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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 29, No. 4, October 1963

THE DETERMINATION OF TRACES OF OSMIUM IN RUTHENIUM SPONGE BY NEUTRON ACTIVATION ANALYSIS

Tracer techniques confirmed that a quantitative separation of osmium and ruthenium is possible by distillation from a hydrogen peroxide–sulphuric acid solution. Osmium distils quantitatively as OsO_4 at a temperature of 105 ± 5° in about 30 min. The ruthenium contamination is approximately 0.01%.

In the present work a neutron activation analysis is described for the determination of traces of osmium in ruthenium sponge. When quantities of osmium below 30 p.p.m. are determined, the ruthenium contamination of the distillate must be taken into account, when the measurement is made with a 3″ × 3″ NaI(Tl) crystal. This can easily be achieved by measurement in two energy regions with a γ-spectrometer or with a multichannel pulse-height analyzer. With a NaI(Tl) wafer as detector, the correction for ruthenium can be omitted for osmium concentrations above 10 p.p.m.

With the addition method of analysis, 10–2000 p.p.m. in 10-mg samples of ruthenium sponge can be determined by neutron activation analysis. Chemical separation is necessary but no carriers are required. The lowest limit of determination is about 3 p.p.m. for a 3″ × 3″ crystal; for the wafer, about 1 p.p.m. can be determined.

R. GIJBELS AND J. HOSTE, *Anal. Chim. Acta*, 29 (1963) 289–302.

THE SOLVENT EXTRACTION OF THE THIOCYANATE COMPLEXES OF TITANIUM, NIOBIUM AND TANTALUM

PART I. GENERAL STUDY OF VARIABLES

The solvent extraction of titanium, niobium and tantalum thiocyanates is studied in detail. The effect of the variables (solvent, concentration of thiocyanate, acidity, etc.) is discussed. There is evidence for the existence of a thiocyanate complex of tantalum.

E.A. MARI, *Anal. Chim. Acta*, 29 (1963) 303–311.

THE SOLVENT EXTRACTION OF THE THIOCYANATE COMPLEXES OF TITANIUM, NIOBIUM AND TANTALUM

PART II. APPLICATION TO THE SEPARATION OF MIXTURES

Solvent extraction of the thiocyanate complexes of titanium, niobium and tantalum allows the separation of micro quantities of these elements. Niobium and tantalum are separated by selective extraction of the fluoro-complexes. Mixtures of Ti and Nb, or of Ti and Ta in ratios of 500 : 1 to 1 : 500 can be separated. For mixtures of the three elements, results were acceptable with Nb : Ta ratios of 100 : 1 to 1 : 100. Colorimetric determinations of the three elements are described.

E. A. MARI, *Anal. Chim. Acta*, 29 (1963) 312–320.

THE REMOVAL OF Ce, Nd, Pr AND La FROM Er, Dy, Gd, Eu AND Sm BY ANION EXCHANGE

An anion-exchange procedure with 35% 3.5 N nitric acid–65% methanol as eluant has been developed for the removal of Ce, Nd, Pr and La from Er, Dy, Gd, Eu and Sm, at the trace concentration level.

R. A. EDGE, *Anal. Chim. Acta*, 29 (1963) 321–324.

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN AND MOLYBDENUM WITH THIOCYANATE AFTER α-BENZOINOXIME EXTRACTION

The extractability of tungsten α-benzoinoximate by chloroform as a function of the reagent concentration and acidity has been studies. In 0.5 M hydrochloric acid solution the extraction coefficient for tungsten (~ 1 p.p.m.) is given by the relation

$$E_w = \frac{[WO_2Bx_2]_{CHCl_3}}{\Sigma[W]_{H_2O}} = K_{ex}[HBx]^2_{H_2O} = 7 \cdot 10^8[HBx]^2_{H_2O}$$

An acidity range of 0.01–1 M provides favorable extraction coefficients. Tungsten can be separated by α-benzoinoxime extraction from much iron and most other metals. Molybdenum accompanies tungsten quantitatively and the two elements can be determined simultaneously by the familiar thiocyanate method if the absorbance of the isopropyl ether extract is measured at 405 mμ and 490 (or 475) mμ. As little as 1 μg W can thus be determined in the presence of 10 μg Mo without separation.

P. Y. PENG AND E. B. SANDELL, *Anal. Chim. Acta*, 29 (1963) 325–334.

MICROANALYSIS WITH THE AID OF ION EXCHANGERS

PART XXII. DETECTION OF NANOGRAM AMOUNTS OF MOLYBDENUM(VI) WITH TIRON

A new sensitive and selective resin spot test for nanogram quantities of molybdenum(VI) with tiron is proposed. The limit of identification is 8 ng (1 : $5 \cdot 10^6$) after 1 hour standing. Vanadium(V), chromium(VI), uranium(VI), titanium(VI), palladium(II), platinum(IV), silver(I) and gold(III) interfere. Uranium(VI) (20 ng, 1 : $2 \cdot 10^6$) can be detected similarly.

M. FUJIMOTO, N. FUKABORI AND Y. NAKATSUKASA, *Anal. Chim. Acta*, 29 (1963) 335–339.

THE DETERMINATION OF IRON IN TUNGSTEN CARBIDE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

An atomic absorption spectrophotometric procedure for the determination of 0.005 to 0.20% iron in a phosphoric acid solution of tungsten carbide is described. The method is rapid, preliminary separations are not required and the results obtained have been compared with those obtained by X-ray fluorescence.

C. B. BELCHER, *Anal. Chim. Acta*, 29 (1963) 340–343.

SPECTROPHOTOMETRIC DETERMINATION OF GALLIUM WITH 1-(2,4-DIHYDROXYPHENYLAZO)-2-NAPHTHOL-4-SULFONIC ACID

A new spectrophotometric method for the determination of gallium is described using 1-(2,4-dihydroxyphenylazo)-2-naphthol-4-sulfonic acid (DHPAN) as a reagent. The color reaction has a sensitivity of 0.013 μg Ga per cm^2 for log $I_0/I = 0.005$ at 560 mμ and obeys Beer's law up to 2.8 p.p.m. The effects of pH, time, order of addition of the reagents, temperature and diverse ions were investigated. Gallium is separated from interfering ions by solvent extraction.

T.-L. CHANG AND J. H. YOE, *Anal. Chim. Acta*, 29 (1963) 344–349.

ANALYSIS OF CORROSIVE FLUORINE COMPOUNDS BY GAS CHROMATOGRAPHY

CONTROL OF FREE FLUORINE

(in French)

A purely chromatographic and sufficiently general method is described for the analysis of molecular fluorine in permanent inert gases or in other corrosive fluorine compounds (UF_6, HF). The method is also applied to the analysis of permanent inert gases (even in trace quantities) in the same fluorine compounds. In this method, one or several chemical "precolumns" are placed in series with a gas–liquid chromatography column. The "precolumns" system retains or destroys the corrosive compounds (UF_6, HF, F_2) and the chromatography column separates the components formed.

O. ROCHEFORT, *Anal. Chim. Acta*, 29 (1963) 350–357.

CARBON PASTE ELECTRODES APPLICATION TO CATHODIC REDUCTIONS AND ANODIC STRIPPING VOLTAMMETRY

The utility of carbon paste electrodes for metal ion reductions and anodic stripping voltammetry is demonstrated. In addition certain organic reductions can be accomplished. Extension of the use of carbon paste electrodes to the cathodic range shows that this electrode has a wide range of potential applications. For anodic oxidations, the carbon paste electrode is perhaps the most versatile and useful stationary electrode available; it possesses practically zero anodic residual current and readily reproducible surfaces, and is simple to prepare and use. On the cathodic side carbon pastes are limited by a non-removable residual current but this difficulty seems readily circumvented.

C. OLSON AND R. N. ADAMS, *Anal. Chim. Acta*, 28 (1963) 358–363.

A METHOD OF AMPEROMETRIC DETERMINATION OF ARSENIC(III)

(Short Communication)

in German

N. Elenkova and G. Todorova, *Anal. Chim. Acta*, 29 (1963) 364–365.

AN IMPROVED GAS ABSORPTION DEVICE FOR CONDUCTOMETRIC MICRO-DETERMINATION OF CARBON DIOXIDE

(Short Communication)

I. Holm-Jensen, *Anal. Chim. Acta*, 29 (1963) 365–368.

A NEW CRITERION FOR THE QUALITATIVE IDENTIFICATION OF SUBSTANCES BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY

(Short Communication)

R. Dybczyński, *Anal. Chim. Acta*, 29 (1963) 369–372.

AN IMPROVED METHOD FOR THE DETECTION AND ESTIMATION OF MICRON-SIZED SULFATE PARTICLES

(Short Communication)

J. P. Lodge, Jr. and K. J. Parbhakar, *Anal. Chim. Acta*, 29 (1963) 372–374.

THE DETERMINATION OF TRACES OF OSMIUM IN RUTHENIUM SPONGE BY NEUTRON ACTIVATION ANALYSIS

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(Received March 15th, 1963)

The six platinum metals Ru, Rh, Pd, Os, Ir and Pt show great analogy in several respects, osmium and ruthenium exhibiting the most striking similarity in their chemical properties. The separation of these metals in a high state of purity therefore causes great difficulties. Until recently, traces of the platinum metals have been mainly determined by spectrographic and spectrophotometric methods. The sensitivity of these techniques is, however, sometimes insufficient[1]. Recently, minute quantities of impurities in platinum metals have been determined by neutron activation analysis[2-15].

The determination of traces of osmium in ruthenium has not been described. A survey of the microgravimetric and colorimetric determination of osmium, after separation from ruthenium is summarized in Table I. No successful spectrographic method has been reported for either the direct or indirect determination of osmium in ores, concentrates or complex alloys[1]. The sensitivity of the osmium determination in high purity platinum is approximately 100 p.p.m.[21]; and a lower limit of detection for the determination of osmium in ruthenium is not to be expected. In the present work, a neutron activation analysis is described which allows a determination down to 1 p.p.m. osmium in 10-mg samples of ruthenium after a quantitative chemical separation.

TABLE I

REVIEW OF Os DETERMINATIONS IN Ru

Author and reference	*Method*	*Amount of Os determined*	*Ratio Os/Ru*	*Error (%)*
PAYNE[16]	Grav. or colorim.	2.5–100 mg	1/1	4–1.8
WESTLAND AND BEAMISH[17]	Colorim.	0.2–0.8 mg	1/2	> 1
WESTLAND AND BEAMISH[18]	Colorim.	16–32 μg	4/10	5–1
GEILMANN AND NEEB[19]	Colorim.	50 μg 60 μg	5/100 1.2/100	1 1.5
SANDELL[20]	Colorim.	5 μg	5/100	6

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NUCLEAR DATA

The natural osmium element consists of the following isotopes: ^{184}Os, ^{186}Os, ^{187}Os, ^{188}Os, ^{189}Os, ^{190}Os and ^{192}Os. Irradiation with thermal neutrons gives rise to a number of radio-nuclides, as shown in Table II[22–24].

After irradiation for 3–5 days at a neutron flux of $4–8 \cdot 10^{11}$ neutrons/cm^2/sec, γ-spectrometric measurement and graphic analysis of the decay-curve from integral NaI(Tl) γ-scintillation counting shows the presence of ^{191}Os (16 days), ^{193}Os (31 h) and a low activity due to ^{185}Os (94 days). The decay of ^{190m}Os (10 min) is complete before the measurements are carried out. A species corresponding to the 14-h half-life of ^{191m}Os could not be detected, because of the small activation cross-section of the reaction: ^{190}Os (n, γ) ^{191m}Os. After decay of ^{193}Os (31 h) the γ-spectrum is mainly due to the 129 KeV photo-peak (^{191}Os–^{191m}Ir), the 65 KeV X-ray from internal conversion, and the 42 KeV peak (^{191}Os–^{191m}Ir) not resolved from the 37 KeV escape peak. A few weeks after irradiation, the 646 KeV photo-peak of ^{185}Os is about 100 times less intense than the X-ray (Fig. 1). It has been estimated[25] that at a thermal neutron flux of 10^{12} neutrons/cm^2/sec, it should be possible, under ideal conditions, to determine 10^{-9} g of osmium by measurement of 31-h ^{193}Os and 16-day ^{191}Os species. In the present case, use was made of the ^{191}Os isotope, as the samples were processed about 14 days after the irradiation.

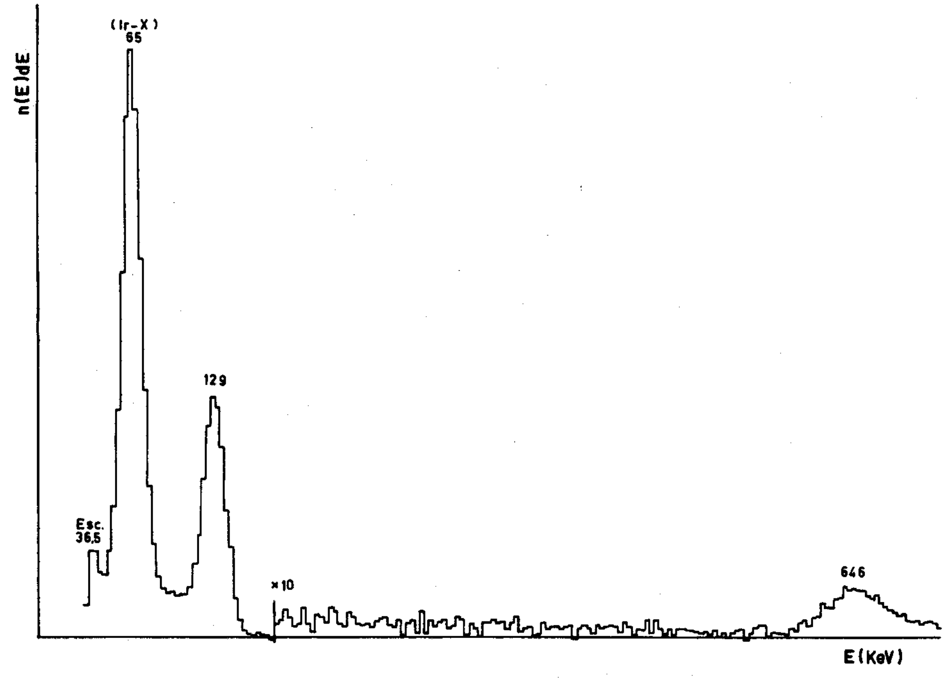

Fig. 1. γ-Spectrum of irradiated osmium sponge.

Naturally occurring ruthenium consists of seven isotopes: ^{96}Ru, ^{98}Ru, ^{99}Ru, ^{100}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru. Irradiation with slow neutrons gives rise to the radio-nuclides summarized in Table III[22–24]. After irradiation under the same conditions as men-

TABLE II

NUCLEAR DATA FOR OSMIUM

Naturally occurring isotope	*Isotopic abundance (%)*	*Radio-nuclide formed by (n, γ) reaction*				*Radioactive daughter*		
			$\sigma_{act}(b)$	$T_{1/2}$	*Radiation (KeV)*		$T_{1/2}$	*Radiation (KeV)*
^{184}Os	0.018	^{185}Os	<200	93.6 days	E.C. γ's (646)	—	—	—
^{189}Os	16.1	^{190m}Os	—	10 min	γ's (39 to 614)	—	—	—
^{190}Os	26.4	^{191m}Os ^{191}Os	— 8 ± 3	14 h 16 days	I.T.(74) β^- (142)	^{191}Os ^{191m}Ir	16 days 6.9 sec	β^- (142) γ's (42,129)
^{192}Os	41	^{193}Os	1.6 ± 0.4	31 h	β^-'s (677 to 1136) γ's (73 to 558) (esp. 281, 321, 388, 460, 558)	—	—	—

TABLE III

NUCLEAR DATA FOR RUTHENIUM

Naturally occurring isotope	*Isotopic abundance (%)*	*Radio-nuclide formed by (n, γ) reaction*				*Radioactive daughter*		
			$\sigma_{act}(b)$	$T_{1/2}$	*Radiation (KeV)*		$T_{1/2}$	*Radiation (KeV)*
^{96}Ru	5.7	^{97}Ru	0.21 ± 0.02	2.88 days	E.C. γ's (216)	—	—	—
^{102}Ru	31.3	^{103}Ru	1.44 ± 0.16	39.8 days	β^-'s (220) γ's (55 to 610) (esp. 498, 610)	^{103m}Rh	57 min	I.T. (40)
^{104}Ru	18.3	^{105}Ru	0.7 ± 0.2	4.5 h	β^- (1150) γ (726)	^{105m}Rh ^{105}Rh	45 sec 37 h	I.T. (130) β^-'s (560) γ (319)

tioned above for osmium, decay measurements with a NaI(Tl) crystal demonstrate the presence of four radio-nuclides: ^{103}Ru (41 days), ^{97}Ru (2.7 days), ^{105}Rh (±36 h) and ^{105}Ru (±4.4 h). The γ-spectrum of irradiated ruthenium shows photo-peaks at 498 and 625 KeV (^{103}Ru), 208 KeV (^{97}Ru), 320 KeV (^{105}Rh) and 726 KeV (^{105}Ru). After distillation of ruthenium from HNO_3–H_2SO_4–$HClO_4$[26], the 320 KeV peak is absent in the distillate, whereas the residue contains carrier-free ^{105}Rh (37 h). In the present case the main activity will obviously be due to ^{103}Ru. Considering atomic weights, isotopic abundances, cross-sections, half-lives, irradiation time and γ-energies, it is obvious that a non-destructive determination of osmium in ruthenium is only feasible if comparable quantities of both elements are present. If traces of osmium are to be determined, chemical separation is inevitable.

RADIOCHEMICAL STUDY OF THE SEPARATION OF OSMIUM FROM RUTHENIUM BY DISTILLATION FROM H_2O_2–H_2SO_4 SOLUTIONS

In an oxidizing medium, osmium and ruthenium form volatile oxides, OsO_4 and RuO_4, which allows an easy separation from Rh, Pd, Ir and Pt. Their mutual separation, however, presents serious difficulties. Distillation of osmium from nitric acid has been suggested although quantitative recovery is difficult and serious ruthenium contamination occurs[27].

SCHOELLER AND POWELL[27] and PAYNE[16] recommended the simultaneous distillation of Os + Ru from sodium bromate or alkaline hypochlorite solution and subsequent separation by selective absorption (ruthenium in hydrochloric acid and osmium in ethanolic sodium hydroxide); this procedure requires a set of 6 absorption flasks and large volumes of absorption liquids. GEILMANN AND NEEB[19] distilled Os + Ru from CrO_3–H_2SO_4–$HClO_4$; the tetroxides are absorbed in hydrochloric acid saturated with sulphur dioxide followed by selective extraction. WESTLAND AND BEAMISH[17,18] used selective distillation of osmium from a sulphuric acid–hydrogen peroxide solution. Ruthenium is thus kept at a lower oxidation state and remains in the residue.

In the present paper, this procedure was investigated using radioactive tracer techniques. Several variables were examined, such as the sulphuric acid and hydrogen peroxide concentrations, and the duration and temperature of the distillation. From these experiments it appeared that the distillation apparatus could be considerably simplified when milligram amounts of the metals were considered.

EXPERIMENTAL

Instrumental

Distillation apparatus (pyrex glass). See Fig. 2.

Multichannel pulse-height analyzer. Intertechnique SA-40.

Detectors. Hilger & Watts, 3" × 3" NaI(Tl) crystal and Quartz & Silice 3" × 1 mm NaI(Tl) wafer with beryllium window of 0.2 mm.

Photomultiplier tube. E.M.I. no. 9531 A.

Precision high voltage supply. Tracerlab RLI-7.

Tracer solutions of ^{103}Ru and ^{191}Os

About 5 mg of finely divided osmium or ruthenium sponge is irradiated during 3–5 days at a neutron flux of 4–$8 \cdot 10^{11}$ neutrons/cm²/sec in BR-1. The metal is intimately mixed with about 0.3 g of sodium peroxide in a nickel crucible and fused. The cold melt is disintegrated with 10 ml of warm water, the crucible rinsed with hydrochloric acid and the black alkaline suspension acidified with the washings.

Procedure

A known amount of tracer solution (0.25–0.50 ml) of adequate activity (approximately 10^5 counts/min), corresponding to about 35–70 μg of the metal is transferred to the distillation flask and 35 ml of sulphuric acid (1 : 2) and 25 ml of hydrogen peroxide (30%) are added. Five ml of 9 *N* sodium hydroxide are placed in the two receivers, an air current is drawn through the apparatus and the flask heated electrically at a temperature of 105±5° for about 30 min, while 15 ml of hydrogen peroxide (30%) is added dropwise over this period. The distillate is absorbed in the receivers. Their contents, with washings (water), are diluted to 25 ml and the activities of distillate and residue are measured by γ-scintillation counting with a pulse-height analyzer. The latter may be necessary to eliminate the interfering daughter activity of ^{105}Rh in the ruthenium tracer solution. The material balance fitted within 2%. Correction for different density of distillate and residue was not required. The results of some typical experiments are summarized in Table IV.

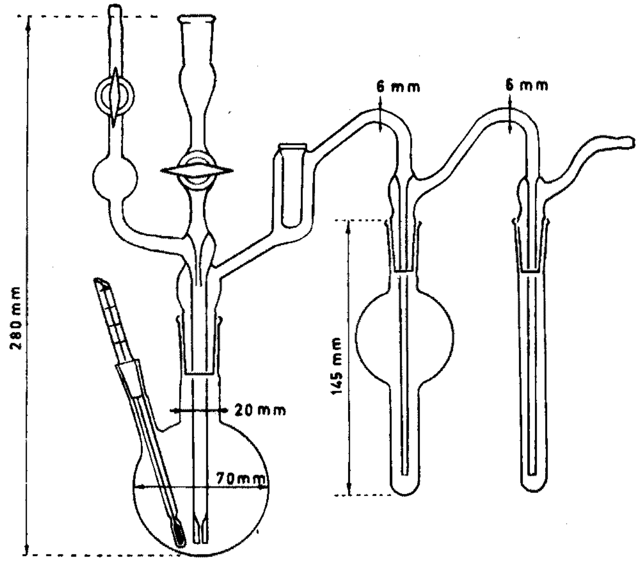

Fig. 2. Micro-distillation apparatus.

Experiments were also made with osmium tracer in the presence of 1–10 mg of osmium or ruthenium carrier and with ruthenium tracer in the presence of 1–10 mg of osmium or ruthenium carrier. The carrier used was osmium or ruthenium sponge, which was weighed in a little nickel crucible; 0.25–0.50 ml of tracer solution of known activity was added and allowed to soak into the metal powder and then carefully evaporated to dryness. When solutions of osmium tracer were to be evaporated, iron(II) sulphate or chloride was added to avoid losses of osmium by volatilization. Sub-

TABLE IV

SEPARATION OF OSMIUM FROM RUTHENIUM BY DISTILLATION (TRACER AMOUNTS)

Osmium tracer			*Ruthenium tracer*		
Temperature (°)	*Duration (min)*	*% dist.*	*Temperature (°)*	*Duration (min)*	*% dist.*
105±5	20	99.60	125–130	60	2.63
105±5	20	99.93	120–125	60	0.24
105±5	20	99.79	120–125	60	2.19
105±5	25	102.30	120–125	50	1.10
			105±5	20	0.02
			105±5	20	0.12
			105±5	20	0.07
			105±5	20	0.08

sequent fusion with sodium peroxide ensured complete exchange between carrier and tracer. After cooling, the melt was disintegrated with 10 ml of warm water and transferred to the distillation flask. The crucible was rinsed with a few ml of hydrochloric acid, 12 ml of sulphuric acid (1 :2) and 25 ml of hydrogen peroxide (30%) and the washings were added to the black alkaline suspension.During this manipulation the flask had to be completely cooled in an ice bath, because the heat of neutralization causes a partial loss of ruthenium[28] or osmium. The distillation apparatus was mounted, 25 ml of sulphuric acid (1 :2) were added and a slow air current was drawn through the apparatus. The contents of the flask were heated to about 70–80°. At this stage the temperature spontaneously rose to 105°. Boiling at 105 ± 5° was then continued for 30–40 min, while 10–15 ml of 30% hydrogen peroxide was added dropwise. Results are given in Table V. The material balance fits within 2%. It appeared that the ruthe-

TABLE V

SEPARATION OF OSMIUM FROM RUTHENIUM BY DISTILLATION (TRACER + CARRIER)

Osmium tracer			*Ruthenium tracer*		
Ru carrier (mg)	*Os carrier (mg)*	*% dist. Os*	*Ru carrier (mg)*	*Os carrier (mg)*	*% dist. Ru*
1.682	—	101.50	1.530	—	0.06
5.012	—	100.96	5.393	—	0.75
6.400	—	99.51	6.510	—	0.00
6.910	—	100.52	6.789	—	0.07
9.712	—	99.62	7.140	—	0.03
—	1.112	102.19	10.525	—	0.00
—	4.840	98.71	—	1.690	0.00
—	6.698	100.52	—	4.955	0.00
—	9.611	100.01	—	5.070	0.02
—	11.510	73.10[a]	—	8.350	0.06
			—	11.296	0.55
			±10	—	0.009[b]

[a] Incomplete absorption of OsO_4 in the receivers because of the too vehement gas development during the decomposition of H_2O_2.

[b] Average of 16 experiments on 10-mg samples of irradiated ruthenium sponge (instead of 10 mg carrier + tracer solution) with an integral activity of about $2 \cdot 10^6$ counts/min. Under the conditions mentioned, an average activity of 180 counts/min was recovered in the distillate, *i.e.* 0.009%.

nium contamination could be reduced to less than 0.01% of the integral ruthenium activity by waiting for several hours before the distillation was started. The ruthenium contamination increases proportionally with the sample size (Fig. 3).

Tables IV and V show that the method allows the quantitative separation of osmium and ruthenium. By boiling at a temperature of 105±5° during 30–40 min, osmium volatilizes quantitatively from a hydrogen peroxide–sulphuric acid solution, while ruthenium is quantitatively retained (distillate less than 0.01% Ru), both with and without carriers. As appeared from tracer experiments, the platinum metals Pt, Ir, Pd and Rh do not distil under these conditions.

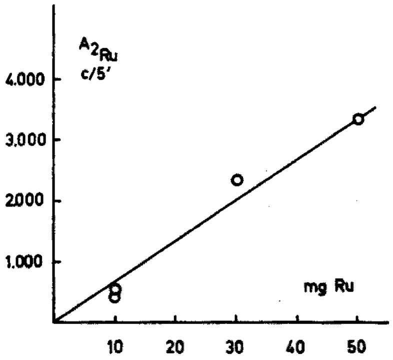

Fig. 3. Ruthenium contamination as a function of sample size.

ACTIVATION ANALYSIS OF TRACES OF OSMIUM IN RUTHENIUM

The described procedure was applied to 10-mg samples of ruthenium sponge, namely a commercial ruthenium and a spectrographically pure ruthenium. γ-Spectrometric

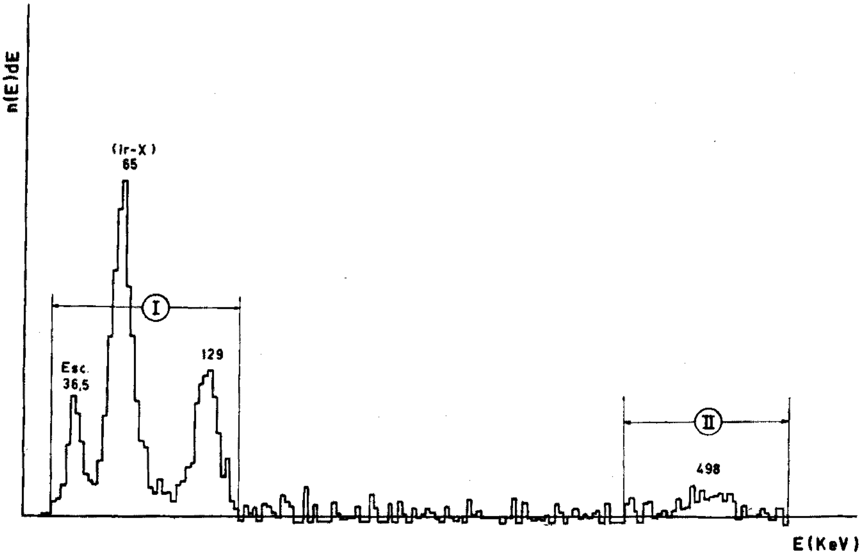

Fig. 4. γ-Spectrum of a typical distillate.

investigation of the distillate showed the presence of osmium, contaminated with a small and almost constant amount of ruthenium. A typical γ-spectrum with the 3″ × 3″ NaI(Tl) detector is represented in Fig. 4. From this Fig. it appears that more than 99% of the osmium activity has an energy below 145 KeV (Region I), whereas the ruthenium activity is essentially located under the photo-peak at 498 KeV (Region II). It is obvious that the ruthenium contamination contributes to the count rate in Region I, owing to the Compton effect, scatter, a 55 KeV γ- and 20.2 KeV X-ray (*cf.* also Fig. 5).

