Vergleichsbestimmung für die bisher vorwiegend eingesetzten, aber durchaus nicht universell anwendbaren Verfahren[3] Elektronendiffraktion, Ellipsometrie und kathodische Reduktion. Die Vorteile der aktivierungsanalytischen Sauerstoffbestimmung sind vor allem in hoher Empfindlichkeit und praktisch unbegrenzter Anwendbarkeit auf alle Metalloberflächen zu sehen; die Ergebnisse fallen — im Gegensatz zur Elektronendiffraktion und Ellipsometrie — in Form von Gewichtsmengen Gesamtsauerstoff je Oberflächeneinheit an, unabhängig vom chemischen Bindungszustand des Sauerstoffs. Zwischen Oberflächensauerstoff und Sauerstoff im Inneren der Probe kann nach verschiedenen Verfahren unterschieden werden. Wir entschieden uns für die Anwendung eines auf der Kernreaktion $^{16}O(t,n)^{18}F$ beruhenden Verfahrens. Es wurde 1954 von OSMOND UND SMALES zur Bestimmung des Sauerstoffs in Berylliumpulver ausgearbeitet. Die Autoren erzeugten die Tritonen nach $^{6}Li(n,\alpha)t$ aus Lithiumfluorid, das sie dem Berylliumpulver zumischten, bei Bestrahlung der Mischung im Reaktor. Anschliessend isolierten sie das gebildete ^{18}F in radiochemisch reiner Form und bestimmten seine Aktivität mit dem Fensterzählrohr[4]. Das Verfahren besitzt gegenüber anderen die Vorteile, dass es mit hoher Empfindlichkeit in jedem Reaktor durchgeführt werden kann und dass das entstan-

---

* Gegenwärtige Adresse: Technische Universität Dresden, Institut für physikalische Chemie, Dresden-A27, Bergstrasse 66.

dene 112-Minuten-^{18}F für radiochemische Trennungen gut geeignet ist. In derFolgezeit wurden daher einige Anwendungen der Reaktionsfolge ^{6}Li(n,α)t, ^{16}O(t,n)^{18}F vorgeschlagen und in einigen Fällen auch erprobt[5-11].

Prinzip der Versuchsdurchführung

Die Metallfolien, deren Oberflächensauerstoff zu bestimmen ist, werden beiderseitig mit Folien aus Polystyrol und Lithiumfluorid (Gewichtsverhältnis 1:1) als Tritonenquellen bedeckt. Dies geschieht, wie bereits beschrieben[11,12], indem Streifen der Metallfolien zwischen Ringe der lithiumhaltigen Folien gesteckt werden. Zwei derart entstandene Ringsätze aus je 3 bis 5 Metallfolien und 4 bis 6 Ringen werden in einer Quarzampulle untergebracht, die evakuiert wird. Nach 3- bis 10-stündiger Bestrahlung im Rossendorfer Forschungsreaktor bei einem thermischen Neutronenfluss von $3 \cdot 10^{12}$ bis 10^{13} n/cm^{2}sec wird das in und auf den Metallfolien entstandene ^{18}F chemisch isoliert und gemessen. Die Menge des Sauerstoffs ergibt sich aus den korrigierten ^{18}F-Aktivitäten durch Bezug auf mitbestrahlte Kupferstandards (als Indikatoren für den Neutronenfluss) bzw. Sauerstoffstandards. Um die pro Gewichtseinheit Sauerstoff entstehende ^{18}F-Aktivität vorausberechnen zu können, ist es zweckmässig, einen Gesamtwirkungsquerschnitt σ_g des Reaktionssystems ^{6}Li(n,α)t, ^{16}O(t,n)^{18}F zu definieren, in den die Wirkungsquerschnitte der beiden Teilreaktionen und die Gesetzmässigkeiten der Tritonenbremsung eingehen sollten.

BERECHNUNG DES GESAMTWIRKUNGSQUERSCHNITTES

Ausgangsdaten

Die Reaktion ^{6}Li(n,α)t ist exotherm und liefert Tritonen der Energie E_t = 2.74 MeV. Ihr Wirkungsquerschnitt für thermische Neutronen beträgt, bezogen auf die natürliche Mischung der Lithiumisotope, 71 barn und nimmt für höhere Neutronenenergien nach dem $1/v$-Gesetz ab.

Die Reaktion ^{16}O(t,n)^{18}F ist mit $Q = +1.28$ MeV ebenfalls exotherm. Ihr Wirkungsquerschnitt nimmt von kleinen Tritonenenergien bis 2.74 MeV sehr steil (ungefähr exponentiell)[13-15] zu.

Die nach der ersten Reaktion produzierten Tritonen verlieren im allgemeinen durch Wechselwirkung mit der Targetsubstanz kinetische Energie, bevor sie mit ^{16}O-Kernen zur Reaktion kommen. Für diesen Bremsprozess erhält man eine von der Bremssubstanz unabhängige Funktion, wenn man die Tritonenenergie E als Funktion des Bremsweges a, dividiert durch die Reichweite R bei der Anfangsenergie, betrachtet. Dies lässt sich nach entsprechenden Umrechnungen an experimentellen Ergebnissen von Wolke und Mitarbeitern[16] zeigen, folgt aber auch aus der Anwendung der Bragg–Kleeman-Regel. Die auf dem letzten Wege erhaltene Funktion ist in Tabelle I dargestellt. Ihre Anwendung vereinfacht die weitere Rechnung beträchtlich.

Homogenes System

Wegen der übersichtlicheren Verhältnisse leiten wir den Gesamtwirkungsquerschnitt zunächst für ein homogenes System ab, in dem die Tritonen in demselben Volumen mit ^{16}O reagieren, in dem sie erzeugt werden. Der Körper soll in seiner Ausdehnung gross gegenüber der Reichweite der Tritonen sein, so dass die Tritonenverluste an seiner Oberfläche nicht ins Gewicht fallen. Andererseits soll er noch so klein

TABELLE I

Tritonenenergie (MeV)	*Normierter Bremsweg a/R*	*Wirkungsquerschnitt (mb)*
2.74	0	650[a]
2.70	0.0235	500
2.55	0.104	255[a]
2.40	0.195	170[a]
2.25	0.260	144
2.10	0.336	124
1.95	0.407	98
1.80	0.477	85
1.65	0.537	78
1.50	0.598	60
1.35	0.648	34
1.20	0.699	20
1.05	0.745	12.8
0.90	0.779	9.5
0.75	0.814	8.0
0.60	0.850	7.1
0.45	0.885	6.2
0.30	0.925	5.5
0.15	0.960	—
0.0	1.000	—

[a] Extra- bzw. interpolierte Werte.

sein, dass ein annähernd ungestörter Neutronenfluss innerhalb des Körpers herrscht. Das trifft z.B. für eine Kugel aus 1.5 mg Li_2CO_3 zu*.

Einen derartigen Körper vom Volumen V betrachten wir als Tritonenquelle mit folgender Quellstärke (Trit./sec):

$$Q = {}^1N_{\mathrm{Li}} \cdot V \cdot \phi \cdot \sigma_{\mathrm{Li}} \qquad (1)$$

${}^1N_{\mathrm{Li}}$ ist die Anzahl der Lithiumatome je ml, ϕ der Neutronenfluss und σ_{Li} der Wirkungsquerschnitt der Reaktion ${}^6\mathrm{Li}(\mathrm{n},\alpha)\mathrm{t}$.

Aus der Tritonenquellstärke erhalten wir die gebildete ^{18}F-Aktivität A, wenn wir den Wachstumsfaktor W der Bestrahlung und eine Wahrscheinlichkeit η einführen, mit der ein Triton die Reaktion mit ^{16}O eingeht. η ist dabei über alle vorkommenden Tritonenenergien zu mitteln ($\bar{\eta}$):

$$A = Q \cdot \bar{\eta} \cdot W \qquad (2)$$

und ist das Verhältnis der Tritonenreichweite R zur mittleren freien Weglänge $({}^1N_{\mathrm{O}}\bar{\sigma})^{-1}$ der Tritonen für die Reaktion mit ^{16}O:

$$\bar{\eta} = R \cdot {}^1N_{\mathrm{O}} \cdot \bar{\sigma} \qquad (3)$$

Hierbei bedeuten ${}^1N_{\mathrm{O}}$ die Anzahl der Sauerstoffatome je ml und $\bar{\sigma}$ der Wirkungsquerschnitt der Reaktion ${}^{16}\mathrm{O}(\mathrm{t},\mathrm{n}){}^{18}\mathrm{F}$, gemittelt über alle Tritonenenergien.

---

* Die Neutronenselbstabsorption wurde abgeschätzt nach MORZEK[17].

Aus der Aktivierungsgleichung (σ_g ist der Gesamtwirkungsquerschnitt):

$$A = {}^1N_{\mathrm{O}} \cdot V \cdot \sigma_g \cdot \phi \cdot W \tag{4}$$

und den Gl. (1), (2) und (3) folgt schliesslich für den Gesamtwirkungsquerschnitt:

$$\sigma_g = {}^1N_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}} \cdot R \cdot \bar{\sigma} \tag{5}$$

Zur Berechnung von $\bar{\sigma}$ kann statt über alle Tritonenenergien auch über alle Tritonenbremswege a gemittelt werden. Mit der im Abschnitt *Ausgangsdaten* behandelten einheitlichen Bremsfunktion mit der Variablen a/R wird der Mittelwert für alle Substanzen gleich:

$$\bar{\sigma} = \frac{1}{R}\int_0^R \sigma(a)\mathrm{d}a = \int_0^1 \sigma\left(\frac{a}{R}\right)\mathrm{d}\left(\frac{a}{R}\right) = 112 \text{ mb} \tag{6}$$

Den Zahlenwert erhielten wir durch graphische Integration der Anregungsfunktion von LORENZEN UND KÖNIG[15] unter Einbeziehung des Messwertes von SHER UND FLOYD[14], die Funktionswerte befinden sich mit in Tabelle I. Dieselben Resultate, wie sie in den Gleichungen (5) und (6) zum Ausdruck kommen, erhielten wir bereits früher bei einer stark vereinfachten Betrachtungsweise. Wir bestätigten dabei die für $LiNO_3$, Li_2CO_3 und LiOH berechneten Gesamtwirkungsquerschnitte durch experimentelle Werte[11].

Schichtauflageverfahren (heterogenes System)

Wie in Fig. 1 skizziert, ist die sauerstoffhaltige Substanz Me (Metallfolie) zu beiden Seiten mit der lithiumhaltigen Folie Li bedeckt. Es wird angenommen, dass ein Triton in A entsteht, bei B in die Metallfolie eindringt und bei C mit einem ^{16}O-Kern reagiert*.

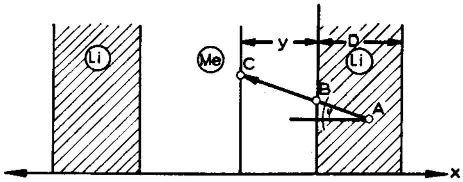


Fig. 1. Schema des Schichtauflageverfahrens.

Von den in einer Li-Folie erzeugten Tritonen fliegt nur die Hälfte in Richtung auf eine Me-Folie. Demnach hat die Tritonenquellstärke den Wert:

$$Q = \tfrac{1}{2} \cdot {}^1N_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}} \cdot \phi \cdot F \cdot D \tag{7}$$

(D ist die Dicke der Li-Folie, die im Vergleich zur Fläche F sehr klein ist). Die mittlere Reaktionswahrscheinlichkeit $\bar{\eta}$ lautet analog zur Gl. (3):

$$\bar{\eta} = R_{\mathrm{Me}} \cdot {}^1N_{\mathrm{O}} \cdot \bar{\sigma} \tag{8}$$

---

* Dass die Bahn des Tritons u.U. komplizierter ist, spielt für die Betrachtung keine Rolle.

(R_{Me} = die Tritonenreichweite im Metall), und die erzeugte ^{18}F-Aktivität ist, da im Metall das Volumen $F \cdot R_{\mathrm{Me}}$ aktiviert wird, gleich:

$$^{1}A \cdot F \cdot R_{\mathrm{Me}} = \bar{\eta} \cdot Q \cdot W \tag{9}$$

(^{1}A ist die Aktivität in der Volumeneinheit). Schliesslich folgt in ähnlicher Weise wie bei der Ableitung von Gl. (5) für den Gesamtwirkungsquerschnitt

$$\sigma_g = {}^{1}N_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}} \cdot \frac{D}{2} \cdot \bar{\sigma} \tag{10}$$

Der Mittelwert $\bar{\sigma}$ soll zunächst für die an der Oberfläche von Me reagierenden Tritonen ($y = 0$) abgeleitet werden. Alle Tritonen, die aus der Tiefe x der Li-Schicht kommen, können je nach dem Winkel φ zwischen ihrer Bahn und derFlächennormalen verschieden lange Bremswege $x/\cos\varphi$ zurücklegen. Da alle Winkel φ mit gleicher Häufigkeit vertreten sind, ergibt die Mittelung für eine bestimmte Tiefe x

$$\bar{\sigma}(x) = \frac{2}{\pi} \int_{0}^{\pi/2} \sigma\left(\frac{x}{\cos\varphi}\right) \mathrm{d}\varphi \tag{11}$$

und schliesslich die Mittelung über alle Schichten x bis zur Dicke D:

$$\bar{\sigma}(D) = \frac{2}{\pi D} \int_{0}^{D} \int_{0}^{\pi/2} \sigma\left(\frac{x}{\cos\varphi}\right) \mathrm{d}x\mathrm{d}\varphi \tag{12}$$

Zur Auswertung dieses Integrals führen wir analog zur Gl. (6) die Variable $x/R_{\mathrm{Li}} = n$ ein. Somit ergibt sich ein für alle Li-haltigen Substanzen gleicher Ausdruck für die Abhängigkeit von σ_g von der Schichtdicke D (bei $y = 0$):

$$\sigma_g(D) = {}^{1}N_{\mathrm{Li}} \cdot R_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}} \int_{0}^{D/R_{\mathrm{Li}}} \int_{0}^{\pi/2} \frac{1}{\pi} \sigma\left(\frac{n}{\cos\varphi}\right) \mathrm{d}n\mathrm{d}\varphi \tag{13}$$

Die Zahlenwerte zu diesem Integral erhielten wir durch numerische Integration; sie sind in Tabelle II enthalten*. Die zweite Spalte enthält das Integral über φ (als Funktion von $n = x/R_{\mathrm{Li}}$) und die dritte Spalte das Integral über x (als Funktion von $n = D/R_{\mathrm{Li}}$). Diese Werte zeigen, dass der Gesamtwirkungsquerschnitt bis etwa $D/R_{\mathrm{Li}} = 0.6$ mit der Dicke D der Li-Schicht zunimmt und dann konstant ist; dickere Schichten sind also unproduktiv.

Mit der allgemeinen Variablen n ist es auch möglich, Gl. (13) auf die Aktivierung im Inneren von Me ($y > 0$) auszudehnen. In der Tiefe y ist der kleinste Bremsweg $y/\cos\varphi$, d.h. in Gl. (13) wird die untere Integrationsgrenze y/R_{Me}. Somit lautet der Ausdruck von σ_g für verschiedene Tiefen y im Metall bei der Dicke der Li-Schicht $D = R_{\mathrm{Li}}$:

$$\sigma_g(y) = {}^{1}N_{\mathrm{Li}} \cdot R_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}} \int_{y/R_{\mathrm{Me}}}^{1} \int_{0}^{\pi/2} \frac{1}{\pi} \sigma\left(\frac{n}{\cos\varphi}\right) \mathrm{d}n\mathrm{d}\varphi \tag{14}$$

---

* Der Rechenweg und Zwischenwerte gehen aus ref.[12] hervor.

Die Werte dieses Integrals befinden sich in Tabelle II, letzte Spalte. Aus ihnen geht hervor, dass der Gesamtwirkungsquerschnitt im Inneren von Me mit der Tiefe y sehr stark (etwa exponentiell) abnimmt und nach einer Reichweite gleich Null wird. Dieser Abnahme muss bei entsprechenden Aktivierungsanalysen Rechnung getragen werden, worauf wir kürzlich in einer Bemerkung zur Arbeit von BAILEY UND ROSS hinwiesen[18].

TABELLE II

Integral als Funktion von

n	x *(mb)*	D *(mb)*	y *(mb)*
0.0	325	0	35.0
0.05	145.7	10.4	24.6
0.1	90.5	16.1	18.9
0.2	56.2	23.0	12.0
0.3	39.3	27.7	7.3
0.4	25.6	30.9	4.11
0.5	17.1	33.0	2.01
0.6	8.4	34.3	0.75
0.7	2.7	34.8	0.24
0.8	0.88	35.0	0.07
0.9	0.29	35.0	0.02
1.0	0	35.0	0.00

Experimentelle Bestätigungen dieses Funktionsverlaufes werden in der Tabelle IV dieser Arbeit angeführt und sind auch aus der Fig. 3 der Arbeit von LORENZEN UND KÖNIG[16] zu entnehmen.

ARBEITSVORSCHRIFTEN

Die bestrahlten Metallfolien werden durch folgende Operationen chemisch aufgearbeitet: (*1*) Auflösen in einer Säuremischung mit eingestelltem Fluoridgehalt, (*2*) Abtrennen des Metalls, (*3*) Ausfällen des Fluorids mit Calciumchloridlösung als CaF_2, (*4*) Destillieren des Fluors als $HF + SiF_4$ und (*5*) Ausfällen des Fluorids mit Bleichloronitrat als PbClF. Nach der Aktivitätsmessung wird die Fluormenge durch Auflösen des PbClF und Titrieren des Cl-Ions mit Silbernitrat bestimmt.

Bei der Aufarbeitung von Aluminiumfolien erübrigt sich die Abtrennung des Metalls, d.h. die Operationen (2) und (*3*) entfallen. Die Arbeiten (*1*) bis (*4*) werden in geschlossenen Gloveboxen ausgeführt.

Auflösen der Proben

Au, Ni, Fe, Cu und Zr. In Polystyrolbecher (lichte Masse 17 Ø × 36 mm) werden mit einer Polyäthylenpipette genau 2 ml einer eingestellten Mischung aus konz. Flusssäure und konz. Salpetersäure 1 : 4 und mit einer Fortunapipette ungefähr 2 ml konz. Salpetersäure gegeben. In dieser Mischung lösen sich die Folien aus Au, Ni, Fe und Cu sofort auf. Die Zr-Bleche werden auf Grund ihrer Dicke von 0.3 mm nur oberflächlich abgetragen, wobei das gesamte dem Oberflächensauerstoff entsprechende ^{18}F in Lösung geht.

Die Pt-Folien werden in Polyäthylenröhrchen gegeben, in denen sich 2 ml der oben beschriebenen Säuremischung und 4 ml Königswasser befinden. Die Röhrchen werden auf dem Sandbad auf 160° erhitzt; die Auflösung dauert je nach der Foliendicke 0.5 bis 2.5 h.

Zur Auflösung der Al-Folien befinden sich in den Polystyrolbechern 10 ml $HClO_4$ 20%, 300 mg NaF und eine Spatelspitze $HgCl_2$. Nach Auflösung des Metalls wird die Lösung unmittelbar in die Fluordestillationsapparatur gegeben.

Abtrennung der Metalle

Die Lösungen von Ni, Fe, Cu und Zr werden in 100-ml Bechergläsern mit 5 ml konz. NaOH und 5 ml Wasser gegeben. Die ausgefallenen Hydroxyde werden abfiltriert.

Die Pt-Lösung gibt man in ein 100-ml Becherglas mit 8 ml konz. NH_3 und 8 ml Wasser. Die Lösung wird zum Sieden erhitzt und mit 5 ml gesättigter Hydrazinhydrochlorid-Lösung versetzt. Das metallische Platin ballt sich gut zusammen und wird abfiltriert.

Das Gold liegt in sehr hohen Aktivitäten vor. Es muss sorgfältig abgetrennt werden, da es bei der Destillation des Fluors mit übergeht. Die hochaktive Lösung wird in einen 100-ml Schütteltrichter zu 20 ml Wasser und 25 ml Essigester gegeben. Nach der Extraktion wird die wässrige, untere Phase in einen zweiten Schütteltrichter, in dem sich 2 ml einer Goldträgerlösung (1 g Gold in 200 ml HCl) befinden, abgelassen. Nach dem Durchschütteln wird die Extraktion in einem dritten und vierten Schütteltrichter, jedes Mal nach Zugabe frischer Gold-Lösung, wiederholt. Es wird ein Dekontaminationsfaktor von 10^8 bis 10^9 erreicht.