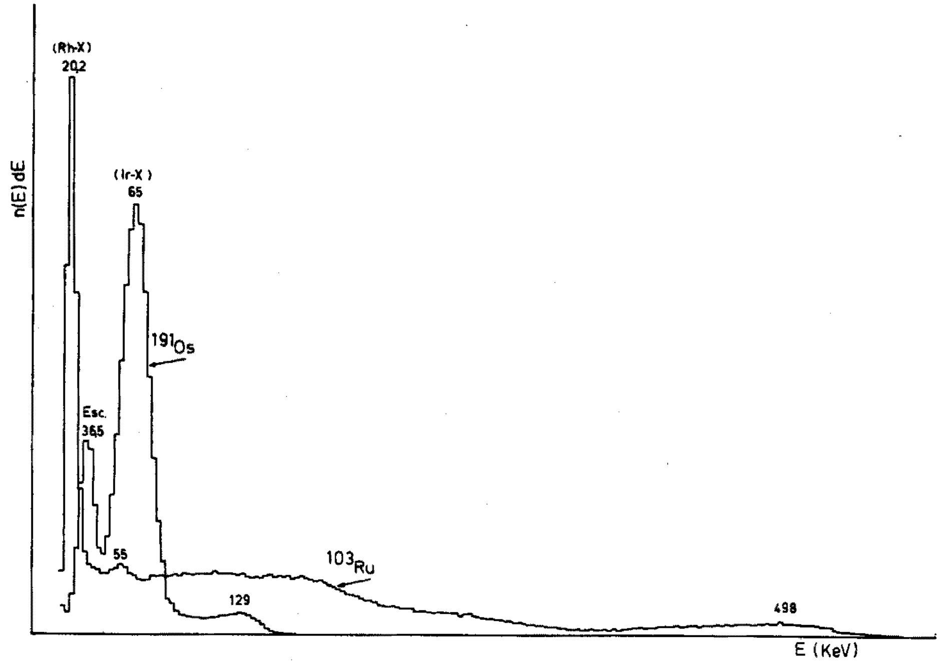

Fig. 5. γ-Spectra of ^{191}Os and ^{103}Ru with 3″ × 1 mm NaI(Tl) wafer.

The ruthenium contamination in Region I will be given by

$$A_{1\,\mathrm{Ru}} = \frac{A_2 - k_{\mathrm{Os}}A_1}{k_{\mathrm{Ru}} - k_{\mathrm{Os}}} \simeq \frac{A_2 - k_{\mathrm{Os}}A_1}{k_{\mathrm{Ru}}},$$

as $k_{\mathrm{Os}} \ll k_{\mathrm{Ru}}$

where

$$k_{\mathrm{Os}} = A_{2\,\mathrm{Os}}/A_{1\,\mathrm{Os}} \text{ and } k_{\mathrm{Ru}} = A_{2\,\mathrm{Ru}}/A_{1\,\mathrm{Ru}}$$

For a given amount of ruthenium sponge (10 mg) the ruthenium interference in the distillate is almost constant (0.01%). The lower, however, the osmium percentage of the investigated ruthenium, the more considerable the relative ruthenium contamination.

The corrected osmium activity in Region I ($A_{1\,\mathrm{Os}}$) is thus given by $A_1 - A_{1_{\mathrm{Ru}}}$, taking, of course, background corrections into account. As the k values are a function of geometry, of radioisotopic composition (thus of time), and even more or less of the integral activity (coincidence for highly active sources), these values must be determined with a standard not exceeding 10^5 counts/min, on the same day and under the same geometrical conditions. Moreover, the standards of ruthenium must be distilled to eliminate the interfering ^{105}Rh daughter activity when measuring shortly after irradiation. k_{Ru} and k_{Os} have approximately values of 3 and 0.003 respectively for a 3″ × 3″ crystal, and 0.5 and 0.0005 respectively for a 3″ × 1 mm wafer. As will be shown below, the described correction can be neglected when the latter detector is used.

As the relative detection efficiency for the photo-electric effect of a thin *vs.* a large NaI(Tl) detector decreases rapidly with increasing γ-energy a substantial reduction of the ruthenium interference can be expected when a 3″ × 1 mm wafer is used instead of a 3″ × 3″ detector. This is apparent from Fig. 6, where the detection efficiency in the photo-peak as a function of energy was computed for a 3″ × 3″ crystal (curve 1) and a 3″ × 1 mm wafer (curve 2). Experimental results of the detection efficiency ratio at different energies are given in curve 3. A further improvement in the detection limit of a low energy γ-emitter is due to a more favourable signal-to-background ratio.

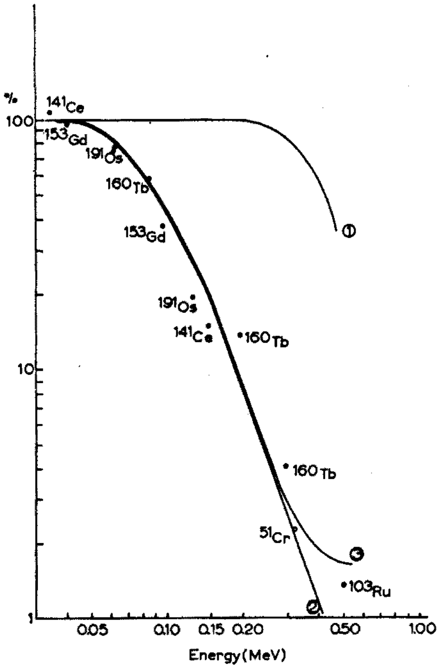

Fig. 6. Calculated percentage detection efficiency of NaI as a function of γ-energy. Curve 1, thickness 3″; curve 2, thickness 1 mm; curve 3, (2) *vs.* (1). o, experimental points.

Experimental values were obtained by measuring ^{191}Os and ^{103}Ru activities in the 65, 129 and 498 KeV regions, after adjusting high voltage and amplifier gain so as to obtain approximately the same spreading of the spectra with either detector. The net count rate to background ratios S of both detectors were determined. The ratios of these values, $S_{\text{wafer}}/S_{\text{crystal}}$, are given in Table VI. From these values it can be seen that the detection limit for ^{191}Os, when measuring in the 65 KeV region, has improved by a factor of 2.2, whereas the ruthenium detection limit is less favourable.

TABLE VI

$S_{\text{wafer}}/S_{3'' \times 3''}$

(S = net count rate to background ratio of the NaI(Tl)-detector)

	65 KeV	*129 KeV*	*498 KeV*
^{191}Os	2.22	1.16	0.98
^{103}Ru	0.87	0.60	0.23

TABLE VII

RATIO OF RELATIVE DETECTION EFFICIENCIES OF ^{191}Os AND ^{103}Ru FOR WAFER *vs.* 3″ × 3″ CRYSTAL

65 KeV	*129 KeV*	*498 KeV*
2.57	1.95	0.42

The relative detection efficiencies of ^{191}Os and ^{103}Ru were measured for the wafer and the 3″ × 3″ crystal. Their ratios are given in Table VII. It appears that in the 65 KeV region the relative detection efficiency of ^{191}Os *vs.* ^{103}Ru has increased by a factor 2.57 when a wafer is used instead of a 3″ × 3″ crystal. This value is valid only if the counting does not include the 20.2 KeV Pd X-ray caused by internal conversion of ^{103}Ru.

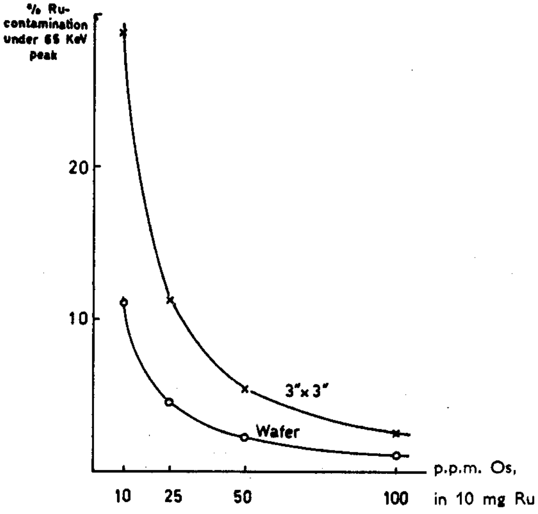

Fig. 7. Percentage contamination of the distillate as a function of the osmium content.

Taking into account that the absolute ruthenium contamination of a distillate is almost constant, namely 0.01% of the total ruthenium activity, one can compute the percentage interference as a function of osmium content. The values for both detectors are given in Fig. 7. This graph was obtained from the most unfavourable data encountered during the analyses performed.

It appears that a correction for the ruthenium contamination is required when measurements are made with the 3″ × 3″ crystal for osmium contents below 30 p.p.m. For the wafer, however, the correction can be omitted for osmium contents above 10 p.p.m., the error being of the same order as the estimated standard deviation of a single activity measurement.

Experimental procedure for the activation analysis

The osmium percentage of "commercial", "spectrographically pure" ruthenium sponge and ruthenium sponge prepared in the laboratory was determined. An addition method of analysis was used[30]. Synthetic samples with increasing percentages of osmium were prepared as follows: 10 mg of ruthenium sponge was weighed and wrapped in Mylar foil (approximately 2×3 cm^2, 15–20 mg), to facilitate the removal of the samples from the aluminium containers (saucers of 15 mm diameter and 2 mm height) after irradiation. In the same "saucer" a piece of Whatman paper no. 1 (15–20 mg) was irradiated, spotted with 100 μl of an osmium solution of known concentration and containing 500 μg of iron(II) chloride per 100 μl. After irradiation for 3–5 days at a neutron flux of $4\text{–}8 \cdot 10^{11}$ neutrons/cm^2/sec, the complete contents of the aluminium container (*i.e.* ruthenium sponge, Mylar and paper) were fused with about 1 g of sodium peroxide, acidified and distilled from hydrogen peroxide–sulphuric acid solution, as described above. No carriers were used as the osmium yield was quantitative. The osmium activity (y), corrected for ruthenium interference if necessary, was then plotted against the added amount of osmium (x); the slope of the straight line and its intercept with the ordinate allowed the calculation of the original osmium content in the investigated ruthenium sponge.

Results

Series A: 10-mg samples of "commercial" ruthenium sponge were spiked with respectively 20.0, 16.0, 10.0, 5.0, 2.5 and 0.0 μg of osmium and irradiated, fused and distilled. The distillates were diluted to 25 ml in a volumetric flask which was placed directly on the 3″ × 3″ crystal and counted for 10 min with the multichannel pulse-height analyzer, the background being subtracted automatically. The activities stocked in the channels of energy region I were totalized and corrected for ruthenium contamination. Measurements were made 13 days after the end of irradiation. The method of least squares was used for fitting the most probable straight line to the points obtained. The standard deviations of the slope and intercept with the ordinate were also calculated[31,32]. Slope: 2295 ± 86 counts/min/μg Os, s.d. = 3.75%; intercept with ordinate 910 ± 985 counts/min, s.d. = 108%. The osmium percentage of the ruthenium sponge is thus given by $(910 \pm 985)/(2295 \pm 86) = 0.04 \pm 0.042$ μg Os/10 mg Ru or 40 ± 42 p.p.m. Os. The amounts of osmium added to the samples were obviously too high to allow a reliable estimate to the osmium content. The standard deviation of the slope (3.75%), however, can be considered as highly satisfactory. The main sources of error were the microlitre pipettes, variations in neutron flux, losses during the neutralization of the sodium peroxide melt, unselected volumetric flasks, ruthenium correction and relatively high background correction.

The average ruthenium contamination in Region I was approximately 75 counts/min. The contamination will be as important as the osmium activity for 75/2295 or 0.03 μg Os/10 mg Ru, *i.e.* 3 p.p.m., this being roughly the lower limit of the method.

Series B: 10-mg samples of "spectrographically pure" ruthenium sponge were spiked with respectively 1.00, 0.80, 0.50, 0.25, 0.10 and 0.00 μg of osmium and irradiated together with 3 samples of 10 mg of "commercial" ruthenium sponge.

The distillates from hydrogen peroxide–sulphuric acid solution were diluted to 25 ml and directly counted for 5 min by placing the volumetric flasks on the detector.

The results of the measurements with the 3″ × 3″ crystal, after correction for ruthenium contamination, are given in Fig. 8 (14 days after the end of irradiation). Slope: 3404±62 counts/min/μg Os, s.d. = 2.04%; intercept with ordinate 1012 ± 35 counts/min, s.d. = 3.28%. Hence the "spectrographically pure" ruthenium contains 33.3±1.3 p.p.m. of Os, whereas the "commercial" ruthenium contains 16.8±2.5 p.p.m. of Os.

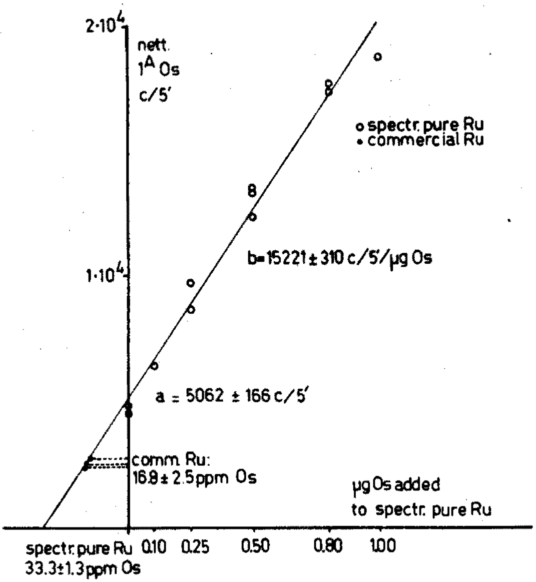

Fig. 8. Calibration curve (series B; 3″ × 3″ crystal).

Remark. Mylar and Whatman paper blanks were irradiated and distilled; no osmium could be detected.

The same osmium distillates were afterwards (35 days after the end of the irradiation) counted with the wafer. No correction for ruthenium contamination was made, but an analogous calibration curve was obtained. Slope = 464±25 counts/min/μg Os, s.d. = 3.2%; intercept with ordinate = 146±4 counts/min., s.d. = 2.9%.

The calculated osmium percentages are consequently 32.4±1.4 p.p.m. for "spectrographically pure" ruthenium and 16.3±4.6 p.p.m. for "commercial" ruthenium.

Series C: Ruthenium sponge was prepared from "commercial" ruthenium, which was fused at first with sodium peroxide and submitted to an osmium distillation. The distillate, absorbed in 9 *N* sodium hydroxide, was discarded. The residue was evaporated in the presence of hydroxylamine hydrochloride. The receivers of the distillation apparatus were refilled with 5 ml of 9 *N* sodium hydroxide and cooled in an ice bath; nitric acid (14 *N*) and perchloric acid (70%) were carefully added to the distillation flask and its contents heated at a temperature of 200–220° until ruthenium had completely distilled[26]. The absorption liquid reduced RuO_4 to $NaRuO_4$. After boiling with ethanol, ruthenium precipitated as hydrated oxide[28]. The precipitate was filtered and after ignition in air, reduced with hydrogen in a Rose crucible[27].

Samples of 10 mg were taken from this sponge and spiked with 1.00, 0.80, 0.50, 0.25, 0.10 and 0.00 μg of osmium. Together with two untreated samples of "commercial" ruthenium they were irradiated as usual. After a sodium peroxide fusion and distillation, the distillates with washings were diluted to 25 ml and counted on the 3″ × 3″ crystal and wafer during 5 min.

The results of the measurements with the Hilger detector, after correction for ruthenium, were as follows (16 days after the end of irradiation). Slope: 1071.6 ± 6.6 counts/min/μg Os, s.d. = 0.61%; intercept with ordinate: 18 ± 4 counts/min, s.d. = 21%. From this calibration curve it appears that the intercept is different from zero, as $t = 18/4 = 4.5 > 2.228$, the latter being the 5% critical value for t, 10 D.F. (12 distillates measured), although no osmium was detected in the unspiked purified ruthenium samples (measured activity below background). The calculated osmium percentage in the "purified" ruthenium sponge was thus 1.67 ± 0.35 p.p.m. For "commercial" ruthenium the osmium content found was 16.4 ± 0.84 p.p.m. in good agreement with the previous determinations.

Measurements during 5 min, without ruthenium correction, were also made with the wafer, 17 days after the irradiation. The results are in agreement with the corrected values obtained with the 3″ × 3″ crystal. Slope: 586 ± 1.6 counts/min/μg Os; intercept with ordinate: 10.3 ± 0.84 counts/min. The "purified" ruthenium thus gave a value of 1.81 ± 0.15 p.p.m. of osmium, whereas for the "commercial" ruthenium a value of 16.2 ± 0.37 p.p.m. was found, both in agreement with the previous determinations.

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SUMMARY

Tracer techniques confirmed that a quantitative separation of osmium and ruthenium is possible by distillation from a hydrogen peroxide–sulphuric acid solution. Osmium distils quantitatively as OsO_4 at a temperature of 105 ± 5° in about 30 min. The ruthenium contamination is approximately 0.01%.

In the present work a neutron activation analysis is described for the determination of traces of osmium in ruthenium sponge. When quantities of osmium below 30 p.p.m. are determined, the ruthenium contamination of the distillate must be taken into account, when the measurement is made with a 3″ × 3″ NaI(Tl) crystal. This can easily be achieved by measurement in two energy regions with a γ-spectrometer or with a multichannel pulse-height analyzer. With a NaI(Tl) wafer as detector, the correction for ruthenium can be omitted for osmium concentrations above 10 p.p.m.

With the addition method of analysis, 10–2000 p.p.m. in 10-mg samples of ruthenium sponge can be determined by neutron activation analysis. Chemical separation is necessary but no carriers are required. The lowest limit of determination is about 3 p.p.m. for a 3″ × 3″ crystal; for the wafer, about 1 p.p.m. can be determined.

RÉSUMÉ

Grâce à l'aide de traceurs, on a pu vérifier qu'une séparation quantitative de l'osmium d'avec le ruthénium est possible par distillation, en présence de peroxyde d'hydrogène et d'acide sulfurique. L'osmium distille quantitativement sous forme de OsO_4, à 105°, en 30 minutes. La contamination en ruthénium est approximativement de 0.01%. Les auteurs décrivent une méthode d'analyse par activation au moyen de neutrons, pour le dosage de traces d'osmium dans le ruthénium. Pour des teneurs en osmium inférieures à 30 p.p.m., la contamination du distillat en ruthénium doit être prise en considération, lorsque les mesures sont effectuées avec un cristal NaI(Tl) 3″ × 3″.

ZUSAMMENFASSUNG

Mit Hilfe von radiochemischen Methoden wird bestätigt, dass eine quantitative Trennung des Osmiums vom Ruthenium durch Destillation aus einer mit Wasserstoffperoxid versetzten schwefelsauren Lösung möglich ist. Das Osmium destilliert in etwa 30 Minuten quantitativ als OsO_4 bei einer Temperatur von $105 \pm 5°$ und ist mit ungefähr 0.01% Ruthenium verunreinigt.

In dieser Arbeit wir eine Neutronenaktivierungsanalyse zur Bestimmung von Spuren Osmium in Ruthenium beschrieben. Liegt der Osmiumgehalt unter 30 p.p.m., so muss der Rutheniumgehalt im Destillat berücksichtigt werden, wenn die Messung mit einem 3″ × 3″ NaJ(Tl)-Kristall durchgeführt wird. Das erreicht man durch Anwendung eines Impulshöhenanalysators. Bei Verwendung eines 3″ × 1 mm NaJ(Tl)-Kristalls kann die Korrektur für das Ruthenium bei Osmiumgehalten über 10 p.p.m. vernachlässigt werden. Die Nachweisgrenze beträgt etwa 3 p.p.m. für den 3″ × 3″ Kristall und etwa 1 p.p.m. für den 3″ × 1 mm Kristall.

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THE SOLVENT EXTRACTION OF THE THIOCYANATE COMPLEXES OF TITANIUM, NIOBIUM AND TANTALUM

PART I. GENERAL STUDY OF VARIABLES*

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The solvent extraction of the thiocyanate complexes of titanium, niobium and tantalum has not been very thoroughly studied; the mechanisms of the processes are not entirely certain, although they are of the ion-association type.

The extraction of titanium thiocyanate with ethyl ether, to form a yellow-orange complex, was first observed by VON DER PFORDTEN[1] in 1886. ROSENHEIM *et al.*[2] synthesized a number of thiocyanate complexes of titanium starting from solutions in ethyl ether; all were strongly coloured, soluble in organic solvents, and decomposed by water. PATSCHEKE AND SCHALLER[3] studied the extraction of titanium(III) and (IV) as thiocyanates with ethyl ether; the extraction was greater with titanium(IV) than with titanium(III). However, BOCK[4] found the opposite. YOUNG AND WHITE[5] and HIBBITS *et al.*[6] reported a very high extraction of titanium thiocyanate with tri-*n*-octyl phosphine oxide.

The extraction of niobium as a thiocyanate complex has been more studied, but more from the point of view of its colorimetric determination than of the extraction process itself. Extraction is good with ethyl ether[7-10], ethyl acetate [11-14], and amines[15]. TROITSKII[16] studied the mechanism of the extraction with butyl alcohol, and concluded that the extracted species is $NbO(SCN)_4H$. WERNER[17] used methyl isobutyl ketone and assigned to the species extracted, the formula $Nb(SCN)_6^-$ associated with oxonium ions of the type $(R_2OH)^+$ where R is an alkyl group.

Tantalum has generally been considered as not extractable as its thiocyanate complex, and the common explanation is its marked tendency to hydrolyze. However, there are some indications that, under particular conditions, extraction is possible[6,15]. VANOSSI[11,12,18] found good extraction of tantalum (as of titanium and niobium) when a solution of these elements in concentrated sulfuric acid was poured into a system consisting of two phases: an aqueous phase containing an adequate concentration of ammonium thiocyanate, equilibrated with an organic phase containing an oxygenated solvent (ethyl acetate).

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In the present work, this extraction system was studied in detail, under different conditions, in order to ascertain if it could be applied to the separation of titanium, niobium and tantalum.

EXPERIMENTAL

Radioactive tracers (^{95}Nb and ^{182}Ta) were used (supplied by the Atomic Energy National Commission of Argentina). Gamma-activity was counted with a scintillation crystal of NaI(Tl), coupled with a photomultiplier tube and a scaler.

Titanium was determined colorimetrically with chromotropic acid[24], using a Beckman B spectrophotometer[25].

Oxides of titanium, niobium and tantalum (Johnson-Matthey spectrographic standard quality) were used. All other reagents were A. R. quality.

The solutions of the elements in concentrated sulfuric acid were stored in semimicro burets (capacity 5 ml, graduated to 0.01 ml and calibrated with concentrated sulfuric acid) with a special container attached (capacity 25 ml), and closed at both ends by tubes containing phosphorus pentoxide. The stopcocks were lubricated with halogenated grease. In this way, hydration was prevented, and the solutions remained stable at least for six months.

Extractions were carried out in 10-ml Pyrex glass tubes, graduated to 0.5 ml, and aliquots of each phase were taken with pipets.

Preparation of the solutions in concentrated sulfuric acid

Titanium and niobium pentoxides were dissolved in hot concentrated sulfuric acid, adding small portions of ammonium sulfate until total dissolution was obtained. About ten parts (by weight) of ammonium sulfate for each part of oxide were necessary. The cold solutions were diluted with concentrated sulfuric acid to a definite volume. Tantalum pentoxide was fused with potassium pyrosulfate (50 parts by weight for each part of oxide), and the melt dissolved with concentrated sulfuric acid and diluted. A small quantity of the corresponding radioisotope was added to the solutions of niobium and tantalum.

Procedure

Equal volumes (4 ml) of aqueous phase (compositions are given below) and organic phase were placed in the extraction tube, and shaken for 30 sec. Then the sulfuric solution was added dropwise and with gentle shaking from the buret. Finally the system was vigorously shaken for 2 min. After 15 to 20 min (to allow phase separation and equilibration with room temperature), the final volumes were read, and aliquots of each phase were taken to measure the activity. In the case of titanium, the aliquots were placed in Pyrex tubes for the colorimetric determination, after destruction of organic matter and fusion with potassium or ammonium pyrosulfate[25].

RESULTS

Effect of the solvent

Table I shows the effect of different solvents on the extraction. It can be seen that extraction is appreciable with oxygenated solvents in the three cases, being better with esters (ethyl and isoamyl acetates) and with isoamyl alcohol. With methyl isobutyl ketone (MIBK), ethyl ether and nitrobenzene, extraction is smaller. Under the same conditions, less titanium is extracted than niobium or tantalum, but the presence of hydrochloric acid enhances remarkably the extraction of titanium.

For the studies of the possibility of separation, ethyl acetate was chosen; this solvent extracts titanium much less than niobium or tantalum, and is easier to evaporate than isoamyl acetate (the other possible solvent). The following data were obtained using ethyl acetate.

TABLE I

EFFECT OF DIFFERENT SOLVENTS ON THE EXTRACTION OF TITANIUM, NIOBIUM AND TANTALUM THIOCYANATES

Element	*Initial concentrations*			*Solvent*	*%E*[a]
	(μg) oxide/ml	*NH_4SCN (M)*	*H_2SO_4 (M)*		
Ti	74	2	1	Ethyl ether	2.0
	30	5	2[b]	Ethyl ether	85.0
	74	0.5	2	Ethyl acetate	*ca.*0
	74	2	1	Ethyl acetate	18.0
	30	5	2[b]	Ethyl acetate	89.5
	74	2	1	Isoamyl alcohol	45.0
	74	2	1	Isoamyl acetate	10.0
	74	2	1	MIBK[c]	3.0
	30	5	2[b]	MIBK[c]	41.7
	74	2	1	Nitrobenzene	0.7
	74	2	1	Chloroform	0.5
	30	5	2[b]	Carbon tetrachloride	3.3
	30	5	2[b]	Benzene	8.3
Nb	40	2	1	Ethyl ether	27.5
	40	1	1	Ethyl acetate	97.8
	40	1	1[b]	Ethyl acetate	99.5
	40	5	2	Ethyl acetate	99.5
	40	2	1	Isoamyl alcohol	99.0
	40	2	1	Isoamyl acetate	99.0
	40	2	1	MIBK[c]	95.0
	40	2	1	Nitrobenzene	85.2
	40	2	1	Chloroform	1.0
Ta	25	2	1	Ethyl ether	18.5
	25	4	0.5	Ethyl ether	73.5
	25	0.5	2	Ethyl acetate	42.0
	25	2	1	Ethyl acetate	99.0
	25	4	2	Ethyl acetate	99.5
	25	4	0.5	Isoamyl alcohol	99.5
	25	2	1	Isoamyl acetate	99.0
	25	4	0.5	Isoamyl acetate	99.5
	25	4	0.5	MIBK[c]	96.0
	25	4	0.5	Nitrobenzene	60.5
	25	4	0.5	Chloroform	6.0

[a] Each figure is the mean of two determinations.
[b] 3 *M* HCl.
[c] Methyl isobutyl ketone.

Variation of the volume of the phases

In all the experiments carried out, a marked increase in the volume of the organic phase was observed. In Table II these variations are expressed as the percentage increase. This increase depends on the concentration of thiocyanate, sulfuric acid and other reagents present. The presence of titanium, niobium or tantalum does not affect the increase in volume.

Extraction of the elements

Figure 1 shows the results for the extraction of titanium thiocyanate for different initial concentrations of ammonium thiocyanate and sulfuric acid. In Figs. 2 and 3 the influence of hydrochloric acid is shown. The sulfate ion has a depressing influence: with 4 M ammonium sulfate the extraction is about 0.1% (instead of 4% in its absence) if the initial conditions are 1 M thiocyanate, 1 M sulfuric acid, and 74 μg TiO_2/ml. Varying the concentration of titanium between 1 and 530 μg TiO_2/ml has no effect on the percentage extraction (with, initially, 1, 2, and 3.5 M thiocyanate and 1 M sulfuric acid).

TABLE II

INCREASE IN VOLUME OF THE ORGANIC PHASE EXPRESSED AS PERCENTAGE INCREASE
(Initial volumes: 4 ml each phase)

NH_4SCN initial (M)	*% Volume increase*				
	H_2SO_4 initial (M)				
	1	*2*	*3*	*4*	*5*
1	0	5	5	5	5
2	5	12	15	12	7
3	7	15	20	20	15
4	8	17	20	22	22
5	10	20	22	25	25

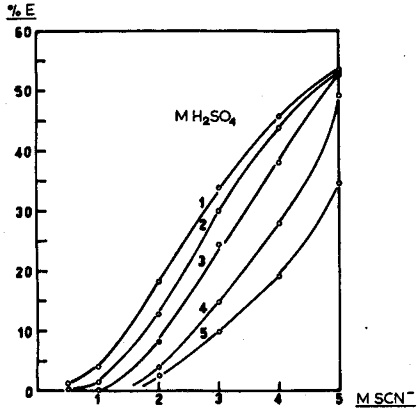

Fig. 1. Effect of sulfuric acid on the extraction of titanium thiocyanate. Initial TiO_2: 74 μg/ml. Initial volumes: 4 ml each phase.

The corresponding data for niobium are summarized in Fig. 4. The presence of hydrochloric acid again enhances the extraction (see Table I). In the presence of 1 M ammonium sulfate, 1 M thiocyanate and 1 M sulfuric acid, extraction is 95%, instead of 98% without sulfate. Varying the concentration of niobium between 0.4 and 360 μg

Nb_2O_5/ml causes no change in the percentage extraction (with, initially, 1 and 2 M thiocyanate and 1 M sulfuric acid).

In the case of tantalum, the extraction for different initial concentrations of thiocyanate and sulfuric acid is given in Fig. 5, and the effect of hydrochloric acid in Fig. 6. The presence of sulfate again decreases the extraction: for 1 M NH_4SCN, 1 M H_2SO_4 and 1.5 M $(NH_4)_2SO_4$ (50 μg Ta_2O_5/ml), extraction is 63% complete, instead of 98% without sulfate. For initial concentrations of 2 M thiocyanate and 1 M sulfuric acid, the percentage extraction remains constant over the range 1–430 μg Ta_2O_5/ml.