Ausfällung von Calciumfluorid

Die Probelösung wird in einem grossen Zentrifugenglas (70 ml) schwach alkalisch gegen Phenolphthalein gemacht. Anschliessend wird mit 5 Tropfen Eisessig und ungefähr 2 g Natriumacetat versetzt und auf dem Wasserbad erwärmt. Das CaF_2 fällt bei langsamer Zugabe einer angewärmten Lösung von $CaCl_2$ (250 g $CaCl_2 \cdot 6\ H_2O/l$) aus und ballt sich nach einiger Zeit zusammen. Es wird abzentrifugiert und ohne zu waschen bei 160° im Trockenschrank getrocknet.

Destillation des Fluors

Die Apparatur besteht aus Glas und arbeitet mit einem kräftigen Strom von überhitztem Wasserdampf. Die Dampfleitung und der Destillationskolben befinden sich in einem Gefäss, das mit siedendem Tetrachloräthan auf 146° gehalten wird. Das trockene CaF_2 wird zusammen mit 8 g Seesand in den Destillationskolben gegeben und aus einem aufgesetzten Zulauftrichter mit 13 ml $HClO_4$ 30% versetzt. Als Vorlage dient ein 100-ml Becherglas mit 10 ml Wasser. Die Destillation ist bei einer Wasserdampfgeschwindigkeit von 3 g H_2O/Min in 15 bis 20 Min beendet. Der Destillationskolben wird über eine Vakuumleitung entleert, mit Wasser gewaschen, getrocknet und ist nach 2 Min für die nächste Destillation bereit[12].

Ausfälllung von Bleichlorofluorid

Die schwach saure Vorlage der Fluordestillation wird nach Zugabe von einigen Tropfen Methylorange auf dem Wasserbad mit 80 ml angewärmter Bleichloronitratlösung (20.5 g $Pb(NO_3)_2$ p.a. + 3.3 g NH_4Cl p.a. pro l) versetzt. Aus einer Bürette wird tropfenweise 1 *N* NaOH zugegeben, bis die Lösung gerade orange ist. Der Niederschlag wird in einer zusammengesetzten Nutsche über mittlerem Filtrierpapier abgesaugt, der Rest wird mit 10 ml Fällungsmittel übergespült. Zum Waschen wird das Vakuum unter der Nutsche aufgehoben, eine Menge von 2 ml Wasser über dem Niederschlag verteilt und danach abgesaugt. Das Papierblatt mit dem feuchten Niederschlag wird zusammengerollt und in ein Reagenzglas gesteckt, das in die Bohrung eines NaJ-Szintillationskristalls passt.

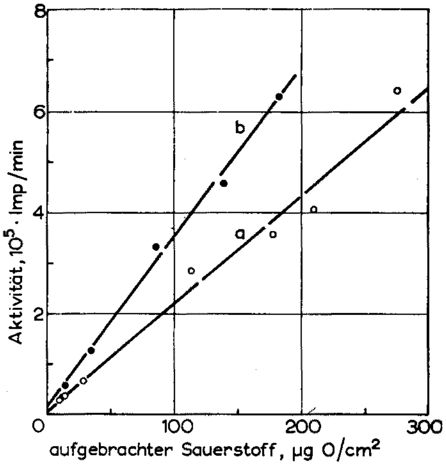
Bestimmung der chemischen Ausbeute

Das Bleichlorofluorid wird nach beendeter Aktivitätsmessung in einem 50-ml Becherglas mit 25 ml halbkonz. Salpetersäure von der Papierscheibe gelöst, am besten mit zwei getrennten Säureportionen. Die Lösung wird in einen 200-ml Messkolben zu 100 ml 0.1 *N* Silbernitratlösung gegeben. Der Kolbeninhalt wird bis zur Marke aufgefüllt, durchgeschüttelt und mit hartem Filtrierpapier filtriert. 20 ml des Filtrats werden mit der Pipette entnommen, mit 2 ml einer $NH_4Fe(SO_4)_2$-Lösung versetzt und mit 0.1 *N* Ammoniumrhodanid bis zur beständigen Braunfärbung titriert. Subtraktion des Rhodanid-Verbrauchs von 10 ergibt die gesuchte Fluorid-Menge in mMol.

Die daraus durch Bezug auf die eingesetzte Fluoridmenge (~5 mMol) berechneten chemischen Ausbeuten liegen im Mittel bei 60% .

VERSUCHSERGEBNISSE ZUR METHODIK

Zur Prüfung des Bestimmungsverfahrens stellten wir mit Sauerstoffstandards Eichkurven auf (Figs. 2 und 3). Abszissenmassstab ist der auf Eisen- bzw. Nickel-



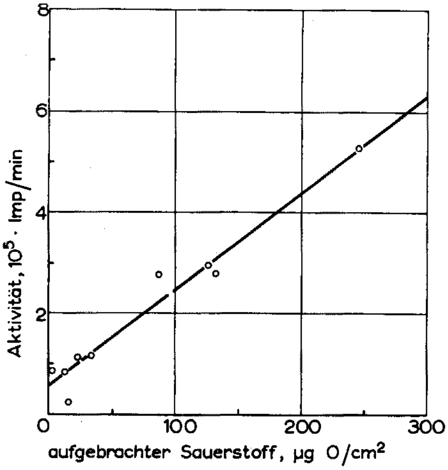


Fig. 2. Eichkurve a) Ni, 20 µ; b) Ni, 3 µ.

Fig. 3. Eichkurve Fe, 18 µ.

folien aufoxydierte Sauerstoff in μg O/cm^2 Folienfläche (die Folien wurden im Muffelofen erhitzt und auf der Mikrowaage ausgewogen) und Ordinatenmassstab die mit dem Hundertkanalanalysator im 0.51 MeV-Peak gezählte ^{18}F-Aktivität (normiert auf das Ende einer Bestrahlung von 3-h Dauer bei einem Fluss von $5 \cdot 10^{12}$ n/cm^2/sec, auf 100% Ausbeute bei der chemischen Aufarbeitung, auf eine totale Zähleffektivität von 24.6% und auf eine Folienfläche von 5 cm^2). In beiden Diagrammen ergeben sich eindeutig lineare Funktionen, die infolge der bereits vor dem Aufoxydieren vorhandenen Sauerstoffschicht die Ordinate oberhalb Null schneiden.

Aus den Geradenneigungen folgen durch Umrechnung mit den genannten Normierungsbedingungen die Gesamtwirkungsquerschnitte σ_g. Sie sind in der folgender Tabelle zusammengefasst und Werten gegenübergestellt, die wir nach $\sigma_g = 35.0 \cdot {}^1N_{\mathrm{Li}} \cdot R_{\mathrm{Li}} \cdot \sigma_{\mathrm{Li}}$(mb) (vergl. Gl. (13) und Tabelle II) berechneten.

TABELLE III

Material	*Dicke* (μ)	σ_b *exptl.* (μb)	σ_g *berechnet* (μb)
Ni	20	230	212
Fe	18	207	212
Ni	3	356	288

Dabei wurden eingesetzt: $\sigma_{\mathrm{Li}} = 71 \cdot 10^{-24}$ cm^2, und für die Mischung aus LiF + Polystyrol 1 : 1 ${}^1N_{\mathrm{Li}} = 1.67 \cdot 10^{22}$ cm^{-3}, $R_{\mathrm{Li}} = 50.8\ \mu$*.

Die Übereinstimmung der berechneten mit den experimentellen Werten in Tabelle III kann angesichts der eingeführten Näherungen bei den Berechnungen als befriedigend bezeichnet werden. Die σ_g-Werte bei verschiedenen Metallen sind ungefähr gleich (Fig. 2,a Ni, Fig. 3 Fe), vorausgesetzt, dass die Folien mindestens eine Tritonenreichweite dick sind ($R_{\mathrm{Ni}} = 17\ \mu$, $R_{\mathrm{Fe}} = 18\ \mu$). Bei der 3.2 μ dicken Ni-Folie (Fig. 2,b) wird die Oberfläche durch Tritonen aktiviert, die sowohl von aussen als auch durch die Folie hindurch auftreffen. Dementsprechend setzt sich σ_g aus zwei Anteilen zusammen, wobei der zweite nach Gl. (14) berechnet wird: $\sigma_g = 212 + 76\ \mu\text{b} = 288\ \mu\text{b}$. Der experimentelle Wert ist in diesem Fall allerdings um rund 20% grösser als der berechnete. Zwei weitere Experimente dienten dazu, die Abnahme der Tritonenaktivierung im Inneren von Metallen nachzuweisen. Für den Bereich bis zur Tiefe einer halben Tritonenreichweite wurden vier 4.9-μ Aluminiumfolien hintereinandergepackt und mit Tritonen aus einer Lithiumfluorid–Polystyrolfolie von einer Seite aktiviert. In einem anderen Experiment wurden acht 5.9-μ Nickelfolien hintereinandergepackt und von beiden Seiten mit Tritonen bestrahlt. In diesem Fall müsste die Aktivierung auf den beiden inneren Folien bis auf Null zurückgehen. Die Tabelle IV zeigt die Ergebnisse. Angegeben werden die auf Nulleffekt, chemische Ausbeute und radioaktiven Zerfall korrigierten ^{18}F-Aktivitäten, die aus den Sauerstoff-Oberflächenschichten der Al- bzw. Ni-Folien entstehen, und die nach Gl. (14) berechneten Gesamtwirkungsquerschnitte σ_g, jeweils gemittelt über die beiden Folienoberflächen.

---

* Die Reichweiten berechneten wir nach der Bragg–Kleeman-Regel[19], nur geringfügig davon abweichende Werte erhielten wir nach Näherungsverfahren, die von JANSSEN[20] bzw. FRIEDLANDER UND KENNEDY[21] beschrieben wurden.

TABELLE IV

Folie Nr.	*Aktivität (Ipm)*	σ_g *(mb)*	*Quot. (mb/Ipm)*
Al			
1	633	0.154	$2.4 \cdot 10^{-4}$
2	218	0.073	$3.3 \cdot 10^{-4}$
3	102	0.036	$3.5 \cdot 10^{-4}$
4	57.3	0.015	$2.6 \cdot 10^{-4}$
	Mittelwert		$3.0 \cdot 10^{-4}$
Ni			
1[a]	$2.24 \cdot 10^5$	0.119	$5.3 \cdot 10^{-7}$
2	$2.19 \cdot 10^4$	0.0136	$6.2 \cdot 10^{-7}$
2′	$2.11 \cdot 10^4$	0.0136	$6.4 \cdot 10^{-7}$
3	$3.87 \cdot 10^2$	$2.7 \cdot 10^{-4}$	$6.9 \cdot 10^{-7}$
3′	$3.52 \cdot 10^2$	$2.7 \cdot 10^{-4}$	$7.6 \cdot 10^{-7}$
4	< 56	0	—
4′	< 64	0	—
	Mittelwert		$6.5 \cdot 10^{-7}$

[a] Die Folie 1′ war verlorengegangen.

Aus den Werten geht hervor, dass die Aktivierung tatsächlich sehr stark mit der Tiefe zurückgeht, wobei die relative Abnahme durch die Berechnungen über mehrere Grössenordnungen richtig wiedergegeben wird.

Sauerstoffwerte auf verschiedenen Metallen

Wir untersuchten eine Reihe von gewalzten Metallfolien, die seit ihrer Herstellung mindestens ein Jahr in Zimmerluft gelagert hatten, blank aussahen und unter dem Mikroskop durchgehende Walzriefen und teilweise geringfügige Oxydablagerungen erkennen liessen: Pt (17 μ), Ni (20 und 3 μ), Cu (19 μ), Al (35 μ) und Fe (18 μ). Aus den Folien wurden jeweils Proben von 1 × 5 cm entsprechend 10 cm^2 Gesamtoberfläche geschnitten und durch Baden in Äther bzw. Extrahieren mit Benzol in einem Soxhlet-Apparat entfettet. In einigen Fällen schlossen sich weitere Behandlungen an (Ätzen bzw. Schmirgeln). Zr und auch Ni wurden in Form von dickeren Blechen (0.3 mm bzw. 0.1 mm) verwendet, Au in Form von Goldschlägerhaut (3 μ) bzw. durch Verdampfen hergestellter Folie (2 μ).

Bei den Sauerstoffbestimmungen bezogen wir die ^{18}F-Aktivitäten auf mitbestrahlte Sauerstoffstandards aus Nickel bzw. Eisen oder auf Neutronenflussstandards aus Kupfer. Wir nutzten dabei die soeben erläuterte Tatsache aus, dass σ_g in erster Näherung unabhängig vom Metall ist.

Die Ergebnisse sind in der Tabelle V zusammengestellt. Die Eigenschaften der Proben werden in der Spalte unter *Charakteristik* wiedergegeben, die Expositionszeit t_E, d.h. die Zeit von der Vorbehandlung bis zum Evakuieren der Proben vor der Bestrahlung, befindet sich in der folgenden Spalte. Die Sauerstoffbedeckungen sind angegeben in μg Sauerstoff pro cm^2 geometrischer Metalloberfläche, hinzugefügt werden die aus den Mehrfachbestimmungen (im allgemeinen 3 bis 6) folgende Standardabweichungen des Mittelwertes.

TABELLE V

Nr.	*Me*	*Charakteristik*	t_E	*Sauerstoffbedeckung* *(µg O/cm²)*	*Rauhigkeitsfaktor* *f*	*Schichtdicke* *(Å)*
1	Au	Durch Verdampfung hergestellte Folie	7 d	$\leqslant 0.51 \pm 0.005$	1.5	$\leqslant 17$
2		Goldschlägerhaut, ausgeheizt bei 950°	4 h	$\leqslant 0.16 \pm 0.025$	2.5	$\leqslant 3.3$
3	Pt	Gewalzte Folie		1.4 ± 0.1	2	40
4	Ni	Gewalzte Folie 20 µ		1.3 ± 0.1	2	45
5		Gewalzte Folie 3 µ		1.4 ± 0.1	1.5	66
6		Älteres Blech 100 µ		9.8 ± 0.25	3	266
7		Wie 6, jedoch geschmirgelt (zuletzt mit Nr. 7.00)	4 h	6.2 ± 0.6	4	107
8	Cu	Gewalzte Folie		2.9 ± 0.3	2	211
9	Al	Gewalzte Folie		4.9 ± 0.9	2.5	106
10		Wie 9, jedoch mit NaOH gebeizt und in HNO$_3$ gespült		3.2 ± 0.5	1.5	115
11	Fe	Gewalzte Folie		7.5 ± 1.1	2	264
12	Zr	Blech 300 µ, mittelfein geschmirgelt	7 d	14.5 ± 2.4	4	244

Diese Standardabweichungen bewegen sich in brauchbaren Grenzen. Wie wir in einer früheren Abschätzung[12] zeigten, beträgt der Maximalfehler einer einzelnen Sauerstoffbestimmung nach dem vorliegenden Verfahren etwa 13%; grössere Schwankungen dürften auf Unterschiede zwischen den Einzelproben zurückzuführen sein.

Relativ schwierig ist die Frage zu klären, inwieweit alle gefundenen Sauerstoffwerte durch einen Blindwert, hervorgerufen durch ^{18}F-Rückstosskerne, die von der LiF–Polystyrol-Folie auf das Metall fliegen, zu hoch ausgefallen sind. Der Blindwert liesse sich mit einer beliebigen Folie bestimmen, die absolut frei von Sauerstoff ist.

Leider lässt sich dieses Experiment kaum mit Sicherheit realisieren. Wir fanden auf ausgeheizter Goldschlägerhaut (Nr. 2) mit 0.16 µg O/cm² einen extrem niedrigen Sauerstoffwert und können vorläufig nur feststellen, dass der Blindwert sicher viel kleiner als dieser Wert ist. Alle Werte der Tabelle V, evtl. mit Ausnahme der Gold-Werte, bedürfen also keiner erheblichen Korrektion.

Vergleichsbestimmungen nach der Vakuumschmelzmethode

In zwei der aktivierungsanalytisch untersuchten Materialien bestimmten wir durch Vakuumschmelze den Gesamtsauerstoffgehalt und rechneten ihn unter der Annahme, dass der Sauerstoffgehalt im Inneren nicht ins Gewicht fällt, in Oberflächenbedeckungen um. Die Tabelle VI enthält die erhaltenen Werte. Sie stimmen mit den Ergebnissen der Aktivierungsanalytischen Bestimmungen ungefähr überein, und eine statistische Prüfung mit dem *t*-Test weist aus, dass Unterschiede in den Mittelwerten nicht signifikant sind.

TABELLE VI

Nr.	*Metall* (*µ*)	*Vakuumschmelze* (% *O*)		*Aktivierung* (*µg O/cm²*)
		(% *O*)	(*µg O/cm²*)	
4	Ni 20	0.018 ± 0.002	1.6 ± 0.2	1.3 ± 0.1
11	Fe 18	0.084 ± 0.005	5.3 ± 0.3	7.5 ± 1.1

DISKUSSION DER SAUERSTOFFWERTE

Da Oxydschichten, die einige 10^5 bis 10^6 Minuten alt sind, in Zimmerluft nur noch äusserst langsam mit der Zeit anwachsen, verdienen die Sauerstoffbedeckungen auf den gewalzten, mindestens ein Jahr alten Folien allgemeines Interesse. Wir haben sie in der Fig. 4 in Form von weissen Säulen dargestellt. Die Nebeneinanderstellung zeigt, dass für die Sauerstoffbedeckungen der einzelnen Metalle sowohl deren Affinitäten zum Sauerstoff—Vergleich von Platin und Eisen—als auch hemmende Einflüsse der entstandenen Sauerstoffschichten—Vergleich von Aluminium und Eisen—verantwortlich sind. Die Art der Herstellung der Metalloberflächen spielt eine untergeordnete Rolle, denn die gefundene Reihenfolge der Metalle stimmt mit Ausnahme von Kupfer mit derjenigen überein, die WEISSMANTEL bei der Adsorption von angefeuchtetem Sauerstoff an aufgedampften Metallschichten[2] feststellte. Bei Nickel, Aluminium und Eisen ergeben sich darüber hinaus etwa dieselben absoluten Sauerstoffbedeckungen*, wenn die von WEISSMANTEL gefundenen Adsorptionsgesetze über zwei bis drei Grössenordnungen der Zeit hinaus extrapoliert werden. Auf Kupfer und auf Platin finden wir höhere Sauerstoffbedeckungen. Das zeigt, das eine so weitreichende Extrapolation dieser Adsorptionsgesetze nicht in jedem Falle erlaubt ist.

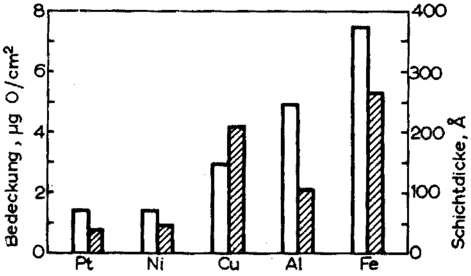


Fig. 4. Sauerstoff auf verschiedenen Metallen.

Die Sauerstoffbedeckung von Gold, Tabelle V Nr. 1, entspricht ungefähr dem Wert[22] einer gesättigten Chemisorptionsschicht von 0.35 *µg* O/cm². Auf der ausgeheizten Goldschlägerhaut (Nr. 2) hat sich nach vierstündiger Luftexposition diese Chemisorptionsschicht noch nicht vollständig ausgebildet.

Auf allen anderen untersuchten Metalloberflächen übersteigen die Sauerstoffbedeckungen den Wert einer Chemisorptionsschicht, und der Oberflächensauerstoff

---

* Die Oberflächen-Rauhigkeitsfaktoren brauchen nicht berücksichtigt zu werden, da sie für gewalzte Folien und verdampfte Filme ungefähr gleich sind.

ist jeweils sowohl in Oberflächenoxyden, als auch in chemisorbierter Form gebunden. Die Chemisorptionsschicht befindet sich dabei nach unseren Vorstellungen als Bindeschicht zwischen dem nackten Metall und dem Oxyd[22–24].