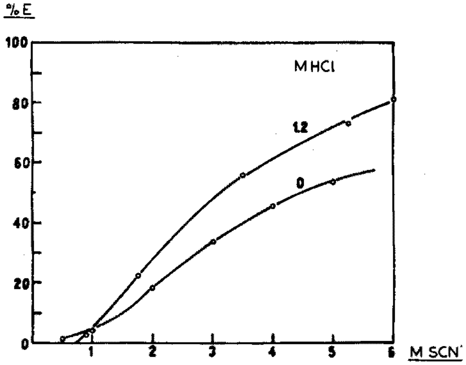

Fig. 2. Effect of hydrochloric acid on the extraction of titanium thiocyanate Initial conditions: 1 M H_2SO_4; 74 μg TiO_2/ml; 4 ml each phase.

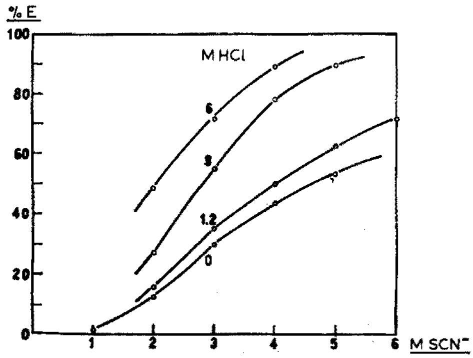

Fig. 3. Effect of hydrochloric acid on the extraction of titanium thiocyanate. Initial conditions: 2 M H_2SO_4; 74 μg TiO_2/ml; 4 ml each phase.

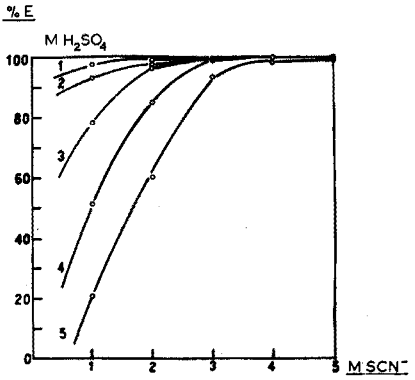

Fig. 4. Effect of sulfuric acid on the extraction of niobium thiocyanate. Initial Nb_2O_5: 40 μg/ml. Initial volumes: 4 ml each phase.

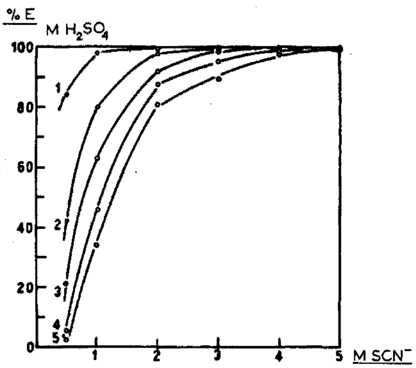

Fig. 5. Effect of sulfuric acid on the extraction of tantalum thiocyanate. Initial Ta_2O_5: 50 μg/ml. Initial volumes: 4 ml each phase.

Back-extraction of the elements

When the organic phase is treated with different reagents, back-extraction occurs in various degrees. Tables III, IV and V show the results for titanium, niobium and tantalum respectively; 4 ml of aqueous phase were always used.

Absorption spectra

Figure 7 shows the absorption spectra of the thiocyanate complexes in ethyl acetate. The presence of tin(II) chloride is necessary to avoid the interference of iron(III), and the hydrochloric acid present comes from the tin(II) solution.

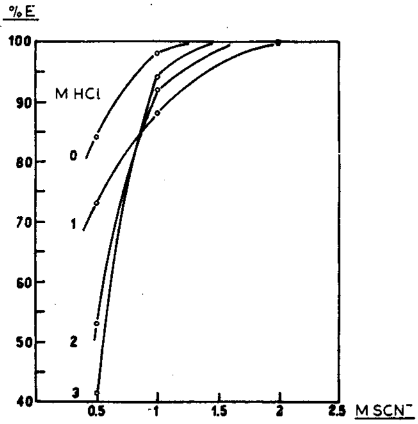

Fig. 6. Effect of hydrochloric acid on the extraction of tantalum thiocyanate. Initial conditions: 1 M H_2SO_4; 50 μg Ta_2O_5/ml; 4 ml each phase.

TABLE III

BACK-EXTRACTION OF TITANIUM

(Initial TiO_2: 74 μg/ml. Initial volumes: 4 ml each phase)

Initial conditions of extraction	*Conditions of back-extraction*	% *R*[a]
1 M SCN^-; 1 M H_2SO_4	0.5 M HCl	>99
1 M SCN^-; 1 M H_2SO_4	1.5 M HCl	>99
1 M SCN^-; 1 M H_2SO_4	0.5 M H_2SO_4	98–99
1 M SCN^-; 1 M H_2SO_4	1.5 M H_2SO_4	98–99
1 M SCN^-; 1 M H_2SO_4	0.05 M HF	>99
1 M SCN^-; 1 M H_2SO_4	0.25 M HF	98–99
2 M SCN^-; 1 M H_2SO_4	0.5 M HCl	98–99
2 M SCN^-; 1 M H_2SO_4	1 M HF–6 M HCl	98–99
4 M SCN^-; 2 M H_2SO_4[b]	0.5 M HCl	*ca.* 80

[a] % R = percentage of Ti recovered compared to the initial concentration in the combined aqueous phases.
[b] 3 M HCl.

Titanium shows a maximum at 395 mμ, and niobium at 385 mμ which agrees with the values given by other authors[8–10,17,19–22] for other solvents. For tantalum a maximum is found between 330 and 335 mμ; this has not been reported previously. The relative positions of the bands are the same as those of the peroxy complexes in concentrated sulfuric acid[23] although in this case the bands are closer together.

DISCUSSION

From the data presented it is possible to draw some general qualitative conclusions.

TABLE IV

BACK-EXTRACTION OF NIOBIUM

(Initial Nb_2O_5: 40 µg/ml. Initial volumes: 4 ml each phase)

Initial conditions of extraction	*Conditions of back-extraction*	% *R*[a]
1 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HCl	*ca.* 0
1 *M* SCN^-; 1 *M* H_2SO_4	1.5 *M* HCl	*ca.* 0
1 *M* SCN^-; 1 *M* H_2SO_4	0.01 *M* HF	86.5
1 *M* SCN^-; 1 *M* H_2SO_4	0.05 *M* HF	>99
1 *M* SCN^-; 1 *M* H_2SO_4	0.10 *M* HF	>99
1 *M* SCN^-; 1 *M* H_2SO_4	0.50 *M* HF	>99
1 *M* SCN^-; 1 *M* H_2SO_4	1.00 *M* HF	>99
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HCl	*ca.* 0
2 *M* SCN^-; 1 *M* H_2SO_4	1.5 *M* HCl	*ca.* 0
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF–4 *M* HCl	98–99
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF–6 *M* HCl	*ca.* 90
2 *M* SCN^-; 1 *M* H_2SO_4	1.0 *M* HF–4 *M* HCl	*ca.* 80
2 *M* SCN^-; 1 *M* H_2SO_4	1.0 *M* HF–6 *M* HCl	*ca.* 65

[a] % R = percentage of Nb recovered compared to the initial concentration in the combined aqueous phases.

TABLE V

BACK-EXTRACTION OF TANTALUM

(Initial Ta_2O_5: 50 µg/ml. Initial volumes: 4 ml each phase)

Initial conditions of extraction	*Conditions of back-extraction*	% *R*[a]
1 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HCl	*ca.* 0
1 *M* SCN^-; 1 *M* H_2SO_4	0.05 *M* HF	71.0
1 *M* SCN^-; 1 *M* H_2SO_4	0.1 *M* HF	53.5
1 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF	27.0
1 *M* SCN^-; 1 *M* H_2SO_4	1.0 *M* HF	18.0
1 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF–4 *M* HCl	10.0
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HCl	*ca.* 0
2 *M* SCN^-; 1 *M* H_2SO_4	1.5 *M* HCl	*ca.* 0
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF–4 *M* HCl	6.0
2 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HF–6 *M* HCl	3.0
2 *M* SCN^-; 1 *M* H_2SO_4	1.0 *M* HF–4 *M* HCl	4.0
2 *M* SCN^-; 1 *M* H_2SO_4	1.0 *M* HF–6 *M* HCl	*ca.* 1
2 *M* SCN^-; 1 *M* H_2SO_4	2% citric acid (w/v)	8.0
2 *M* SCN^-; 1 *M* H_2SO_4	2% tartaric acid (w/v)	33.5
2 *M* SCN^-; 1 *M* H_2SO_4[b]	4% ammonium oxalate (w/v) + 1% H_2SO_4	>99.0
3 *M* SCN^-; 1 *M* H_2SO_4[b]	0.5 *M* HF	17.0
4 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* HCl	*ca.* 0
4 *M* SCN^-; 1 *M* H_2SO_4	0.5 *M* H_2SO_4	*ca.* 0

[a] % R = percentage of Ta recovered compared to the initial concentration in the combined aqueous phases.

[b] 3 *M* HCl.

In the first place, it is clear that a thiocyanate complex of tantalum exists and that the described procedure allows its formation and extraction.

The increase in volume of the organic phase during the extraction is probably due to the extraction of thiocyanic acid which carries water of hydration. The extraction of thiocyanic acid increases as the concentrations of thiocyanate and acid increase[4].

With high acid concentrations, the solubility of ethyl acetate in the aqueous phase increases, and the relative increase in volume of the organic phase is smaller.

The extraction of the three elements increases as the concentration of thiocyanate increases, but decreases as the concentration of sulfuric acid is increased. This may have two causes: (*a*) competition between thiocyanate complexes in the organic phase and sulfate complexes in the aqueous phase (as is shown by the influence of sulfate ions), and (*b*) the decrease in the concentration of thiocyanate in the aqueous phase owing to an increase in the extraction of thiocyanic acid and as the acidity is augmented. The results for niobium and tantalum are very similar, and suggest an identical mechanism.

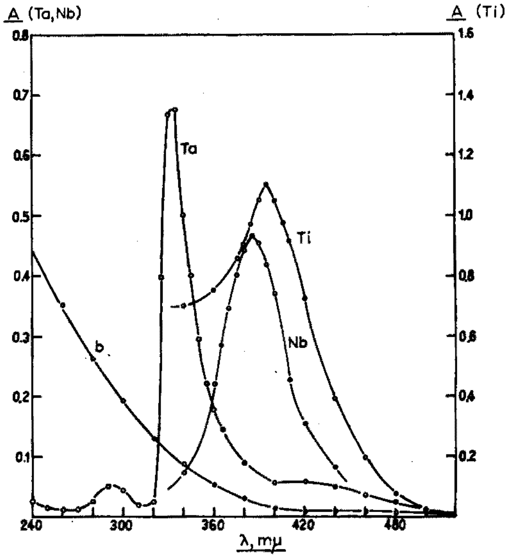

Fig. 7. Absorption spectra of titanium, niobium and tantalum thiocyanates in ethyl acetate Reagent blank as reference. Composition of the initial aqueous phase: 1.6 *M* NH_4SCN, 0.8 *M* H_2SO_4, 0.8 *M* HCl, 0.14 *M* $SnCl_2$, 62.5 μg TiO_2/ml, 4.25 μg Nb_2O_5/ml, 74.5 μg Ta_2O_5/ml. Initial volumes: aqueous phase 26 ml; organic phase 20 ml. Under these conditions, the values of extraction are approximately 20% for Ti, 98% for Nb, and 99% for Ta. b = reagent blank.

The effect of hydrochloric acid may be explained on the basis of an ion-association mechanism. Increasing the acidity increases the concentration of oxonium ions in the aqueous phase, and extraction is enhanced. The lowering of the dielectric constant of the aqueous phase at higher acidity may also be important. Increasing the concentration of hydrochloric acid and decreasing that of thiocyanate, decreases the extraction of the metals because of the extraction of thiocyanic acid, as shown above. This effect is very marked with tantalum. However, for high concentrations of hydrochloric acid, extraction of tantalum increases again. For example, with 0.5 *M* thiocyanate, 1 *M* sulfuric acid, 5 *M* hydrochloric acid and 50 μg Ta_2O_5/ml, the percentage extraction lies between 70 and 80%. This suggests the possibility of extraction of chloro-complexes of tantalum. It was found that when 6 *M* hydrochloric and 1 *M* sulfuric acid were applied without thiocyanate, the extraction was about 5–10 % complete; however, the reproducibility under these conditions was very poor, probably owing to the hydrolysis of tantalum.

Finally, the constant values found for the percentage extractions over a wide concentration range of the elements, may be due to the low dielectric constant of ethyl acetate, which made the dissociation of ionic associations in the organic phase negligible.

The author wishes to thank Professor Dr. R. VANOSSI (University of Buenos Aires, Argentina) for helpful advice during this work, and Drs. A. E. LAGOS and H. A. MOTTOLA for valuable suggestions on the manuscript.

SUMMARY

The solvent extraction of titanium, niobium and tantalum thiocyanates is studied in detail. The effect of the variables (solvent, concentration of thiocyanate, acidity, etc.) is discussed. There is evidence for the existence of a thiocyanate complex of tantalum.

RÉSUMÉ

L'auteur a effectué une étude sur l'extraction dans un solvant des thiocyanates de titane, de niobium et de tantale. L'influence de divers facteurs a été examinée (solvant, concentration du thiocyanate, acidité, etc.). L'existence d'un complexe du tantale avec le thiocyanate est indiquée.

ZUSAMMENFASSUNG

Es wird die Extraktion der Titan-, Niob- und Tantalthiocyanate untersucht. Der Einflusz des Lösungsmittels, der Thiocyanat-Konzentration, der Säurekonzentration u.a. wird diskutiert und die Existenz eines Thiocyanatkomplexes des Tantals aufgewiesen.

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THE SOLVENT EXTRACTION OF THE THIOCYANATE COMPLEXES OF TITANIUM, NIOBIUM AND TANTALUM

PART II. APPLICATION TO THE SEPARATION OF MIXTURES

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The data on the extraction of thiocyanate complexes collected in Part I of this work[1] suggested the possibility of separating micro quantities of titanium, niobium and tantalum by extraction with ethyl acetate at low concentrations of ammonium thiocyanate (1 or 2 *M*) and sulfuric acid (1 *M*), and back-extraction of the titanium with dilute hydrochloric acid (0.5 *M*). It is possible to recover the small residual quantities of niobium when 1 *M* thiocyanate is used, by carrying out a re-extraction after the addition of more thiocyanate. In the case of tantalum, this procedure is ineffective because of hydrolysis effects. When 2 *M* thiocyanate is used, extraction of niobium and tantalum is essentially quantitative, and re-extraction is unnecessary. Table I

TABLE I

RECOVERY OF NIOBIUM AND TITANIUM USING DOUBLE EXTRACTION AND SUBSEQUENT BACK-EXTRACTION WITH 0.5 *M* HCl

Element	*Conditions of extraction*	*Conditions of re-extraction*	$\% E'$[a]	$\% R$[b]
Ti	1 *M* SCN^-, 1 *M* H_2SO_4	c	0	99
	1 *M* SCN^-, 1 *M* H_2SO_4	d	5.0	99
	1 *M* SCN^-, 1 *M* H_2SO_4	e	10.0	97–98
	2 *M* SCN^-, 1 *M* H_2SO_4	c	0	99
	2 *M* SCN^-, 1 *M* H_2SO_4	d	10.0	98–99
	2 *M* SCN^-, 1 *M* H_2SO_4	e	20.0	97–98
Nb	1 *M* SCN^-, 1 *M* H_2SO_4	c	0	98.0
	1 *M* SCN^-, 1 *M* H_2SO_4	d	*ca.* 95	99
	1 *M* SCN^-, 1 *M* H_2SO_4	e	*ca.* 99	99
	2 *M* SCN^-, 1 *M* H_2SO_4	c	0	98–99
	2 *M* SCN^-, 1 *M* H_2SO_4	d	98–99	99
	2 *M* SCN^-, 1 *M* H_2SO_4	e	99	99

[a] $\% E'$ = percentage extracted in the re-extraction referred to the amount of the element remaining in the aqueous phase after the first extraction.

[b] $\% R$ = percentage recovery of the element referred to the initial value. For Ti, in the combined aqueous phases and for Nb in the combined organic phases.

[c] Without adding NH_4SCN.

[d] Adding half of the initially added NH_4SCN.

[e] Adding an amount equal to the initially added NH_4SCN.

summarizes the results obtained by double extraction. In the case of tantalum, any further extraction occurred during the re-extraction, whatever initial conditions were used.

From Table I it can be observed that there are two possibilities for mixtures of titanium and niobium: (*a*) to extract with 1 *M* thiocyanate and 1 *M* sulfuric acid, repeat the extraction with half the amount of thiocyanate initially added, and then back-extract the titanium with 0.5 *M* hydrochloric acid, or (*b*) to extract with 2 *M* thiocyanate and 1 *M* sulfuric acid (without re-extraction) and back-extract the titanium as before.

For mixtures of titanium and tantalum, recoveries of tantalum are acceptable only by the second alternative. When the ratio Ti/Ta is high, it is necessary to back-extract the last traces of titanium with a mixture of hydrofluoric and hydrochloric acids, if tantalum is to be determined colorimetrically by the usual pyrogallol method.

Further separation of niobium and tantalum is accomplished by back-extracting the niobium with a mixture of hydrofluoric and hydrochloric acids. In this case, the last traces of titanium accompany niobium, but this does not cause an appreciable error in the determination of the elements.

The following procedures were checked with mixtures of the elements concerned. The final determinations were made colorimetrically, but any other suitable method could be applied after the separations.

EXPERIMENTAL

Apparatus and reagents

Absorptiometric determinations were made in a Beckman Model B spectrophotometer, with Pyrex cells of 1 cm.

Oxides of titanium, niobium and tantalum (Johnson-Matthey "Spec-pure" quality) were used as standards and for the preparation of the mixtures.

Separatory funnels (Pyrex, 100 ml) were used. The relatively low concentrations of hydrofluoric acid used attack Pyrex glass very little; however, polyethylene funnels may be used advantageously.

Procedures for the separations

Mixtures of the oxides of the elements were dissolved in concentrated sulfuric acid as described previously[1]. The sulfuric acid solutions were made up to a standard volume, with the same solvent, and aliquots of these solutions were added to the system containing aqueous phase and organic phase, by means of a pipet previously calibrated with concentrated sulfuric acid. The quantity of acid added in this way must be taken into account for the final acidity.

Procedure A: *For mixtures of titanium and niobium.* Place in a separatory funnel 10 ml of 1 *M* ammonium thiocyanate and 10 ml of ethyl acetate, and shake for 30 sec. Add dropwise with gentle shaking 0.5 ml of the sulfuric acid solution. Shake vigorously for 2 min and allow to stand for about 15 min. Transfer the aqueous phase to another funnel, add 2.5 ml of 2 *M* thiocyanate and 10 ml of ethyl acetate, shake for 2 min and allow to stand for 15 min. Transfer the aqueous layer to a volumetric flask (25 or 50 ml). Transfer the organic layer to the first funnel, add 10 ml of 0.5 *M* hydrochloric acid and shake for 2 min. Allow to stand for 15 min and transfer the aqueous phase to the flask. Dilute to the mark with sulfuric acid (1:9), and take an aliquot for the determination of titanium. Transfer the organic phase to a volumetric flask (25 or 50 ml), dilute to the mark with ethyl acetate, and take an aliquot for the determination of niobium.

Procedure B: *For mixtures of titanium and niobium.* Place in a separatory funnel 10 ml of 2 *M* ammonium thiocyanate and 10 ml of ethyl acetate. Shake for 30 sec. Add 0.5 ml of the sulfuric acid solution as described in Procedure A. Shake vigorously for 2 min and allow to stand for 15 min. Transfer the aqueous phase to a volumetric flask. Add to the funnel 10 ml of 0.5 *M* hydrochloric acid and shake for 2 min. Allow to stand 15 min, and transfer the aqueous layer to the flask. Complete the procedure as described for Procedure A, for dilution and aliquotting.

Procedure C: *For mixtures of titanium and tantalum.* Operate in the same way as in Procedure B, up to the back-extraction of titanium. If $TiO_2:Ta_2O_5$ exceeds 1, repeat the washing of the organic phase with 10 ml of 0.5 *M* hydrochloric acid, adding 1 ml of ethyl acetate (in order to compensate for the solubility of ethyl acetate in the aqueous phase). If the ratio exceeds 50/1, wash the organic phase (after the two washings with 0.5 *M* HCl) with 10 ml of 1 *M* HF–6 *M* HCl, adding 2 ml of ethyl acetate. In each case, collect the aqueous phases in a volumetric flask, dilute to a definite volume with sulfuric acid (1:9), and take an aliquot for the determination of titanium. Transfer the organic layer to a volumetric flask, and dilute to the mark with ethyl acetate; take an aliquot for the determination of tantalum.

Procedure D: *For mixtures of titanium, niobium and tantalum.* Operate in the same way as in Procedure B, up to the back-extraction of titanium. For large quantities of titanium (see Procedure C), repeat the treatment of the organic layer with 0.5 *M* hydrochloric acid. Collect all the aqueous phases in a volumetric flask, dilute to the mark with sulfuric acid (1:9), and determine titanium in an aliquot. Adding 2 ml of ethyl acetate each time, wash the organic layer three times with 10-ml portions of 1 *M* HF–6 *M* HCl. Collect the aqueous phases in a volumetric flask, dilute to the mark with sulfuric acid (1:9), and take an aliquot for the determination of niobium. Transfer the organic layer to a volumetric flask, dilute to the mark with ethyl acetate, and determine tantalum in an aliquot.

General procedure for decomposition of organic matter before colorimetry. Place the aliquots taken for the determinations of the elements in Pyrex tubes (*ca.* 10 × 1.5 cm). Evaporate cautiously to near dryness. Cool and add several drops of concentrated sulfuric acid and concentrated nitric acid and heat until sulfur trioxide fumes are evolved. Repeat the operation with more sulfuric and nitric acids with the addition of 2–3 drops of concentrated perchloric acid. Add about 100 mg of ammonium sulfate, and heat until the excess of sulfuric acid is eliminated and ammonium bisulfate begins to boil[2]. In all these operations it is advantageous to blow air into the tube to accelerate evaporation. Cool and dissolve the solid melt in the appropriate reagent (see below).

When hydrofluoric acid is present, place the aliquot in a quartz tube (*ca.* 10 × 1.5 cm) and add a few drops of concentrated sulfuric acid and 5–10 mg of boric acid. Evaporate to sulfur trioxide fumes. Add 3–4 ml of methyl alcohol and evaporate again to fumes. Repeat, if necessary, the treatment with methyl alcohol until boric acid has been eliminated. Then add more concentrated sulfuric and nitric acids and proceed as described above.

Determination of titanium

The chromotropic acid (CTA) method was chosen because it is sensitive and there is no interference from niobium. This method has been widely used[3-8]. For the determination of titanium in the presence of niobium, oxalic acid has been proposed in the medium[9]. This technique with some modifications (mainly in the reagent solution) was adapted for the present work.

KLINGER AND KOCH[9] recommended a 6% (w/v) solution of CTA, and added 10 ml for a final volume of 100 ml. However, such solutions are unstable and become dark with time, owing to oxidation of CTA. Solutions of CTA are more stable when dilute and stored in the dark, and when sulfurous acid is added. In this work, the solutions were prepared in the following way. Dissolve 1 g of CTA (disodium salt, recrystallized) and 0.1 g of sodium bisulfite in 50 ml of water, warming to 70–80°. Cool, filter and dilute to 100 ml. These solutions are stable for more than six months.

Solutions of CTA absorb strongly in the near ultraviolet region but above 400 mμ absorption is negligible. The spectrum of the Ti–CTA complex shows a maximum at 470 mμ in sulfuric or oxalic acid medium. At this wavelength the absorbance increases as the concentration of CTA increases. The optimum quantity of reagent was found to be 1 ml of the CTA solution for a final volume of 10 ml. With larger amounts of CTA, the sensitivity was higher, but blanks were also very high, and the solutions became more unstable towards light.

Procedure. Dissolve the melt obtained after decomposition of organic matter, in the same tube with 3–4 ml of 2% oxalic acid and boil until complete dissolution is achieved. Cool and transfer to a 10-ml volumetric flask. Wash the tube with a few portions of 2% oxalic acid and transfer to the flask. Add 1 ml of CTA solution and dilute to the mark with 2% oxalic acid. The colour develops almost instantaneously. Read the absorbance at 470 mμ against a reagent blank.

For the calibration curve, between 0 and 150 μg TiO_2/10 ml, the plot of absorbance *vs.* μg TiO_2 is a straight line, with a sensitivity[10] of 0.025 μg TiO_2/cm^2.

In this procedure, 800 μg of Nb_2O_5, 320 μg of Ta_2O_5, 32 μg of Fe_2O_3, and 100 mg of $(NH_4)_2SO_4$ do not interfere (the error in the determination of 10 μg of TiO_2 is less than 2%).

Determination of niobium

Extraction-colorimetry with thiocyanate was used, because of its high sensitivity and few interferences compared with other methods for niobium[10-24]. The directions of BUKHSH AND HUME[13] were followed, with some modifications: (*a*) the use of ethyl acetate instead of ethyl ether, since the latter is so volatile; (*b*) the use of only one extraction, because the sensitivity so achieved sufficed for the present purpose.

Procedure. Dissolve the melt in the digestion tube with 3 ml of 5% tartaric acid by boiling gently. Cool. Transfer to an extraction tube (Pyrex, 12 × 2.5 cm) and dilute to 5 ml with the 5% tartaric acid with which the tube has been washed. Add 2 ml of 8 *M* ammonium thiocyanate, 5 ml of 10% tin(II) chloride (in hydrochloric acid 1 : 3), and 5 ml of 8 *M* hydrochloric acid. Shake for 30 sec. Add 10 ml of ethyl acetate, and shake vigorously for 2 min. Let stand for 15 min. Use a dry pipet to transfer an appropriate quantity of the organic layer to fill the cells of the spectrophotometer. Read the absorbance at 385 mμ against a reagent blank.

The calibration curve must be constructed starting from a standard solution of niobium and following the described procedure (including evaporation, destruction and fusion with ammonium bisulfate). Between 0 and 20 μg Nb_2O_5 the plot of absorbance *vs.* μg Nb_2O_5 is a straight line. The sensitivity is 0.002 μg Nb_2O_5/cm^2.

The extraction was checked by means of niobium-95 (see Part I[1] for details) with three different solvents; the procedure described for the determination of niobium was applied. With ethyl acetate, 86.5% extraction was found, with ethyl ether 88.5%, and with isoamyl acetate 85.5%. In all three cases, the absorption maximum was found at 385 mμ, and the sensitivity was of the same order.

In the described procedure, 400 μg of TiO_2 and 400 μg of Ta_2O_5 do not interfere in the determination of 20 μg of Nb_2O_5 (error less than 2%). Sulfuric acid interferes, but its interference is avoided by running the calibration curve as described.

Determination of tantalum

For the determination of tantalum the pyrogallol method was used. This is the colorimetric method most widely applied for tantalum[25-37], but it has two main disadvantages: low sensitivity, and high interference from titanium. The directions of HUNT AND WELLS[31] were followed, but the solution of pyrogallol was prepared as described by MARZYS[27], because the solutions recommended by the former authors were stable only for a few days.

Solutions of pyrogallol absorb continuously between 360 and 560 mμ. The tantalum–pyrogallol complex shows a maximum at 400 mμ under the described conditions. As the concentration of pyrogallol is increased, the absorbance due to the same quantity of tantalum increases, and with 8 g of pyrogallol/100 ml, precipitation occurs. The optimum quantity of reagent was found to be 2 ml of the 20% solution for final volume of 10 ml.

Pyrogallol solution (*20%, w/v*). Dissolve 50 g of pyrogallol (resublimated) in boiled water; add 25 ml of concentrated HCl and 10 ml of 2 *M* $SnCl_2$ (in 1:3 HCl). Filter and dilute to 250 ml with distilled and boiled water. This solution is stable at least for three months if stored in the dark.

Procedure. Dissolve the melt in the decomposition tube with 3–4 ml of a boiling saturated ammonium oxalate solution; boil gently to complete the dissolution. Cool. Transfer to a 10-ml volumetric flask. Wash the tube with the boiling ammonium oxalate solution, and transfer the washings to the flask. Add 2 ml of the pyrogallol solution and dilute to the mark with the ammonium oxalate solution. Homogenize and let stand for 15 min. Read the absorbance at 400 mμ against a reagent blank.

The calibration curve must be constructed by taking a standard solution of tantalum through the described procedure (including evaporation, etc.). Between 0 and 225 μg Ta_2O_5 in 10 ml, Beer's law holds. The sensitivity is 0.044 μg Ta_2O_5/cm^2.

Interference of titanium is very serious. This element forms a complex with pyrogallol which shows an absorption maximum at 400 mμ. One part of TiO_2 produces, at this wave length, the same absorbance as 4 parts of Ta_2O_5. This means that, even although the separations by the described procedure are effective (*e.g.* 99.5% of the titanium can be recovered), the data obtained for tantalum would be very erroneous if the ratio $TiO_2:Ta_2O_5$ were high. In this work, this problem was solved (for the Ti : Ta ratios studied), by using the back-extractions for titanium with 0.5 *M* HCl and HF–HCl mixtures.

The presence of 660 μg of Nb_2O_5 and 32 μg of Fe_2O_3 produces an error of less than 2% in the determination of 50 μg of Ta_2O_5. The interference of sulfate is eliminated by preparing the calibration curve as described.

Boric acid depresses the absorbance, probably owing to combination with the phenolic groups of pyrogallol. In the presence of 800 µg of boric acid per ml, 8.5 µg of Ta_2O_5 were found instead of the 10 µg added. It is important, therefore, to eliminate completely all the boric acid if this was used to assist the removal of hydrofluoric acid in the evaporation.

TABLE II

SEPARATION OF TITANIUM AND NIOBIUM BY "PROCEDURE A"
(Results are the mean of two determinations)

Added (µg)		*Ratio*	*Found (µg)*		*Absolute error (µg)*		*Relative error (%)*	
Nb_2O_5	TiO_2	$Nb_2O_5:TiO_2$	Nb_2O_5	TiO_2	Nb_2O_5	TiO_2	Nb_2O_5	TiO_2
4	1998	1 : 500	4.0	2000	—	+2.0	—	+0.1
8	592	1 : 75	8.0	597	—	+5.0	—	+1.0
40	666	1 : 17	39.9	665	−0.1	−1.0	−0.3	−0.2
200	370	1 : 2	198.0	369	−2.0	−1.0	−1.0	−0.3
384	29.5	13 : 1	379.0	29.2	−5.0	−0.3	−1.3	−1.0
360	7.5	50 : 1	362.0	7.4	+2.0	−0.1	+0.5	−2.0
1080	7.5	145 : 1	1080.0	8.0	—	+0.5	—	+6.0
3600	7.5	480 : 1	3589.0	7.5	−11.0	—	−0.3	—

TABLE III

SEPARATION OF TITANIUM AND NIOBIUM BY "PROCEDURE B"
(Results are the mean of two determinations)

Added (µg)		*Ratio*	*Found (µg)*		*Absolute error (µg)*		*Relative error (%)*	
Nb_2O_5	TiO_2	$Nb_2O_5:TiO_2$	Nb_2O_5	TiO_2	Nb_2O_5	TiO_2	Nb_2O_5	TiO_2
4	1998	1 : 500	5.8	1995.0	−0.2	−0.3	−5.0	−0.2
80	7.5	10 : 1	79.0	7.4	−1.0	−0.1	−1.1	−2.0
1080	7.5	145 : 1	1062.0	7.5	−18.0	—	−2.0	—

TABLE IV

SEPARATION OF TITANIUM AND TANTALUM BY "PROCEDURE C"
(Results are the mean of two determinations)

Added (µg)		*Ratio*	*Found (µg)*		*Absolute error (µg)*		*Relative error (%)*	
Ta_2O_5	TiO_2	$Ta_2O_5:TiO_2$	Ta_2O_5	TiO_2	Ta_2O_5	TiO_2	Ta_2O_5	TiO_2
4298	7.5	574 : 1	4225.0	7.5	−7.3	—	−2.0	—
965	7.5	130 : 1	956.5	7.3	−8.5	−0.2	−1.0	−4.0
772	148	5.2 : 1	761.0	147.5	−11.0	−0.5	−1.5	−0.5
386	444	1 : 1.1	380.0	440.0	−6.0	−4.0	−1.5	−1.0
42	740	1 : 17	41.0	738.0	−1.0	−2.0	−2.5	−0.3
10	6168	1 : 635	11.0	6150.0	+1.0	−18.0	+10.0	−0.3

RESULTS

Tables II, III, IV and V show the results obtained with various mixtures of titanium, niobium and tantalum when the corresponding procedures were applied.

TABLE V

SEPARATION OF TITANIUM, NIOBIUM AND TANTALUM BY "PROCEDURE D"
(Results are the mean of two determinations)

No.	*Composition of the mixtures*				*Results of the separation*								
	Added (µg)			*Approximate ratio*	*Found (µg)*			*Absolute error (µg)*			*Relative error (%)*		
	TiO_2	Nb_2O_5	Ta_2O_5	$TiO_2 : Nb_2O_5 : Ta_2O_5$	TiO_2	Nb_2O_5	Ta_2O_5	TiO_2	Nb_2O_5	Ta_2O_5	TiO_2	Nb_2O_5	Ta_2O_5
1	518	8	96.5	50 : 1 : 10	519.0	7.8	95.0	+1.0	−0.2	−1.5	+0.2	−2.5	−1.5
2	2825	320	10	300 : 30 : 1	2817.5	312.5	9.5	−7.5	−7.5	−0.5	−0.3	−2.0	−5.0
3	74	1080	10	7 : 100 : 1	72.5	1050.0	9.5	−1.5	−30.0	−0.5	−2.0	−3.0	−5.0
4	7.5	1080	96.5	1 : 100 : 10	7.5	1052.5	95.0	—	−27.5	−1.5	—	−3.0	−1.0
5	74	8	772	10 : 1 : 100	73.0	7.7	762.0	−1.0	−0.3	−10.0	−1.5	−4.0	−1.5
6	7.5	80	772	1 : 10 : 100	7.5	78.0	762.0	—	−2.0	−10.0	—	−2.5	−1.5

DISCUSSION

The methods outlined may be applied directly to mixtures of titanium, niobium and tantalum in their maximum valence states. In the mixtures studied, the amounts of "total oxides" ($TiO_2 + Nb_2O_5 + Ta_2O_5$) varied from a few micrograms to about 6 mg, volumes of 10 ml being used for each phase. This indicates a wide possibility of application at the level of micro-quantities and, with some modifications, for sub-micro and also macro quantities.

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SUMMARY

Solvent extraction of the thiocyanate complexes of titanium, niobium and tantalum allows the separation of micro quantities of these elements. Niobium and tantalum are separated by selective extraction of the fluoro-complexes. Mixtures of Ti and Nb, or of Ti and Ta in ratios of 500 : 1 to 1 : 500 can be separated. For mixtures of the three elements, results were acceptable with Nb : Ta ratios of 100 : 1 to 1 : 100. Colorimetric determinations of the three elements are described.

RÉSUMÉ

L'extraction par solvant des complexes thiocyanés du titane, du niobium et du tantale permet la séparation de microquantités de ces éléments. Nb et Ta sont séparés par extraction sélective des fluorocomplexes. Des mélanges de Ti et Nb ou Ti et Ta, dans des rapports de 500 : 1 à 1 : 500 peuvent être séparés. Pour des mélanges des 3 éléments, les résultats sont acceptables pour des rapports Nb : Ta 100 : 1 à 1 : 100. Des dosages colorimétriques de ces 3 éléments sont décrits.

ZUSAMMENFASSUNG

Mikromengen der Elemente Titan, Niob und Tantal können durch Extraktion ihrer Thiocyanat-Komplexe getrennt werden. Vorher werden Niob und Tantal durch selektive Extraktion der Fluoro-Komplexe abgetrennt. Es lassen sich Mischungen von Titan und Niob oder von Titan und Tantal im Verhältnis von 500 : 1 bis 1 : 500 trennen. Für Mischungen dieser drei Elemente werden brauchbare Ergebnisse erzielt bei Niob : Tantal von 100 : 1 bis 1 : 100. Kolorimetrische Bestimmungen der drei Elemente werden beschrieben.

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THE REMOVAL OF Ce, Nd, Pr AND La FROM Er, Dy, Gd, Eu AND Sm BY ANION EXCHANGE

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In the spectrochemical analysis of trace amounts of Er, Dy, Gd, Eu and Sm (rare earths with high thermal neutron absorption cross-sections) isolated from thorium and uranium compounds by ion exchange[1-4], solvent extraction[5,6] or precipitation procedures[7,8], the presence of other rare earth elements, especially Ce, Nd and Pr, must be considered**. The complex emission spectra of Ce, Nd and Pr lower the sensitivity and cause line interference[9-11]. Separation of the interfering rare earths from those of analytical interest would reduce the spectral difficulties.

An anion-exchange procedure, based upon the relatively high adsorption of Ce, Nd and Pr compared with Er, Dy, Gd, Eu and Sm on strong base anion exchangers from nitric acid–aliphatic alcohol media[12-14], was therefore developed for this purpose. To eliminate determinative errors, yttrium (which has similar physical and chemical properties to Er, Dy, Gd, Eu and Sm) was used as a carrier for Er, Dy, Gd, Eu and Sm during the separation procedure and as an internal standard for subsequent spectrochemical analysis[4,10,15,16].

It should be emphasised that the effluent from the column in the proposed method does not contain materials which are difficult to remove, *e.g.* citric, lactic or ethylenediaminetetraacetic acids (widely used as eluants in ion-exchange separations of rare earths) or which cause serious interference in the subsequent spectrochemical determination of the rare earths; only nitric acid and an aliphatic alcohol, *e.g.* methanol, are present and these are readily removed by evaporation.

Although the separation procedure is primarily considered in combination with emission spectrography, it could also be combined with other quantitative techniques, *e.g.* X-ray fluorescence.

EXPERIMENTAL

Ion-exchange columns

Columns 9 cm long and 1.4 cm internal diameter of strongly basic DeAcidite FF, 7–9 ×, 100–200 mesh (nitrate form) were used.

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** The composition of a typical rare earth mixture isolated from Th and U compounds was: 500 p.p.m. Ce, 190 p.p.m. La, 200 p.p.m. Nd, 55 p.p.m. Pr, 30 p.p.m. Sm, 1 p.p.m. Eu, 25 p.p.m. Gd, 8 p.p.m. Tb, 10 p.p.m. Dy, 5 p.p.m. Er and 10 p.p.m. Y.

Reagents

Specpure CeO_2, La_2O_3, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3 and Y_2O_3. National Carbon S.P.-2 graphite powder. Reagent-grade nitric acid (d. 1.42) and methanol. Deionised water.

Nitric acid–methanol eluant. The eluant containing 35% of 3.5 *N* nitric acid and 65% of methanol was prepared by diluting the required percentage volume of 3.5 *N* nitric acid to the mark in a standard flask with methanol. The eluant was freshly prepared as needed.

Standard Ce, La, Nd, Pr, Sm, Eu, Gd, Dy and Er stock solutions. These were prepared by dissolving appropriate amounts of the specpure oxides in concentrated nitric acid (CeO_2 was dissolved by treatment[17] with concentrated nitric acid and 100-volume hydrogen peroxide) removing excess nitric acid by evaporation and making up to volume with the above eluant solution. From these stock solutions, mixtures of rare earths similar to those isolated from Th and U compounds were prepared (see Table I).

DEVELOPMENT OF THE SEPARATION PROCEDURE

A survey of the distribution coefficients of the rare earths between strong base anion-exchange resins and dilute nitric acid–aliphatic alcohol media[12-14] revealed that 35% 3.5 *N* nitric acid–65% methanol should be the most favourable eluant concentration for the contemplated separation. The distribution coefficients (K_D's) for Ce, Nd, Pr and La in this solution were shown to be 140, 90, 100 and 180 respectively, while those for Er, Dy, Gd, Eu, Sm and Y were 4, 4, 4, 8, 10 and 8 respectively (the resin used was similar to that mentioned above but 50–100 mesh). With the specified nitric acid–methanol eluant, Er, Dy, Gd, Eu, Sm and Y should be eluted rapidly and with very little resolution from an anion-exchange column, while Ce, Nd, Pr and La, which have much larger distribution coefficients, should be retained by the resin.

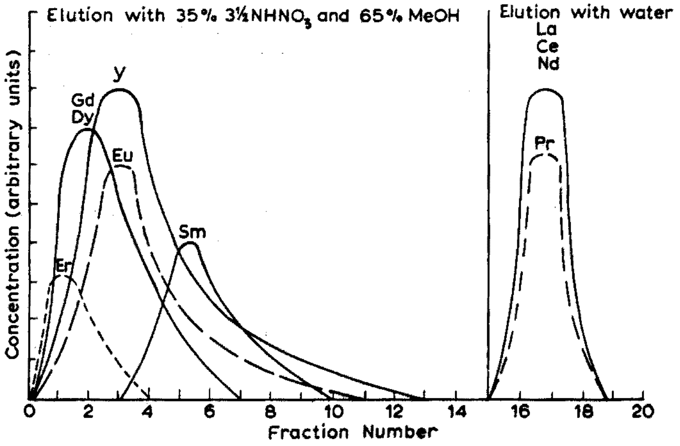

Fig. 1. Semiquantitative elution curves for Er, Dy, Gd, Eu, Sm, Y, Ce, Nd, Pr and La. Column: 9 cm × 1.4 cm, DeAcidite FF, 7–9×, 100–200 mesh (nitrate form). Flow rate for nitric acid–methanol eluant: 0.75 ml/min. Flow rate for water elution: 1 ml/min. Volume/fraction: 14 ml. Sample: Mixture of specpure rare earth nitrates equivalent to 8 mg Y, 0.8 mg each of Er, Dy, Gd, Eu and Sm and 1 mg each of Ce, Nd, Pr and La, dissolved in 5 ml of the eluant mixture.

These rare earths can subsequently be eluted with an eluant (*e.g.* water) in which the adsorbed Ce, Nd, Pr and La "complexes" are no longer stable.

Semiquantitative elution curves obtained using the procedures outlined previously[12,18], confirmed the above predictions. A typical semiquantitative elution curve is shown in Fig. 1. It is apparent from the asymmetrical appearance of the elution bands of Er, Dy, Gd, Eu, Sm and Y that the rate of equilibration was slow. Sharper elution bands would be expected, of course, with a finer resin of lower cross-linkage, with slower flow rates and an increase in the temperature of operation of the column (unsuitable for the reactive eluant employed here).

PROCEDURE

The mixture of rare earths (see Table I) together with 24.4 mg of specpure $Y(NO_3)_3$ and contained in 3-4 ml of the 35% 3.5 *N* nitric acid-65% methanol eluant solution was soaked into the top of an anion-exchange column at a flow rate not exceeding 0.1 ml/min. Before the sorption step the column was washed with 4-5 column volumes of the eluant solution at a flow rate of 1 ml/min. The column was eluted with 15 column volumes of the eluant solution at a flow rate of 0.2 ml/min. The arrangement described by EDGE[19] was employed to obtain the slow, steady flow rate required.

The effluent, containing the Er, Dy, Gd, Eu, Sm and Y was slowly evaporated to 5-10 ml and the residual solution transferred to a 20-ml porcelain evaporating basin containing 10 mg of graphite powder; the mixture was then evaporated carefully to dryness. The resultant residue was analysed spectrographically as described by CARTER AND DEAN[4].

Ce, Nd, Pr and La were removed from the column by elution with 5 column volumes of water, a flow rate of 1 ml/min being employed. All elutions were carried out at room temperature.

RESULTS AND DISCUSSIONS

In Table I the results of a series of separations, in which the amounts of rare earths employed were equivalent to those isolated from uranium and thorium compounds (see footnote on p. 321) are recorded.

TABLE I

RECOVERIES OF Er, Dy, Gd, Eu AND Sm FROM RARE EARTH MIXTURES

Sample composition (μg)	*Rare earth recovered (μg)*					*Remarks*
	Er	*Dy*	*Gd*	*Eu*	*Sm*	
500 Ce, 170 La, 200 Nd,	4.9	9.8	24.0	6.7	48.3	
50 Pr, 50 Sm, 7 Eu,	5.1	10.0	25.6	7.1	51.0	
25 Gd, 10 Dy and 5 Er	4.7	9.4	23.8	6.6	67.8	
1000 Ce, 340 La, 400 Nd,	9.8	19.4	48.9	13.7	98.4 →	18 μg Nd and 3 μg Pr were found in the Er, Dy, Gd, Eu and Sm fraction
100 Pr, 100 Sm, 14 Eu,	9.7	19.3	48.5	13.5	97.0	
50 Gd, 20 Dy and 10 Er	9.5	19.0	48.0	13.3	96.3	
1000 Ce, 340 La, 400 Nd,	4.8	9.5	24.2	6.7	47.5	
100 Pr, 50 Sm, 7 Eu,	4.9	9.8	24.0	6.8	48.6 →	7 μg Nd was found in the Er, Dy, Gd, Eu and Sm fraction
25 Gd, 10 Dy and 5 Er	5.1	9.9	25.6	7.0	49.5	

A reagent blank carried through the separation procedure showed no detectable Sm, Eu, Gd, Dy and Er.

The results show that the anion-exchange procedure effectively removes Ce, Nd, Pr and La and that good recoveries of Er, Dy, Gd, Eu and Sm may be obtained. The recommended procedure should be equally effective for separating trace amounts of other heavy rare earths from Ce, Nd, Pr and La.

The author wishes to thank Mr. E. H. CHAN-HENRY for help with the spectrochemical determinations and the South African Atomic Energy Board for the award of a Senior Bursary.

SUMMARY

An anion-exchange procedure with 35% 3.5 *N* nitric acid–65% methanol as eluant has been developed for the removal of Ce, Nd, Pr and La from Er, Dy, Gd, Eu and Sm, at the trace concentration level.

RÉSUMÉ

Une méthode par échange d'anions avec, comme éluant, un mélange de 35% d'acide nitrique 3.5 *N* et 65% de méthanol, a été mise au point pour l'élimination de Ce, Nd, Pr et La d'avec Er, Dy, Gd, Eu et Sm.

ZUSAMMENFASSUNG

Es wird die Trennung von Spuren Er, Dy, Gd, Eu und Sm von Ce, Nd, Pr und La mit Hilfe eines Anionenaustauschers beschrieben. Als Eluationsmittel diente ein Gemisch aus 35% 3.5 *N* Salpetersäure und 65% Methanol.

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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN AND MOLYBDENUM WITH THIOCYANATE AFTER α-BENZOINOXIME EXTRACTION

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A number of workers have applied chloroform extraction of the α-benzoinoxime complexes of molybdenum[1-4] and tungsten[1,5] to separate small amounts of these elements from others. The separation is selective and very useful in practice. The work described here was concerned primarily with the extraction of tungsten in this way, to supplement the available information on this separation. Since molybdenum accompanies tungsten quantitatively in the extraction, it would be desirable to have a simple spectrophotometric method allowing the determination of both elements simultaneously. Such a determination can be based on measurement of the absorbance of an isopropyl ether extract of the molybdenum(V) and tungsten(V) thiocyanate complexes at two wave lengths. The simultaneous determination of the two elements with dithiol has already been described by JEFFERY[1].

Chloroform extraction of tungsten α-benzoinoximate

This extraction has been studied especially by PFEIFER AND HECHT[5] with particular reference to the determination of tungsten in steel. Some additional observations are recorded here. A systematic study of the extraction was not made because of the instability of α-benzoinoxime in mineral acid solutions.

The extractability of tungsten as a function of the α-benzoinoxime concentration in the aqueous phase at a constant acidity (0.5 *M* hydrochloric acid) is shown in Fig. 1. The composition of the tungsten complex is $WO_2(C_{14}H_{12}O_2N)_2$ or WO_2Bx_2 (HBx = α-benzoinoxime)[4]. In accordance with the ratio Bx/W = 2 in the extracted compound, the slope of the straight line in the plot of the log of the tungsten extraction coefficient E_W (= $[WO_2Bx_2]_{CHCl_3}/\Sigma[W]_{H_2O}$) against the log of the benzoinoxime concentration in the aqueous phase at equilibrium is very nearly 2, namely 1.97.

Assume tungsten at very low concentrations in acidic solutions to be present chiefly as WO_3 (disregarding combined water). α-Benzoinoxime is very weakly acidic (dissociation constant reported[6] as $\sim 10^{-6}$), so that its reaction with tungsten in acidic solutions (> 0.01 *M* HCl) may be represented by

$$WO_3 + 2\ HBx \rightleftharpoons WO_2Bx_2 + H_2O$$

(or, what is the same, by

$$WO_2^{2+} + 2\ Bx^- \rightleftharpoons WO_2Bx_2)$$

The dissociation constant of the complex in water solution is given by

$$K = \frac{[\mathrm{WO_3}][\mathrm{HBx}]^2}{[\mathrm{WO_2Bx_2}]} \tag{1}$$

Let P_w be its partition coefficient:

$$P_w = \frac{[\mathrm{WO_2Bx_2}]_o}{[\mathrm{WO_2Bx_2}]} \tag{2}$$

(concentrations without subscripts refer to aqueous solutions, *o* to chloroform). Then the extraction coefficient for tungsten is

$$E_w = \frac{\Sigma[\mathrm{W}]_o}{\Sigma[\mathrm{W}]} = \frac{[\mathrm{WO_2Bx_2}]_o}{[\mathrm{WO_3}] + [\mathrm{WO_2Bx_2}]} = \frac{P_w[\mathrm{WO_2Bx_2}]}{[\mathrm{WO_3}] + [\mathrm{WO_2Bx_2}]} = \frac{P_w[\mathrm{WO_3}][\mathrm{HBx}]^2}{K\{[\mathrm{WO_3}] + [\mathrm{WO_2Bx_2}]\}} \tag{3}$$

The extraction coefficient of α-benzoinoxime itself increases with its concentration in chloroform (Table I). This behavior points to association in the chloroform phase. The concentration of benzoinoxime in an aqueous phase in equilibrium with a chloroform phase of known initial concentration must therefore be found with the aid of a distribution curve.

TABLE I

DISTRIBUTION OF α-BENZOINOXIME BETWEEN CHLOROFORM AND AQUEOUS SOLUTIONS[a]

pH	*HBx in CHCl₃* (*μg/ml*)	*HBx in H₂O* (*μg/ml*)	$E = \frac{\Sigma[HBx]_{CHCl_3}}{\Sigma[HBx]_{H_2O}}$
4.45	280	19.8	14.1
4.45	1420	84	16.9
4.45	2850	152	18.7
4.45	5980[b]	300	19.9
3.95	5980[b]	300	19.9

[a] Disodium citrate buffer, $\mu = 0.3$ *M*. Room temperature: *ca.* 26° in the first three experiments and 25° in the last two. Benzoinoxime concentrations determined by measurement of absorbance at 290 mμ (chloroform) or 300 mμ (aqueous phase made basic with sodium hydroxide).
[b] Both phases saturated with α-benzoinoxime.

When $[\mathrm{WO_3}] \gg [\mathrm{WO_2Bx_2}]$, the extraction of tungsten being quite incomplete, the following approximation may be written:

$$E_w \sim \frac{P_w[\mathrm{HBx}]^2}{K} \sim K_{ex}[\mathrm{HBx}]^2 \tag{4}$$

A plot of log E_w against log [HBx] should give, initially, a straight line with a slope of 2, since

$$\log E_w = \log K_{ex} + 2 \log [\mathrm{HBx}] \tag{5}$$

The extraction equilibrium constant, K_{ex}, has an average value of $7.2 \cdot 10^8$, with a range from 6.9 to $7.7 \cdot 10^8$, calculated from the 7 points in Fig. 1.

P_w has not been determined, but it is certainly greater than 100, since E_w values at least this large have been found in the present work. From the figure 99.2% extraction of tungsten by 10 ml of chloroform–HBx from 50 ml aqueous phase given in a Table by PFEIFER AND HECHT[5], P_w is ~ 500 or greater. If $P_w > 500$, $K > 500/7 \cdot 10^8 > 7 \cdot 10^{-7}$. Accordingly, when $[HBx] = 2.5 \cdot 10^{-4}$, corresponding to $[HBx]_o \sim 3.9 \cdot 10^{-3}$, $[WO_3]/[WO_2Bx_2]$ in the aqueous phase exceeds 10 and the deviation of E_w from the E_w calculated on the assumption that all tungsten in the aqueous phase is present as WO_3 (or analogous species) should not exceed 10%. The outermost point in Fig. 1 still falls close to the straight line.

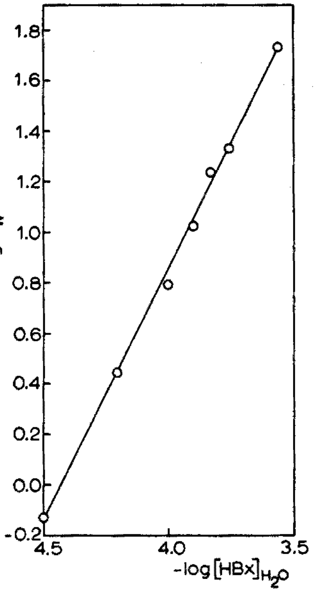

Fig. 1. Log E_w(= log $\frac{[WO_2Bx_2]_{CHCl_3}}{\Sigma[W]_{H_2O}}$) as a function of log $[HBx]_{H_2O}$. Volume of aqueous phase 23 ml, of chloroform 10 ml; 20 μg W; *ca.* 26°.

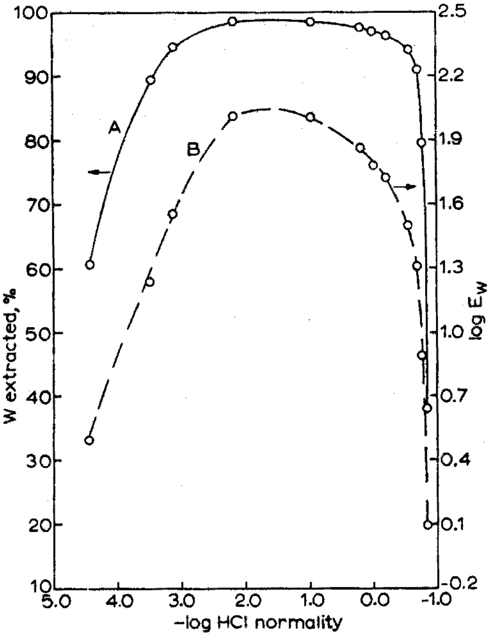

Fig. 2. Percentage extraction of tungsten (A) and log E_w (B) as functions of log hydrochloric acid concentration. Volume of aqueous phase 20 ml, of chloroform phase 10 ml (containing 15 mg α-benzoinoxime); 20 μg W.

The effect of acidity on the extraction is shown in Fig. 2. The extraction coefficient of tungsten should remain essentially constant over the acidity range in which the reagent is present as HBx and tungsten predominantly as WO_3 or a similar (hydrated) species. In this range the increase in the concentration of WO_2^{2+} is counterbalanced by the decrease in the concentration of Bx^- as the acidity is increased. The extraction coefficient of tungsten does remain substantially constant in the approximate range 0.01 to 0.1 *M* hydrochloric acid. Its decrease at lower hydrogen ion concentrations is no doubt due to the increase in anionic tungsten and anionic α-benzoinoxime species. The reason for its decrease above 0.1–1 *M* hydrochloric acid is uncertain. In part at least, the decrease may be due to the instability of α-benzoinoxime in strongly acidic solutions; this instability also makes it difficult to determine whether cationic species of the reagent (H_2Bx^+) are formed. Moreover, the tungsten species in strong hydrochloric acid solution are uncertain. In practice, extractions can be made from 0.01

to *ca.* 1 *M* hydrochloric acid. The concentration of α-benzoinoxime need be no greater than 1.5 mg per ml of chloroform if a double extraction is made. Even one extraction of 20 ml of aqueous solution with 10 ml of chloroform having this benzoinoxime concentration removes *ca.* 97% of 10–20 μg W. Shaking for 2 min suffices for attaining equilibrium.

The benzoinoxime extraction is suitable only for low concentrations of tungsten, because of the small solubility of tungstic acid in water and of WO_2Bx_2 in chloroform. The latter solubility has been reported[4] as 0.12 mg per ml of chloroform at room temperature, corresponding to 0.033 mg W per ml. Some association of tungsten species in acidic solution is to be expected. The extraction of tungsten seems to be a little smaller with 50 μg than with 10 μg W as indicated by the following results for which 20 ml of aqueous phase, 0.6 *M* in hydrochloric acid, was shaken for 2 min with 10 ml of chloroform containing 15 mg of α-benzoinoxime:

W(μg)	*W extracted (%)*
10	97
50	95.3
100	94.9 (slight turbidity in chloroform)
500	91.6 (strong turbidity in chloroform)

The tungsten extraction separation is especially suitable for less than 10–20 μg W.

Separations of tungsten

The results tabulated in Table II show that microgram amounts of tungsten in the

TABLE II

SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN AS THIOCYANATE AFTER α-BENZOINOXIME EXTRACTION

(Twenty ml of aqueous phase containing 1 ml concentrated HCl extracted with 10 + 5 ml of chloroform solution of α-benzoinoxime containing 1.5 mg per ml; α-benzoinoxime in extracts destroyed with H_2SO_4–$HClO_4$. The following elements in the amounts (mg) indicated showed no interference (4.9 to 5.1 μg W found when 5.0 was taken): Mg and Ca (50 each); Mn, Cu, Zn (5 each); Ni, Co, Cd, Hg (1 each); As, Sb, Bi (0.5 each))

Foreign elements (mg)	*W taken (μg)*	*W found (μg)*
Al, 100	5.0	5.0, 5.0
Fe(III), 100	1.0	1.0, 1.0
Fe(III), 100	5.0	5.0, 5.0
Fe(III), 100	10.0	9.8, 10.0
Ti(IV), 5	5.0	5.0, 5.0
Cr(VI), 5[a]	5.0	5.0, 5.0
V(V), 10[a]	5.0	5.1, 4.9
Re(III), 1	5.0	4.9, 5.1
Pt(IV), 0.5	5.0	5.0, 5.0
Pd, 1.0	5.0	43.5
H_3PO_4, 8.5	5.0	5.0
H_3PO_4, 170	5.0	4.2
H_3PO_4, 1700	5.0	1.3

[a] 100 mg Fe(II) as ferrous ammonium sulfate for reduction.

presence of various elements can be extracted with α-benzoinoxime and subsequently determined satisfactorily by the spectrophotometric thiocyanate method involving isopropyl ether extraction. Chromium(VI) and vanadium(V) must be reduced with iron(II) or a similar reducing agent, else they are also extracted by α-benzoinoxime. Palladium, but not platinum(IV), causes high results. Phosphate hinders the extraction of tungsten and may be present in small amounts only (up to 1–2 mg of phosphoric acid per ml of aqueous phase). Fluoride interferes more seriously than phosphate, but it can be removed by evaporation of the sample solution to fumes with sulfuric acid.