Hinweise auf die Wirksamkeit von zwei verschiedenen Verfahren zur Abtragung der Metalloberfläche vermitteln die Werte der Tabelle V, Nr. 7 und 10. Durch intensives Schmirgeln eines Nickelbleches mit matter, stark oxydierter Oberfläche gelingt es, die Sauerstoffbedeckung herabzusetzen, jedoch nicht bis zu derjenigen, die die blanken gewalzten Folien aufweisen. Besser ist trotz einer längeren nachfolgenden Exposition an der Luft der Erfolg eines bekannten Beizverfahrens[25] für Aluminiumoberflächen.

In Tabelle V, letzte Spalte, und in Fig. 4 (schraffierte Säulen) haben wir die Sauerstoffbedeckungen in der anschaulicheren Grösse von Schichtdicken angegeben. Die Umrechnung erfolgte mit den Rauhigkeitsfaktoren in der vorletzten Spalte. Diese Faktoren wurden von uns nach mikroskopischen Untersuchungen der einzelnen Oberflächen geschätzt; sie haben erfahrungsgemäss[26] ungefähr die Grösse zwei.

Für die jeweils wahrscheinlichsten Oxydstrukturen benutzten wir folgende Umrechnungsfaktoren: NiO 69.4; Al_2O_3 54.3; ZrO_2 67.2; Fe_2O_3 70 und Cu_2O 145.1 Å/μg O/cm^2. Diese Faktoren liegen mit einer Ausnahme bei dem metallreichen Cu_2O nicht viel über 51.1 Å/μg O/cm^2, dem Wert der dichtesten Kugelpackung von O^{2-}-Ionen, und gelten deshalb einerseits auch angenähert für etwas andere Oxydzusammensetzungen als angenommen, z.B. $AlOOH$, FeO usw., und andererseits auch ungefähr für die Chemisorptionsschicht. Im Falle des Goldes[27] bzw. des Platins[28] ist die Existenz von Oberflächenoxyden noch recht umstritten. Solche Verbindungen wie Au_2O_3, PtO und PtO_2 können sich wahrscheinlich bei Zimmertemperatur nicht bilden. Unsere Bestimmungen ergaben für Gold nur Chemisorptionsschichten, deren Dicken wir mit dem Umrechnungsfaktor der dichtesten O^{2-}-Packung berechneten. Bei Platin ist nach SCHISCHAKOW *et al.*[3] die Bildung von Peroxyden wahrscheinlich; wir entnahmen dieser Arbeit den Umrechnungsfaktor 56.8 Å/μg O/cm^2 für die Verbindung Pt_3O_8.

Die berechneten Schichtdicken der Tabelle V stimmen im wesentlichen mit den Ergebnissen optischer Messungen überein, die in dem Buch von SCHISCHAKOW *et al.*[3] zusammengetragen sind.

Schlussfolgerungen

Aus den diskutierten Ergebnissen geht hervor, dass das beschriebene aktivierungsanalytische Verfahren für die Bestimmung von Sauerstoff-Oberflächenschichten sehr gut geeignet ist. Seine untere Grenze für quantitative Bestimmungen liegt auf Grund eines möglichen ^{18}F-Leerwertes bei etwa 0.1 μg O/cm^2, d.h. ungefähr einem Drittel einer monomolekularen Sauerstoffschicht. Dies ist für Metalloberflächen, die sich einige Zeit an der Luft befanden, völlig ausreichend.

Es ist mir ein Bedürfnis, meinem verehrten Lehrer, Herrn Prof. Dr. Dr. h.c. K. SCHWABE, an dieser Stelle für die ausserordentliche Förderung dieser Arbeit und für zahlreiche wertvolle Hinweise zu danken. Mein Dank gebührt ferner der Bestrahlungsgruppe des Rossendorfer Forschungsreaktors für die durchgeführten Bestrahlungen.

ZUSAMMENFASSUNG

Aktivierungsanalytische Bestimmungen des Oberflächensauerstoffs auf Metallfolien werden auf der Grundlage der Reaktionsfolge ^{6}Li(n,α)t, ^{16}O(t,n)^{18}F ausgeführt. Hierzu werden die Metallfolien zwischen Folien aus Lithiumfluorid und Polystyrol, die als Tritonenquelle dienen, gepackt und in evakuierten Ampullen im Reaktor bestrahlt. Das entstandene ^{18}F wird chemisch abgetrennt und durch seine Vernichtungsstrahlung bei 0.51 MeV gemessen. Die Gesamtwirkungsquerschnitte derartiger Folienanordnungen werden nach einfachen Formeln berechnet und mit experimentellen Werten verglichen. Es werden Arbeitsvorschriften für die chemische Aufarbeitung von bestrahlten Folien aus Au, Pt, Ni, Cu, Al, Fe und Zr mitgeteilt. Folgende Sauerstoffbedeckungen werden auf gewalzten Folien gefunden: Pt 1.4, Ni 1.4, Cu 2.9, Al 4.9 und Fe 7.5 μg O/cm^2 geometrischer Oberfläche. Weitere Sauerstoffwerte beziehen sich auf Au, Zr und auf verschiedene Vorbehandlungen der Metalloberflächen. Die untere Grenze für eine quantitative Bestimmung liegt bei 0.1 μg O/cm^2.

SUMMARY

Surface oxygen on metal foils was determined by activation analysis on the basis of the reaction sequence ^{6}Li(n,α)t, ^{16}O(t,n)^{18}F. The metal foils were placed between foils consisting of lithium fluoride and polystyrene, sealed in evacuated ampoules, and irradiated in the reactor. The produced ^{18}F was radiochemically separated, and measured by its annihilation radiation at 0.51 MeV. The overall cross-sections of such foil arrangements were computed by simple formulas and compared with experimental data. Instructions are given for the chemical treatment of irradiated foils of Au, Pt, Ni, Cu, Al, Fe and Zr. The following values of oxygen coverage were found on rolled foils: Pt 1.4, Ni 1.4, Cu 2.9, Al 4.9 and Fe 7.5 μg O/cm^2 of geometrical surface. Other oxygen values refer to Au, Zr and to different pretreatments of the metal surfaces. The lower limit of determination is about 0.1 μg O/cm^2.

RÉSUMÉ

L'oxygène à la surface de feuilles métalliques a été déterminé par analyse par activation, sur la base de la séquence de réaction: ^{6}Li(n,α)t et ^{16}O(t,n)^{18}F. Les feuilles métalliques sont placées entre fluorure de lithium et polystyrène, en ampoules scellées, irradiées dans le réacteur. ^{18}F produit est séparé radiochimiquement et mesuré par sa radiation d'annihilation à 0.51 MeV. Des renseignements sont donnés en ce qui concerne le traitement chimique de feuilles irradiées d'Au, Pt, Ni, Cu, Al, Fe et Zr. La limite inférieure du dosage est d'environ 0.1 μg d'oxygène/cm^2.

LITERATUR

1 K. Hauffe, *Oxydation von Metallen und Metallegierungen*, Springer-Verlag, Berlin, 1956.
2 Ch. Weissmantel, *Werkstoffe und Korrosion*, 13/11 (1962) 682.
3 N. A. Schischakow, W. W. Andrejewa und N. K. Andruschenko, *Bau und Bildungsmechanismus von Oxydfilmen auf Metallen* (in russian), Akad. Wiss. UdSSR, Moskau, 1959.
4 R. G. Osmond und A. A. Smales, *Anal. Chim. Acta*, 10 (1954) 117.

5 G. W. Leddicotte, W. T. Mullins, L. C. Bate, J. F. Emery, R. E. Druschel und W. A. Brooksbank, *PUAE P/927*, 28 (1958) 478.
6 J. W. Winchester, R. E. Meyer und G. W. Leddicotte, *Rept. CF-59-7-128*, 1959.
7 H.-J. Born und N. Riehl, *Angew. Chem.*, 72 (1960) 559.
8 H.-J. Born und P. Wilkniss, *Intern. J. Appl. Radiation Isotopes*, 10 (1961) 133.
9 P. Wilkniss, *Untersuchungen zur Frage der Sauerstoffbestimmung in Festkörpern mittels Aktivierungsanalyse*, Dissertation an der Fakultät f. Allg. Wissensch. d. TH München, 1961.
10 R. F. Bailey und D. A. Ross, *Anal. Chem.*, 35 (1963) 791.
11 W. Leonhardt, *Kernenergie*, 5 (1962) 166.
12 W. Leonhardt, *Die Bestimmung von Sauerstoff und Fluor durch Aktivierung im Reaktor*, Dissertation an der Fak. f. Math. u. Naturwiss. der TU Dresden, 1962.
13 N. Jarmie, *Phys. Rev.*, 98 (1955) 41.
14 R. Sher und J. J. Floyd, *Phys. Rev.*, 102 (1956) 242.
15 K. Lorenzen und D. König, *Z. Naturforsch.*, 16a (1961) 933.
16 R. L. Wolke, W. N. Bishop, E. Eichler, N. R. Johnson und G. D. O'Kelly, *Phys. Rev.*, 129 (1963) 2591.
17 P. Morzek, *Kernenergie*, 5 (1962) 839.
18 W. Leonhardt, *Anal. Chem.*, 36 (1964) 1879.
19 R. D. Evans, *The Atomic Nucleus*, McGraw Hill, 1956.
20 P. Jannssen, *Compt. Rend.*, 232 (1961) 825.
21 G. Friedlander und J. Kennedy, *Lehrbuch der Kern- und Radiochemie*, Thiemig, München, 1962.
22 K. Schwabe und Ch. Weissmantel, *Monatsber. Deut. Akad. Wiss. Berlin*, 5/1 (1963) 23.
23 K. Schwabe, *Electrochim. Acta*, 3 (1960) 186.
24 K. Schwabe, *Mitteilungsbl. d. Chem. Ges. in der DDR*, 7/6 (1960) 105.
25 *Aluminium-Taschenbuch*, Aluminium-Verlag, Düsseldorf, 1955.
26 T. Hickmott, *Advan. Catalysis*, 9 (1957) 167.
27 D. Clark, T. Dickinson und W. Mair, *Trans. Faraday Soc.*, 55 (1959) 1937.
28 L. Hunt, *Platinum Metals Rev.*, 1 (1957) 55.

SEPARATION OF SELENITE, SULFATE AND IRON BY CATION-EXCHANGE RESIN

M. YAMAMOTO AND H. SAKAI
Institute for Thermal Spring Research, Okayama University, Misasa, Tottori-ken (Japan)

(Received June 30th, 1964)

In the course of a study on the distribution of sulfur isotopes in various sulfides and its bearing on the distribution of trace elements such as selenium in the sulfides, the total size of a sample was often so small that the whole sample had to be used for the determination of both the isotope ratio and the selenium. It was therefore essential to separate selenite, sulfate and iron(III) in solutions obtained by oxidative decomposition of sulfides.

The application of anion-exchange resins for the separation of the group VIB elements has been studied by SASAKI[1], who found that selenium is adsorbed on anion-exchange resins from concentrated hydrochloric acid solution, while sulfate passes through; selenium can be eluted with 6 *N* hydrochloric acid. The procedure, however, did not seem practical for the present purpose because of the high volatility of selenium in concentrated hydrochloric acid.

Cation-exchange resin has been used for the separation of micro amounts of selenite from iron and other cations. YOSHINO[2] has called attention to the fact that selenite is partially held by cation-exchange resins when a solution of pH 3 containing more iron(III) than selenite is passed through the resin.

In the present paper, it is shown that selenite in the presence of a large excess of iron(III) can be quantitatively retained by a cation-exchange resin, whereas sulfate shows no tendency to be adsorbed. The further separation of selenite and iron(III) is then achieved by elution of selenite with weak hydrochloric acid.

The procedure has been satisfactorily used for the analysis of micro amounts of selenium in iron sulfides.

EXPERIMENTAL

Reagents and materials

Standard solution of selenite. Standard solution I (243.1 μg Se/ml) was prepared by direct weighing of purified anhydrous selenous acid and subsequent dissolution and dilution. Standard solution II (4.86 μg/ml) was prepared by dilution of standard solution I.

Standard solution of iron(III). A solution (1.0858 mg Fe^{3+}/ml) was prepared by dissolving weighed Merck iron wire in nitric acid followed by dilution.

Iron alum solution. 50.4 g of iron alum crystals were dissolved in 200 ml of 1 : 9 hydrochloric acid.

EDTA solution. A 0.01 *M* EDTA solution was stored and standardized against the standard iron(III) solution before use.

Resin. Dowex 50W-X8, 100–200 mesh, was used in all experiments. After fine particles had been removed by washing with distilled water and hydrochloric acid and decantation, a resin bed about 1 cm in diameter and 10 cm long was prepared; the volume of the resin bed was 15 ml. The resin was washed further with 6 *N* hydrochloric acid and distilled water before use.

Analytical methods for selenite, sulfate and iron(III)

Selenite. Selenite was determined spectrophotometrically with 3,3′-diaminobenzidine (DAB) as described by CHENG[3]. To 50 ml of solution containing less than 50 μg Se, 2 ml of 2.5 *M* formic acid and 1 ml of 0.01 *M* EDTA were added and the pH was adjusted to 2 with formic acid and ammonia; 2 ml of freshly prepared 0.5% DAB solution was added and the mixture was left for about 1 h. The pH was then adjusted to 7 and the yellow organoselenium complex was extracted with 10 ml of toluene. The absorption at 420 mμ was measured against pure toluene by a conventional spectrophotometer. The addition of 0.01 *M* EDTA was usually effective in preventing the oxidation of DAB by trace amount of iron and other oxidizing ions present in the selenite solutions which had been separated from large excesses of iron(III).

Iron(III). A known volume of 0.01 *M* EDTA solution was mixed with a sample solution of iron(III). After heating the mixture to about 80°, excess of EDTA was titrated with copper(II) nitrate solution in the presence of copper–PAN (a mixture of Cu–EDTA and 1-(2-pyridylazo)-2-naphthol) as indicator[4]. The copper solution was standardized against the standard solution of iron(III); the solution during the titration was buffered with ammonium acetate–acetic acid buffer.

Sulfate. Unless otherwise mentioned, sulfate was determined by the usual gravimetric method as barium sulfate, but treatment of the ignited precipitates with sulfuric acid to convert any sulfide to sulfate was avoided, because the precipitates were kept for the isotopic analysis of sulfur.

Adsorption of selenite and iron(III) by the cation-exchange resin

YOSHINO[2] observed that the separation of selenite from iron(III) by cation-exchange resin was incomplete at pH 3 when the ratio of iron to selenite exceeded 10; 20–30% of the selenite was adsorbed when the ratio of iron to selenite in the original solution was 118. These observations indicated that quantitative retention of selenite by cation-exchange resins should be attained if a much larger excess of iron(III) were present.

The effect of the amount of iron(III) on the adsorption of selenite was checked by the following two methods.

(1) Batch method. Four 50-ml solutions containing different ratios of selenite to iron were prepared, each of which contained 24.3 μg of selenium and an amount of iron(III) varying from zero to 127 mg. The pH of each solution was adjusted to 2 with ammonia before the final dilution to 50 ml and 0.5 g of Dowex 50W, 100–200 mesh, was added to each of the solutions. After standing overnight at room temperature, the selenium contents of the liquid phases were measured.

(2) Column method. A similar series of selenium–iron solutions were prepared;

the solutions were passed through the resin beds which had been equilibrated with 0.01 *N* hydrochloric acid. The resins were then washed with 50 ml of 0.01 *N* hydrochloric acid (pH 2), at a flow rate of about 1 ml/min. The first and second effluents were combined and half (50 ml) was analysed for selenium.

The results of these experiments are shown in Table I and Fig. 1, respectively. The adsorption of selenite on the resin rapidly increased with increasing amount of iron(III) until the iron content in the solution reached *ca.* 70 mg. Fig. 1 shows that 24.3 μg of selenium was quantitatively retained by the resin when more than 80 mg of iron(III) was present. In another experiment, 243 μg of selenium as selenite was passed through the resin together with 100 mg of iron(III) under the conditions for the column tests. No selenite could be detected in the first and second effluents.

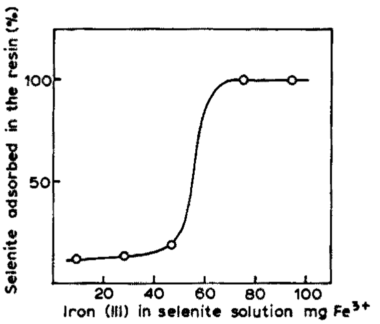


Fig. 1. The effect of iron(III) on the adsorption of selenite on cation-exchange resin (column method).

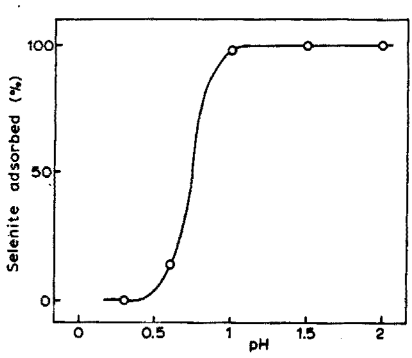


Fig. 2. The effect of pH on the adsorption of selenite on cation-exchange resin.

In Fig. 2 is shown the effect of the pH of the selenite solutions on the adsorbability of selenite on the cation-exchange resin. The experiments were carried out as for the column method (2), but the iron(III) content was maintained at 127 mg in all solutions, while the hydrochloric acid concentration was varied. The results indicate that the pH of the selenite solutions should be higher than 1.5 to ensure complete adsorption.

TABLE I

EFFECT OF IRON(III) ON SELENITE ADSORPTION BY THE BATCH METHOD

Iron content in the original solution (mg)	0.0	31.74	63.48	127.0
Selenite adsorbed (%)	0	58.2	87.0	87.5

These results suggest that there is a strong interaction between iron(III) and selenite in the solutions or in the resin phase. There seem to be two possible explanations for the selenite retention in cation-exchange resins. Selenite may be adsorbed as an iron(III)–selenite complex, such as $FeHSeO_3^{2+}$, or may be coprecipitated with iron(III) in the interstitial solution of the resin phase where the pH could be higher than in the surrounding solution and hydrolysis of iron(III) might occur. In either case, the adsorbability of selenite would depend on the pH and on the iron(III) concentration.

Further experiments are necessary before any definite conclusion can be drawn about the actual mechanism.

The separation of selenite, sulfate and iron(III)

Figure 3 shows an elution curve of selenite, sulfate and iron(III). Sulfate in the effluents was determined spectrophotometrically with barium chloranilate[4]. Tailing of the sulfate ions in the effluents was not significant under the conditions studied; of 584.6 mg of sulfate added, 100% was recovered.

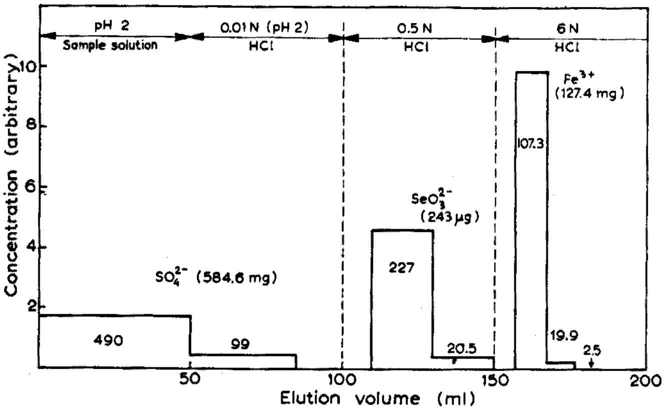


Fig. 3. Elution curve of sulfate, selenite and iron. The figures in brackets are the amounts added and those assigned to each column represent the amount found.

The recovery of selenite was also checked for 3 mixtures of selenite and iron alum solution. With 24.3 µg of selenium and 2 ml of the iron alum solution present, results were 24.3 and 24.9 µg of selenium; with 243 µg of selenium and 4 ml of iron alum solution, the result was 247 µg of selenium.

Analysis of Se, S, Co and Fe in iron sulfides

About 200 mg of pyrite or pyrrhotite was decomposed with 10 ml of reversed aqua regia in a 200-ml beaker. After vigorous reaction ceased at room temperature, the covered beaker was heated on a water bath for about 15 min. The solution was then evaporated almost to dryness.

The residue was taken up with 1 ml of concentrated hydrochloric acid and diluted to about 50 ml with distilled water. Undissolved silica was filtered off and the filtrate further diluted to 100 ml. The pH of the final solution was adjusted to 1.8 to 2 with ammonia. The solution was passed through a 15-ml Dowex 50W resin bed which was pre-conditioned as described before. The resin was then washed with 50 ml of 0.01 *N* hydrochloric acid and the combined effluents were analyzed for sulfate.

Selenite was eluted with 50 ml of 0.5 *N* hydrochloric acid and measured spectrophotometrically as described before.

Iron and cobalt were then eluted with 80 ml of 6 *N* hydrochloric acid. Further separation of cobalt and iron was achieved by means of the anion-exchange resin, Dowex 1-X8; they were first adsorbed from 9 *N* hydrochloric acid solution, and cobalt was eluted with 4 *N* hydrochloric acid and iron with 0.5 *N* hydrochloric acid. Cobalt was determined spectrophotometrically with *o*-nitrosoresorcinol monomethylether[6].

No serious loss of selenite was found when a model solution of 24.3 μg of selenium, 2 ml of iron alum solution and 10 ml of reversed aqua regia was completely evaporated to dryness. In the case of pyrite decomposition, however, the selenite loss might be higher than in the case of pyrrhotite because of the presence of free sulfuric acid after decomposition.

TABLE II

SOME RESULTS OF Se, S, Co AND Fe DETERMINATIONS OF IRON SULFIDES

Sample	*Sample wt. (mg)*	*Se (p.p.m.)*	*S (%)*	*Co (p.p.m.)*	*Fe (%)*
Pyrite-10	256.7	95.4	48.88	27.4	42.6
	253.5	99.1	48.43	28.2	42.8
	258.0	98.8	48.88	27.7	42.9
Pyrrhotite-11	248.1	119	37.79	33.9	58.3
	248.5	124	37.99	33.9	58.4
	180.4	125	—	34.6	57.8
Pyrrhotite 15-2	249.1	65.2	37.76	14.7	59.1
	250.1	70.5	37.66	14.4	58.8
Pyrite 15-2	255.5	75.6	51.75	46.4	44.7
	258.1	74.3	51.75	46.4	44.8

Some of the results of the analyses obtained for natural iron sulfides are summarized in Table II.

The authors are indebted to Dr. UMEMOTO of this Institute for valuable suggestions and discussion, and to Dr. MATSUI and Mr. IKEDA of this Institute, for helpful advice on EDTA titrations.

SUMMARY

Selenite, sulfate and iron(III) are separated by cation-exchange resin. Microgram amounts of selenite in iron(III) sulfate solution at pH 2 are completely adsorbed on the resin together with the large excess of iron(III), while sulfate passes through.

Selenite is eluted with 0.5 *N* hydrochloric acid, leaving iron(III) in the resin. The procedure is applied to the determination of these elements in natural iron sulfides.

RÉSUMÉ

Sélénite, sulfate et fer(III) sont séparés au moyen d'une résine échangeuse de cations. De faibles quantités de sélénite (de l'ordre du microgramme) dans des solutions de sulfate de fer(III), au pH 2, sont complètement adsorbées sur la résine, de même que le grand excès de fer(III), tandis que le sulfate n'est pas retenu. Le sélénium est ensuite élué par l'acide chlorhydrique 0.5 *N*. Ce procédé est appliqué pour le dosage de ces éléments dans les sulfures de fer naturels.

ZUSAMMENFASSUNG

Selenit, Sulfat und Eisen(III) werden mit einem Kationenaustauscher getrennt. Mikrogramme Selenit in Eisen(III)-Sulfatlösung werden zusammen mit einem grossen Überschuss des Eisen(III) beim pH-Wert 2 völlig vom Harz adsorbiert, während das Sulfat den Austauscher passiert. Das Selenit wird mit 0.5 *N* Salzsäure eluiert, das Eisen(III) bleibt auf dem Austauscher zurück. Das Verfahren wird zur Bestimmung dieser Elemente in natürlichen Eisensulfiden angewandt.

REFERENCES

1 Y. SASAKI, *Bull. Chem. Soc. Japan*, 28 (1955) 89.
2 Y. YOSHINO, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 71 (1950) 577.
3 K. L. CHENG, *Anal. Chem.*, 28 (1956) 1738.
4 H. FLASCHKA AND H. ABDINE, *Chemist Analyst*, 45 (1956) 58.
5 R. J. BERTOLACINI AND J. E. BARNEY, *Anal. Chem.*, 29 (1957) 281.
6 T. TORII, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 76 (1955) 328.

STUDIES IN THE TETRAARYLBORATES

PART I. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-CHLOROPHENYL)BORATE

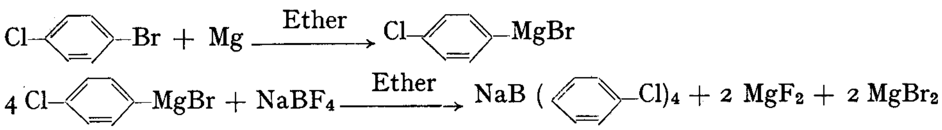
FRANK P. CASSARETTO, JOHN J. McLAFFERTY AND CARL E. MOORE*
Department of Chemistry, Loyola University, Chicago-26, Ill. (U.S.A.)
(Received June 22nd, 1964)

The first of the tetraarylborates, tetraphenylborate, was introduced into analytical chemistry in the years 1949–1951[1–3]. This compound, as the sodium or lithium salt, was recommended for the precipitation of potassium, rubidium, cesium, protonated basic nitrogen and quarternary ammonium compounds. It soon became available commercially and an extensive literature has subsequently developed on its applications[4–6]. The reagent has a limited stability in aqueous solution; this fact prompted us to look into the possibilities of preparing a similar molecule that would be more stable. Of the numerous tetraarylborates synthetically possible but hitherto unprepared, the sodium tetrakis(*p*-chlorophenyl)borate was chosen as the first of a series of molecules in which the substituents on the benzene ring would be varied in such a way as to modify the inductive and resonance effects of the benzene ring on the carbon–boron bond.

EXPERIMENTAL

Synthesis of sodium tetrakis(p-chlorophenyl)borate

Sodium tetrakis(*p*-chlorophenyl)borate is synthesized by the following sequence of reactions.



To a 1-l 3-necked flask equipped with a stirrer, water-cooled condenser and a dropping funnel, add 9.7 g (0.4 mole) of magnesium turnings. Sweep the assembly with dry nitrogen. Add 250 ml of ether previously dried over sodium to the flask. Dissolve 76.6 g (0.4 mole) of *p*-bromochlorobenzene in 100 ml of dry ether and arrange for dropwise addition into the flask. Add approximately 10 ml of the *p*-bromochlorobenzene solution to the flask and stir the solution. Bring to reflux temperature. The

---

* Direct all inquiries to this author.

reaction generally starts within 20 min. Add the remaining 90 ml of solution dropwise over a period of 1 h. Continue the reflux and stirring for an additional hour.

To the cold solution of *p*-chlorophenyl Grignard reagent, add 11.0 g (0.1 mole) of sodium borofluoride which has been previously dried at 110° for 1 h. Blanket with nitrogen; stir and reflux for 2 h while maintaining the blanket of nitrogen. Pour the contents of the reaction flask into 400 ml of ice-cold saturated sodium chloride solution. A white precipitate of inorganic material forms in the aqueous layer. Separate the ether layer with a separatory funnel and extract the aqueous phase 3 times with 50-ml portions of ether. Add these to the previously separated ether layer. The reaction mixture need not be worked up immediately and may be left standing several days before adding it to the sodium chloride solution. Evaporate the major portion of ether under vacuum at room temperature and the remainder under vacuum at 40°. A yellow viscous liquid remains. Pour this into 300 ml of dry xylene and cool in an ice bath. The crystals of the mixed salts, sodium-magnesium tetrakis(*p*-chlorophenyl)-borate, will separate. The yield is about 25 g.

To prepare the pure sodium salt, pass 3 g of the mixed salt in 100 ml of water through an ion-exchange column of Dowex 50W-X4, in its sodium form, at a rate of 3–5 ml per min. It is best to prepare the column with 4% sodium hydroxide. It appears that the acid residue left on the column after the usual HCl–NaCl cycle decomposes the borate. Saturate the eluate, which amounts to about 175 ml, with sodium chloride and extract with three 50-ml portions of ether. Combine the extracts and evaporate under vacuum. Pour the clear viscous liquid into 200 ml of dry xylene. Cool in an ice bath and collect the resulting crop of crystals. Yield: 1.9 g. An analysis of the dried sodium salt yielded the following results: C 59.13%, H 3.49%, Cl 29.73%; calculated: C 60.00%, H 3.36%, Cl 29.54%.

Reagent properties of the tetrakis(p-chlorophenyl)borate anion

A 1% solution of the reagent as the mixed Na–Mg salt was used for qualitative testing. About 2 ml of the reagent were added to 2 ml of the 0.1 *M* test solution. The following ions gave heavy precipitates: K^+, NH_4^+, Rb^+, and Cs^+, while Ba^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Cd^{2+} and Co^{2+} gave no precipitates.

The reagent was also tested for its ability to precipitate quaternary ammonium compounds and other compounds containing a basic nitrogen which had been protonated. Precipitates in such cases are of interest for possible quantitative methods as well as for qualitative identification purposes. Sodium tetraphenylboron has been extensively used as a reagent for the preparation of derivatives of compounds of these types[7]. The nitrogen-containing compound was dissolved in dilute hydrochloric acid and a 1% solution of the reagent was added. The following compounds gave heavy precipitates: 1-phenyl-ethylamine, N-ethylamine, diethylamine, dibenzylamine, atropine, hexamethylenetetramine, 1,6-diaminohexane, glycine and tetrabutylammonium chloride, while pyridine and quinine gave light precipitates. A few of the precipitates were filtered, dried, and analyzed for nitrogen and melting points were taken on a melting point block. The results are summarized in Table I.

The reagent was then tested for its ability to precipitate the potassium ion by mixing 2 ml of a 1% solution of the reagent with 2 ml of test solution. For a comparison tetraphenylborate was used in a similar series of tests. The results are summarized in Table II.

TABLE I

ANALYSIS OF REPRESENTATIVE PRECIPITATES

Material tested	*M.P.(°)*	*%N*	
		Calculated	*Found*
Benzidine	173–176	4.24	4.43
n-Butylamine	117–118	2.63	2.52
Brucine	148–149	3.29	3.24
Quinine	146–151	3.58	2.79

TABLE II

COMPARISON OF SODIUM TETRAKIS(*p*-CHLOROPHENYL)BORATE AND SODIUM TETRAPHENYLBORATE AS A PRECIPITANT FOR POTASSIUM

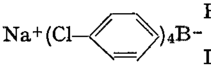
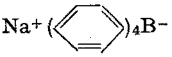
Reagent	*Concentration of potassium ion (mg/ml)*						
	2.0	*0.2*	*0.15*	*0.10*	*0.01*	*0.005*	*0.002*
	Heavy Immediate	Heavy Immediate	Slight Immediate	Trace Slow	None	None	None
	Heavy Immediate	Heavy Immediate	Slight Immediate	Slight Immediate	Slight Immediate	Trace Slow	None

TABLE III

SOLUBILITY OF POTASSIUM TETRAKIS(*p*-CHLOROPHENYL)BORATE IN WATER AT 25° AT DIFFERENT pH VALUES

pH of solution	*Solubility (mole/l)*
3.7	$6.0 \cdot 10^{-4}$
6.7	$6.5 \cdot 10^{-4}$
6.8	$7.5 \cdot 10^{-4}$

The solubility values were obtained by determining the potassium in the supernatant liquid by flame photometry. These values are shown in Table III.

The reagent solutions of sodium tetrakis(*p*-chlorophenyl)borate were tested for stability by observation of the appearance of cloudiness and by checking the activity of the solution against the potassium ion. It was noted that alcoholic solutions of 25% and above by volume remained clear and appeared to be stable for several weeks. Aqueous solutions tested concurrently developed a turbidity after 5 days and were inactive after sixteen days.

Sodium tetrakis(p-chlorophenyl)borate as a reagent for potassium

The procedure described by Gloss[8] in the determination of potassium by sodium tetraphenylborate was selected for the study of the precipitation of potassium with sodium-magnesium tetrakis(*p*-chlorophenyl)borate. A 2% solution of the reagent in water was prepared from the sodium tetrakis(*p*-chlorophenyl)borate. To this was added 1 g of reagent-grade aluminium hydroxide and the solution filtered and the filtrate reserved for analytical use.

Duplicate 10.00-ml aliquots of a standard solution of potassium chloride (2 mg/ml) were pipetted into 250-ml beakers and water was added to bring the volume to 100 ml. They were heated to 70°, and 40 ml of a 2% reagent solution was added slowly to each beaker. The heavy white precipitate which formed immediately was allowed to stand for 30 min, and finally cooled in an ice bath for 30 min. The precipitate was filtered through a fine-porosity, sintered-glass crucible. Four 5-ml portions of ice-cold water were used for transferring and washing the precipitate. The precipitate was dried for 30 min at 110°, cooled in a desiccator and weighed. The recovery of potassium was calculated using the theoretical gravimetric factor 0.07882. The results are summarized in Table IV.

TABLE IV

RESULTS OF QUANTITATIVE TESTS USING SODIUM TETRAKIS(*p*-CHLOROPHENYL)BORATE

K^+ *taken (mg)*	K^+ *found (mg)*
47.6	45.6
47.6	44.9
47.6	44.9
47.6	45.1
20.0	19.7
20.0	19.5
20.0	19.6
21.4	21.0
21.4	21.0

DISCUSSION

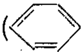
The potassium salt was examined for thermal stability by drying at 110°. After the initial constant weight was established, no further weight was lost during a normal drying interval. Constant weight was usually achieved in about 30 min. Drying for periods of 54 h resulted in losses of less than one part per thousand. The precipitate appeared somewhat more crystalline in character than potassium tetraphenylborate. It flocculated more readily, settled more rapidly and was generally easier to handle than potassium tetraphenylborate. It should be an excellent reagent for use in qualitative analysis schemes. The compound has the serious disadvantage as a precipitation reagent for potassium of yielding a compound of potassium of moderate solubility ($6.5 \cdot 10^{-4}$ mole/l at 25° at pH 6.5).

As shown in Table I the compound has possibilities as a reagent for the formation of derivatives of quarternary ammonium and protonated basic nitrogen compounds. A few of the compounds tested yielded precipitates which were not suitable for derivative purposes. Notable among these were aniline and atropine. Compounds containing two basic nitrogens formed mono or di salts. Benzidine produced a compound that was difficult to recrystallize; this analyzed as the mono salt. These derivatives were characterized by several phase changes before the final melt was achieved.

SUMMARY

Sodium tetrakis(*p*-chlorophenyl)borate was synthesized. It formed precipitates with K^+, Rb^+, Cs^+, quarternary ammonium and protonated basic nitrogen compounds. The potassium salt was more soluble than potassium tetraphenylborate but flocculated more readily and filtered more easily. The salts formed with nitrogen compounds offer possibilities as derivatives suitable for qualitative analysis.

RÉSUMÉ

Le *p*-chlorophénylborate de sodium (NaB(-Cl)$_4$), synthétisé par les auteurs, donne des précipités avec le potassium, le rubidium, le caesium, l'ammonium quaternaire et des composés azotés basiques. Le sel de potassium est plus soluble que le tétraphénylborate de potassium, mais il flocule plus facilement et il se filtre plus aisément.

ZUSAMMENFASSUNG

Es wurde Natriumtetrakis(*p*-chlorophenyl)borat hergestellt, das mit K^+, Rb^+, Cs^+, quaternärem Ammonium und protonisierten basischen Stickstoffverbindungen Niederschläge bildet. Das Kaliumsalz war löslicher als das Kaliumtetraphenylborat, flockte jedoch leichter aus und liess sich besser filtrieren. Die mit Stickstoffverbindungen gebildeten Salze bieten sich für die qualitative Analyse an.

REFERENCES

1 G. Wittig, G. Keicher, A. Ruckert and P. Raff, *Liebigs Ann.*, 563 (1949) 114.
2 G. Wittig, *Angew. Chem.*, 63 9/10 (1950) 231.
3 P. Raff and W. Brotz, *Z. Anal. Chem.*, 133, 4 (1951) 241.
4 A. J. Barnard, *Chemist Analyst*, 44 (1955) 104.
5 A. J. Barnard, *Chemist Analyst*, 45 (1956) 110.
6 A. J. Barnard and H. Buechl, *Chemist Analyst*, 46 (1957) 16.
7 H. M. Koehler and E. G. Feldman, *Anal. Chem.*, 32 (1960) 28.
8 G. H. Gloss, *Chemist Analyst*, 42 (1953) 50.

Anal. Chim. Acta, 32 (1965) 376–380

THE COMPOSITION OF TETRAPHENYLARSONIUM THIOCYANATOTUNGSTATE IN CHLOROFORM

H. E. AFFSPRUNG AND J. W. MURPHY
Department of Chemistry, The University of Oklahoma, Norman, Okla. (U.S.A.)

(Received July 26th, 1964)

In a recent article describing the determination of tungsten by the extraction of a tungsten thiocyanate complex as a tetraphenylarsonium ion-pair[1], it was suggested that the extracted species might have a stoichiometry corresponding to that reported by Gottschalk[2] for the aqueous tungsten–thiocyanate complex. Gottschalk used the method of Asmus[3] to determine the reaction coefficients for the reduction of tungsten with titanium(III) in the presence of thiocyanate and concluded that the tungsten species formed was $[\mathrm{W(OH)_2(SCN)_4}]^-$. The spectrum of the aqueous tungsten complex is very similar to the spectrum of the ion-pair in chloroform, so it seemed likely that the extracted tungsten complex had the same composition as the aqueous complex. However, it appeared necessary to study the composition of the extracted species in order to confirm the assumed stoichiometry. Subsequent variational analyses applied to the results of the extraction procedure indicated that, in contrast to the aqueous system, the stoichiometric molar ratio of thiocyanate to tungsten is 2:1 and of tetraphenylarsonium (TPA) to tungsten is 1:1. The method used is a modification of that presented by Bent and French[4].

Consider the reaction

$$\begin{array}{l} r\mathrm{SCN}^- + n(\mathrm{C_6H_5})_4\mathrm{As}^+ + \mathrm{WX}_z{}^{n-} \rightleftharpoons \{[(\mathrm{C_6H_5})_4\mathrm{As}]_n{}^+\,[\mathrm{WX}_{z-r}\,(\mathrm{SCN})_r]^{n-}\}_{\mathrm{aq.}} + r\mathrm{X}^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow\!\uparrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \{[(\mathrm{C_6H_5})_4\mathrm{As}]_n{}^+\,[\mathrm{WX}_{z-r}\,(\mathrm{SCN})_r]^{n-}\}_{\mathrm{o}} \end{array}$$

where X^- is OH^- or Cl^- which can be neglected in the equilibrium since the concentration will be relatively very large and constant, and the subscript o indicates the organic layer and aq. the aqueous. An equilibrium expression can be written as

$$\frac{\{[(\mathrm{C_6H_5})_4\mathrm{As}]_n{}^+\,[\mathrm{WX}_{z-r}(\mathrm{SCN})_r]^{n-}\}_{\mathrm{o}}}{(\mathrm{SCN}^-)^r{}_{\mathrm{aq.}}\,(\phi_4\mathrm{As}^+)^n{}_{\mathrm{aq.}}\,(\mathrm{WX}_z{}^{n-})_{\mathrm{aq.}}} = K_{\mathrm{o}}$$

The extraction is made from 8 M hydrochloric acid, so the activity coefficients may be assumed to be constant. For brevity, let

$$[(\phi_4\mathrm{As})_n\mathrm{WX}_{z-r}\,(\mathrm{SCN})_r]_{\mathrm{o}} = (W)_{\mathrm{o}} \text{ and } (\phi_4\mathrm{As}^+) = (T)$$

then

$$\frac{(W)_{\mathrm{o}}}{(\mathrm{SCN}^-)^r{}_{\mathrm{aq.}}\;(T)^n{}_{\mathrm{aq.}}\;(\mathrm{WX}_z{}^{n-})_{\mathrm{aq.}}} = K_{\mathrm{o}} \qquad (1)$$

When the extraction is carried out, all tetraphenylarsonium species are quantitatively extracted into the chloroform layer. These species include tetraphenylarsonium chloride (TPACl), tetraphenylarsonium thiocyanate (TPASCN), and the tungsten complex. A large amount of thiocyanate is also extracted as thiocyanic acid. The total analytical concentration of TPA is thus the sum of n times the concentration of tungsten in the chloroform layer plus the sum of the concentrations of a number of partitioned TPA species. These concentrations can be expressed in terms of $(T)_{\text{aq.}}$ as follows:

$$D_1 = \frac{(\phi_4\text{As}^+\text{SCN}^-)_\text{o}}{(\phi_4\text{As}^+\text{SCN}^-)_\text{aq.}} \qquad D_2 = \frac{(\phi_4\text{As}^+\text{Cl}^-)_\text{o}}{(\phi_4\text{As}^+\text{Cl}^-)_\text{aq.}}$$

$$K_1 = \frac{(\phi_4\text{As}^+)_\text{aq.}\,(\text{SCN}^-)_\text{aq.}}{(\phi_4\text{As}^+\text{SCN}^-)_\text{aq.}} \qquad K_2 = \frac{(\phi_4\text{As}^+)_\text{aq.}\,(\text{Cl}^-)_\text{aq.}}{(\phi_4\text{As}^+\text{Cl}^-)_\text{aq.}}$$

$$\begin{aligned}(T)_\text{total} &= (\phi_4\text{AsSCN})_\text{o} + (\phi_4\text{AsSCN})_\text{aq.} + (\phi_4\text{AsCl})_\text{o} + (\phi_4\text{AsCl})_\text{aq.} + (\phi_4\text{As}^+)_\text{aq.}\\ &\quad + n(W)_\text{o} = \left(\frac{D_1+1}{K_1}\right)(\text{SCN}^-)\,(\phi_4\text{As}^+)_\text{aq.} + \left(\frac{D_2+1}{K_2}\right)(\text{Cl}^-)(\phi_4\text{As}^+)_\text{aq.}\\ &\qquad + (\phi_4\text{As}^+)_\text{aq.} + n(W)_\text{o}\end{aligned}$$

Thus,

$$\begin{aligned}(T)_\text{total} - n(W)_\text{o} &= \left\{\left(\frac{D_1+1}{K_1}\right)(\text{SCN}^-) + \left(\frac{D_2+1}{K_2}\right)(\text{Cl}^-) + 1\right\}(\phi_4\text{As}^+)_\text{aq.} \qquad (2)\\ &= K_3(\phi_4\text{As}^+)_\text{aq.}\end{aligned}$$

K_3 is constant provided that (SCN^-) and (Cl^-) are large and constant.