Niobium, tantalum and, especially, silicic acid have been reported to interfere by forming precipitates which strongly adsorb tungsten[5]. Molybdenum accompanies tungsten and interferes strongly, of course, unless the absorbance of the thiocyanate complexes of the two elements is determined at two suitable wave lengths.

Simultaneous spectrophotometric determination of tungsten and molybdenum as thiocyanates

The absorbance peaks of the tungsten and molybdenum thiocyanate complexes in isopropyl ether solution lie sufficiently far apart to enable the concentrations of the elements to be determined by measurement at or near these wave lengths if their amounts are not too disproportionate (Fig. 3). At 405 mμ the absorbance due to tungsten is approximately 6 times that of an equal weight of molybdenum, whereas at 490 mμ the absorbance of molybdenum is several hundred times that of tungsten

TABLE III

EFFECT OF ACIDITY AND TIME OF STANDING AFTER DILUTION ON COLOR INTENSITIES OF TUNGSTEN AND MOLYBDENUM

(W or Mo solution, 5 ml of 1 *M* NaOH, 2.0 ml of 2 *M* KSCN, 5.0 ml of 15% $SnCl_2 \cdot 2H_2O$ and HCl diluted to 30 ml and allowed to stand 1 h; then diluted to 50 ml with water, allowed to stand for the time indicated, and extracted with 5 ml isopropyl ether. When Mo was present, 5 mg Fe(II) was added before dilution)

W (μg)	*Mo (μg)*	*HCl concn. before diln. (M)*	*HCl concn. after diln. (M)*	*Time of standing after diln. (min)*	*Absorbance*[a]
0	—	6.0	3.6	0	0.012
20	—	6.0	3.6	0	0.364
20	—	5.0	3.0	0	0.323
20	—	4.0	2.4	0	0.273
20	—	6.0	3.6	90	0.361
20[b]	—	6.0	3.6	90	0.374
—	—	6.0	3.6	90	0.009
—	20	6.0	3.6	1	0.343
—	20	6.0	3.6	5	0.356
—	20	6.0	3.6	30	0.411
—	20	6.0	3.6	60	0.428
—	20	6.0	3.6	90	0.434
—	20	6.0	3.6	120	0.438

[a] At 400 mμ for W, 490 mμ for Mo.

[b] 5 mg Fe(II) added before dilution.

(30 μg Mo and 30 μg W in 5 ml of isopropyl ether give respective absorbances of 0.64 and *ca.* 0.002 against an ether blank). Conditions are thus especially favorable for the determination of molybdenum in the presence of tungsten. However, the determination of tungsten in the presence of as much as 10–20 times its weight of molybdenum can still be carried out with an accuracy often sufficing for trace analysis. The sensitivities of the determinations are approximately 0.011 μg W/cm² and 0.009 μg Mo/cm² for $\log I_0/I = 0.001$.

The formation of the tungsten–thiocyanate complex requires a high hydrochloric acid concentration and relatively long standing. We have adopted a procedure similar to that of GRAN[7] for the development of the tungsten color, followed by isopropyl ether extraction. In GRAN's method, the color development is carried out in 6 *M* hydrochloric acid, followed by dilution to *ca.* 4.8 *M* hydrochloric acid. The acidity of 6 *M* should be controlled to ±0.1 *M* (Table III). The time of standing after dilution and the presence or absence of iron have little effect on the color intensity of tungsten. The absorbance of the ether extract remains constant for an hour or more. Little color is given by molybdenum unless iron is present (5 mg suffices) and it may be added before dilution. The absorbance given by molybdenum increases with the time of standing after dilution, but there is little change after 1 h. The absorbance of the ether extract shows little change in 15 min. The concentration of stannous chloride has little effect on the tungsten absorbance in the range 0.75–3% $SnCl_2 \cdot 2H_2O$ (after dilution), but a definite one on the molybdenum absorbance ($A = 0.475$ for 0.6% $SnCl_2 \cdot 2H_2O$, 0.425 for 1.5%, 0.375 for 3.0%).

Trials of the proposed method (Table IV) show that as little as 1 μg W can be determined to within 5–10% in the presence of 10 μg Mo, and 1 μg Mo can be determined to within a few per cent in the presence of 10–20 μg W. Determination of tungsten in the presence of up to 10 times as much molybdenum after separation from calcium,

TABLE IV

SIMULTANEOUS DETERMINATION OF TUNGSTEN AND MOLYBDENUM IN PURE SOLUTIONS

W added (μg)	*Mo added (μg)*	*W found (μg)*	*Mo found (μg)*
1.0	20.0	0.95	20.0
1.0	20.0	1.00	19.9
2.0	20.0	1.93	20.1
2.0	20.0	1.93	20.1
5.0	20.0	5.0	20.1
5.0	20.0	5.0	20.4
1.0	5.0	0.92	5.0
1.0	5.0	0.95	5.0
1.0	10.0	0.95	10.0
1.0	10.0	0.99	10.0
10.0	1.0	10.0	0.98
10.0	1.0	10.1	0.98
20.0	1.0	20.2	0.98
20.0	1.0	20.2	0.98
30.0	1.0	30.5	0.97
20.0	20.0	20.2	20.0

magnesium, iron, titanium and small amounts of phosphorus by α-benzoinoxime extraction is also satisfactory (Table V).

Considering only the photometric error, the standard deviation in the determination of 1 μg W in the absence of molybdenum is approximately 5% or ±0.05 μg W if the standard deviation of a transmittance reading is ±0.2% (absolute), since 1 μg W in 5 ml of isopropyl ether in a 1-cm cell has an absorbance of 0.0177 at 405 mμ:

TABLE V

SIMULTANEOUS DETERMINATION OF TUNGSTEN AND MOLYBDENUM AFTER α-BENZOINOXIME EXTRACTION

Foreign elements	*W taken (μg)*	*Mo taken (μg)*	*W found (μg)*	*Mo found (μg)*
Fe(III), 100 mg	—	—	0.00	0.00
	—	10.0	0.00	9.8
	1.0	10.0	1.00	9.7
	1.0	10.0	0.96	9.8
	3.0	10.0	2.9	9.9
	5.0	10.0	4.7	9.8
	10.0	10.0	9.5	9.9
Ca and Mg, 50 mg each	—	—	0.00	0.00
	1.0	10.0	1.04	10.0
	1.0	10.0	1.00	9.9
	3.0	10.0	2.8	10.1
	10.0	10.0	9.7	10.1
H_3PO_4, 8.5 mg	1.0	10.0	1.00	9.9
	1.0	10.0	0.97	9.9
	3.0	10.0	2.8	10.0
	10.0	10.0	9.6	10.0
Ti, 10 mg	—	—	0.00	0.00
	1.0	10.0	0.97	9.9
	1.0	10.0	1.05	9.8
Ti, 5 mg	10.0	10.0	9.8	10.0

$$s_w = \frac{0.0009}{0.0177} \cdot 1 = 0.051\ \mu\text{g or } 5.1\%.$$

The factor 0.0177 is taken to have an indeterminate error so small in comparison with the absorbance error that it need not be considered. The indeterminate error in setting the wave length or in the color development may be neglected in comparison with the error in transmission measurement at low absorbance values.

When molybdenum is present, the error in absorbance reading resulting from the error in setting the wave length at 490 mμ must be taken into account. At this wave length an error of ± 1 mμ causes an error of 2% in the molybdenum absorbance. The indeterminate error in the tungsten determination also includes the indeterminate errors in the absorbance readings at 405 and 490 mμ, irrespective of wave length error. If a_{405} and a_{490} are the standard deviations in absorbance measurements at 405 and

490 mμ, the percentage standard deviation in the determination of tungsten is given by the expression

$$\overset{\%}{s_w} = \frac{100\{(\overset{\mathrm{Mo}}{k}_{490}a_{405})^2 + (\overset{\mathrm{Mo}}{k}_{405}a_{490})^2 + (0.02\,\overset{\mathrm{Mo}}{k}_{405}A_{490})^2\}^{1/2}}{\overset{\mathrm{Mo}}{k}_{490}A_{405} - \overset{\mathrm{Mo}}{k}_{405}A_{490}}$$

$$= \frac{100\{(0.0213a_{405})^2 + (0.0029a_{490})^2 + (0.02\cdot 0.0029A_{490})^2\}^{1/2}}{0.0213A_{405} - 0.0029A_{490}}$$

(*cf.* formula given under *Procedure*). The values of a correspond to the deviation in A equivalent to ±0.2% (absolute) transmittance.

The percentage standard deviation in the determination of 1 μg of tungsten in the presence of various amounts of molybdenum (5 ml of isopropyl ether, 1-cm absorption cell) by absorbance measurement at 405 and 490 mμ is graphed as A in Fig. 4. When Mo/W < 5, the determination of tungsten can be made with almost the same accuracy as in the absence of molybdenum. At Mo/W $= 15$, the photometric error has increased by about 50% over that for 1 μg W alone.

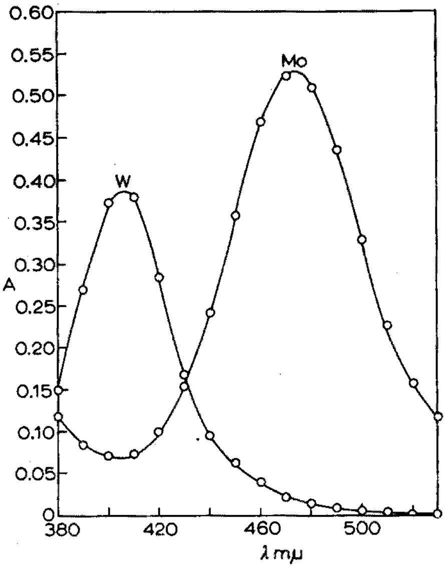

Fig. 3. Absorbance curves of tungsten and molybdenum thiocyanate complexes in isopropyl ether. 20.0 μg W, 20.0 μg Mo, 5 ml of isopropyl ether, 50 ml of aqueous phase. Beckman B spectrophotometer, 1-cm cell. Absorbance measured against pure isopropyl ether (not blank).

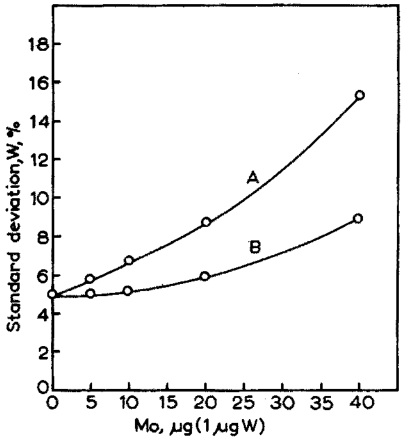

Fig. 4. Standard deviation (%) in determination of 1 μg W in presence of Mo if (A) standard deviation in transmission measurement at 405 and 490 mμ is ± 0.2% (absolute) and standard deviation in wave length setting at 490 mμ is 1 mμ ($\equiv \pm 0.02\,\overset{\mathrm{Mo}}{A}_{490}$); if (B) standard deviation in transmission measurement at 405 and 475 mμ is ± 0.2 % (absolute) and standard deviation in wave length setting at 475 mμ causes a negligible error in absorbance.

When tungsten only is to be determined, it may be preferable to make the second absorbance measurement at the molybdenum peak, 475 mμ, so that the absorbance error due to wave length setting will be decreased or practically eliminated. Curve B represents the percentage standard deviation in the tungsten determination by absorbance measurement at 405 and 475 mμ, if the deviations in absorbance values at these wave lengths correspond to a standard deviation of 0.2% (absolute) in the transmission and there is no error in the absorbance at 475 mμ (or 405 mμ) resulting from variation in wave length setting.

EXPERIMENTAL

Special solutions

α-Benzoinoxime. 0.15 g in 100 ml of chloroform. If the purity of the benzoinoxime is uncertain, recrystallize from 95% ethyl alcohol. Keep the solution in a dark glass bottle, and prepare fresh weekly.

Potassium thiocyanate. 10% (w/v) in water.

Stannous chloride. 5.0 g $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid. Prepare fresh weekly.

Ferrous ammonium sulfate. 7 g of the hexahydrate in 100 ml of 0.2 N sulfuric acid.

Isopropyl ether. Purify daily by shaking 100 ml of reagent-grade product for 2 min with 100 ml of water to which 5 ml of 5% stannous chloride solution has been added.

Standard tungsten solution. 100 μg W per ml. Dissolve 0.0897 g of clear crystals of $Na_2WO_4 \cdot 2H_2O$ in water and dilute to 500 ml. This solution may be diluted five- or ten-fold if desired. The tungsten content of the sodium tungstate should be determined gravimetrically if there is any doubt about its water content.

Standard molybdenum solution. 100 μg Mo per ml. Dissolve 0.1261 g of $Na_2MoO_4 \cdot 2H_2O$ in water and dilute to 500 ml. The molybdenum content of the sodium molybdate should be checked by a gravimetric determination as lead molybdate.

Procedure

Acidify 20–25 ml of neutral sample solution, containing at least 1 μg W (or Mo) and not more than 20–25 μg Mo (or W), with 1 ml of concentrated hydrochloric acid. Shake well for 2 min with 10 ml of α-benzoinoxime solution in chloroform and draw off the latter. Extract the aqueous phase with 5 ml of α-benzoinoxime solution and combine the chloroform extracts in a separatory funnel. Shake the combined extracts with 1–2 ml of 0.5 M hydrochloric acid to remove any droplets of entrained aqueous sample solution and run the chloroform phase into a 100-ml beaker.

Evaporate the chloroform, cool, and add 0.5 ml each of concentrated nitric acid and 1 :3 sulfuric acid. Heat to fumes of sulfuric acid, cool, and add 0.5 ml of 70% perchloric acid. Heat until fuming ceases. If the residue still has some dark color, repeat the heating with 0.5 ml of perchloric acid. Cool and add 5 ml of 1 M sodium hydroxide. Heat almost to boiling and stir to make sure that all tungsten and molybdenum has been dissolved.

Transfer the solution to a 50-ml volumetric flask and rinse the beaker with a total of 8 ml of water. Add 2.0 ml of potassium thiocyanate and 15 ml of stannous chloride solution and mix. Allow to stand at room temperature for 60 min. Then add 0.5 ml of ferrous ammonium sulfate solution, dilute to the mark with water and allow to stand for 90 min. Transfer the solution to a separatory funnel, drain well, and rinse the flask with 2 ml of water. Extract with 5.0 ml of isopropyl ether, shaking vigorously for 30 sec. Allow to stand for 1–2 min for clarification of the ether phase. Run the clear ether layer into a 1-cm cell and measure the absorbance at 405 and 490 mμ against an ether extract of a blank. If only tungsten is to be determined, it is preferable to make the second absorbance measurement at 475 mμ. Use a spectrophotometer, not a filter photometer.

Establish the standard curves by taking 5, 10, 15, 20, 25 μg of Mo and W separately and treating as described in the preceding paragraph.

Obtain the amount of tungsten and molybdenum from the relations:

$$C_{W} = \frac{\overset{Mo}{k}_{490}A_{405} - \overset{Mo}{k}_{405}A_{490}}{\overset{W}{k}_{405}\overset{Mo}{k}_{490} - \overset{W}{k}_{490}\overset{Mo}{k}_{405}} \quad \text{and} \quad C_{Mo} = \frac{\overset{W}{k}_{490}A_{405} - \overset{W}{k}_{405}A_{490}}{\overset{Mo}{k}_{405}\overset{W}{k}_{490} - \overset{Mo}{k}_{490}\overset{W}{k}_{405}}$$

The values of k are found from the slopes of the standard curves in which the absorbances produced by tungsten and molybdenum at 405 and 490 mμ are plotted against the concentrations (μg in 5 ml) in isopropyl ether. The value of $\overset{W}{k}_{490}$ should be so small that the term $\overset{W}{k}_{490}\overset{Mo}{k}_{405}$ in the denominator can be neglected when less than 10 μg W is present.

SUMMARY

The extractability of tungsten α-benzoinoximate by chloroform as a function of the reagent concentration and acidity has been studied. In 0.5 M hydrochloric acid solution the extraction coefficient for tungsten (~ 1 p.p.m.) is given by the relation

$$E_{w} = \frac{[WO_2Bx_2]_{CHCl_3}}{\Sigma[W]_{H_2O}} = K_{ex}[HBx]^2{}_{H_2O} = 7 \cdot 10^8[HBx]^2{}_{H_2O}$$

An acidity range of 0.01–1 M provides favorable extraction coefficients. Tungsten can be separated by α-benzoinoxime extraction from much iron and most other metals. Molybdenum accompanies tungsten quantitatively and the two elements can be determined simultaneously by the familiar thiocyanate method if the absorbance of the isopropyl ether extract is measured at 405 mμ and 490 (or 475) mμ. As little as 1 μg W can thus be determined in the presence of 10 μg Mo without separation.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du tungstène, avec l' α-benzoïnoxime, par le chloroforme, en fonction de la concentration de réactif et de l'acidité. Une équation est donnée pour déterminer le coefficient d'extraction du tungstène (env. 1 p.p.m.) en milieu acide chlorhydrique 0.5 M. Le tungstène peut être séparé par extraction à l' α-benzoïnoxime d'avec de grandes quantités de fer et de nombreux autres métaux. Le molybdène accompagnant souvent le tungstène, ces deux éléments peuvent être dosés simultanément par la méthode habituelle au thiocyanate, par extraction dans l'éther isopropylique et mesure à 405 mμ et 490 (ou 475) mμ. On peut ainsi déterminer jusqu'à 1 μg de tungstène, en présence de 10 μg de molybdène, sans séparation.

ZUSAMMENFASSUNG

Die Extrahierbarkeit des Wolfram-α-Benzoinoximats durch Chloroform wurde in Abhängigkeit von der Reagenz- und Säurekonzentration untersucht. Zur Bestimmung des Extraktionskoeffizienten des Wolframs (*ca.* 1 p.p.m.) aus 0.5 M Salzsäure wird eine Gleichung angegeben. Säurekonzentrationen von 0.01 – 1 M ergeben günstige Extraktionskoeffizienten. Wolfram kann durch die α-Benzoinoxim-Extraktion von grossen Mengen Eisen und zahlreichen anderen Metallen getrennt werden. Molybdän begleitet das Wolfram quantitativ. Die beiden Elemente können nebeneinander mit der bekannten Thiocyanatmethode bestimmt werden, wenn die Absorption des Isopropylätherextrakts bei 405 mμ und 490 (oder 475) mμ gemessen wird. 1 μg Wolfram kann in Gegenwart von 10 μg Molybdän ohne Trennung bestimmt werden.

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MICROANALYSIS WITH THE AID OF ION EXCHANGERS

PART XXII[1]. DETECTION OF NANOGRAM AMOUNTS OF MOLYBDENUM(VI) WITH TIRON

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Tiron (sodium 1,2-dihydroxybenzene-3,5-disulphonate) was reported in the preceding papers as an excellent reagent for a resin spot test[2] for iron(III)[3] and titanium(IV)[4]. In the present paper, methods for the detection of molybdenum(VI) with ion-exchange resin beads[5,6] are extended by means of a resin spot test based on the intense yellow coloration of the pale-coloured anion-exchanger phase on adsorption of the chelate anion formed between tiron and molybdenum(VI)[7]. A similar method can be applied to the sensitive detection of uranium(VI).

EXPERIMENTAL

Reagents

The chemicals used were of analytical grade.

Stock solution of molybdenum(VI). Molybdenum(VI) oxide was dissolved in a minimum amount of aqueous ammonia and diluted with water to prepare a stock solution containing 1 mg molybdenum(VI) per ml, which was diluted with 0.01 *F* aqueous ammonia, if necessary.

4% aqueous stock solution of tiron (Wako) and 0.05 *F* aqueous solution of disodium ethylenediaminetetraacetate (EDTA, Dojindô) were used.

1 F buffer solutions. pH 2.0 and 3.0 (monochloroacetic acid–sodium monochloroacetate) and pH 4.1, 4.7, 5.0 and 6.0 (acetic acid–sodium acetate). The pH values were determined with a Horiba glass electrode pH-meter, model M-3.

Ion-exchange resins and dropping capillary pipettes

The following commercial strongly basic anion-exchange resins conditioned beforehand[8] were used mainly in the chloride form, or in the nitrate form, if necessary: Dowex 1-X1, -X2, -X4, -X10 and Dowex 2-X2. Dropping capillary pipettes as in a preceding paper[8] were used.

RESULTS AND DISCUSSION

Determination of the optimum conditions

The following general procedure[2] was applied. On a white spot plate, mix a few grains of a pale-coloured strongly basic anion-exchange resin, successively with 1 drop each of the test solution, 0.05 *F* EDTA[4], the reagent solution and finally the buffer solution*. After several minutes, observe the yellowish orange to yellow colour in the resin phase. The use of a fluorescent lamp under magnification of *ca.* 20 × is recommended.

The following comparison tests were carried out semiquantitatively[9] with a solu tion containing 1.00 p.p.m. molybdenum(VI).

The optimum sensitivity of the test was displayed at pH values between 4 and 5; at lower pH values the coloration was less sensitive, and at pH values higher than 6, a pale red colour by the gradual oxidation of the reagent[10] masked the yellow colour of the chelate in the resin phase. A buffer solution of pH 4.7 was thus used in the following tests.

Varying the concentration of the reagent between 0.01 and 4% affected the sensitivity to some extent; 0.5% tiron was the optimum concentration.

Among the anion-exchange resins applied, Dowex 1-X1 and Dowex 1-X2 gave the highest sensitivity (see below).

Increasing concentration of indifferent salts in the sample solution depressed the sensitivity of the test; the addition of 1 or 2 drops of 5 *F* sodium chloride to a drop of the test solution reduced the sensitivity by about 50 or 70% respectively, and saturating the solution with the salt (*ca.* 5 *F* in NaCl) reduced the sensitivity by two orders of magnitude.

Recommended procedure and the limit of identification

From the above results, the resin spot test for molybdenum(VI) with tiron is carried out most efficiently by the application of a pale-coloured strongly basic anion-exchange resin of low cross-linkage, a 1 *F* acetate buffer solution of pH 4.7 and a 0.5% solution of tiron. Addition of a drop of 0.05 *F* solution of EDTA before the test is necessary to mask the strong interference by iron(III)[3], which is often present in the usual sample solution.

TABLE I

INFLUENCE OF THE SAMPLE SIZE ON THE LIMIT OF IDENTIFICATION FOR MOLYBDENUM(VI) WITH TIRON IN THE VARIOUS DETECTION TECHNIQUES

Detection method applied	*Volume of the sample solution (ml)*	*Number of drops of the 4% reagent added*	*Limit of identification for molybdenum(VI) (ng)*		*Dilution limit*
Resin spot test[a]	0.04	1[b]	8	after 1 hour standing	1 : 5·10^6
	0.1	2	10		1 : 1·10^7
	0.3	2	20		1 : 1·5·10^7
	1	2	100		1 : 1·10^7
Resin centrifuge method[a]	1	3	80	after 5 to 10 min standing	1 : 1·3·10^7
	5	3	200		1 : 2·5·10^7
Resin-powder flotation method[a]	1	3	160		1 : 6·3·10^6
	5	3	200		1 : 2·5·10^7
Usual spot test	0.04	1	200		1 : 2·10^5

[a] Dowex 1-X2 was used.
[b] 0.5% solution was used.

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* The order of mixing does not affect the sensitivity of the test.

TABLE II

INFLUENCE OF FOREIGN SUBSTANCES ON THE DETECTION OF MOLYBDENUM(VI) WITH TIRON BY THE RESIN SPOT TEST

Foreign ion	*Added form*	*Coloration of the resin phase*[a]	*Amount of foreign ion (μg)*	*Amount of detectable molybdenum(VI) (μg)*	*Limiting proportion*	*Remark*
La(III)	$La(NO_3)_3$	Colourless	270	0.027	$1:1\cdot10^4$	
Ce(IV)	$Ce(SO_4)_2$	Dark yellow-orange ~ yellowisch brown	27	0.027	$1:1\cdot10^3$	b
		Colourless	160	0.01	$1:1.8\cdot10^4$	c,d
Zr(IV)	$ZrO(NO_3)_2$	Colourless	200	0.04	$1:5\cdot10^3$	b
Th(IV)	$Th(NO_3)_4$	Colourless	680	0.027	$1:2.5\cdot10^4$	
V(V)	NH_4VO_3	Dark grey	0.4	0.04	$1:1\cdot10$	
		Dark grey	5.3	0.27	$1:2\cdot10$	
Cr(III)	$KCr(SO_4)_2$	Greenish grey	40	0.04	$1:1\cdot10^3$	e
		Greenish grey	530	0.27	$1:2\cdot10^3$	e
Cr(VI)	$K_2Cr_2O_7$	Greenish grey (dark yellow orange)	530	0.27	$1:2\cdot10^3$	e,f
W(VI)	Na_2WO_4	Colourless ~ pale yellow	2.6	0.016	$1:1\cdot6.10^2$	
		Colourless	800	0.08	$1:1\cdot10^4$	d,g
U(VI)	$UO_2(OAc)_2$	Colourless (dull yellow ~ dark yellow orange)	800	0.04	$1:2\cdot10^4$	h
Mn(II)	$MnSO_4$	Pink	1300	0.027	$1:5\cdot10^4$	
Ti(IV)	$TiOSO_4$	Colourless (yellow)	130	0.02	$1:6.5\cdot10^3$	h,i
Fe(III)	$FeCl_3$	Yellowish grey	130	0.027	$1:5\cdot10^3$	e
Co(II)	$CoCl_2$	Pale red	1300	0.027	$1:5\cdot10^4$	e
Ni(II)	$NiCl_2$	Colourless	160	0.016	$1:1\cdot10^4$	e
		Bluish white	1000	0.04	$1:2.5\cdot10^4$	e
Pd(II)	$PdCl_2$	Yellow ~ yellowing brown	5.3	0.016	$1:3\cdot10^2$	
		Colourless	120	0.04	$1:3\cdot10^3$	d,j
Pt(IV)	H_2PtCl_6	Colourless ~ pale pink	5.3	0.027	$1:2\cdot10^2$	
		Colourless	530	0.027	$1:2\cdot10^4$	d,f
Cu(II)	$CuSO_4$	Light olive	1000	0.04	$1:2.5\cdot10^4$	e
Ag(I)	$AgNO_3$	Pale blue	1.3	0.027	$1:5\cdot10$	k
		Coulorless	3500	0.02	$1:1.8\cdot10^5$	d,k,l
Au(III)	$HAuCl_4$	Greyish blue	1.2	0.016	$1:7.5\cdot10$	
		Colourless	450	0.04	$1:1.1\cdot10^4$	d,m
Zn(II)	$ZnSO_4$	Colourless	1300	0.027	$1:5\cdot10^4$	
Cd(II)	$CdSO_4$	Colourless	1000	0.04	$1:2.5\cdot10^4$	
Hg(II)	$Hg(NO_3)_2$	Colourless	1300	0.027	$1:5\cdot10^4$	b
Al(III)	$KAl(SO_4)_2$	Colourless	1000	0.04	$1:2.5\cdot10^4$	b
Ga(III)	$GaCl_3$	Colourless	640	0.016	$1:4\cdot10^4$	b
In(III)	$In(NO_3)_3$	Colourless	250	0.027	$1:9\cdot10^3$	
Tl(I)	Tl_2SO_4	Colourless	640	0.016	$1:4\cdot10^4$	
Ge(IV)	Na_2GeO_3	Colourless	89	0.016	$1:5.6\cdot10^3$	
Sn(IV)	$SnCl_4$	Colourless	130	0.027	$1:5\cdot10^3$	d,i
As(V)	Na_2HAsO_4	Colourless	320	0.016	$1:2\cdot10^4$	
Sb(III)	$SbCl_3$	Colourless	270	0.027	$1:1\cdot10^4$	b,d,i
Bi(III)	$Bi(NO_3)_3$	Colourless	3200	0.016	$1:2\cdot10^5$	d,i

TABLE II (Continued)

Foreign ion	*Added form*	*Coloration of the resin phase*[a]	*Amount of foreign ion (µg)*	*Amount of detectable molybdenum(VI) (µg)*	*Limiting proportion*	*Remark*
Se(IV)	H_2SeO_3	Colourless	640	0.016	$1:4\cdot10^4$	
Te(IV)	K_2TeO_3	Colourless	530	0.027	$1:2\cdot10^4$	b
F^-	KF	Colourless	880	0.027	$1:3.3\cdot10^4$	
Br^-	KBr	Colourless	1300	0.027	$1:5\cdot10^4$	
I^-	KI	Colourless	360	0.008	$1:4.5\cdot10^4$	
NO_3^-	KNO_3	Colourless	1600	0.016	$1:1\cdot10^5$	
SO_4^{2-}	K_2SO_4	Colourless	1300	0.027	$1:5\cdot10^4$	
HPO_4^{2-}	Na_2HPO_4	Colourless	1600	0.016	$1:1\cdot10^5$	
$B_4O_7^{2-}$	$Na_2B_4O_7$	Colourless	650	0.027	$1:2.4\cdot10^4$	
$HCOO^-$	HCOONa	Colourless	1600	0.016	$1:1\cdot10^5$	
$C_2O_4^{2-}$	$(NH_4)_2C_2O_4$	Colourless	270	0.027	$1:1\cdot10^4$	
$C_4H_4O_6^{2-}$	Rochelle salt	Colourless	1600	0.016	$1:1\cdot10^5$	
$C_6H_5O_7^-$	Ammonium citrate	Colourless	1600	0.016	$1:1\cdot10^5$	
EDTA	Disodium salt	Colourless	2200	0.008	$1:2.8\cdot10^5$	n

[a] In parentheses is shown the coloration of the resin phase without removing the foreign compound.
[b] A drop of 4% tiron was used.
[c] A drop of 2% ammonium oxalate was added to precipitate cerium(IV).
[d] The precipitate was filtered off on a tiny wad of glass wool or filter paper.
[e] The coloration was observed after repeated rinsing of the resin beads with a few drops of deionized water or of 0.05 *F* EDTA.
[f] A drop of alkaline formaldehyde was added as a reducing agent.
[g] The test was carried out on the evaporation residue from the sample solution acidified with a few drops of concentrated hydrochloric acid.
[h] The effluent from a micro column of Dowex 50W-X8 (NH_4R) was tested[5].
[i] The sample solution was neutralised beforehand with a dilute solution of sodium hydroxide and the precipitate was removed.
[j] Palladium(II) was reduced with a minimum amount of zinc dust.
[k] The nitrate-form resin beads were used.
[l] A drop of 10% potassium iodide was added beforehand.
[m] Gold(III) was reduced with a drop of 10% oxalic acid.
[n] 4 drops of the sample solution were used.