The analytical concentration of thiocyanate can be written in a similar manner where D_3 is the distribution coefficient for HSCN and K_a is the ionization constant of HSCN in water.

This leads to

$$(\text{SCN}^-)_\text{total} - r(W)_\text{o} = (\text{SCN}^-)_\text{aq.}\left\{1 + \frac{(\text{H}^+)}{K_a} + \frac{(\text{H}^+)D_3}{K_a} + \left(\frac{D_1+1}{K_1}\right)(\phi_4\text{As}^+)\right\}$$

or

$$(\text{SCN}^-)_\text{total} - r(W)_\text{o} = (\text{SCN}^-)_\text{aq.}K_4 \qquad (3)$$

where K_4 is a constant if (H^+) and $(\phi_4\text{As}^+)$ are large and constant.

Equations (2) and (3) may be rearranged to give

$$(T)_\text{free} = 1/K_3\{(T)_\text{total} - n(W)_\text{o}\} \qquad (4)$$

and

$$(\text{SCN}^-)_\text{free} = 1/K_4\{(\text{SCN}^-)_\text{total} - r(W)_\text{o}\} \qquad (5)$$

Making the appropriate substitutions, eqn. (1) becomes

$$\frac{(W)_\text{o}}{(\text{WX}_z{}^{n-})\{(\text{SCN}^-)_\text{total} - r(W)_\text{o}\}^r\{(T)_\text{total} - n(W)_\text{o}\}^n} = K_5 \qquad (6)$$

The tungsten in the chloroform solution is analyzed spectrophotometrically so that

$$(W)_\text{o} = A/a$$

where A is the absorbance and a the absorptivity at 406 mμ. For the given total amount of tungsten used in one equilibration, complete extraction would give an absorbance of A_0. Since the tungsten remaining in the aqueous phase is the difference between the total amount taken and the amount extracted, the amount left unextracted is given by

$$(WX_z^{r-}) = (A_0 - A)/a$$

assuming that all of the tungsten complexed with the thiocyanate is extracted. Making these substitutions into eqn. (6), we have

$$\frac{A/a}{(A_0-A)/(a)[(SCN^-)_{total} - rA/a]^r[(T)_{total} - nA/a]^n} = K_5$$

or

$$A/(A_0 - A) = K_5[(SCN)_{total} - rA/a]^r[(T)_{total} - nA/a]^n \tag{7}$$

Taking logarithms of eqn. (7),

$$\log A/(A_0-A) = \log K_5 + r\log\{(SCN^-)_{total} - rA/a\} + n\log\{(T)_{total} - nA/a\} \tag{8}$$

If the thiocyanate concentration is large compared to the tungsten concentration, and is held constant for a series of extractions while the TPA concentration is varied, then

$$\log A/(A_0-A) = \log K_6 + n\log[(T)_{total} - nA/a] \tag{9}$$

To a first approximation, a plot of $\log A/(A_0-A)$ *vs.* $\log (T)_{total}$ yields a straight line of slope n. After a value of n is obtained, a better fit can be made by plotting $\log A/(A_0-A)$ *vs.* $\log[(T)_{total} - nA/a]$.

The same procedure can be used for the thiocyanate variation if $(T)_{total}$ is kept large and constant. This gives

$$\log A/(A_0-A) = \log K_7 + r\log[(SCN)_{total} - rA/a] \tag{10}$$

A and A_0 are measured and $(T)_{total}$ and $(SCN^-)_{total}$ are known. In the case of thiocyanate, the correction term is negligible so the absolute thiocyanate concentration need not be known. In this case, a variable volume of a stock solution of thiocyanate was used and the appropriate equation was

$$\log A/(A_0-A) = \log K_8 + r\log V_{KSCN} \tag{11}$$

EXPERIMENTAL

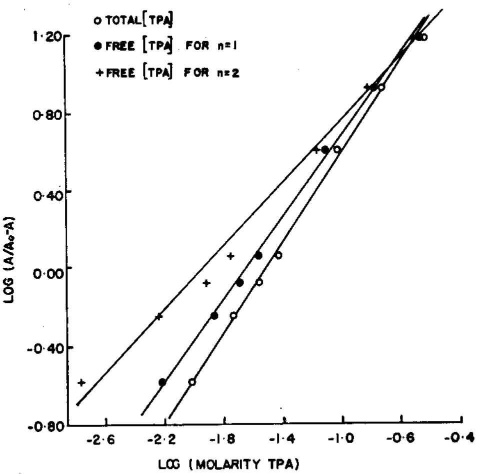
(1) TPA/tungsten ratio

Five ml (0.500 μmoles) of 10^{-4} M tungsten(VI) in concentrated hydrochloric acid were reduced by boiling with 2 ml of tin(II) chloride in concentrated hydrochloric acid. The reduced solution was chilled and transferred to a 60-ml separatory funnel with 10 ml of cold 6 M hydrochloric acid. An aliquot (x ml) varying in volume from 0.5 to 2 ml of $5 \cdot 10^{-3}$ M TPACl or $5 \cdot 10^{-4}$ M TPACl was pipetted into the separatory funnel. Three ml of 1.5 M potassium thiocyanate and $(5-x)$ ml of cold, distilled water were added, and the mixture was swirled to mix. 25 ml of chloroform were pipetted in, the mixture shaken, the layers allowed to settle, and the absorbance of the chloroform layer was measured at 406 mμ. A_0 was 0.294.

(2) *Thiocyanate/tungsten ratio*

Ten ml (1.00 μmole) of 10^{-4} M tungsten(VI) in concentrated hydrochloric acid was reduced with 3 ml of 10% tin(II) chloride in concentrated hydrochloric acid, chilled, and transferred to a 60-ml separatory funnel using $(10-x)$ ml of cold water as a rinse. Two ml of 0.005 M TPACl and x ml of a stock potassium thiocyanate solution were added. (Two stock solutions of potassium thiocyanate were used. Solution "*a*" was approximately 0.05 M and solution "*b*" was one-fifth the concentration of "*a*". x was 1, 2, and 3 ml for "*a*" and 3, 4, and 6 ml for "*b*".) 25 ml of chloroform were added to extract the complex, and the absorbance was measured at 406 mμ. A_0 was 0.590.

The data are plotted according to eqns. (8) and (11) in Figs. 1 and 2, respectively.



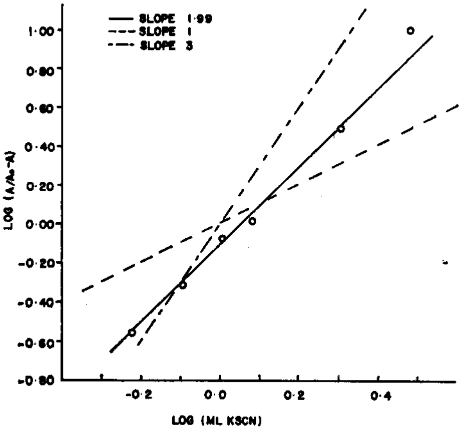


Fig. 1. Plot for determining stoichiometric molar ratio of TPA to tungsten.

Fig. 2. Plot for determining stoichiometric molar ratio of thiocyanate to tungsten.

The slope of the tetraphenylarsonium plot is 1.02, indicating an n value of 1, and the slope of the thiocyanate plot is 1.99, indicating an r value of 2. The formula of the extracted species is thus

$$(\phi_4\mathrm{As})^+[\mathrm{W}\ (\mathrm{SCN})_2\mathrm{X}_z]^-$$

A pure sample of a salt of the complex has not been obtained since every attempt has resulted in a decomposition of the compound. However, qualitative analysis of the partially decomposed tetraphenylarsonium salt of the complex has shown chloride ion to be absent, which would imply that the coordination sphere of the tungsten is completed by oxy or hydroxy groups.

The difference in composition between that reported by GOTTSCHALK for the aqueous phase and that found in the organic phase may be due partially to the assumption of GOTTSCHALK that titanium(IV) does not form a thiocyanate complex, although such a complex has been reported[5], or it may be that the composition of the tungsten complex is changed by the extraction procedure. In any case a determination of the stoichiometry of extracted complexes is important and helps to establish the conditions necessary for complete extraction. The results of this study illustrate the possibility that complexes extracted into organic media may be significantly different from the most stable forms found in the aqueous phase.

SUMMARY

The variation of extraction efficiency as a function of thiocyanate concentration and of tetraphenylarsonium concentration has established part of the composition of the extracted species which is involved in the determination of tungsten by extraction as the tetraphenylarsonium tungsten–thiocyanate ion-pair. The thiocyanate:tungsten ratio is 2:1, and the tetraphenylarsonium:tungsten ratio is 1:1, indicating an anionic charge of one for a mononuclear complex.

RÉSUMÉ

A propos du dosage du tungstène par extraction sous forme de thiocyanatotungstate de tétraphénylarsonium, les auteurs ont examiné l'influence de la concentration en thiocyanate et de la concentration en tétraphénylarsonium sur le rendement de l'extraction. Les rapports établis sont les suivants: thiocyanate–tungstène 2:1 et tétraphénylarsonium–tungstène 1:1, indiquant une charge anionique de 1 pour un complexe mononucléaire.

ZUSAMMENFASSUNG

Die Zusammensetzung des Tetraphenylarsonium–thiocyanatowolframats in Chloroform wurde bestimmt, indem der Extraktionsgrad in Abhängigkeit von der Thiocyanat- und der Tetraphenylarsonium-Konzentration untersucht wurde. Im einwertig negativ geladenen Komplex beträgt das Verhältnis von Thiocyanat: Wolfram 2:1, das von Tetraphenylarsonium: Wolfram 1:1.

REFERENCES

1 H. E. Affsprung and J. W. Murphy, *Anal. Chim. Acta*, 30 (1964) 501.
2 G. Gottschalk, *Z. Anal. Chem.*, 187 (3) (1962) 164.
3 E. Asmus, *Z. Anal. Chem.*, 178 (1960) 104.
4 H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, 63 (1941) 568.
5 D. Delafosse, *Compt. Rend.*, 236 (1953) 2313.

THE THERMAL DECOMPOSITION OF METAL ETHYLENEDIAMINE OXALATE COMPLEXES

JOHN M. HASCHKE* AND WESLEY W. WENDLANDT
Department of Chemistry, Texas Technological College, Lubbock, Texas (U.S.A.)
(Received August 7th, 1964)

Bis- and tris(ethylenediamine) metal complexes, such as $[Cu(en)_2]\ [CdI_4]$[1], $[Cr(en)_3]SbS_4$[2], $[Cu(en)_2]\ [HgI_4]$[3], $[Co(en)_2(SCN)_2]\ [Ag(SCN)_2]$[4], and others, have long been used in gravimetric analysis. Of great importance in these determinations are the drying and/or ignition temperatures of the precipitated complexes. DUVAL[5] has studied the thermal stability of a large number of compounds of the above formulas as well as others. WENDLANDT and his coworkers have also studied the thermal dissociation of a large number of ethylenediamine complexes; among them are: $[Cr(en)_3]\ X_3$[6], $[Cr(en)_2(H_2O)_4]X_3$[7], $[Ni(en)_3]X_2$[8,9], platinum ethylenediamine complexes[10], cobalt ethylenediamine complexes[11], and copper ethylenediamine complexes[12]. In continuing with this work, the thermal decomposition of a series of metal ethylenediamine oxalates was studied by thermogravimetry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and high temperature reflectance spectroscopy.

EXPERIMENTAL

Thermobalance

The automatic recording thermobalance was previously described[11]. Sample sizes ranged in weight from 50 to 70 mg and were pyrolyzed in a static air atmosphere at a heating rate of 5°/min.

DTA apparatus

The DTA apparatus was previously described[13]. Sample sizes ranged in weight from 60 to 70 mg and were pyrolyzed in a dynamic helium atmosphere at a furnace heating rate of 10°/min.

DSC apparatus

A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was employed. Sample sizes ranged in weight from 2 to 5 mg and were pyrolyzed in a static air atmosphere at a heating rate of 5°/min.

Reflectance studies

The reflectance spectra of the samples at ambient and elevated temperatures

---

* Present address: Fulbright Fellow, University of Mainz, Mainz, Germany, 1964–1965.

were measured with a Beckman Model DK-2A spectroreflectometer equipped with a heated sample holder[14,15]. Measurements were made at fixed elevated temperatures in the 350–750 mμ wavelength range.

Preparation of complexes

Although a number of nickel, zinc, copper, and cadmium ethylenediamine complexes were prepared by WERNER[16], the oxalate compounds were not synthesized. However, in connection with the purification of ethylenediamine, BAILAR[17] described the preparation of Zn(en)C_2O_4. The methods described here were developed for the synthesis of the ethylenediamine metal oxalates.

The metal oxalates of Zn, Cd, Co, Ni, and Cu were prepared by the addition of an equivalent amount of a sodium oxalate solution to solutions containing the above metal ions. The precipitated compounds were all air-dried for 24 h at room temperature before use in the synthesis of the ethylenediamine complexes.

All of the tris(ethylenediamine) metal oxalates were prepared in the same general manner, such as is illustrated here by $[Zn(en)_3]C_2O_4$. A two-fold excess of ethylenediamine was added to 2 g of zinc oxalate. The latter was covered completely with the amine, triturated, and allowed to stand for 1 h. The resulting white precipitate was filtered off and dissolved in a minimum amount of hot water. Acetone was then added to the solution to effect crystallization of $[Zn(en)_3]C_2O_4$. The crystals were filtered off, washed with acetone, and dried in a vacuum desiccator. The yield was approximately quantitative. The cobalt and cadmium complexes were not redissolved in hot water but were washed with 100% ethanol and then acetone. The $[Cd(en)_3]C_2O_4$ required storage at 0° to prevent decomposition.

TABLE I

ANALYTICAL RESULTS FOR METAL COMPLEXES

Compound	*% Metal*		*%N*		*%C_2O_4*	
	Theoretical	*Found*	*Theoretical*	*Found*	*Theoretical*	*Found*
$[Zn(en)_3]C_2O_4$	19.59	20.2	25.19	23.4	26.38	26.8
$[Cd(en)_3]C_2O_4$	29.52	29.6	—	—	23.12	22.7
$[Cu(en)_2(H_2O)_2]C_2O_4$	20.64	20.4	18.20	18.8	28.60	27.6
$[Cu(en)_3]C_2O_4$	19.15	19.6	25.32	25.0	26.52	25.8
$[Ni(en)_3]C_2O_4 \cdot 2H_2O$	16.17	15.2	23.15	24.6	24.24	24.8
$[Co(en)_3]C_2O_4$	18.01	18.8	25.68	24.5	—	—

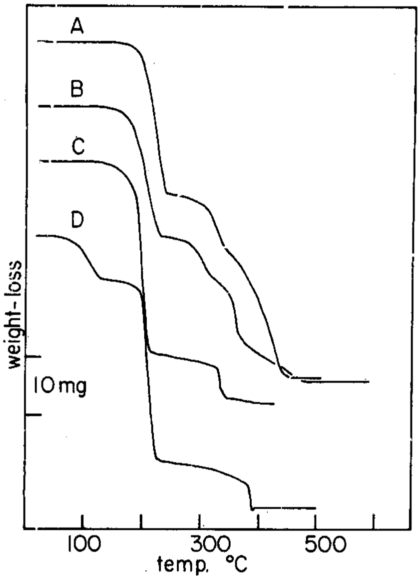
The $[Cu(en)_2(H_2O)_2]C_2O_4$ was prepared by the addition of an excess of ethylenediamine to solid copper oxalate hemihydrate followed by enough water to effect solution. The dark purple colored solution was filtered, and acetone was added to the filtrate to cause crystallization of $[Cu(en)_2(H_2O)_2]C_2O_4$. After filtration, the crystals were washed with acetone and dried in a vacuum desiccator. Yield was approximately quantitative.

The compounds were analyzed for nitrogen content by use of a Coleman Nitrogen Analyzer; for oxalate content by titration with standard potassium permanganate; and for metal ion content by ignition of the compounds to the metal oxide. The results of the analyses are given in Table I.

RESULTS AND DISCUSSION

Weight-loss studies

The weight-loss curves of the ethylenediamine metal complexes are given in Figs. 1 and 2.



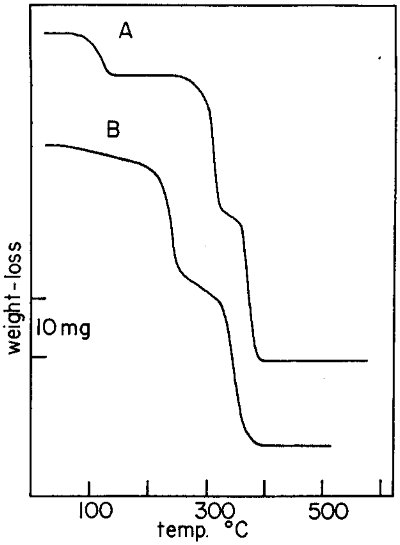


Fig. 1 .Weight-loss curves of metal complexes. (A) $[Zn(en)_3]C_2O_4$; (B) $[Cd(en)_3]C_2O_4$; (C) $[Cu(en)_3]C_2O_4$; (D) $[Cu(en)_2(H_2O)_2]C_2O_4$.

Fig. 2. Weight-loss curves of metal complexes. (A) $[Ni(en)_3]C_2O_4 \cdot 2H_2O$; (B) $[Co(en)_3]C_2O_4$.

In general, the tris(ethylenediamine) complexes evolved 2 moles of amine per mole of complex, to form the mono(ethylenediamine) complex. Well-defined curve plateaus were observed, indicating that the monoamine compounds were quite stable. The remainder of the ethylenediamine was evolved at still higher temperatures but no curve plateaus were observed for the anhydrous metal oxalate. Instead, the oxalate ion began to dissociate before all of the amine was evolved, resulting in only a curve inflection point rather than a plateau.

The decomposition temperatures for the tris- to mono(ethylenediamine) transition were as follows: $[Zn(en)_3]C_2O_4$, 150–240°; $[Cd(en)_3]C_2O_4$, 140–230°; $[Ni(en)_3]C_2O_4$, 250–325°; and $[Co(en)_3]C_2O_4$, ambient–*ca.* 300°. The curve for $[Cu(en)_3]C_2O_4$ did not show a weight-change which corresponded to the above transition but instead, evolved all 3 amines in one step, from 140–220°.

Water of hydration of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ was evolved in the temperature range 70°–130°, resulting in the formation of anhydrous $[Ni(en)_3]C_2O_4$. The coordinated water in $[Cu(en)_2(H_2O)_2]C_2O_4$ was evolved over a similar temperature range, 60°–130°, resulting in the formation of $Cu(en)_2C_2O_4$. The two ethylenediamines were then evolved from 170°–230°.

In all cases, the residue of the thermal decomposition reaction was the metal oxide.

DTA studies

The DTA curves of the complexes are given in Figs. 3 and 4.

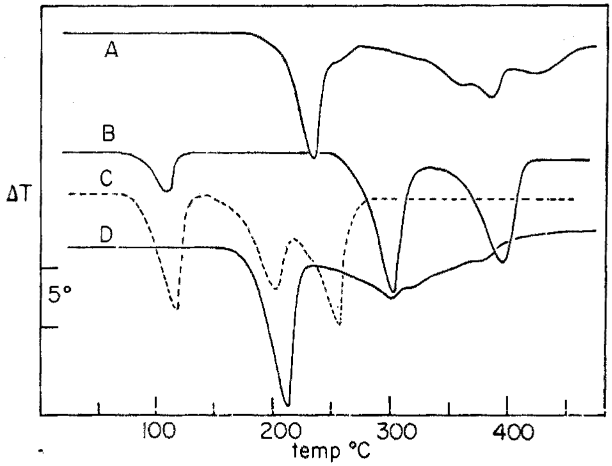


Fig. 3. DTA curves of metal complexes. (A) $[Co(en)_3]C_2O_4$; (B) $[Ni(en)_3]C_2O_4 \cdot 2H_2O$; (C) $[Cu(en)_2(H_2O)_2]C_2O_4$; (D) $[Zn(en)_3]C_2O_4$.

The curves all contained endothermic peaks which were due to dehydration, deamination, and decomposition reactions. The transitions involved were the same as previously discussed in the weight-loss studies. The curve for $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ contained 3 endothermic peaks. The first peak, with a T_{max} of 110° was due to the dehydration reaction; the second at 300°, due to the loss of 2 moles of ethylenediamine; and the third, at 400°, to the loss of the remaining ethylenediamine and the decomposition of the oxalate ion. A similar interpretation can be made for $[Cu(en)_2(H_2O)_2]C_2O_4$. The first peak, at 115°, to the dehydration reaction; the other peaks, at 200° and 255°, to the deamination and decomposition reactions.

The DTA curves of $[Zn(en)_3]C_2O_4$, $[Co(en)_3]C_2O_4$, and $[Cd(en)_3]C_2O_4$ were all similar to each other. The first endothermic peak was due to the tris → mono amine transition, while the other smaller peaks were due to the deamination and decomposition reactions of the mono(ethylenediamine) complex.

Gas evolution (GE) curves were obtained simultaneously with the DTA curves, but only the GE curve for $[Cu(en)_3]C_2O_4$ is shown. The GE curves for the other compounds indicated that all of the DTA curve peaks involved gaseous products, as was expected. The GE curve for $[Cu(en)_3]C_2O_4$ indicated that each DTA peak was due to a reaction which evolved a gaseous product. However, an exact interpretation of the peaks was not possible because from the weight-loss curve, no stable amine intermediates were observed.

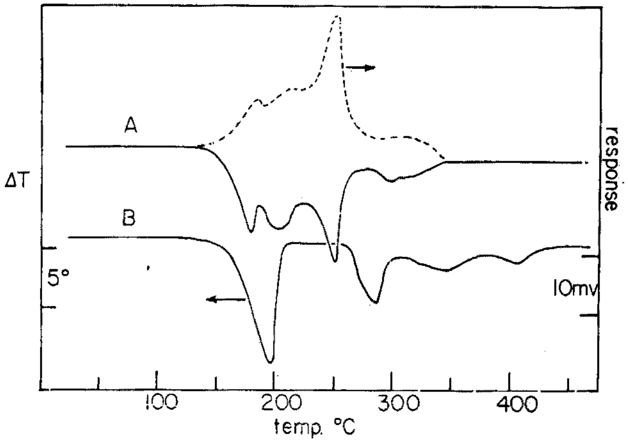


Fig. 4. DTA and GE curves of metal complexes. (A) $[Cu(en)_3]C_2O_4$; (B) $[Cd(en)_3]C_2O_4$.

DSC studies

It was possible to study only some of the dehydration and deamination reactions calorimetrically. Difficulty was encountered due to the overlapping of curve peaks. Results that were obtained, however, are shown in Table II. The heat of dissociation of the coordinated water, such as in $[Cu(en)_2(H_2O)_2]C_2O_4$, was greater than for the hydrate-bound water in $[Ni(en)_3]C_2O_4 \cdot 2H_2O$. In fact, on the basis of kcal per mole of water, the values are 13.1 and 7.2, respectively. Practically identical ΔH values were obtained for the deamination of the cadmium and zinc complexes; both values were higher than those obtained for the dehydration reactions.

TABLE II

HEATS OF DISSOCIATION OF THE METAL COMPLEXES

Reaction	*ΔH (kcal/mole)*	*Temperature (°K)*
$[Ni(en)_3]C_2O_4 \cdot 2H_2O(s) \rightarrow [Ni(en)_3]C_2O_4(s) + 2H_2O(v)$	14.2	350–
	14.7	405
$[Cu(en)_2(H_2O)_2]C_2O_4(s) \rightarrow [Cu(en)_2C_2O_4](s) + 2H_2O(v)$	26.2	335–
	26.3	385
$[Zn(en)_3]C_2O_4(s) \rightarrow [Zn(en)C_2O_4](s) + 2en(v)$	36.7	
	35.7	
$[Cd(en)_3]C_2O_4(s) \rightarrow [Cd(en)C_2O_4](s) + 2en(v)$	35.8	
	35.9	

Reflectance studies

The total diffuse reflectance curves of $[Cu(en)_2(H_2O)_2]C_2O_4$ and $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ are shown in Figs. 5 and 6. The reflectance curve of $[Cu(en)_2(H_2O)_2]C_2O_4$ contained a single absorption peak (reflectance minimum) at 535 mμ. On heating the compound to 160°, the peak intensity changed but did not shift to a different wavelength. Thus, the anhydrous complex, $[Cu(en)_2C_2O_4]$, was of a lighter blue color than the initial compound. This behavior was similar to that observed for the dehydration of $[Cu(en)(H_2O)_2]SO_4$[12].

The reflectance curve of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ at 25° contained 2 absorption peak maxima, at 525 mμ and 335 mμ, respectively. On heating the compound to 130°, the 525 mμ peak shifted slightly to 535 mμ and also increased in intensity. The 335 mμ peak shifted to 325 mμ but underwent a pronounced intensity change. Thus, the visual change in color was from a dark pink to a lighter pink. Apparently, no structural change in the coordination of ligands to the nickel or copper ions was involved in either dehydration reaction.

Kinetics studies

BORCHARDT AND DANIELS[18] have derived general expressions for calculating kinetic data from enthalpy measurements. If it is assumed that the heat evolved (or absorbed) is proportional to the number of moles reacted, then

$$-\frac{dn}{dt} = \frac{n_0}{A}\frac{dH}{dt}$$

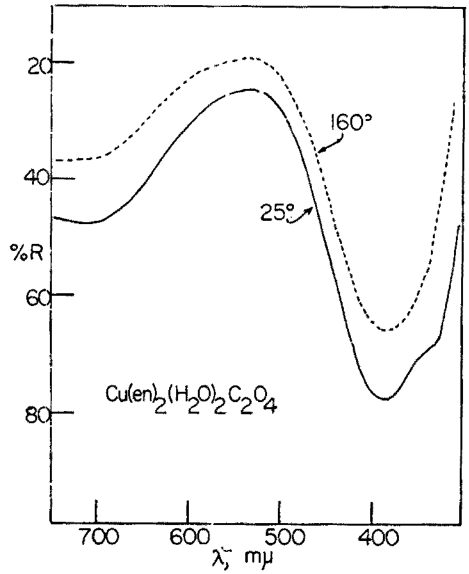


Fig. 5. Reflectance curves of $[Cu(en)_2(H_2O)_2]C_2O_4$.

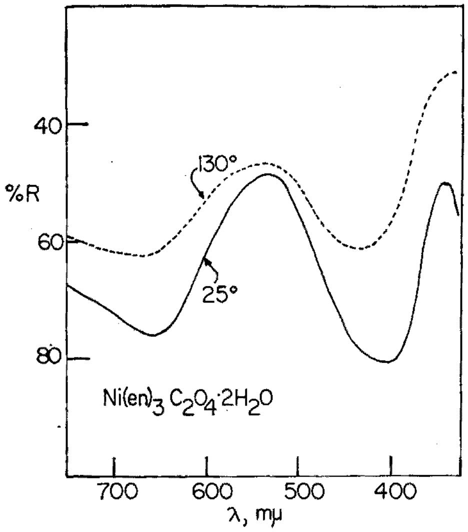


Fig. 6. Reflectance curves of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$.

where n_0 is the initial number of moles of reactant, and $A = \Delta H$, the relationship between total peak area to heat transferred. The amount of reactant present at any instant is given by

$$n = n_0 - \frac{n_0 a}{A}$$

where a is the peak area up to a certain time or temperature. The rate constant, k, is given by

$$k = \frac{\left(\frac{AV}{n_0}\right)^{x-1} \frac{\mathrm{d}H}{\mathrm{d}t}}{(A - a)^x}$$

where V/n_0 is the reciprocal of the initial concentration of reactants. Then, assuming a first order reaction, the previous equation becomes

$$k = \frac{\mathrm{d}H/\mathrm{d}t}{(A - a)}$$

The assumptions under which the above equations apply have previously been discussed[18] in detail.

Typical kinetics plots for the deamination of $[\mathrm{Cd(en)_3}]\mathrm{C_2O_4}$ and $[\mathrm{Zn(en)_3}]\mathrm{C_2O_4}$ are given in Fig. 7. Activation energies, E_a, for these 2 complexes were both 51 kcal/mole. Kinetics data were also obtained for the dehydration of $[\mathrm{Cu(en)_2(H_2O)_2}]\mathrm{C_2O_4}$, $E_a = 38$ kcal/mole, and $[\mathrm{Ni(en)_3}]\mathrm{C_2O_4} \cdot 2\mathrm{H_2O}$, $E_a = 27$ kcal/mole. The value for the

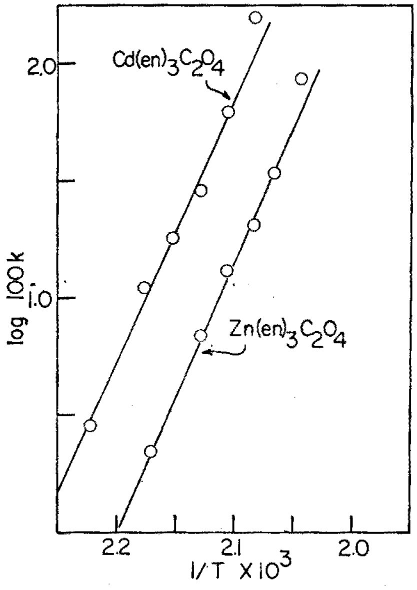


Fig. 7. Kinetics plots.

copper complex was somewhat larger than the $E_a = 29$ kcal/mole, previously calculated for $[Cu(en)(H_2O)_2]SO_4$ using a DTA method[12].

The support of this work by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-23-63, is gratefully acknowledged.

SUMMARY

The thermal dehydration and deamination of some ethylenediamine complexes of Zn, Cd, Cu, Ni and Co oxalate were studied by TGA, DTA, DSC, reflectance spectroscopy, and by GE. The tris(amine) complexes deaminated to mono(amine) compounds which then decomposed directly to the metal oxide. The kinetics and heats of dehydration and deamination of several of the complexes were determined.

RÉSUMÉ

Les auteurs ont examiné la décomposition thermique de complexes oxalates métalliques (Zn, Cd, Cu, Ni, Co)–éthylènediamine, par analyse thermogravimétrique, analyse thermique différentielle, calorimétrie différentielle, spectroscopie et par dégagement gazeux. Les complexes étudiés donnent d'abord des composés monoaminés; ils se décomposent ensuite directement en oxyde métallique.

ZUSAMMENFASSUNG

Die thermische Zersetzung einiger Äthylendiaminkomplexe der Oxalate des Zn, Cd, Cu, Ni und Co wurden mit verschiedenen Methoden wie z.B. der TGA, DTA u.a. untersucht. Die Trisaminkomplexe zersetzen sich zu Monoaminverbindungen und weiter direkt zum Metalloxyd.

REFERENCES

1 G. Spacu and G. Suciu, *Z. Anal. Chem.*, 77 (1929) 340.
2 G. Spacu and A. Pop, *Z. Anal. Chem.*, 111 (1937–38) 254.
3 G. Spacu and G. Suciu, *Z. Anal. Chem.*, 78 (1929) 329.
4 G. Spacu, *Bull. Soc. Stiinte Cluj*, 7 (1934) 568.
5 C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd Ed., Elsevier, Amsterdam, 1963.
6 W. W. Wendlandt and J. L. Bear, *J. Inorg. & Nucl. Chem.*, 17 (1961) 286.
7 W. W. Wendlandt and W. R. Robinson, *J. Inorg. & Nucl. Chem.*, 26 (1964) 531.
8 T. D. George and W. W. Wendlandt, *J. Inorg. & Nucl. Chem.*, 25 (1963) 395.
9 T. D. George and W. W. Wendlandt, *Texas J. Sci.*, 14 (1962) 47.
10 W. W. Wendlandt, *Texas J. Sci.*, 14 (1962) 264.
11 W. W. Wendlandt, T. D. George and K. V. Krishnamurty, *J. Inorg. & Nucl. Chem.*, 21 (1961) 69.
12 W. W. Wendlandt, *J. Inorg. & Nucl. Chem.*, 25 (1963) 833.
13 W. W. Wendlandt, *Anal. Chim. Acta*, 27 (1962) 309.
14 W. W. Wendlandt, P. H. Franke and J. P. Smith, *Anal. Chem.*, 35 (1963) 105.
15 W. W. Wendlandt and T. D. George, *Chemist-Analyst*, 53 (1964)100.
16 A. Werner, *Z. Anorg. Allgem. Chem.*, 21 (1899) 201.
17 J. C. Bailar, *J. Am. Chem. Soc.*, 56 (1934) 955.
18 H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.

SHORT COMMUNICATIONS

The determination of trace amounts of silicon in copper and copper-base alloys

The presence of small amounts of silicon in certain grades of brass is known to cause undesirable discoloration of the material, and for this reason specifications for leaded brass often impose a maximum limit of 50 p.p.m. of silicon.

Spectrographic methods are satisfactory for determining silicon at these low levels, provided that reference standards containing known amounts of silicon are available.

The procedure previously used in this laboratory for the colorimetric determination of silicon in these materials is the British Standard method[1], based on the formation of silicomolybdic acid, which is subsequently reduced to "molybdenum blue" with a mixture of sodium sulphite, 1-amino-2-naphthol-4-sulphonic acid and sodium metabisulphite[2]. This method is restricted in its application to the analysis of copper-base samples containing silicon in excess of about 50 p.p.m., because the optical density of the complex is measured in the presence of copper(II), which also imparts a blue colour to the solution, and a "background" correction has to be made. Thus even in the absence of silicon, unless a very small sample is used, the solution has a significantly high optical density at the wavelength at which the optical density is measured.

It seemed logical that if copper could be removed from solution before the colorimetric reaction, the method could be extended to the determination of silicon in copper-base materials at much lower levels than 50 p.p.m., and such a procedure would enable standards to be made for spectrographic analysis.

Several features of this modified determination had to be investigated. Copper is not easily removed by electrodeposition on to a platinum electrode from a solution containing nitric/hydrochloric acid, similar to the solvent used in the British Standard method. However, it is known that the electrodeposition of copper can be made from a nitric/sulphuric acid electrolyte, and that a solution containing these acids can also be used in the "molybdenum blue" reaction. Accordingly, in the proposed simplified procedure the concentration of the nitric/sulphuric acid solvent is chosen to be suitable for the electrodeposition of copper, as well as for the colorimetric reaction. The removal of copper also enables a larger sample weight to be used, thereby improving the accuracy of the method.

Preliminary tests

In preliminary experiments, 1-g samples of vacuum-cast copper were dissolved in 10 ml of a nitric/sulphuric acid mixture and diluted to 100–150 ml, and copper was removed conventionally by electrodeposition. Each solution was evaporated to less than 100 ml, cooled, diluted to 100 ml in a calibrated flask, then divided into two equal aliquots; the determinations were completed by the "molybdenum blue" reaction.

Satisfactory conditions were thus obtained for development of the coloured silicon complex, but blank values were very high and variable. It was suspected that this was due, at least in part, to contamination of the solution with silicate from the glass apparatus. Accordingly, during electrodeposition of the copper the electrolyte was contained in a polythene beaker, and the need to evaporate the solution after electrolysis was eliminated by increasing the weight of copper to 2 g. After electrolysis the solution was diluted to 250 ml, and the characteristic colour of the silicon complex was developed in a 50-ml aliquot. With these modifications lower blank values were obtained, amounting to the equivalent of about 1 μg of silicon in the final solution, or 2.5 p.p.m. of silicon, calculated on a 0.4-g sample basis.

To simplify the preparation of the calibration graph, the addition of copper and the subsequent electrolysis were omitted, but it was found that the acidity of the solution was too high for satisfactory development of the silicomolybdic acid. The acidity aspect of this determination could have been investigated further, to establish optimum conditions, comparable with the acidity of a solution in which copper had been dissolved and subsequently removed. It seemed more expedient to prepare the calibration graph using high-purity copper under conditions comparable with those proposed for the analysis of samples.

In preparing the calibration graph a compensating (electrolysed) solution was used, similar to that used in the British Standard, *i.e.*, prepared from a second 50-ml aliquot of the test solution. In the British Standard, the compensating solution is indispensable in the presence of copper(II), and whilst this may be unnecessary in the modified procedure, it provides a safeguard in the analysis of samples containing an appreciable amount of metals such as nickel and chromium that give coloured solutions, and in the event of any residual copper being present in the electrolyte.

Effect of other elements

The effects of arsenic, phosphorus and germanium were investigated. Arsenic and phosphorus seemed likely to interfere, and both are frequently present in copper-base samples. Germanium is the only other element likely to react with molybdic acid and subsequently to form "molybdenum blue".

Solutions of vacuum-cast copper, to which were added known volumes of standard solutions of silicon, arsenic, phosphorus and germanium, corresponding to 50 p.p.m. of silicon and 0.1% of each of the other three elements, were examined by the proposed procedure. The results (Table I) indicate that interference by 0.1% of either arsenic or phosphorus is negligible, but that germanium seriously interferes. However,

TABLE I

EFFECT OF OTHER ELEMENTS ON THE RECOVERY OF SILICON

Added	*Silicon (p.p.m.)*	
	Added	*Found*
Arsenic (0.1%)	50	50
Phosphorus (0.1%)	50	52
Germanium (0.1%)	50	—[a]

[a] The optical density of the final solution was too high to be measured accurately.

germanium occurs only rarely in copper-base alloys and this interference was not investigated further.

RECOMMENDED PROCEDURE FOR DETERMINATION OF SILICON (UP TO 50 p.p.m.) IN COPPER AND COPPER-BASE ALLOYS

Reagents

Standard silicon solution. Transfer 0.214 g of finely ground fused silica (ignited at 1000°) to a small platinum dish. Fuse with 2 g of anhydrous sodium carbonate, then cool. Transfer the dish to a nickel beaker, dissolve the melt in about 100 ml of water, then dilute the solution to 1 l. Store this solution in a polythene bottle. Immediately before use, dilute 25 ml of this solution to 250 ml (1 ml $\equiv$ 10 μg of silicon).

Nitric/sulphuric acid mixture. Transfer 60 ml of water to a polythene beaker, and add 40 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid. Store the mixture in a polythene vessel.

Reducing solution. Dissolve 2 g of sodium sulphite in about 25 ml of water, and add 0.4 g of 1-amino-2-naphthol-4-sulphonic acid. Add this solution to 25 g of sodium metabisulphite dissolved in about 200 ml of water. Dilute the mixture to 250 ml.