Limits of identification determined after 1 hour standing with various resins in the chloride form* are: Dowex 1-X1: 12 ng, -X2: 8 ng, -X4: 12 ng, -X10: 16 ng, and Dowex 2-X2: 12 ng.

The influence of the sample volume on the sensitivity of the present resin spot test was also studied; the results are shown in Table I along with those obtained with the aid of a resin centrifuge method[11], a resin-powder flotation method[12] and the usual spot test.

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* The resins in the nitrate form gave the same values.

Influences of foreign substances

The data obtained with Dowex 1-X2 are summarized in Table II. Vanadium(V), chromium(VI), uranium(VI), titanium(IV), palladium(II), platinum(IV), silver(I) and gold(III) interfere with the test.

ULTRAMICRO DETECTION OF URANIUM(VI) WITH TIRON

A resin spot test for uranium(VI) was successfully carried out by exactly the same procedure as that described above for molybdenum (VI). The yellow uranium(VI) chelate[13] gave the strongly basic resin beads an intense yellow colour. The limit of identification was found to be 20 ng uranium(VI), per 0.04 ml of the test solution ($1:2\cdot10^6$) after standing for 1 h with Dowex 1-X2 in the chloride form*.

SUMMARY

A new sensitive and selective resin spot test for nanogram quantities of molybdenum(VI) with tiron is proposed. The limit of identification is 8 ng ($1 : 5\cdot10^6$) after 1 hour standing. Vanadium(V), chromium(VI), uranium(IV), titanium (IV), palladium(II), platinum(IV), silver(I) and gold(III) interfere. Uranium(VI) (20 ng, $1 : 2\cdot10^6$) can be detected similarly.

RÉSUMÉ

Une nouvelle méthode ultramicrochimique utilisant une résine échangeuse d'ion est proposée pour l'identification du molybdène(IV) avec le tiron comme réactif. Limite d'identification: 8 ng de molybdène(VI) après 1 heure. Gênent: vanadium(V), chrome(VI), uranium(VI), titane(IV), palladium(II), platine(IV), argent(I) et or(III). On peut aussi déceler jusqu'à 20 ng d'uranium-(VI) par la même méthode.

ZUSAMMENFASSUNG

Es wird eine empfindliche und selektive Harztüpfelmethode mit Tiron zum Nachweis von Nanogrammen Molybdän(VI) vorgeschlagen. Die Erfassungsgrenze beträgt 8 ng($1:5\cdot10^6$). Vanadium-(V), Chrom(VI), Uran(VI), Titan(IV), Palladium(II), Platin(IV), Silber(I) und Gold(III) stören. Uran(VI) kann auf ähnliche Weise nachgewiesen werden (20 ng, $1:2\cdot10^6$).

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* The resins in the nitrate form gave the same values.

THE DETERMINATION OF IRON IN TUNGSTEN CARBIDE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Iron is a deleterious element[1] in tungsten carbide and although the literature does not contain any specific reference to quantitative determinations, various procedures have been proposed for the determination of iron in tungsten metal or oxide. HOLT AND SWALHEIM[2] and SAKURABA AND SUZUKI[3,4] determined iron by electrolyzing a solution of sodium tungstate in sodium carbonate; the deposited iron was dissolved in acid, separated by ammonia precipitation and determined iodometrically; the cobalt (4–25%) present in tungsten carbide would increase the complexity of this method. CRAWLEY AND ASPINAL[5] determined iron in tungsten by extracting the iron(II)–tris-(bathophenanthroline) complex, but it was found that each 1% cobalt increased the apparent iron content by 0.018%. Emission spectrographic[6–9] procedures have been used for the determination of iron in tungsten metal or oxide but the intense tungsten spectrum causes difficulties. WALSH[10] has indicated that atomic absorption spectrophotometry is practically interference free and GATEHOUSE AND WILLIS[11] and ALLAN[12] have reported iron sensitivities (1% absorption 2483.3 Å) of 0.1 p.p.m. The present study has shown that atomic absorption spectrophotometry is a suitable method for the determination of minor percentages of iron in tungsten carbide powders or sintered pieces.

EXPERIMENTAL AND DISCUSSION

The equipment used in the study consisted of a Hilger large quartz E492 spectrograph, an E.M.I. 9558-QB photomultiplier tube, a modulated argon-filled iron hollow-cathode lamp[13] and a tuned amplifier[13]. The iron present in unsintered tungsten carbide powders is distributed heterogeneously, being derived from tungstic acid, carbon black, cobalt and austenitic grinding balls. Therefore any acid dissolution process requires a preliminary attack with a reducing acid and a subsequent attack with an oxidizing acid; tungsten hydrolyzes in the presence of oxidizing acids and co-precipitates a variable proportion of the iron present. Co-precipitation losses and evaporation or filtration difficulties can be avoided by retaining the tungsten in solution as a complex. Phosphoric acid, hydrofluoric acid and citric acid were considered as complexing agents and of these phosphoric acid seemed the most suitable. Sintered pieces passing a 18 B.S. mesh or less than 0.05″ thick and tungsten carbide powder are readily soluble in phosphoric acid.

A number of experimental difficulties with iron hollow-cathode lamps have been reported. ALLAN[12] experienced poor line-to-background ratios and was unable fully to resolve the 2483.3 Å line from neighbouring lines, whereas GATEHOUSE AND WILLIS[11] found that absorption sensitivity was markedly dependent on slit width. WILLIS[14] found an iron sensitivity (1% absorption) of 0.17 p.p.m. using an argon-filled lamp, and 0.10 p.p.m. using a neon-filled lamp. A sensitivity of only 0.30 p.p.m. was obtained with the argon-filled iron lamp used in this study, but lamps with much improved line-to-background ratios are now in the course of manufacture[15].

A preliminary investigation was carried out to determine the influence of phosphoric acid on the absorption sensitivity of iron and the results which were obtained using an air–acetylene flame, the 2483.3 Å iron resonance line and a 10 cm slot burner are shown in Fig. 1.

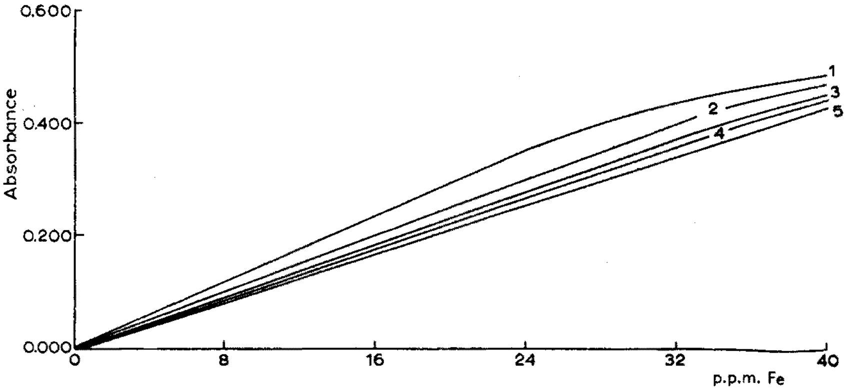

Fig. 1. The influence of phosphoric acid concentration on the absorption sensitivity of iron at a tungsten concentration of 20,000 p.p.m. Hollow-cathode lamp current, 30 mA. 1, aqueous; 2, 2% (v/v) H_3PO_4; 3, 4% (v/v) H_3PO_4; 4, 8% (v/v) H_3PO_4; 5, 16% (v/v) H_3PO_4.

Increasing phosphoric acid concentration caused a decrease in the absorption sensitivity of iron and 8% (v/v) phosphoric acid was finally selected as a suitable acid concentration, the sensitivity being 0.4 p.p.m. The iron content of tungsten carbide is in the range 0.00%–0.20% and an acceptable reproducibility is ±0.005%. These requirements could be met by dissolving a 1-g sample of tungsten carbide in 4 ml of phosphoric acid (s.g. 1.75), diluting to a final volume of 50 ml and using a lamp current of 30 mA; a calibration curve was prepared for the range 0–0.20% iron and found to be linear. The absorbance was not markedly dependent on flame type and the highest readings were obtained in a slightly rich flame (10.4 l/min air and 2.2 l/min acetylene at S.T.P.).

An interference study was carried out at the 0.000, 0.100 and 0.200% iron levels, the possible interfering elements being added as spectrographically pure metals. Any interference greater than 0.003% Fe was considered to be significant and using the selected conditions, no interference was encountered from 12% Co^{2+}, 24%Co^{2+} or varying tungsten contents between 70% and 100%. Sodium tungstate is less expensive than spectrographically pure tungsten metal and it was confirmed that substitution of sodium tungstate for tungsten metal in the calibration series did not cause any significant deviation from the established calibration curve.

The results obtained indicated that under the conditions recommended in this study, iron in tungsten carbide could be satisfactorily determined by atomic absorption spectrophotometry.

EXPERIMENTAL

Reagents

AnalaR hydrochloric (s.g. 1.16), orthophosphoric (s.g. 1.75) and nitric (s.g. 1.42) acids were used. Iron solution: dissolve 0.2 g spectrographically pure iron (Johnson-Matthey) in 10 ml of 50% (v/v) orthophosphoric acid, oxidise with dropwise additions of nitric acid and evaporate to fumes; fume for 1 min, add 50 ml of water, simmer to dissolve, cool and dilute to 1 l (1 ml ≡ 0.2 mg Fe). Spectrographically pure tungsten (Johnson-Matthey) or AnalaR sodium tungstate (hydrated) were used.

Recommended procedure

Transfer 1 g of tungsten carbide powder to a 125-ml conical beaker. Add 4 ml of orthophosphoric acid and 4 ml of hydrochloric and, cover and simmer for 30 min. Add slowly 4 ml of nitric acid and simmer until dissolution is complete. Evaporate to light fumes and fume gently for 1 min. Cool, add 20 ml of water, simmer to dissolve all soluble salts, filter if necessary, cool and dilute to 50 ml in a graduated flask. Using the 2483.3 Å iron line, measure the absorbance by atomising the solution in a slightly rich air–acetylene flame and operating the iron hollowcathode lamp at 30 mA. The calibration graph is prepared for the range 0.00–0.20% Fe by making additions of iron solution to several 1.0-g samples of tungsten or several 1.8-g samples of sodium tungstate and treating in a similar manner to the assays.

RESULTS

Some experimental tungsten carbide powders were analyzed by the proposed method and by X-ray fluorescence and the results are compared in Table I. The X-ray fluorescence analyses were obtained with a Philips X-ray Spectrograph PW 1520. The results obtained confirm the accuracy of the proposed procedure and certain advantages over other techniques are indicated.

TABLE I

IRON CONTENT OF TUNGSTEN CARBIDE POWDERS

Sample	*% Iron*	
	Atomic absorption spectrophotometry	*X-ray fluorescence*
C 1885–0	0.025	0.02
C 1885–12	0.060	0.05
C 1885–48	0.115	0.11
C 1885–84	0.185	0.20

Appreciation is expressed to T. R. THOMSON who carried out the X-ray fluorescence analyses and the Chief Research Officer, The Broken Hill Proprietary Company Limited for permission to publish this work.

SUMMARY

An atomic absorption spectrophotometric procedure for the determination of 0.005 to 0.20% iron in a phosphoric acid solution of tungsten carbide is described. The method is rapid, preliminary

separations are not required and the results obtained have been compared with those obtained by X-ray fluorescence.

RÉSUMÉ

Une méthode spectrophotométrique par absorption atomique est proposée pour le dosage du fer (0.005 à 0.20%) dans une solution de carbure de tungstène dans l'acide phosphorique. La méthode est rapide; aucune séparation préalable n'est nécessaire. Les résultats ont été comparés avec ceux obtenus par fluorescence aux rayons X.

ZUSAMMENFASSUNG

Es wird eine Methode der atomaren Absorptionsspektroskopie zur Bestimmung von 0.005–0.20% Eisen in einer Lösung von Wolframcarbid in Phosphorsäure beschrieben. Das Verfahren ist schnell und erfordert keine vorhergehenden Trennungen. Die Ergebnisse wurden mit denen, die mit der Röntgenfluoreszenzanalyse erhalten wurden, verglichen.

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SPECTROPHOTOMETRIC DETERMINATION OF GALLIUM WITH 1-(2,4-DIHYDROXYPHENYLAZO)-2-NAPHTHOL-4-SULFONIC ACID

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In 1958, POLUEKTOV AND KISELEVA[1] studied a number of *o,o'*-dihydroxyazo dyes and reported 1-(2,4-dihydroxyphenylazo)-2-naphthol-4-sulfonic acid to be a sensitive colorimetric reagent for gallium. During the same year, NAZARENKO AND VINKOVETSKAYA[2] proposed this compound as a reagent for the fluorimetric determination of gallium. However, no extensive study of this compound as a spectrophotometric reagent for gallium has been made. This paper describes such a study and presents a sensitive method for the spectrophotometric determination of gallium. Gallium is separated from interfering ions by solvent extraction with isopropyl ether. The method has been applied successfully to a variety of salt solutions containing various small amounts of gallium.

EXPERIMENTAL

Apparatus

Absorbance curves were obtained with a Beckman ratio recording spectrophotometer, Model DK-2. For measurements at a single wavelength a Beckman spectrophotometer, Model DU, was used. Measurements were made in matched 1.00-cm Corex cells.

A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated with certified buffer solutions.

Reagents

1-(2,4-Dihydroxyphenylazo)-2-naphthol-4-sulfonic acid (DHPAN). $C_{16}H_{12}N_2O_6S$. Dissolve 0.3603 g of DHPAN (Eastman 9999) in distilled water and dilute to 100 ml to give a $1.00 \cdot 10^{-2}$ *M* reagent stock solution.

Standard gallium solution. Dissolve 0.1344 g of pure gallium sesquioxide (Ga_2O_3, A. D. Mackay, New York) in 1 or 2 ml of aqua regia, evaporate to a syrupy consistency, add about 5 ml of 12 *N* hydrochloric acid and again evaporate almost to dryness. Add 5 ml of 12 *N* hydrochloric acid, repeat the evaporation and then dilute with water to 100 ml in a volumetric flask. The concentration of gallium ion is $1.41 \cdot 10^{-2}$ *M*, or 984 p.p.m. Prepare more dilute standard solutions as required.

Buffer solutions. Buffer solutions were prepared by mixing 0.5 *N* sodium acetate solution and 0.5 *N* hydrochloric acid in various proportions and checking their pH with a meter.

Other reagents. All other reagents were analytical grade and were used without further purification.

Reagent and complex

1-(2,4-Dihydroxyphenylazo)-2-naphthol-4-sulfonic acid (DHPAN) can be made by coupling 1-diazo-2-naphthol-4-sulfonic acid with resorcinol. The compound is a dark greenish brown solid, readily soluble in water and ethanol. The solutions are dark red (reddish brown in dilute solution) when neutral or acidic. Basic solutions are purple. No fluorescence was observed in either acidic or basic solutions. At pH 5.8, the absorbance maximum is at about 485 mμ, when a distilled water blank is used (see curve I, Fig. 1).

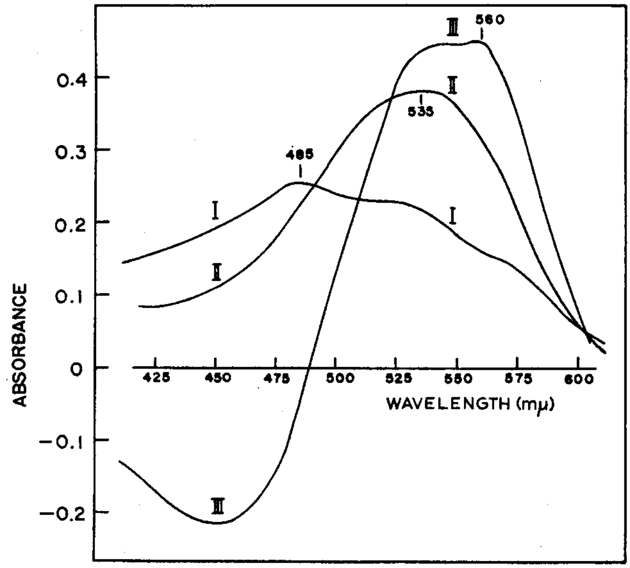


Fig. 1. Curve I: DHPAN $2 \cdot 10^{-5}$ *M*, at pH 5.8 *vs.* water. Curve II: DHPAN $2 \cdot 10^{-5}$ *M*, gallium 0.4 p.p.m., at pH 5.8 *vs.* water. Curve III: DHPAN $1 \cdot 10^{-4}$ *M*, gallium 1.18 p.p.m., at pH 5.8 *vs.* reagent solution.

An immediate color change was observed in spot tests by adding gallium to the reagent solution. The complex is bright pink in neutral and acidic solutions but purple in basic solution. Fluorescence was observed in neutral and acidic solutions. The absorbance of the complex was measured at pH 5.8 against a distilled water blank and has a maximum at about 535 mμ (see curve II, Fig. 1).

Curve III in Fig. 1 was obtained for the complex with the reagent solution as reference. It shows negative absorbance from 400 to 490 mμ and positive absorbance over the 490–600 mμ range. Maximum absorption is at 560 mμ.

Effect of pH

The effect of hydrogen-ion concentration on the absorbance of the complex is shown in Fig. 2. A reagent blank was employed. The absorbance at low pH is not strong. Above pH 3.5 the absorbance increases sharply with increasing pH, reaching a maximum at about pH 4, then decreases with increase in pH. At pH 5.8, Beer's law is obeyed and all the following experiments were carried out at this pH.

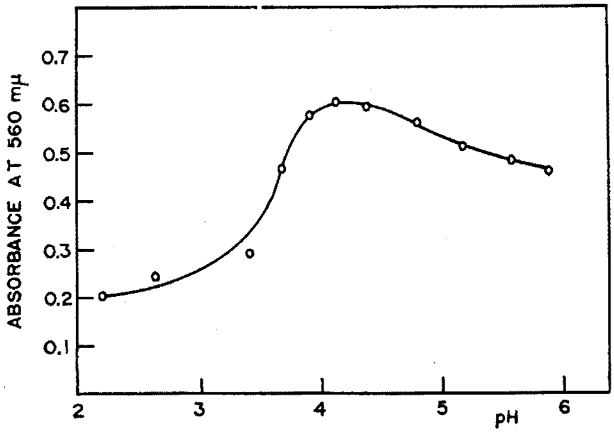


Fig. 2. Effect of pH on absorbance.

Order of addition of reagents

The order of addition of the reagents was found to have an effect upon the absorbance of the complex. For good reproducibility a certain order of addition must be followed, namely, reagent, buffer, gallium.

Rate of color formation

The color formation is instantaneous, reaching almost the maximum absorbance in 10 min. However, there is a small increase, about 2% per hour, during the first few hours. Thirty min for color developing was employed in this study.

Effect of temperature

Absorbance measurements at 15°, 25° and 35°, respectively, showed the complex to be independent of normal variations in laboratory temperature.

Conformity to Beer's law

Beer's law is obeyed from 0.04 to 0.4 p.p.m. gallium at $4.0 \cdot 10^{-5}$ *M* reagent concentration and from 0.4 to 2.8 p.p.m. gallium at $2.0 \cdot 10^{-4}$ *M* reagent concentration. All measurements were made against reagent blank solutions.

Sensitivity

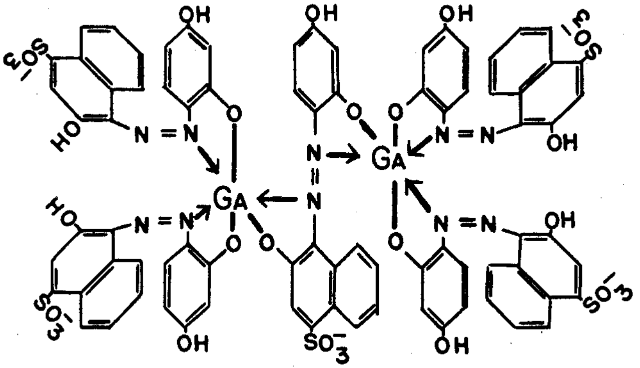
The sensitivity of the color reaction is 0.0026 μg Ga per cm^2 for $\log I_0/I = 0.001$, *i.e.*, one part of gallium in 385 million parts of solution. A more practical sensitivity, however, based on a reproducible absorbance reading of 0.005 unit, is 0.013 μg, *i.e.*, one part of gallium in 77 million parts of solution. The spot-plate sensitivity is 0.025 μg of gallium per 0.05 ml of test solution, with a dilution limit of 1 to 2,000,000.

Optimum concentration range

The most sensitive range for absorbance measurement is 0.2 to 0.7 unit[3]. This range corresponds to a gallium concentration of 0.52 to 1.8 p.p.m. for the gallium–DHPAN complex.

Mole ratio studies

The empirical formula of the gallium complex in solution was established by three independent techniques: the mole ratio method of YOE AND JONES[4], the continuous variations method of JOB[5] as modified by VOSBURGH AND COOPER[6], and the slope ratio method proposed by HARVEY AND MANNING[7]. These studies indicate that the complex has a 2:5 ratio of gallium to the organic ligand. The structure formula for the $Ga_2(DHPAN)_5$ complex may be written thus:



Effects of diverse ions

An error of ± 3% was arbitrarily taken as the tolerance of the complex. If more than 100 p.p.m. concentration of ion can be tolerated in a solution containing 1 p.p.m. gallium, it was considered to have no interference. Of the ions tested, the following were found to have no interference: Ba^{2+}, BO_3^{3-}, Br^-, Ca^{2+}, Cd^{2+}, F^-, I^-, La^{3+}, NO_2^-, Pb^{2+}, PO_4^{3-}, Rb^+, Ru^{3+}, S^{2-}, Sr^{2+} and TeO_4^{2-}. Ions interfering at less than 1 p.p.m. for a gallium concentration of 1 p.p.m. are: Al^{3+}, Au^{3+}, Be^{2+}, Co^{2+}, Fe^{3+}, In^{3+}, Ni^{2+}, OsO_4^{2-}, Th^{4+}, VO_2^+ and Zr^{4+}. The following ions are tolerated at the concentration in p.p.m. given in parentheses: As^{5+}(5), Bi^{3+}(10), Ce^{3+}(50), Ce^{4+}(5), Cr^{3+}(1), Cr^{6+}(10), Cs^+(50), Cu^{2+}(1), Er^{3+}(10), Eu^{3+}(1), Gd^{3+}(10), Hg^+(1), Hf^{4+}(1), Ir^{4+}(5), Mg^{2+}(50), Nb^{3+}(5), Pr^{3+}(5), Sb^{4+}(50), Se^{4+}(10), Sn^{4+}(10), Ta^{3+}(10), Ti^{4+}(100), Tl^{3+}(5), Tm^{3+}(1), UO_2^{2+}(1), W^{6+}(1), Y^{3+}(1) and Zn^{2+}(1).

SEPARATION OF GALLIUM

Gallium must be separated from many interfering ions before making the spectrophotometric determination. Extraction of gallium ions into isopropyl ether is an excellent method for the separation[8]. The optimum hydrochloric acid concentration is

6.5 to 8 *N* [9]. Under these conditions only iron(III), gold and thallium(III) are extracted in large amount. If a suitable reducing agent, such as stannous chloride, is added, iron(III), gold and thallium(III) are reduced to iron(II), metal and thallium(I), respectively, and are not extracted. Antimony, arsenic, germanium, molybdenum, tellurium and tin are extracted to some extent. Ether extraction followed by back-extraction with hydrochloric acid solution, however, will decrease the interfering ion content in the ether layer to a negligible amount.

The following procedure was used in this study and is recommended for use in the determination of gallium by our method.

Method

Transfer the sample solution containing 1 to 10 μg of gallium to a separatory funnel, add an excess of 15% (w/v) stannous chloride (about 1 ml) and then hydrochloric acid to bring the acidity to 7.5 *N* and the volume of the solution to about 10 ml. After about 5 min, extract twice with 10-ml portions of isopropyl ether. Wash the combined ether phase with a mixture of 10 ml of 7.5 *N* hydrochloric acid and a drop of stannous chloride. Then wash 2 or 3 times with 10 ml of 7.5 *N* hydrochloric acid saturated with isopropyl ether. Transfer the organic phase containing the gallium to a 25-ml beaker and evaporate just to dryness on a water-bath. To the residue add about 5 ml of distilled water and 2 to 3 drops of 0.5 *N* hydrochloric acid. Transfer the solution quantitatively to a 25-ml volumetric flask, dilute to the mark and mix. Pipet out an aliquot sufficient

TABLE I

ANALYSIS OF SALT SOLUTIONS[a]

Ions	*1*	*2*	*3*	*4*	*5*	*6*
Series A[b]						
Ga^{3+}	1.0	1.0	1.0	1.0	1.0	1.0
Al^{3+}	2.0	5.0	—	—	2.0	5.0
In^{3+}	—	—	2.0	5.0	2.0	5.0
Ga^{3+} found	0.99	0.99	0.99	0.99	0.98	0.98
Series B[c]						
Ga^{3+}	1.28	1.47	0.59	0.98	1.77	0.49
Al^{3+}	0.5	1.0	1.0	0.5	1.0	1.0
Co^{2+}	0.5	1.0	1.0	—	—	—
Cr^{3+}	0.5	1.0	1.0	0.5	1.0	1.0
Cu^{2+}	0.5	1.0	1.0	0.5	1.0	1.0
Fe^{3+}	—	—	—	0.5	1.0	1.0
In^{3+}	0.5	1.0	1.0	0.5	1.0	1.0
Ni^{2+}	0.5	1.0	1.0	0.5	1.0	1.0
Th^{4+}	0.5	1.0	1.0	0.5	1.0	1.0
Tl^{3+}	—	—	—	0.5	1.0	1.0
Zn^{2+}	0.5	1.0	1.0	0.5	1.0	1.0
Zr^{4+}	0.5	1.0	1.0	0.5	1.0	1.0
Ga^{3+} found	1.27	1.47	0.58	0.99	1.77	0.48

[a] All concentrations are in p.p.m.

[b] Prepared by T. L. Chang.

[c] Prepared by Dr. T. Arita.

to give an absorbance between 0.2 and 0.7, and transfer to a 25-ml volumetric flask containing 5 ml of $1.00 \cdot 10^{-3}$ M DHPAN solution buffered at pH 5.8. Measure the absorbance at 560 mμ, using the reagent as a blank, and read the amount of gallium from a standard curve.

Analysis of salt solutions

Two series of salt solutions were prepared and analyzed for gallium. The results are summarized in Table I.

SUMMARY

A new spectrophotometric method for the determination of gallium is described using 1-(2,4-dihydroxyphenylazo)-2-naphthol-4-sulfonic acid (DHPAN) as a reagent. The color reaction has a sensitivity of 0.013 μg Ga per cm² for log $I_0/I = 0.005$ at 560 mμ and obeys Beer's law up to 2.8 p.p.m. The effects of pH, time, order of addition of the reagents, temperature and diverse ions were investigated. Gallium is separated from interfering ions by solvent extraction.

RÉSUMÉ

Une nouvelle méthode spectrophotométrique est proposée pour le dosage du gallium, au moyen de DHPAN. L'influence de divers facteurs a été examinée. On procède à la séparation d'avec d'autres éléments gênants par extraction dans un solvant.

ZUSAMMENFASSUNG

Es wird eine neue spektrophotometrische Methode zur Bestimmung von Gallium mit Hilfe von DHPAN beschrieben. Der Einfluss verschiedener Faktoren wurde untersucht. Die Abtrennung von störenden Elemente erfolgte durch Lösungsmittelextraktion.

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ANALYSE DES COMPOSES FLUORES CORROSIFS PAR CHROMATOGRAPHIE GAZEUSE

CONTROLE DU FLUOR LIBRE

O. ROCHEFORT

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La séparation des isotopes de l'uranium par diffusion gazeuse nécessite la mise en oeuvre de composés fluorés corrosifs volatils auxquels sont liés un certain nombre de problèmes analytiques.

Nous nous sommes proposés de décrire une méthode d'analyse, par chromatographie gazeuse, du fluor moléculaire, gaz incondensable et corrosif, pour résoudre les problèmes suivants:

(*1*) Contrôle du fluor libre à la sortie des cellules d'électrolyse.