Preparation of calibration graph

Transfer 2 g of high-purity copper into each of six 250-ml glass beakers, and add 20 ml of the nitric/sulphuric acid mixture. Warm gently to assist solution of the copper, add about 20 ml of water and boil gently to expel oxides of nitrogen. Transfer the solutions immediately to separate 250-ml polythene beakers.

Add, separately, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of the standard silicon solution (1 ml $\equiv$ 10 μg Si) to five of the beakers; use the sixth beaker for a blank determination.

Dilute each solution to 100–150 ml, insert a pair of platinum-gauze electrodes of conventional design, and electrolyse at 3–4 A (d.c.) until the solution is colourless. Lower the beaker, wash down the electrodes with water, then cool. Transfer the solution to a 250-ml calibrated flask, dilute to the mark, mix and transfer two 50-ml aliquots into independent 100-ml calibrated flasks.

To one aliquot (T) in each of the series, add 10 ml of ammonium molybdate solution (10%), mix the solution and allow to stand for 5 min, then add 10 ml of citric acid solution (25%). To the second aliquot (C), add 10 ml of citric acid solution (25%) followed by 10 ml of ammonium molybdate solution (10%); wash down the neck of the flask, mix the solution and allow to stand for 5 min.

To each solution add 5 ml of the reducing solution, place the flasks *in* a water bath, maintained at 50°, for 15 min, then cool. Dilute each solution to the mark, mix, and measure the optical densities of the solutions at a wavelength of 820 mμ, using 4-cm cells.

From the optical density value of each test solution (T), subtract that of the corresponding compensating solution (C). Correct for the blank value on the high-purity copper, and prepare a calibration graph by plotting the corrected values against the weights of silicon added.

Procedure

Dissolve 2 g of the sample in 20 ml of the nitric/sulphuric acid mixture, and continue as described under "*Preparation of calibration graph*". With each batch of samples, simultaneously determine a blank value, using 2 g of high-purity copper.

TABLE II

DETERMINATION OF SILICON IN COPPER AND BRASS SAMPLES

Sample no.	*Sample*	*Silicon found (p.p.m.)*	*Mean (p.p.m.)*	*Standard deviation (p.p.m.)*
S279	80/20 Brass	47, 48, 50, 52, 52	49.8	2.3
S279[a]	—	24, 24, 26, 26, 27	25.4	1.3
S280	85/15 Brass	<1,1	—	—
S283	Copper	2,4	—	—

[a] Sample S279 (1 g) added to 1 g of high-purity copper to simulate a sample containing 25 p.p.m. of silicon.

Precision of the recommended procedure

This is indicated in Table II. The mean value of 49.8 p.p.m. of silicon, found in the brass sample S279, compares with duplicate silicon values of 56 and 59 p.p.m., determined by the existing British Standard.

CONCLUSIONS

The proposed modifications to the British Standard make possible the determination of silicon in copper and brass, down to about 10 p.p.m. The standard deviation of the modified procedure, at the 25 p.p.m. silicon level, is about 1.3. Interference from arsenic and phosphorus, each at the 0.1% level, is negligible, but the presence of germanium cannot be tolerated.

This procedure has been applied to the analysis of spectrographic standards, and a correlation of spectrographic and chemical data supports the validity of this recommended chemical procedure.

I thank Messrs. W. T. ELWELL and I. R. SCHOLES for helpful suggestions, and for their assistance in the preparation of this paper.

Research Department, Imperial Metal Industries
(Kynoch) Ltd., Witton, Birmingham 6 (Great Britain)
J. M. STURTON

1 BRITISH STANDARDS INSTITUTION, B.S. 1748: Part 7: 1960, *Methods for the Analysis of Copper Alloys. Part 7. Silicon (photometric method)*.
2 E. J. KING AND H. STANTIAL, *Biochem. J.*, 27 (1933) 990.

(Received October 18th, 1964)

Fluorimetric mole ratio studies of aluminum and gallium chelates of *o,o'*-dihydroxyazobenzene*

In a continuing study of *o,o'*-dihydroxyazo chelates, it was desirable to determine if the 2:1 chelates of aluminum and gallium with *o,o'*-dihydroxyazobenzene would fluoresce and if a fluorimetric mole ratio determination would indicate a 2:1 composition. These 2:1 chelates have been shown spectrophotometrically to exist[1] and fluorimetric mole ratio determinations are possible with similar 1:1 chelates[2].

It was found in earlier studies[3-6] that the pH values for maximum fluorescence of aluminum–*o,o'*-dihydroxyazo chelates are about 4.5 to 5.5 whereas with the gallium chelates the corresponding values are lower (3.0–4.0). The fluorescence decreases significantly with increasing pH. At the above pH values, only the 1:1 chelates have been shown to exist, so there has been no evidence for the fluorescence of the 2:1 chelates which exist above pH 6.

Apparatus and chemicals

The fluorescence spectra were recorded with a Cary Model 14 Recording Spectrophotometer equipped with a fluorescence attachment. The pH measurements were made with a Beckman Zero-Matic pH meter calibrated with aqueous buffers and are referred to as "measured values".

The *o,o'*-dihydroxyazobenzene, abbreviated DHAB in this paper, was prepared in this laboratory by Dr. RONALD MILBURN by the method of WESELSKY AND BENEDIKT[7]. The purified product melted at 176° on a Koefler micro hot stage. The DHAB was dissolved in 95% ethanol to make a $1.00 \cdot 10^{-3}$ *M* solution. The aluminum and gallium solutions were prepared by dissolving the metals in hydrochloric and sulfuric acid, respectively, and diluting. Analysis[8,9] showed the aluminum solution to be $8.07 \pm 0.03 \cdot 10^{-3}$ *M* and the gallium solution to be $5.95 \pm 0.02 \cdot 10^{-3}$ *M*.

Mole ratio studies

Series of solutions for each metal were prepared, each containing $4.00 \cdot 10^{-5}$ *M* DHAB, 0.1 *M* potassium chloride and 35% ethanol which was necessary to maintain the DHAB in solution. The aluminum and gallium concentrations were varied from zero to 10^{-4} *M*. The pH values of the aluminum and gallium solutions were adjusted to 6.3 and 6.2 respectively by the addition of 2.5 *M* sodium acetate from a micropipet. The fluorescence spectra of the solutions were recorded after equilibrium had been established. This was two days for aluminum and less than a day for gallium. The fluorescence spectra for the solutions with high aluminum concentrations consisted of one band with a maximum at 573 mμ. The spectra for solutions with low aluminum concentrations had a maximum at 575 mμ. The fluorescence intensity at 573 mμ as a function of aluminum concentration is plotted in Fig. 1. The fluorescence spectra of all gallium solutions consisted of one band with a maximum at 580 mμ. The fluorescence intensity at this wavelength is plotted against the gallium concentration in Fig. 2.

---

* Taken in part from the dissertation submitted by JOHN W. LEDBETTER in partial fulfilment of the requirements for the Ph.D. degree in Chemistry at Duke University, September 1962.

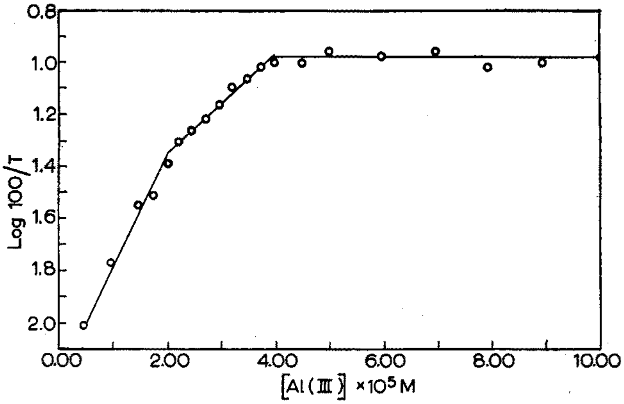


Fig. 1. Fluorimetric mole ratio plot for aluminum-*o,o'*-dihydroxyazobenzene (T = percent fluorescence).

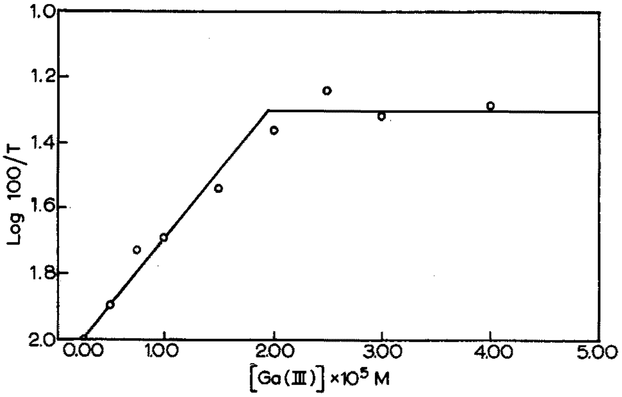


Fig. 2. Fluorimetric mole ratio plot for gallium-*o,o'*-dihydroxyazobenzene.

Results

From the mole ratio plot of the aluminum–DHAB system, the existence of the 1:1 and 2:1 chelates was established at a pH of 6.3 by fluorimetric techniques. Between 2.00 and 4.00 · 10^{-5} *M* aluminum, an equilibrium exists between the two chelates. It was also clearly established that the 2:1 chelate does fluoresce. An indication of the fluorescence of the 2:1 chelate occurred when the spectrum shifted 2 mμ bathochromically at low aluminum concentrations.

For the gallium–DHAB system, the mole ratio plot indicated a 2:1 chelate at a pH of 6.2. At this pH, there was no evidence from the mole ratio plot or from the spectra at different gallium concentrations for the 1:1 chelate. It was therefore established that the 2:1 chelate also fluoresces.

It has been found that the 2:1 chelate of indium–DHAB exists at pH 6.50[1]; however, the fluorescence intensity at this pH is too low for a fluorimetric mole ratio determination.

Department of Chemistry,
Duke University,
Durham,
N. C. (U.S.A.)

JOHN H. SAYLOR
JOHN W. LEDBETTER*

1 J. R. KIRBY, R. M. MILBURN AND J. H. SAYLOR, *Anal. Chim. Acta*, 26 (1962) 458.
2 J. H. SAYLOR AND J. W. LEDBETTER, *Anal. Chim. Acta*, 30 (1964) 427.
3 W. A. POWELL AND J. H. SAYLOR, *Anal. Chem.*, 25 (1953) 960.
4 J. W. LEDBETTER, *Master's Thesis*, Duke University, 1961.
5 P. SCHATZBERG, *Master's Thesis*, Duke University, 1954.
6 D. C. FREEMAN AND C. E. WHITE, *J. Am. Chem. Soc.*, 78 (1956) 2678.
7 P. WESELSKY AND R. BENEDIKT, *Ann.*, 196 (1879) 339.
8 R. BERG, *Z. Anal. Chem.*, 71 (1927) 369.
9 E. GASTINGEN, *Z. Anal. Chem.*, 126 (1943) 373.

(Received August 20th, 1964)

---

* Present address: U.S.A. Chemical R. & D. Laboratories, Edgewood Arsenal, Maryland.

Gravimetric determination of palladium with salicyloylhydrazide

Dimethylglyoxime is probably the best-known organic reagent for the precipitation of palladium; hydroxytriazines[1] and dalzin[2] have also been employed. In the present work, salicyloylhydrazide, first prepared by STRAUVE AND RADENHAUSEN[3], was found to be an effective and selective reagent for the gravimetric determination of this metal. If palladium is precipitated with salicyloylhydrazide in cold solution in presence of tartrate (when necessary) at pH 1.0–1.5 metallic ions such as Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Ru^{3+}, Th^{4+}, Zr^{4+}, Ti^{4+}, MoO_4^{2-}, WO_4^{2-}, UO_2^{2+}, do not interfere. Gold(III) is reduced to the metal by the reagent in hot solution, and palladium can be subsequently determined in the filtrate.

Preparation and properties of salicyloylhydrazide

Mix 1 g of methyl or ethyl salicylate and 1 ml of 85% hydrazine hydrate and heat under reflux for 15 min. Add just enough ethanol through the condenser to obtain a clear solution. Reflux again for 2 h, evaporate the alcohol and cool the residue. Filter the crystals of salicyloylhydrazide and recrystallise from water.

Salicyloylhydrazide, $C_6H_4(OH)CO \cdot NHNH_2$, is a white crystalline compound, m.p. 144–145°. It is slightly soluble in cold water, but appreciably soluble in hot water, 50% ethanol, acetic acid, ether and chloroform.

Reactions with metal ions

Salicyloylhydrazide was found to be a selective reagent for the precipitation of palladium and copper[4]. It also precipitates Zr^{4+}, Ti^{4+}, Th^{4+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, VO^{2+} and VO_3^- in weakly acidic or alkaline medium. The palladium and copper complexes of salicyloylhydrazide are, however, stable in presence of mineral acids. The wine-red colour which it forms with VO^{2+} has been utilised in the titrimetric determination of vanadium with EDTA[5].

Palladium was precipitated from aqueous solution by adding a slight excess of the reagent in 50% ethanol; the precipitate was thoroughly washed with hot water and dried at 110–120°. The yellow, granular complex obtained from palladium chloride solution at pH 1.0–1.5 had the composition $Pd(C_7H_8O_2N_2)_2Cl_2$. It was practically insoluble in chloroform, ether, carbon tetrachloride, benzene, alcohol; moderately soluble in 50% dioxan; and completely soluble in dilute alkali and strong mineral acids. The complex decomposed at 233–234°. Elemental analysis gave the following results: found C 22.05%, H 3.51%, N 11.85%, Pd 22.05%, Cl 14.80%; theoretical C 22.14%, H 3.36%, N 11.62%, Pd 22.14%, Cl 14.71%.

Palladium was also precipitated as $Pd(C_7H_8O_2N_2)_2SO_4$ from palladium sulphate solution at pH 1.0–1.5. The complex was greenish yellow and slimy in nature. Its solubility behaviour was similar to that of the chloride, except that it was slightly soluble in chloroform. The complex decomposed at 223–224°.

The dissociation of acidic hydrogen in the reagent appears to be checked because of the formation of the complex in strong acidic medium, and the palladium complex has the general formula: $Pd(C_7H_8O_2N_2)_2X$ where $X = 2\ Cl^-$ or SO_4^{2-}.

Determination of palladium

(a) In chloride solution. Dilute a measured amount of palladium chloride with distilled water to 75–100 ml, and adjust the pH to 1.0–1.5 with dilute hydrochloric acid. To the cold solution, add salicyloylhydrazide (0.15–0.50 g) in 50% ethanol (5–10 ml) dropwise with stirring; continue stirring for 5–10 min. Allow the precipitate to settle on a hot water bath or in the cold for 20–25 min. Filter, wash with hot water, dry at 110–120° and weigh as $Pd(C_7H_8O_2N_2)_2Cl_2$. The palladium content was calculated on the basis that the precipitate contained 22.14% of the metal. The results are shown in Table I.

TABLE I

DETERMINATION OF PALLADIUM BY DIRECT WEIGHING OF $Pd(C_7H_8O_2N_2)_2Cl_2$

Pd taken (mg)	*Pd found (mg)*	*Error (mg)*	*Pd taken (mg)*	*Pd found (mg)*	*Error (mg)*
3.24	3.21	−0.03	9.20	9.23	+0.03
	3.29	+0.05		9.29	+0.09
	3.19	−0.05	9.72	9.74	+0.02
6.90	6.86	−0.04		9.78	+0.06
6.48	6.50	+0.02	12.96	12.90	−0.06
	6.46	−0.02		12.99	−0.03
	6.42	−0.06		12.95	−0.01

(b) In sulphate solution. Dilute a measured amount of palladium sulphate solution to 100–150 ml, and adjust the pH to 1.0 with dilute sulphuric acid. Heat to 40–50° and precipitate palladium as described above. Digest the gelatinous precipitate on a boiling water bath for 30–40 min, filter, wash with hot water, dry, and weigh as $Pd(C_7H_8O_2N_2)_2SO_4$. The precipitate contains 21.04% of the metal. The results were similar in accuracy to those shown in Table I but it was more convenient to determine palladium as the chloro complex which was easily obtained in a granular form from the cold solution.

Effect of variables

With the palladium chloride solutions, approximately 20 times the theoretical quantity of the reagent was necessary for complete precipitation of the metal at pH 1.5 in a total volume of 100 ml of solution. When this excess of reagent was used, no precipitate was formed from 1 *N* hydrochloric acid, but precipitation was complete from 0.5 *N* hydrochloric acid solution. The precipitate conformed to the above-mentioned composition up to pH 2.0, but at higher pH values, the composition was altered.

TABLE II

SEPARATION OF PALLADIUM FROM DIVERSE IONS

Pd taken (mg)	*Foreign ion added (mg)*	*Pd found (mg)*	*Error (mg)*	*Pd taken (mg)*	*Foreign ion added (mg)*	*Pd found (mg)*	*Error (mg).*
2.30	Cu^{2+} (20)	2.32	+0.02	2.30	Pt^{4+} (3)	2.34	+0.04
4.60	Cu^{2+} (80)	4.64	+0.04	4.60	Pt^{4+} (6)	4.68	+0.08
				2.30	Pt^{4+} (6)	2.29	−0.01
2.30	Ni^{2+} (60)	2.28	−0.02				
2.30	Ni^{2+} (120)	2.29	−0.01	4.60[b]	Au^{3+} (15.8)	4.64	+0.04
2.30	Ni^{2+} (180)	2.32	+0.02	4.60[b]	Au^{3+} (16.9)	4.68	+0.08
				4.60[b]	Au^{3+} (14.3)	4.58	−0.02
2.30	Zn^{2+} (16)	2.29	−0.01				
4.60	Zn^{2+} (64)	4.54	−0.06	4.60[a]	Th^{4+} (7)	4.56	−0.04
				4.60[a]	Th^{4+} (70)	4.53	−0.07
2.30	Ni^{2+} (60) Cu^{2+} (20) Zn^{2+} (16)	2.29	−0.01	4.60[a]	MoO_4^{2-}(50)	4.62	+0.02
		2.32	+0.02	4.60[a]	MoO_4^{2-} (100)	4.56	−0.04
4.60	Fe^{2+} (74)	4.67	+0.07	4.60[a]	WO_4^{2-}(20)	4.60	0.00
4.60	Fe^{2+} (148)	4.67	+0.07	4.60[a]	WO_4^{2-}(40)	4.64	+0.04
2.30[a]	Fe^{3+} (11)	2.32	+0.02	4.60	UO_2^{2+} (10)	4.60	0.00
2.30[a]	Fe^{3+} (11)	2.34	+0.04	4.60	UO_2^{2+} (60)	4.58	−0.02
2.30[a]	Fe^{3+} (22)	2.32	+0.02				
				4.60	Co^{2+} (5)	4.54	−0.06
2.30[a]	Ti^{4+} (11.7)	2.36	+0.06	4.60[a]	Co^{2+} (50)	4.64	+0.04
2.30[a]	Ti^{4+} (23.4)	2.28	−0.02				
				4.60[a]	Zr^{4+} (30)	4.62	+0.02
2.30[a]	Rh^{3+} (7)	2.36	+0.06	4.60[a]	Zr^{4+} (50)	4.67	+0.07
2.30[a]	Rh^{3+} (7)	2.26	−0.04				
				4.60[a]	Hg^{2+} (15)	4.60	0.00
2.30[a]	Ru^{3+} (9)	2.29	−0.01	4.60[a]	Hg^{2+} (30)	4.68	+0.08
2.30[a]	Ru^{2+} (9)	2.32	+0.02				

[a] Separations were done in the presence of tartrate.
[b] See text.

Separation of palladium from diverse ions

The metal was precipitated from a mixture containing known amounts of palladium chloride, and copper nitrate, zinc sulphate, nickel sulphate, cobalt nitrate, zirconium chloride, platinic chloride, thorium nitrate, iron(II) ammonium sulphate or uranyl nitrate solution, at pH 1.0–1.5 (adjusted with dilute hydrochloric acid) in the cold exactly as described above, and the precipitate was weighed as $Pd(C_7H_8O_2N_2)_2Cl_2$. The amounts of metal which could be tolerated are shown in Table II. As salicyloylhydrazide reduces platinum(IV) in hot solutions, its separation should be carried out in the cold.