(*2*) Contrôle du fluor libre dans l'hexafluorure d'uranium produit par la réaction du fluor sur le tétrafluorure d'uranium.

En outre la solution adoptée trouve une application intéressante dans l'analyse des gaz permanents non-corrosifs (O_2, N_2, CO, CF_4) (même à l'état de traces) dans certains composés fluorés corrosifs tels que le fluor, l'hexafluorure d'uranium et l'acide fluorhydrique anhydre.

Différentes méthodes ont déjà été proposées et utilisées pour l'analyse du fluor libre. Elles sont toutes délicates à mettre en oeuvre par suite de la très grande réactivité du fluor. De plus la facilité avec laquelle il libère de l'oxygène de tous les composés qui en contiennent, accroît encore les difficultés s'il est nécessaire de doser également l'oxygène dans le fluor; c'est en particulier le cas du contrôle de la pureté du fluor engendré par l'électrolyse du KF, 2 HF. Compte-tenu de la nature de cet élément, les possibilités d'emploi d'une méthode d'analyse *purement physique* sont fortement compromises.

L'absorption du fluor par les solutions aqueuses de sulfite de sodium, déjà préconisée[1], est inutilisable pour l'analyse d'un fluor pur puisqu'elle libère fatalement un peu d'oxygène. Il en sera de même pour toutes les absorptions en solution aqueuse comme celle des mélanges de gaz inertes et de fluor à des concentrations de ce dernier de moins de 10%, par une solution diluée d'acide iodhydrique[2].

Il est donc préférable de s'orienter vers une réaction du fluor en milieu anhydre. Cependant les composés comportant de l'oxygène dans leur molécule sont aussi prohibés. La réaction des halogènes sur les métaux peut être envisagée, mais à part les métaux nobles, ils contiennent des oxydes qui peuvent dégager des traces d'oxygène. Ainsi nous avons employé avec succès l'absorption du fluor par le mercure[3,4], mais cette méthode est très laborieuse. Elle permet cependant d'isoler les impuretés du fluor qui peuvent être alors analysées (par spectrographie de masse par exemple).

Un procédé d'absorption du fluor par le brome dissous dans le trifluorure de brome a été également proposé[5]. Le déplacement de l'halogène d'un halogénure métallique, par le fluor donne lieu à des méthodes intéressantes qui conduisent au dosage de l'halogène libéré. Ainsi le déplacement du brome du bromure de sodium et son dosage semi-automatique par colorimétrie a été proposé[6]. De même le déplacement du chlore du chlorure de sodium anhydre a été décrit; le chlore est ensuite dosé volumétriquement après absorption soit par la soude[2,7], soit par l'iodure de chlore[8]. Il est ainsi possible d'analyser les impuretés du fluor (O_2, N_2, CO_2), en particulier après élimination de HF par le fluorure de sodium. Ces réactions gaz–solide ont été réalisées en statique.

Nous avons fondé nos analyses du fluor sur ces réactions avec le fluorure et le chlorure de sodium, en les couplant à la chromatographie gazeuse comme moyen d'analyse du chlore et des impuretés. Les réactions sont alors toutes réalisées en dynamique par passage du fluor, entraîné par le gaz porteur, sur le fluorure et le chlorure de sodium.

ANALYSE DU FLUOR LIBRE

Comme pour tous les gaz permanents, la chromatographie de partage gaz–liquide n'est pas applicable à la séparation du fluor libre, à moins de travailler à très basse température.

L'analyse par chromatographie d'adsorption gaz–solide du fluor moléculaire, gaz incondensable, n'est pas possible directement en raison de son affinité pour la plupart des adsorbants classiques qui sont en outre tous des produits hydrophiles, difficiles à déshydrater parfaitement sans leur faire perdre leur activité.

Au contraire l'analyse du chlore par chromatographie gaz–liquide est possible en appliquant la technique proposée et mise au point par ELLIS et ses collaborateurs[9–12] pour la séparation de gaz corrosifs et condensables tels que HF, ClF_3, UF_6 et le chlore.

Principe

Le principe de l'analyse du fluor est alors le suivant: le fluor est remplacé quantitativement par du chlore par réaction sur du chlorure de sodium *absolument anhydre* suivant l'équation réactionnelle:

$$NaCl + 1/2\ F_2 \rightarrow NaF + 1/2\ Cl_2$$

Le chlore est ensuite séparé des autres constituants contenus dans le fluor au moyen d'une huile de type "Kel-F" comme phase stationnaire et d'un polymère solide du même type comme support; il est détecté avec un catharomètre à fil de nickel.

Dispositif expérimental (Fig. 1)

On dispose en série à la suite de l'échantillonneur (4):

(*a*) une "précolonne" (6) de chlorure de sodium anhydre, de 10 cm de long (le sel est granulé à 70/100 A.S.T.M. et desséché sous vide à 350–400° durant 3 h);

(*b*) une colonne (8) d'huile "Voltalef no. 3" sur support résine "Voltalef 300 LD" granulée à 40/70 A.S.T.M. et à raison de 40 : 100 en poids (de 1.80 à 2 m de longueur);

(*c*) un catharomètre (3) à fil de nickel, de préférence du type conçu pour l'analyse des gaz fluorés corrosifs au cas où le détecteur viendrait en contact avec le fluor.

L'ensemble des colonnes est maintenu entre 60 et 70° au moyen d'une enceinte calorifugée.

Les seuls matériaux utilisés, en particulier pour les pièces en contact avec le fluor, sont le nickel, le monel, les résines fluorées et chlorofluorées (Téflon, Kel-F, Voltalef).

L'hélium, gaz porteur, est parfaitement décontaminé sur tamis moléculaires (1) à −196°.

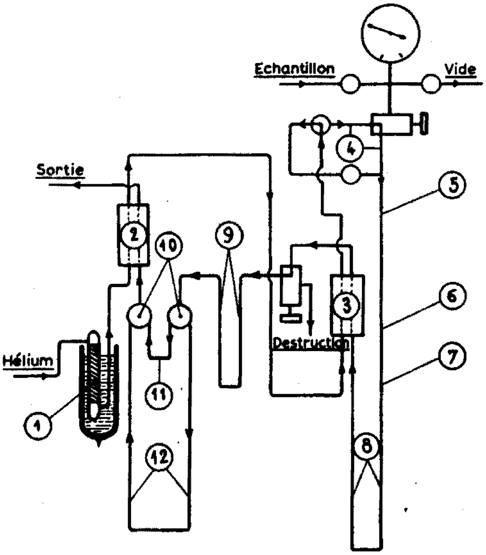

Fig. 1. Dispositif expérimental.

Résultats

Avec un débit d'hélium de 2.4 l/h, le chromatogramme d'un fluor pur (ne contenant que des impuretés telles que O_2, N_2, CF_4 et HF en faibles quantités) ne doit présenter que deux pics: (*1*) celui des "inertes" (O_2, N_2, CF_4) de temps de rétention 1 min environ et (*2*) celui du chlore de temps de rétention 2 min environ.

Réponse du fluor en chlore. Dans un large domaine de pression d'échantillonnage on obtient une réponse en "surface" de pics (produit de la hauteur par la largeur à mi-hauteur) proportionnelle aux pressions de fluor introduites (de quelques mm Hg à 500 mm Hg) (Fig. 2) ce qui montre que la transformation du fluor en chlore est *quantitative* même pour des pressions d'introduction proches de l'atmosphère.

Remarquons que, lorsque la réponse est exprimée en hauteurs de pics, les plages de linéarité sont beaucoup plus étroites comme le montre la Fig. 2, ce qui peut s'expliquer par un retard dans la libération du chlore du réseau du sel entraînant un étalement du pic. Ainsi la réponse est bien linéaire de 0.25 à 20 mm Hg de fluor engagé.

La limite de détection est de 0.0005 cm^3 T.P.N. soit 100 à 200 v.p.m. de fluor dans l'échantillon.

Afin de connaître la capacité et le rendement de transformation du NaCl en NaF par F_2 à 70°, nous avons effectué des introductions répétées de fluor. Nous observons ainsi la saturation de NaCl, mise en évidence simultanément par une annulation in-

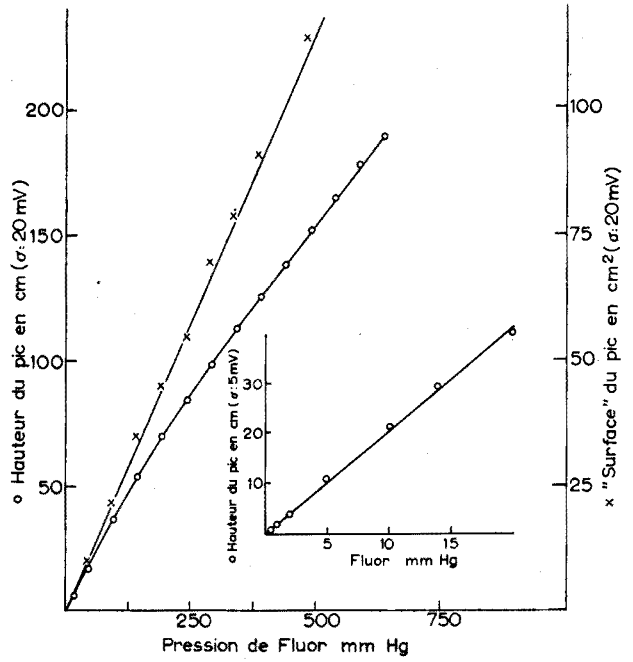

Fig. 2. Réponse du fluor en chlore.

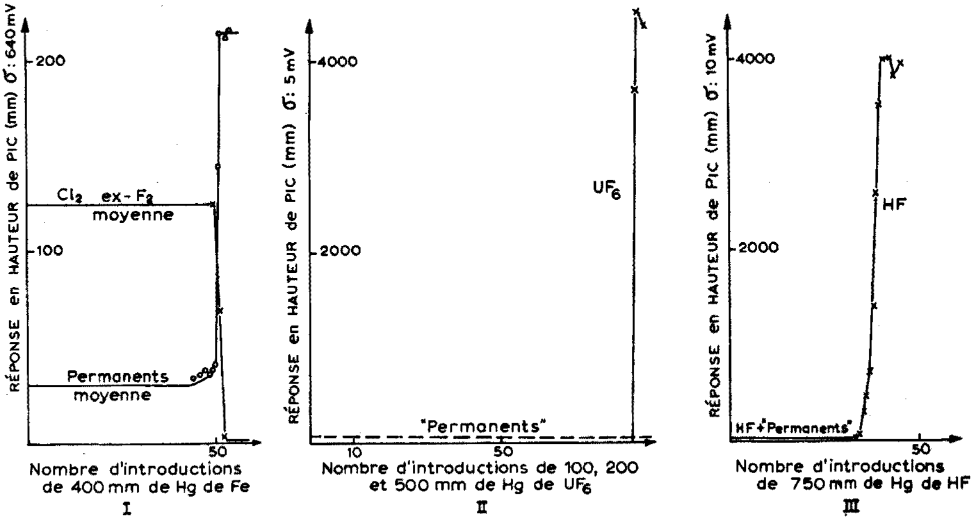

Fig. 3. Reaction de F_2 sur NaCl(I); reaction de UF_6 sur NaF(II); absorption de HF par NaF(III).

stantanée du pic de chlore et une augmentation rapide du pic des permanents (Fig. 3).

L'activité de la précolonne s'annule lorsque 95% environ du NaCl engagé sont transformés en NaF.

La précision des mesures sur le chlore (ex-fluor) est de ± 4% d'après les hauteurs de pic.

Discussion

(*a*) Il est très important que le chlorure de sodium soit parfaitement anhydre, donc déshydraté sous la forme la plus divisée possible, et conservé à l'abri de l'humidité atmosphérique, sinon les résultats obtenus sont complètement aberrants: le fluor peut ne pas réagir ou être décomposé plus ou moins par l'humidité présente. Mais dans de bonnes conditions, la réaction avec NaCl s'effectue très bien quelle que soit la concentration du fluor dans l'hélium.

(*b*) Le comportement du F_2O n'est pas bien connu, mais il semble logique de penser qu'il se comportera comme le fluor en donnant du fluorure et du chlore[13]. SiF_4, s'il est présent, sera retenu par le fluorure formé en donnant un fluosilicate.

(*c*) Cependant de nombreux fluorures volatils (UF_6, ClF_3, ClF, etc.) peuvent libérer du chlore par réaction avec NaCl. Ainsi le dispositif décrit n'est *directement* applicable qu'à la recherche du fluor libre dans un gaz inerte vis à vis du chlorure; c'est le cas du contrôle du fluor à la sortie des cellules d'électrolyse.

(*d*) Si le fluor contient de l'HF en faible quantité et bien que celui-ci ne réagisse pas avec le chlorure dans les conditions indiquées, le fluorure, formé par réaction du fluor sur NaCl, fixera l'acide fluorhydrique présent.

S'il s'agit d'analyser de petites quantités de fluor en présence d'une forte proportion de HF, il est possible de faire précéder la précolonne de NaCl, d'une petite quantité de NaF, comme nous le verrons ci-après.

(*e*) Enfin notons qu'une application très intéressante de la précolonne de NaCl peut se ramener à la simple destruction du fluor (sans le doser) pour permettre l'analyse des autres gaz permanents par chromatographie d'adsorption. Nous reviendrons un peu plus loin sur les détails de cette application.

ANALYSE DU FLUOR DANS UF_6

Différentes méthodes sont à envisager pour résoudre ce problème: le dosage du fluor peut être réalisé par débitmétrie différentielle au cours de la transformation du fluor en SO_2F_2 par SO_2 (méthode de WEBER[14]). Cependant cette méthode reste délicate à mettre en oeuvre, en particulier, les difficultés de stabilisation des multiples débits gazeux étant importantes. Le SO_2F_2 formé est aussi dosable par spectrométrie infrarouge. La spectrographie de masse a également servi à analyser le fluor dans l'hexafluorure d'uranium[15].

Nous avons donc mis au point une méthode chromatographique d'analyse du fluor en présence d'UF_6 et de faibles quantités de HF, N_2, O_2 et CF_4.

Principe

Comme l'hexafluorure d'uranium peut réagir plus ou moins avec le chlorure de sodium de la précolonne, il est nécessaire de le fixer ou de le séparer avant d'introduire le fluor sur le chlorure. Pour résoudre ce problème nous avons utilisé la propriété connue du NaF de fixer UF_6 sous forme de complexe 3 NaF, UF_6[16-18].

L'hélium entraînant l'échantillon traverse une précolonne de NaF qui retient UF_6 et également HF; le fluor inaltéré est alors remplacé quantitativement par du chlore libre par passage sur la précolonne de NaCl. Ensuite le chlore est séparé et dosé sur une colonne "classique" à huile "Voltalef" comme phase stationnaire.

Dispositif expérimental (Fig. 1)

Il est semblable à celui décrit pour l'analyse du fluor pur, excepté l'adjonction de la précolonne (5) de NaF anhydre, préparé par décomposition de NaF, HF en pastilles à 300°, puis broyé et granulé à 40/70 ou 70/100 A.S.T.M. et régénéré sous vide à 300–350°. La température de l'ensemble est maintenue entre 60 et 70°.

Nous voyons qu'un tel dispositif permet de doser de petites quantités de fluor dans HF sans craindre une interférence éventuelle de ce dernier.

Résultats

Avec un débit d'hélium de 2.4 l/h et en présence d'UF_6, la réponse en hauteur de pic est une droite; elle est identique à celle obtenue avec le fluor ne contenant pas d'UF_6, pour des pressions d'échantillonnage correspondant de 0 à 20% de fluor (en pression) dans 100 mm Hg d'UF_6.

Le chromatogramme ne doit présenter normalement que le pic des "permanents" et celui du chlore. Les autres constituants tels que UF_6 et HF ne doivent donner aucune réponse.

Etude de l'absorption de UF_6 et HF par NaF

Afin de connaître la capacité et les limites d'absorption de UF_6 et HF par du fluorure de sodium de granulométries différentes et utilisé dans les conditions expérimentales de l'analyse, nous avons effectué les essais suivants.

Hexafluorure d'uranium. Des introductions d'UF_6 à des pressions partielles relativement élevées (jusqu'à 500 mm Hg) ont permis de saturer systématiquement le NaF.

La saturation du NaF est mise en évidence par l'apparition instantanée du pic d'UF_6 qui atteint rapidement son maximum (Fig. 3) (en deux ou trois introductions) pour une pression d'échantillonnage constante. La granulométrie optimale adoptée pour le NaF est de 70/100 A.S.T.M. (grains de 150 à 200 μ de diamètre). Pour cette granulométrie le rendement d'absorption d'UF_6 par NaF est de 30% par rapport à la stoéchiométrie de la formule UF_6, 3 NaF. Si l'on utilise un échantillonneur de 5 cm^3 de volume, une précolonne de 20 cm de longueur est suffisante pour absorber quantitativement chaque introduction d'UF_6 à des pressions allant jusqu'à 760 mm Hg. La capacité d'une telle précolonne est d'environ 300 cm^3 T.P.N. d'UF_6 (5 g) ce qui représente environ 450 introductions de 100 mm Hg.

Acide fluorhydrique anhydre. De même des introductions systématiques de HF sous 760 mm Hg de pression d'échantillonnage, sur une précolonne de 9 cm de NaF (2.7 g), montrent que durant quelques dizaines d'introductions, la proportion de produit détecté par la cellule à fil représente moins de 0.5% en volume de la quantité détectée lorsque le NaF est saturé; cette saturation est également mise en évidence par une augmentation brusque et rapide du pic enregistré et elle correspond à 65% du poids théorique d'HF qui peut être fixé par NaF sous forme de NaF, HF (granulométrie 40/70 A.S.T.M.) (Fig. 3).

Une longueur de précolonne de 15 à 20 cm donne alors toute satisfaction.

Remarques

Quant au dosage de UF_6 et de HF, il pourra être réalisé par chromatographie directe sur huile "Voltalef no. 3" selon la technique décrite par ELLIS[9,10]. Il suffit de supprimer ou mieux de détourner les précolonnes par un système de dérivation.

Enfin il est possible d'analyser les gaz permanents non-corrosifs en adjoignant une seconde colonne de chromatographie en série avec le montage décrit ci-dessus.

ANALYSE DES GAZ PERMANENTS

La séparation de l'oxygène, de l'azote et du CF_4 s'effectue très facilement par chromatographie d'adsorption gaz–solide sur tamis moléculaires 13 A à température ambiante ou même un peu plus élévée.

Pour analyser les gaz permanents dans le fluor, l'UF_6 ou l'HF il est absolument nécessaire d'éliminer le chlore (ex-fluor), l'UF_6 et l'HF du gaz porteur, avant de le véhiculer sur la colonne de tamis.

Ainsi la précolonne de NaF fixe UF_6 et HF, et une colonne supplémentaire de silicagel va nous permettre d'éliminer le chlore.

Le principe de l'analyse est alors le suivant (Fig. 1).

L'hélium entraînant l'échantillon (qui peut contenir UF_6, HF, F_2, O_2, N_2, CF_4) traverse la précolonne (5) de NaF (elle retient UF_6 et HF), puis celle de NaCl (6) où le fluor est remplacé quantitativement par du chlore, les autres gaz permanents (O_2, N_2, CF_4) restant inaltérés. Le chlore est normalement séparé de ces permanents par la colonne (8) d'huile Voltalef no. 3 à 70° et détecté par le premier catharomètre (3). Il est ensuite momentanément retenu sur une colonne (9) de silicagel à 50° pour permettre aux gaz permanents d'être séparés sur la colonne (12) de tamis moléculaires à 40° et d'être détectés par la 2ème cellule (2). Lorsque le pic de CF_4 est enregistré, on dérive (10, 11) le courant de gaz porteur vers cette seconde cellule en détournant les tamis.

Le chlore, à son tour est détecté par le 2ème catharomètre. Un tel système rend possible l'analyse, en un même échantillonnage de F_2, O_2, N_2, et CF_4; il peut être simplifié, si l'on ne désire pas connaître la teneur en fluor, par la suppression de la première colonne (8) et du premier catharomètre (3).

Enfin si l'on veut doser des traces de gaz permanents ($<$ 100 v.p.m.) il faudra utiliser un détecteur à gaz rare rendu sensible aux gaz minéraux en faisant fonctionner un détecteur de ce type avec de l'hélium[19] selon le principe de son fonctionnement habituel avec l'argon. Dans ce cas la très grande pureté de l'hélium nécessite un dispositif très efficace de fixation du chlore, faisant appel à des pièges à carboglace et à azote liquide, pour éviter que ce gaz ne vienne contaminer le détecteur.

CONCLUSIONS

Nous avons donné une solution chromatographique et assez générale pour l'analyse du fluor moléculaire dans les gaz permanents non-corrosifs ou dans des composés fluorés corrosifs (UF_6, HF). La méthode est aussi étendue à l'analyse des gaz permanents "inertes" (même à l'état de traces) dans ces mêmes composés fluorés. Ainsi moyennant l'adjonction de colonnes et d'un catharomètre supplémentaires en série, l'appareillage permet alors le dosage simultané du fluor, de l'oxygène, de l'azote et du tétrafluorure de carbone.

L'analyse du fluor par l'intermédiaire du chlore en utilisant des précolonnes chimiques et la chromatographie gazeuse s'est révélée commode et sensible. La méthode permet un contrôle rapide (5 à 10 min) du fluor dans le cas d'un échantillonnage en ligne. La chromatographie a l'avantage de ne demander que de très petits volumes d'échantillons gazeux. Elle est susceptible de pouvoir être automatisée pour des contrôles industriels.

Ce travail a été effectué dans les laboratoires du Centre de Recherches de Lyon de la Société d'Electro-Chimie d'Ugine dans le cadre d'un contrat avec le Commissariat à l'Energie Atomique. Nous remercions vivement cet organisme de nous avoir autorisé à publier cette étude.

RÉSUMÉ

Il est donné une solution purement chromatographique et assez générale de l'analyse du fluor moléculaire dans les gaz permanents inertes ou dans d'autres composés fluorés corrosifs (UF_6, HF). Puis la méthode est étendue à l'analyse des gaz permanents inertes (même à l'état de traces) dans ces mêmes composés fluorés. La solution consiste à mettre en série une ou plusieurs "précolonnes" dites chimiques avec une colonne de chromatographie gaz–liquide. Le système de "précolonnes" est destiné à retenir ou à détruire les composés corrosifs (UF_6, HF, F_2) et la colonne chromatographique à séparer les constituants formés.

SUMMARY

A purely chromatographic and sufficiently general method is described for the analysis of molecular fluorine in permanent inert gases or in other corrosive fluorine compounds (UF_6, HF). The method is also applied to the analysis of permanent inert gases (even in trace quantities) in the same fluorine compounds. In this method, one or several chemical "precolumns" are placed in series with a gas–liquid chromatography column. The "precolumn" system retains or destroys the corrosive compounds (UF_6, HF, F_2) and the chromatography column separates the components formed.

ZUSAMMENFASSUNG

Es wird eine nahezu allgemein anwendbare chromatographische Methode beschrieben zur Analyse von molekularem Fluor in permanenten Inertgasen oder in anderen korrodierenden Fluorverbindungen (UF_6, HF). Die Methode kann ebenso zur Analyse von permanenten Inertgasen (auch wenn sie in Spuren vorliegen) in den genannten Fluorverbindungen angewendet werden.

Bei dieser Methode werden eine oder mehrere "Vorkolonnen" in Reihe mit einer chromatographischen Kolonne angewandt. Das "Vorkolonnen-System" dient dazu, die korrodierenden Verbindungen zurückzuhalten oder zu zerstören. Die chromatographische Kolonne trennt die gebildeten Komponenten.

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CARBON PASTE ELECTRODES APPLICATION TO CATHODIC REDUCTIONS AND ANODIC STRIPPING VOLTAMMETRY

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The value of carbon paste electrodes for anodic oxidations has been firmly established[1-3]. Since this electrode material showed a considerable hydrogen overpotential, the potentialities for cathodic reductions were investigated in detail. The results were most promising and establish carbon paste as a practical, dual-purpose electrode material. Nujol pastes, as described previously, were used in this study. Such electrodes are designated CE-NjP[3].

(A) *Cathodic range and residual currents*

Current–voltage curves were run in a variety of supporting electrolytes to establish the usuable cathodic potential range over which the CE-NjP could be used. Fig. 1 shows typical results. The greatest range is, of course, obtained in neutral and basic

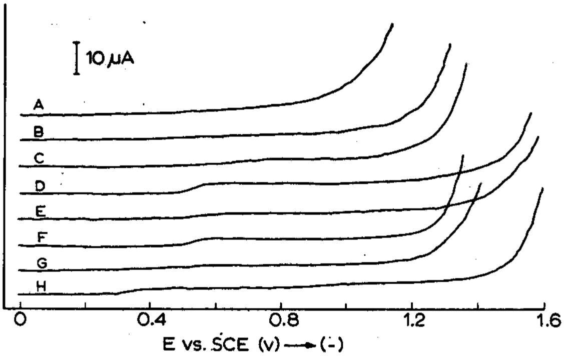

Fig. 1. Typical cathodic background runs for CE-NjP.
A. 1 *M* perchloric acid;
B. 1 *M* hydrochloric acid;
C. 1 *M* sodium acetate–acetic acid;
D. 1 *M* sodium perchlorate;
E. 1 *M* potassium chloride;
F. 1 *M* potassium nitrate;
G. 1 *M* ammonia–ammonium chloride;
H. 1 *M* sodium hydroxide.

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media. In general, the cathodic range extends to *ca.* -1.2 to -1.4 V *vs.* S.C.E., excluding strong acid media. This, of course, is not as great as mercury, but is a decided improvement over noble metals.

However, a relatively small but non-removable residual current is found on the cathodic side with the CE-NjP. This can be seen in Fig. 1 as the small wave between -0.4 and -0.6 V. This is a marked contrast to the anodic residual current which is almost nil up to the onset of background oxidation. Attempts to remove this residual current completely were not successful. It appears to be an oxygen wave, as suggested by the pH dependence and the fact that it decreases significantly on thorough deaeration. It was reasoned that it was due to oxygen in the paste itself which obviously could not be removed completely by solution deaeration. Accordingly, the Nujol was deaerated before mixing, and, in other attempts, the carbon was degassed and then an attempt made to sorb nitrogen on the carbon at low temperatures. None of these treatments (in addition to others) *completely* eliminated the residual current and it is believed that the mixing process which obviously is most conveniently done in the ordinary atmosphere would re-introduce oxygen in the paste even after the most careful removal.

Fortunately, the residual wave has a very flat plateau and it was found that cathodic reductions could be carried out "on top" of this wave, *i.e.*, using it as a base line for peak current measurements. In fact, although low level determinations are difficult by direct cathodic reduction, otherwise the residual current is not troublesome at all. All electroactive species studied were 10^{-3} *M* or greater in concentration.

(*B*) *Reduction of metal ions*

Figure 2 illustrates analytical results for the reduction of cadmium (II) in 1 *M*

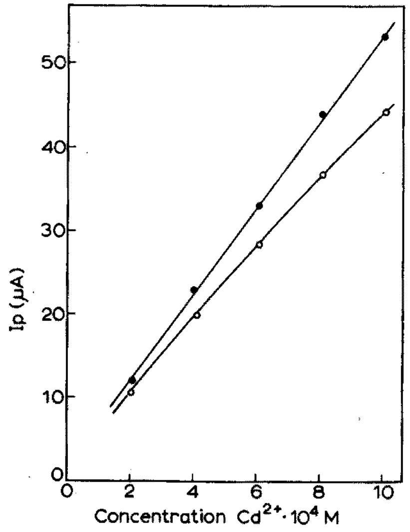

Fig. 2. Peak current *vs.* concentration for cadmium(II) reduction.
○ Experimental currents,
● Corrected for *iR*.

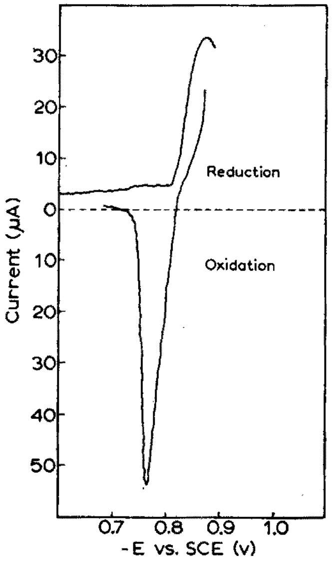

Fig. 3. Reduction and anodic stripping of thallium(I). $1 \cdot 10^{-3}$ *M* Tl(I) in 1 *M* ammonia–ammonium chloride.

potassium chloride as an example of a reduction carried out "on top" of the residual current. The lower line is for data directly from a Leeds and Northrup Electrochemograph with a scan rate of 200 mV/min. The upper curve represents the peak currents corrected for *iR* drop by the method of DELAHAY AND STIEHL[4]. Either line functions satisfactorily as a working curve but the advantages of a controlled potential polarograph are obvious. Satisfactory results similar to that of Fig. 2 were obtained for other metal ion systems.