When mixtures containing known amounts of palladium chloride, and titanium sulphate, iron(III) chloride, ruthenium chloride, rhodium chloride, mercury(II) chloride, sodium molybdate or sodium tungstate were analyzed, it was necessary to add sodium potassium tartrate (0.5–1.0 g) to prevent the interference of the foreign ion. The pH of the solution was adjusted to 1.5 with dilute hydrochloric acid, if necessary; care was needed to avoid any precipitation of tartaric acid. To the cold solution 0.5 g of salicyloylhydrazide in 10 ml of 50% ethanol was added dropwise with stirring, which was continued for at least 5 min until the precipitate had separated. The precipitate was allowed to settle for 30–45 min with occasional stirring, filtered, washed first with cold and then with hot water, dried and weighed as $Pd(C_7H_8O_2N_2)Cl_2$. The amounts of foreign ion which could be tolerated are shown in Table II.

Since gold(III) chloride was reduced by salicyloylhydrazide in either hot or cold solution, palladium could be determined in the filtrate after separation of metallic gold. Measured quantities of palladium chloride and gold(III) chloride were mixed and diluted to 150–200 ml. The solution was made 2 *N* with hydrochloric acid, and 0.2–0.5 g of the reagent in 10–15 ml of ethanol was added. The solution was then heated near boiling for 45–60 min and filtered. The filtrate was evaporated to 75 ml, cooled and adjusted to the proper acidity, and palladium was determined as described initially. The results are given in Table II.

The precipitation of palladium is not quantitative in the presence of large excess of nitrate. The metal can be precipitated as the chloride complex in the presence of sulphate if chloride : sulphate is $\leqslant 1 : 12$; and as the sulphate complex in the presence of chloride if chloride : sulphate $\geqslant 1 : 25$. Platinum(IV) interferes when Pt : Pd exceeds 5 : 1.

Presidency College,
Calcutta (India)

S. C. SHOME
H. R. DAS

1 S. K. BHATTACHARYA AND N. C. SONGANI, *J. Indian Chem. Soc.*, 37 (1960) 531.
2 N. K. DUTTA AND K. P. SEN SARMA, *Anal. Chim. Acta*, 23 (1960) 531.
3 STRAUVE AND RADENHAUSEN, *J. Prakt. Chem.*, [2] 52 (1930) 239.
4 H. R. DAS AND S. C. SHOME, unpublished work.
5 H. R. DAS AND S. C. SHOME, unpublished work.

(Received September 15th, 1964)

BOOK REVIEWS

Advances in Analytical Chemistry and Instrumentation, Vol. 2, Edited by CHARLES N. REILLEY, Wiley–Interscience, New York, 1963, vi + 408 pp., price 115 s.

To appreciate the coverage of this book the reader need only glance at the main headings of its several parts, namely *Progress in Qualitative Organic Analysis, Laboratory pH Measurements, Application of Hanging Mercury Drop Electrodes in Analytical Chemistry, Mass Spectra of Organic Molecules, Some Techniques in Organic Polarography* and *Reaction Rate Methods.* These contributions bear the names of authors universally known for their expert knowledge, and the choice of subjects is supported by an Advisory Board of eminent scientists of no less repute.

The scope and applications of analytical chemistry have made such rapid advances in recent years that even the dedicated analyst finds it difficult to keep abreast with developments in his particular field, and this is even more difficult where some new chemical or physico-chemical technique, developed for another purpose, might have useful applications. The purpose of this book is to bridge that gap by presenting a series of volumes with chapters dealing with new techniques, and a critical evaluation and up-to-date account of the more established principles of analytical chemistry.

This is a book that the progressive analyst should read, but the price is such that it is more likely to find its way into reference libraries rather than among the treasured possessions of the private individual.

W. T. ELWELL (Birmingham)

Anal. Chim. Acta, 32 (1965) 404

A. GEMANT, *Ions in Hydrocarbons*, John Wiley, Inc., New York, 1962, viii + 261 pp., price 94 s.

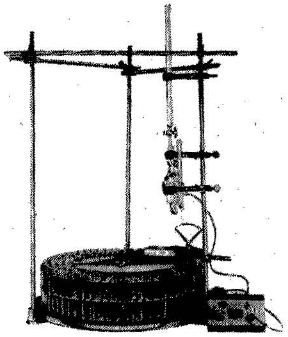
The author states in the preface that "the book will be of interest to three major classes of readers: the electrochemists, who will discover an extension of electrochemistry of aqueous and alcoholic solutions to hydrocarbon solvents; the organic chemists, who are concerned with the role of ionic intermediates in organic reaction mechanisms; and those researchers who are engaged in the work on liquid electrical insulation . . .". While I would not care to predict the response of the latter two categories of research workers, I suspect that the interest of electrochemists will not be very great.

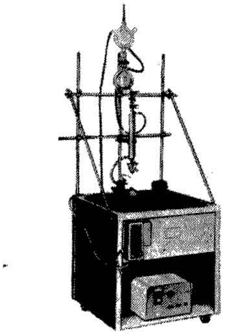
The book appears to be based significantly upon the author's own researches, and discusses a wide variety of topics including properties of electrolytes in medium low dielectric constants, ions present in amine–aliphatic acid solutions and ions formed from oxidation of ortho-substituted aromatics, and ozonolysis of aromatics.

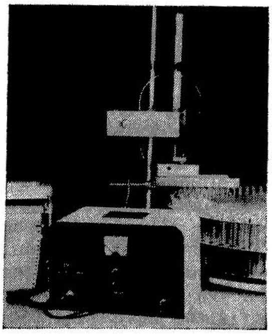
In my opinion, anyone attracted by the title of this book would be wise to browse through it in a library before purchasing it.

S. BRUCKENSTEIN (Minneapolis)

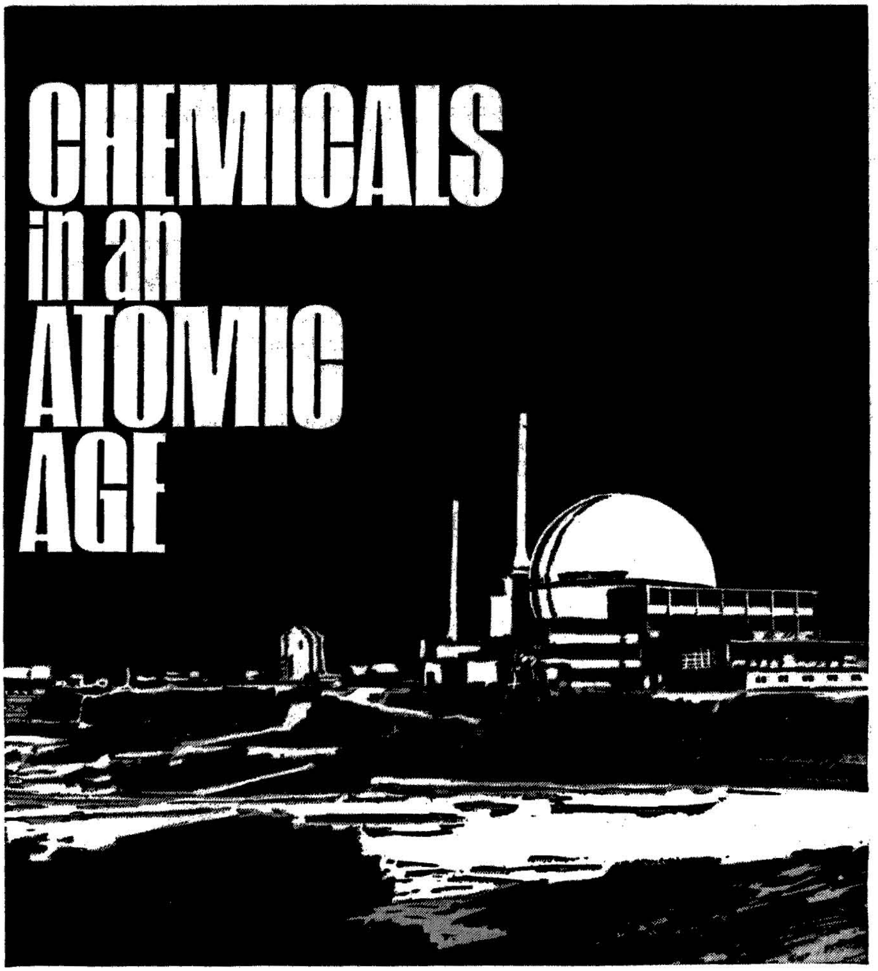
Anal. Chim. Acta, 32 (1965) 404








SPECTROSIL
Standard 10mm
Ultra Violet
SPECTROPHOTOMETER
CELLS
* WITH WINDOWS OF SYNTHETIC FUSED SILICA


CHEMICALS
in an
ATOMIC
AGE

SPRINGER-VERLAG
BERLIN·HEIDELBERG·NEW YORK

RESIDUE REVIEWS

Residues of Pesticides and other Foreign Chemicals in Foods and Feeds

Rückstands-Berichte

Rückstände von Pesticiden und anderen Fremdstoffen in Nahrungs- und Futtermitteln

Edited by **Francis A. Gunther**
Riverside, Calif.,
with the co-operation of numerous experts

Volume VII

In English. With 8 figures
and 31 tables. VI, 161 pages 8vo. 1964
Cloth DM 24,—

Contents: C. Logothetis and W. E. Westlake: The role of the Food and Agriculture Organization of the United Nations in the pesticide residue problem. — R. P. Myers: Antibiotic residues in milk. — W. Horwitz: The Association of Official Agricultural Chemists (AOAC). — D. E. Coffin: Residues of parathion, methyl parathion, EPN, and their oxons in Canadian fruits and vegetables. — S. E. Katz and K. Helrich: The determination of penicillins and chlortetracycline in premixes and mixed feeds. — I. Hoffmann and E. V. Parups: Mode of action of maleic hydrazide in relation to residues in crops and soils. — E. J. Miller, I. Granhall, and J. W. Cook: Collaborative studies on the analysis of pesticide residues. — E. Hindin, D. S. May, and G. H. Dunstan: Collection and analysis of synthetic organic pesticides from surface and ground water. — Subject index.

Volume VIII

With 26 figures. VI, 183 pages
(85 pages in English, 73 pages in
French) 8vo. 1965
Cloth DM 26,—

Contents: Anna Rajzman: Les résidus de biphényle dans les agrumes. — J. L. Henderson: Insecticide residues in milk and dairy products. — G. Unterstenhöfer, W. Bartels und M. Boness: Ergebnisse, Probleme und Tendenzen bei der Entwicklung von Pesticiden. — H. F. Linskens, W. Heinen, and A. L. Stoffers: Cuticula of leaves and the residue problem. — Subject index.

■ *General prospectus on request!*

Eastman Organic Chemicals around the world

Workers in the countries served by these distributors of Eastman Organic Chemicals can avoid the paperwork involved in importing. Some of these distributors maintain their own rather substantial stocks from which they can fill orders immediately. All can give you the benefit of the consolidated orders they place.

Among the 4000 Eastman Organic Chemicals these firms distribute are uncommon ones as well as uncommonly pure ones—organics that are often more economical to purchase than to make. These firms make it easier to purchase them. Get in touch with the one best located to serve you.

Distillation Products Industries
Eastman Organic Chemicals Department
Rochester 3, N. Y., U.S.A.

DPi

Distributors

AUSTRALIA

H. B. Selby & Co. Pty. Ltd.
35 York Street
Sydney, N.S.W.

H. B. Selby & Co. Pty. Ltd.
393 Swanston Street
P. O. Box 409G
Melbourne, C.1

H. B. Selby & Co. Pty. Ltd.
Box 606J, G.P.O.
Brisbane, Queensland

AUSTRIA

Heilmittelwerke Wien
G.m.b.H.
III/40, Rennweg 12
Vienna

W. J. Rohrbecks Nachf.
Wehrgasse 18
Vienna V

BELGIUM

Analis, S. A.
14, Rue Dewez
Namur

DENMARK

H. Struers Chemiske
Laboratorium
38, Skindergade
Copenhagen K

FINLAND

G. W. Berg & Co.
Fabiansgatan 14
Helsinki

Havulinna Oy
P. O. Box 468
Helsinki

FRANCE

Touzart & Matignon
3, Rue Amyot
Paris V^e

Substantial stocks maintained

GERMANY

Serva-Entwicklungslabor
Romerstrasse 45
Heidelberg

GREAT BRITAIN

Kodak Limited
Kirkby
Liverpool

Substantial stocks maintained

HOLLAND

N. V. Holland Indonesia
Agenturen Mij.
HIAM
139 De Ruyterkade
Amsterdam C

INDIA

The Andhra Scientific Co., Ltd.
4, Blacker's Road,
Mount Road
Madras

Raj-Der-Kar & Co.
Sadhana Rayon House
Dr. D. Naoroji Road
Bombay

INDONESIA

N. V. Chemicalienhandel
Rathkamp and Co.
18 Djalan Madja Pahit
Djakarta

ITALY

Prodotti Gianni, s.r.l.
Via Mecenate, 30/14
Milano

JAPAN

Tokyo Tsusho Kaisha, Ltd.
New Kaijo Building
6, Marunouchi 1-chome,
Chiyoda-ku
Tokyo

NEW ZEALAND

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 1495
Wellington, C.1

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 319
Dunedin, C.1

NORWAY

Norliens Kemisk-Tekniske
Aktieselskap
Tollbodgt. 32
Oslo

PORTUGAL

Soquimica, Sociedada de
Representacoes de
Quimica, Lda.
Rua dos Correeiros, 113-3°
Lisbon

SOUTH AFRICA

Kodak (South Africa) (Pty.)
Limited
"Kodak House"
45 Shortmarket Street
Cape Town

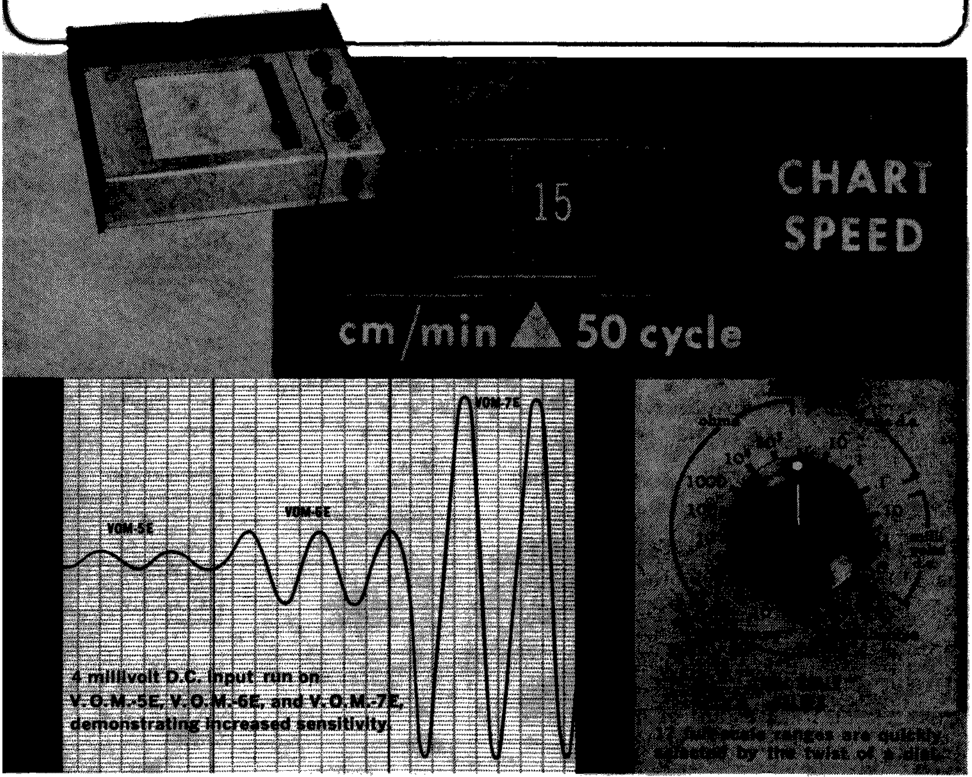
SWEDEN

Rudolph Grave A/B
Pyramidvagen 9, Fack Solna 1
Stockholm 3

SWITZERLAND

Dr. Bender & Dr. Hobein AG.
Riedtlistrasse 15a
Zurich 6

Distillation Products Industries *is a division of* **Eastman Kodak Company**


15
CHART SPEED
cm/min 50 cycle
VOM-5E
VOM-6E
VOM-7E
4 millivolt D.C. input run on V.O.M.-5E, V.O.M.-6E, and V.O.M.-7E, demonstrating increased sensitivity.
17 full-scale ranges are quickly selected by the twist of a dial.

Vol. 32 No. 4 ANALYTICA CHIMICA ACTA APRIL 1965

CONTENTS

Short Communications

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

RODD'S CHEMISTRY OF CARBON COMPOUNDS

Second Edition

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

This completely revised edition of this standard work has been undertaken to take into account the important advances in theoretical and experimental organic chemistry recorded since the appearance of the first edition.
The treatment has remained largely unchanged although the sheer extent of new material has made it necessary to create further subdivision in order to reduce publication delay.

VOLUME IA - GENERAL INTRODUCTION, HYDROCARBONS, HALOGEN DERIVATIVES
General Introduction
1. The saturated or paraffin hydrocarbons. Alkanes. 2. Unsaturated acyclic hydrocarbons. 3. Halogen derivatives of the aliphatic hydrocarbons.
6 × 9″ xx + 569 pages, 1964, subscription price £7.0.0.
non-subscription price £8.0.0.

VOLUME IB - MONOHYDRIC ALCOHOLS, THEIR ETHERS AND ESTERS, SULPHUR ANALOGUES; NITROGEN DERIVATIVES; ORGANOMETALLIC COMPOUNDS
4. Monohydric alcohols, their ethers and esters. 5. Sulphur analogues of the alcohols and their derivatives. 6. Nitrogen derivatives of the aliphatic hydrocarbons.
7. Aliphatic organometallic and organometalloidal compounds.
6 × 9″ xvi + 313 pages, 16 tables, 1964, subscription price £4.8.0.
non-subscription price £5.0.0.

VOLUME IC - MONOCARBONYL DERIVATIVES OF ALIPHATIC HYDROCARBONS; THEIR ANALOGUES AND DERIVATIVES
8. Aldehydes and ketones. 9. Monobasic carboxylic acids. 10. Carbon monoxide, isocyanides and fulminic acid. 11. Carbonic acid and its derivatives.
6 × 9″ xvi + 432 pages, 17 tables, April 1965, subscription price £5.17.0.
non-subscribtion price £7.10.0.

VOLUME ID - DIHYDRIC ALCOHOLS, THEIR OXIDATION PRODUCTS AND DERIVATIVES
12. Dihydric alcohols or glycols and their derivatives. 13. Hydroxyaldehydes and ketones and related compounds; dicarbonyl compounds. 14. Aliphatic hydroxycarboxylic acids and related compounds. 15. Nitro- and amino-acids and their derivatives. 16. Aldehydic and ketonic carboxylic acids and related compounds. 17. Dicarboxylic acids.

VOLUME IE - TRI- AND TETRA-HYDRIC ALCOHOLS, THEIR OXIDATION PRODUCTS AND DERIVATIVES
18. Trihydric alcohols and carbonyl compounds derived from them. 19. Phospholipids and glycolipids. 20. Dihydroxycarboxylic and tricarboxylic acids and their derivatives. 21. Tetrahydric alcohols and their oxidation products.

VOLUME IF - PENTA-, HEXA- AND HIGHER POLYHYDRIC ALCOHOLS, THEIR OXIDATION PRODUCTS AND DERIVATIVES; SACCHARIDES
22. Penta-, hexa- and higher polyhydric alcohols. 23. Monosaccharides. 24. Oligosaccharides and polysaccharides.

VOLUME IG - ENZYMES; MACROMOLECULES; CUMULATIVE INDEX TO VOLUME I A-G
25. Enzymes. 26. Synthetic macromolecules. 27. Rubber.
To follow
Volume II Alicyclic Compounds; Volume III Aromatic Compounds; Volume IV Heterocyclic Compounds; Volume V Miscellaneous; General Index

Multi-volume works such as Rodd's Chemistry of Carbon Compounds represent a considerable outlay for the purchaser. In order to alleviate this to a certain extent, the publishers offer a discount of 15% on the publication price. Subscribers to the complete series will thus be able to acquire the work for only 26s. (approx.) per 100 pages.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

380 E