In all metal ion reductions, anodic stripping procedures were checked. That most of the reductions involved deposition as the metal was evident from the fact that the

TABLE I

REDUCTION OF METAL IONS AT STATIONARY CE-NjP ELECTRODES

Electroactive species	*Medium*	$E_{p/2}$ (*V vs. S.C.E.*)
Bismuth(III)	*M* $HClO_4$	(−) 0.19
	M $NaClO_4$	0.25
	M HCl	0.19
	M KNO_3	0.12
	M NaAc–*M* HAc	0.32
Tin(II)	*M* HCl	0.57
	M $HClO_4$	0.54
	M $NaClO_4$	0.61
Cadmium(II)	*M* $HClO_4$	0.88
	M HCl	0.84
	M KCl	0.84
	M $NaClO_4$	0.78
	M NH_4Cl–*M* NH_4OH	0.99
	M NaAc–*M* HAc	0.86
Load(II)	*M* $NaClO_4$	0.53
	M $HClO_4$	0.56
	M HCl	0.56
	M KNO_3	0.53
	M NaAc–*M* HAc	0.61
Cobalt(II)	*M* NH_4Cl–*M* NH_4OH	0.98
	M $NaClO_4$	0.82
Iron(II)	*M* KCl	0.99
	M $NaClO_4$	0.98
Copper(II)	*M* $HClO_4$	0.23
	M HCl (2nd wave)	0.46
	M KCl (1st wave)	0.20
	M KCl (2nd wave)	0.40
	M NH_4Cl–*M* NH_4OH (1st wave)	0.18
	M NH_4Cl–*M* NH_4OH (2nd wave)	0.67
Thallium(I)	*M* $HClO_4$	0.83
	M HCl	0.83
	M $NaClO_4$	0.84
	M KCl	0.84
	M NH_4Cl–*M* NH_4OH	0.83
Nickel(II)	*M* KNO_3	0.97

anodic peak current (i_p) was far greater than that expected if the re-oxidation process involved a solution component. Further, after reduction, the solutions were stirred to destroy any concentration gradients at the electrode before re-oxidation. Figure 3 shows a typical example of a cathodic reduction and the corresponding anodic stripping for thallium in an ammonia–ammonium chloride buffer. No attempts were made to carry out extensive quantitative studies of the anodic stripping. The theory and utility of such processes is well established and applications are straightforward. Obviously, for metal ions, the use of anodic stripping completely eliminates any worry about the carbon paste residual current while, at the same time, it affords far greater sensitivity.

Table I summarizes the $E_{p/2}$ values for some typical metal ion reductions in a variety of background electrolytes. Specific points of interest on the individual systems are discussed briefly below.

Bismuth(III). In general the reproducibility of i_p for bismuth(III) reductions was good in all media. However, when the same electrode surface was used for several runs, the $E_{p/2}$ tended to shift slightly and then become stabilized. This shift in perchlorate media was toward more cathodic potentials but toward anodic values in hydrochloric acid. Excellent stripping patterns were obtained in perchlorate, chloride and acetate media.

Tin(II). The reduction of tin(II) in 1 *M* hydrochloric and perchloric acids and 1 *M* sodium perchlorate was successful. However, no reduction was obtained in 1 *M* sodium hydroxide. Satisfactory stripping patterns were obtained in both chloride and perchlorate backgrounds.

Cobalt(II). The reduction of cobalt(II) was possible in 1 *M* sodium perchlorate, 1 *M* potassium chloride, and ammonia–ammonium chloride medium but no reduction waves were obtained in 1 *M* hydrochloric or perchloric acids.

The shape of the cobalt(II) reduction wave was very non-reproducible. Anodic strippings in both ammoniacal and perchlorate media verified metal deposition.

Iron(II). Iron(II) could be reduced in 1 *M* potassium chloride, 1 *M* sodium perchlorate and 0.2 *M* sodium sulfate media. In all three supporting electrolytes, anodic stripping patterns confirmed the presence of deposited metal.

Nickel(II). Nickel ion reduction is one of the most interesting studies at the carbon paste electrode. A well-defined reduction peak was obtained in 1 *M* potassium nitrate. After deposition, the electrode was removed from solution, rinsed with distilled water and anodically stripped into sodium acetate containing dimethylglyoxime. No red color appeared until the potential necessary for stripping was applied showing definitely the metal had been deposited.

The interesting feature of the nickel(II)–nickel metal system is the extremely large degree of irreversibility. Thus, the $E_{p/2}$ for reduction is -0.97 V *vs.* S.C.E. The anodic stripping occurs at about $+1.0$ V *vs.* S.C.E. — about 2 V between the two processes. Clearly such an observation would be difficult to make at any other electrode.

The reductions of cadmium(II) and lead(II) were conventional in all respects and copper(II) showed stepwise reduction to copper(I) and the metal.

A comparison of $E_{p/2}$ values at the CE-NjP with $E_{1/2}$'s at the D.M.E. afford some interesting observations. In nearly all cases the $E_{p/2}$ for a given metal ion reduction at CE-NjP is different from that at the D.M.E., as well could be expected. For thallium(I), cadmium(II), and lead(II), the reduction is at more cathodic potentials for CE-NjP. However, cobalt(II) and iron(II) deposit at more anodic potentials on carbon paste. It is interesting to note that the former group of metals readily form amalgams with mercury while cobalt(II) and iron(II) do not form amalgams readily. Further interpretation of such results must await more careful studies of these and other metal ion systems.

Although metal ion reduction potentials at carbon paste differ from those at the D.M.E., they are relatively reproducible and in no way hamper analytical applications. It is safe to conclude that a number of metal ions can be determined successfully at the CE-NjP either by cathodic reduction or anodic stripping. If one examines all the metal ions studied herein, a reproducibility of ± 20 mV is the best that can be claimed for $E_{p/2}$ values. Thus for analytical work the anodic stripping technique would be recommended.

(C) *Organic reductions*

The cathodic range of the CE-NjP obviously will not allow as wide a spectrum of organic reductions to be accomplished as is possible with the D.M.E. However, determinations of easily reducible groups like the nitro function are quite possible. To indicate the potential scope, Table II shows results on a variety of aromatic and aliphatic nitro compounds. In almost all cases, as was expected, the reductions were irreversible, but the peak polarograms were well defined and suitable for analytical determinations.

TABLE II

REDUCTION OF NITRO COMPOUNDS AT STATIONARY CE-NjP ELECTRODES

Electroactive species	*Medium*	$E_{p/2}$ *(V vs. S.C.E.)*
p-Nitrodimethylaniline	*M* HCl	(−) 0.38
p-Chloronitrobenzene	*M* HCl	0.42
p-Nitrostyrene	*M* HCl + acetone	0.32
p-Nitrobenzoic acid	*M* HCl	0.29
Nitrocyclohexane	*M* HCl	0.87
1-Nitropropane	*M* HCl	0.92
2-Nitropropane	*M* HCl	1.00
Nitrodiphenyl	*M* HCl + acetone	0.43

This work was supported by the Research Corporation and this support is gratefully acknowledged.

SUMMARY

The utility of carbon paste electrodes for metal ion reductions and anodic stripping voltammetry is demonstrated. In addition certain organic reductions can be accomplished. Extension of the use of carbon electrodes to the cathodic range shows that this electrode has a wide range of potential applications. For anodic oxidations, the carbon paste electrode is perhaps the most versatile and useful stationary electrode available; it possesses practically zero anodic residual current and readily reproducible surfaces, and is simple to prepare and use. On the cathodic side carbon pastes are limited by a non-removable residual current but this difficulty seems readily circumvented.

RÉSUMÉ

Les électrodes en pâte de carbone conviennent très bien pour les réductions d'ions métalliques et pour la voltammétrie anodique ("stripping voltammetry"). En plus, certaines réductions organiques peuvent être affectuées. Ces électrodes présentent de nombreux avantages: un courant résiduel anodique pratiquement nul, des surfaces bien reproductibles; d'autre part, elles sont faciles à préparer.

ZUSAMMENFASSUNG

Es wird gezeigt, dass sich Kohlenpaste-Elektroden für die Reduktion von Metallen und anodische "stripping" voltammetrie sehr gut eignen. Ausserdem können damit Reduktionen gewisser organischer Verbindungen erzielt werden. Kohlenpaste-Elektroden zeigen im kathodischen Bereich eine weite Anwendungsmöglichkeit. Sie zeigt praktisch keinen anodischen Reststrom, besitzt eine gut reproduzierbare Oberfläche und ist leicht herzustellen. Ihre Anwendung als Kathode ist etwas begrenzt wegen einem nicht entfernbaren Reststrom.

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Short Communications

Eine Methode zur amperometrischen Bestimmung von Arsen(III)

Die bestehenden Methoden zur amperometrischen Bestimmung von Arsen(III) weisen gewisse Mängel auf[1-4]. Wir untersuchten deshalb die amperometrische Titration von Arsen(III) mit Weinsäure, bei der ein polarographisch aktiver Komplex entsteht[5].

Die Versuche wurden mit dem Polarographen Lp 55-A durchgeführt, der eine Empfindlichkeit von $1.3 \cdot 10^{-9}$ A/mM besitzt. Das Kapillarröhrchen hatte folgende Werte: $m = 2.18$ mg/sec; 3.0 sec Tropfzeit. Als Bezugselektrode diente eine gesättigte Kalomelelektrode. Der Sauerstoff wurde durch Stickstoff vertrieben. Als Grundlösung wurden für jede Titration 50 ml eines Gemisches von 0.10 M Natriumsulfatlösung, 20 Vol.% Äthanol und 0.005% Gelatine verwendet. Die alkalische Arsen(III)-oxid-Lösung wurde mit Schwefelsäure neutralisiert.

Wurde der Grundlösung kein Äthanol zugesetzt, so waren die Titrierkurven infolge des unvollständigen Ablaufs des Komplexbildungsvorganges unbrauchbar. Der komplexbildende Prozess verlief quantitativ, wenn der Äthanolgehalt 10–30 Vol.% betrug. Höhere Äthanolgehalte bewirkten eine Verminderung der Leitfähigkeit und Streckung der polarographischen Kurven.

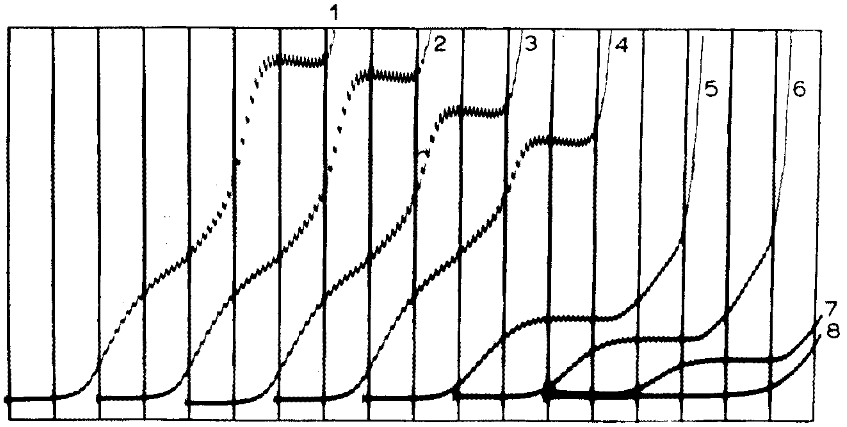

Fig. 1. Polarographische Stufen des Arsen(III) in Gegenwart von Weinsäure. $3.02 \cdot 10^{-4}$ g mol/l Arsen(III)-oxid. Weinsäurekonzentrationen: 1 = $3.32 \cdot 10^{-3}$ M, 2 = $3.18 \cdot 10^{-3}$ M, 3 = $2.88 \cdot 10^{-3}$ M, 4 = $2.56 \cdot 10^{-3}$ M, 5 = $8.00 \cdot 10^{-4}$ M, 6 = $6.1 \cdot 10^{-4}$ M, 7 = vollständige Komplexbildung, 8 = ohne Weinsäure.
Empfindlichkeit: 1/200, 200 MV/Absz. Beginn der Kurven −0.6 V gegenüber der G.K.E.

Bei Abwesenheit von Weinsäure entstand keine polarographische Stufe (Fig. 1, Kurve 8). Lag nur Weinsäure vor, so erhielten wir eine Stufe bei −1.8 V, deren Höhe proportional der Konzentration war. Bei der Titration von Arsen(III) mit Weinsäure erschien zuerst die Komplexstufe mit dem Halbwellenpotential −1.16 V. Diese wurde mit der Erhöhung der Weinsäurekonzentration immer höher bis zur vollständigen Komplexbildung des Arsen(III) (Kurven 5–7). Bei einem Überschuss an Weinsäure änderte sich die Höhe der Komplexstufe nicht, es erschien dagegen die negativere Stufe der freien Weinsäure (Kurven 1–4). Die Versuche zeigten, dass sich ein Arsen-Ion mit 2 Molekülen Weinsäure verbindet. Als günstigste Spannung ergab sich der Plateau-Ansatz der polarographischen Komplexstufe mit der Spannung −1.25 V. Bei negativeren Potentialen störte die Stufe der freien Weinsäure. Eine unter diesen Bedingungen durchgeführte Titrationskurve zeigt Fig. 2.

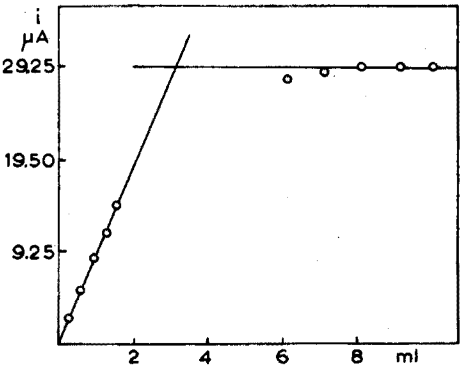

Fig. 2. Kurve einer amperometrischen Titration des Arsen(III)-oxids mit Weinsäure. 108.8 mg Arsen(III)-oxid; $7.58 \cdot 10^{-2}$ *M* Weinsäure.

Gehaltsbestimmungen von Lösungen mit bekannten Mengen Arsen(III)-oxid von *ca.* 3–20 mg ergaben Unterbefunde, die sich mit steigendem Arsengehalt von *ca.* 0 bis −3% änderten. Die Messungen liessen sich gut reproduzieren.

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Anal. Chim. Acta, 29 (1963) 364–365

An improved gas absorption device for conductometric micro-determination of carbon dioxide

The gas absorption device described in this paper was developed from a spiral absorber furnished with electrodes which was described previously[1] for visual titrimetric as well as for conductometric determinations of micro-mole quantities of carbon dioxide in air.

The original apparatus is similar in principle to the present modified design shown in Fig. 1, the principal differences being in the length of the spiral tube (A) and in the positioning of the electrodes. In the original apparatus the absorption liquid, usually 0.5 ml of 5.0 m*M* strontium hydroxide solution, was circulated from below upwards through a spiral tube of length about 160 cm, by passing a stream of the air to be analysed through the apparatus at a flow rate up to about 15 ml/min. The droplets of liquid ascending through the spiral renewed and stirred the thin layer of liquid wetting the inside of the spiral. On arrival at the bulb similar to B in Fig. 1, the liquid was returned to the bottom end of the spiral through a capillary tube. No air passed through this tube, which, because of capillarity, remained full of liquid. The electrodes for the measurement of the conductivity were placed at the lower bend of this capillary tube.

Owing to the extensive area of contact between air and absorbing liquid (about 160 cm^2), the escape of unabsorbed carbon dioxide was negligible even when only a very small surplus of alkali remained in the spiral; accordingly the apparatus could be used not only for conductometric analyses, but also for a titrimetric determination of carbon dioxide in which the strontium hydroxide was "titrated" with the air-stream in the presence of a visual indicator, no back-titration of the excess of alkali being needed. During the last three years the above spiral absorber has been in daily use in this laboratory for conductometric determinations of carbon dioxide. The experience gained has led to the introduction of certain minor changes in the design of the absorber.

The modified spiral absorber described below (Fig. 1) differs from the above device with respect to the following details:

(*1*) The shape and site of the electrodes are changed.

(*2*) The electrodes are not coated with platinum black.

(*3*) The length of the absorption tube is reduced.

(*4*) The distance between the upper and lower ends of the U-shaped capillary tube has been reduced.

Discussion

(*1*) When the absorption liquid is introduced in the original spiral absorber, an air bubble may be trapped between the electrodes protruding into the bore of the tube (C). When this happens, the absorber cannot be used for conductometric analyses or, if recirculation of the liquid ceases, for visual titration. However, the use of cylindrical hollow electrodes melted on to the inside of the left ascending limb of the capillary tube as shown in Fig. 1 eliminates the risk of trapping air between the electrodes.

(*2*) In the previous paper[1] it was pointed out that the conductivity of the strontium hydroxide solution is influenced by concentration changes caused by the adsorption of strontium hydroxide on the exposed inner glass surfaces of the spiral absorber. However, it was overlooked that the adsorption of the strontium hydroxide on the platinum black-coated electrodes also influences the measurements, even though it amounts to only a small fraction of the quantity adsorbed on the glass.

When the hydroxide is introduced in the spiral absorber through the inlet tube (D) as recommended previously, the major part of the solution passes into the horizontal lower part of the absorption tube adjacent to the inlet tube, and only a small fraction of the volume of the liquid enters and fills the capillary and the space between the electrodes. Under these conditions, the initial conductivity measured before the first circulation of the hydroxide through the spiral has been completed is about 4% lower than the initial conductivity measured in experiments in which the hydroxide is introduced through the outlet tube. In the latter case the space between the electrodes is washed with practically the total volume of the solution before the initial measurement of the conductivity can be made. In accordance with these observations the sudden drop of conductivity measured after the completion of the first circulation of the liquid through the spiral absorber, was smaller (about 4%) when the liquid (0.5 ml of 5.0 mM strontium hydroxide solution) was introduced through the inlet tube than when it was introduced through the outlet tube (in which case it was about 8%).

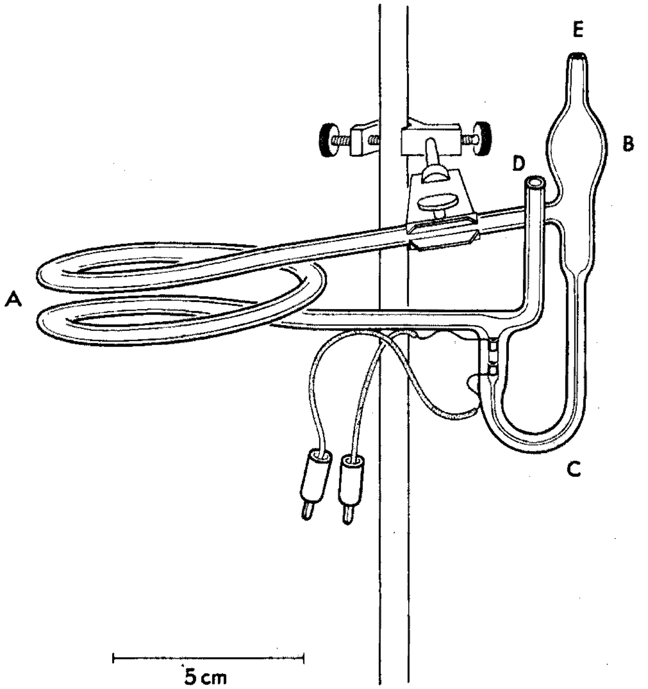

Fig. 1. The modified spiral absorber. A: Absorption tube, length about 40 cm, internal diameter 0.32 cm ± 0.01 cm, diameter of the helix about 7 cm. B: Bulb, outer diameter about 1.5 cm. C: Capillary tube; internal diameter of the right limb 0.070 cm ± 0.005 cm. The distance between the levels of the upper ends of the two limbs of the U-shaped capillary tube is 1.6 cm ± 0.2 cm. The ascending part of the capillary adjacent to the lower branch of the absorption tube is widened to a bore of about 0.22 cm to accommodate the cylindrical electrodes.

The electrodes are hollow cylinders made of a platinum–rhodium alloy (10% rhodium). Height of each electrode 0.2 cm, external diameter about 0.22 cm, internal diameter 0.15 cm. The outer surfaces of the electrodes are melted on to the inner surface of the capillary. The upper electrode is placed a few millimetres below the lower branch of the absorption tube (A). The distance between the electrodes is 0.4–0.5 cm. The lead-in platinum wires, diameter 0.04 cm, which are welded to the electrodes traverse the wall of the capillary tube. Outside the tube the wires are cemented to the glass by Araldite cement to make the joins less fragile.

Of course, the above experiments were carried out in a carbon dioxide-free atmosphere, and under constant temperature conditions.

In similar experiments carried out with spiral absorbers with uncoated electrodes the conductivity drop occurring after the first circulation of the hydroxide was constantly about 8%, independent of which orifice was used for the introduction of the strontium hydroxide solution. As the quantities of strontium hydroxide adsorbed on the platinum black-coated electrodes appeared to be variable, and as the coating was not essential for the accuracy of the conductivity measurements, it was decided to improve the reproducibility of the determinations by using uncoated electrodes.

(*3*) After the coating of the electrodes had been dispensed with, it became apparent that the adsorption of the strontium hydroxide on the glass was not quite so constant as had hitherto been assumed. Consequently, it was decided to reduce the length of the absorption tube from 160 cm to about 40 cm. On account of the shorter tube the quantity of strontium hydroxide adsorbed on the glass as well as the error caused by variations in the adsorption were reduced by about 75%. This modification did not measurably reduce the completeness of the uptake of carbon dioxide during the first 90% of the maximum absorption capacity of the hydroxide, which percentage need not be exceeded in conductometric analyses.

(*4*) The slight reduction of the difference in height between the upper and lower ends of the U-shaped capillary tube is of only minor importance for the function of the spiral absorber. It was made to compensate for the influences on the flow of the liquid caused by the shortening of the absorption tube and of the narrow part of the capillary tube.

It is recommended that readers who may decide to use the modified spiral absorber briefly described in this paper should also study the previous paper[1] for a more detailed description of the functioning of the spiral absorber. The use of the spiral absorber for various analytical purposes will be described elsewhere.

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A new criterion for the qualitative identification of substances by means of ion-exchange chromatography

As is known, column chromatography on ion-exchange resins can be used for the qualitative detection of various substances. Under a given set of conditions, the distribution coefficient λ (amount per g of dry resin/amount per ml of solution) is a characteristic property and can be simply evaluated by determination of the volume U_{max} at which the adsorbed material appears in the effluent in maximum concentration:

$$\lambda = \frac{U_{max} - (U_0 + V)}{m_j} \qquad (1)$$

where U_0 is the dead volume of the column, V is the free volume of the resin bed and m_j is the weight of the oven-dried resin.

The identification of substances according to their distribution coefficients appears to be very successful in the biochemical field (analysis of mixtures of amino acids and related compounds), and in the analysis of rare earths as well as in the discovery of transplutonium elements. In some laboratories this method has also been used for almost routine identification of radioactive tracers[1]. In spite of such successes, this type of qualitative analysis has not been exploited to the extent that it deserves, principally because the analysis is not specific. It often happens that different substances have in a given system almost the same distribution coefficients, so that it is impossible to identify a substance unambiguously, simply from the location of the peak on the elution curve when some property common to several components (*e.g.* radioactivity, conductivity) is measured in the effluent.

It is suggested that the method may be made specific, if the change of the distribution coefficient with temperature (or better, the analogous change of the selectivity coefficient for the ion-exchange reaction) is taken as the criterion of identity, instead of a single value of the distribution coefficient.

For most practical applications of ion-exchange chromatography, the concentration of the species being separated is negligible in comparison with the eluant concentration, and exchange isotherms are linear. Thus a relatively simple calculation of the selectivity coefficient from the experimentally determined value of the distribution coefficient is possible. Let us consider, for instance, a cation-exchange reaction:

$$\frac{1}{q}\,R_qA + \frac{1}{p}\,B^{p+} \rightleftharpoons \frac{1}{p}\,R_pB + \frac{1}{q}\,A^{q+} \qquad (2)$$

where A^{q+} and B^{p+} are exchangeable ions, q and p are their valencies, and R is the symbol of the resin matrix.

The selectivity coefficient (equilibrium quotient) of this reaction is given by:

$$k = \frac{N_{\mathrm{R_pB}}^{1/p}\, m_{\mathrm{A}^{q+}}^{1/q}}{N_{\mathrm{R_qA}}^{1/q}\, m_{\mathrm{B}^{p+}}^{1/p}} \qquad (3)$$

where N and m denote mole fraction and molality respectively.

As B^{p+} is present in trace amounts, $N_{\mathrm{R_qA}} \simeq 1$. Introducing the total concentration of the resin phase, C_r (mmol per g of dry resin), we have finally:

$$k = \frac{\lambda_{\mathrm{B}^{p+}}^{1/p}\, m_{\mathrm{A}^{q+}}^{1/q}\, d^{1/p}}{C_r^{1/p}} \qquad (4)$$

where λ is defined by equation (1) and d is the density of the eluant solution.

The enthalpy change (ΔH) for the ion-exchange reaction is not large but is usually sufficient to cause distinct changes of λ with temperature. Moreover, the heat capacity change (ΔC_p) in most cases is not negligible and a plot of log k *vs.* $1/T$ has a characteristic curvature[2-5]. Thus, the plot of log k *vs.* $1/T$ should be a characteristic property of the substance and it seems highly unlikely that such plots over a wide range of temperature would be identical for two different substances. Once a dependence of log k upon temperature has been established in a given system for the substance in question, it can later be unequivocally identified in mixtures by measuring the peak position of the substance at a few different values of temperature. Some examples of such identifications are quoted below.

In the course of our work on the separation of rare earths on anion-exchange resins, the exchange reaction:

$$1/2\ \mathrm{R_2H_2Y} + \mathrm{LnY}^- \rightleftharpoons \mathrm{RLnY} + 1/2\ \mathrm{H_2Y}^{2-} \qquad (5)$$

in the system: Amberlite IRA-400 [$\mathrm{H_2Y}^{2-}$]–$\mathrm{Na_2H_2Y}$ aq., was examined at different temperatures (Ln denotes a lanthanide or Sc or Y, and Y^{4-} is the anion of ethylenediaminetetraacetic acid). With the use of radioactive tracers, selectivity coefficients for this reaction were determined by the column method within the temperature range 2–92° for all the rare earths[3,6]. Experimental data were elaborated by means of the "least squares" method and the values of log k computed in this way are plotted in Fig. 1 as a function of $1/T$.

In the experiments with ^{159}Gd which was prepared by irradiation of $\mathrm{Gd_2O_3}$ in a reactor, a small peak whose activity was too small to permit accurate evaluation of half-life, always preceded the gadolinium peak on the elution curves. When selectivity coefficient values had been computed for this small peak they were found to lie accurately on the curve which had been previously obtained for terbium with the use of ^{160}Tb (*cf.* Fig. 1).

In a single experiment a larger amount of $\mathrm{Gd_2O_3}$ was irradiated and the half-life of the isolated small peak was measured. This was about 7.5 days which is in reasonable agreement with the value of 7.15 days given in the literature for ^{161}Tb (ref. 7); in fact, ^{161}Tb can be formed according to the reaction:

$$^{160}\mathrm{Gd}(n,\gamma)^{161}\mathrm{Gd} \xrightarrow{\beta^-} {}^{161}\mathrm{Tb} \quad .$$

As can be seen from Fig. 1, any other rare earth element can be easily identified in a similar way to terbium.

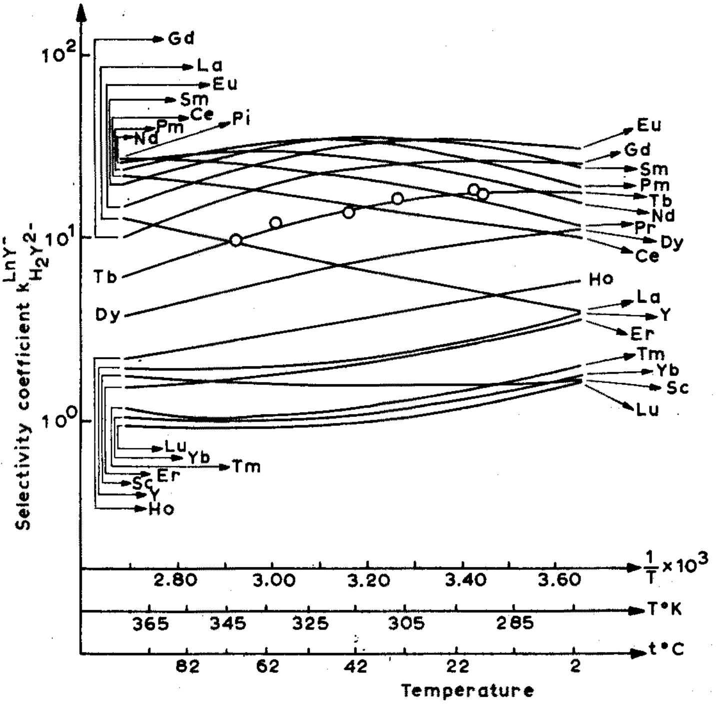

Fig. 1. Identification of traces of terbium by means of ion-exchange chromatography at different temperatures. System: Amberlite IRA-400 [H_2Y^{2-}]–Na_2H_2Y aq. Solid lines = selectivity coefficients for the ion-exchange reaction: $1/2\ R_2H_2Y + LnY^- \rightleftharpoons RLnY + 1/2\ H_2Y^{2-}$ as a function of temperature[3,6]. ○ = experimental values for the peak being identified.

In further work, the temperature dependence of the selectivity coefficients was determined for the ion-exchange reaction:

$$RH + Me^+ \rightleftharpoons RMe + H^+ \qquad (6)$$

in the system: MK-3 cation exchanger (phenol sulfonic acid type)–HCl aq., where Me denotes alkali metal. The results are presented in Fig. 2. By means of this graph the presence of trace amounts of alkali metals in some pure materials could be confirmed by radioactivation followed by cation-exchange chromatography.

The results of identification of sodium and potassium admixtures in a very pure rubidium specimen are shown in Fig. 2.

In general, it can be concluded that the determination of the selectivity coefficient for an ion-exchange reaction over some range of temperature is a sensitive and

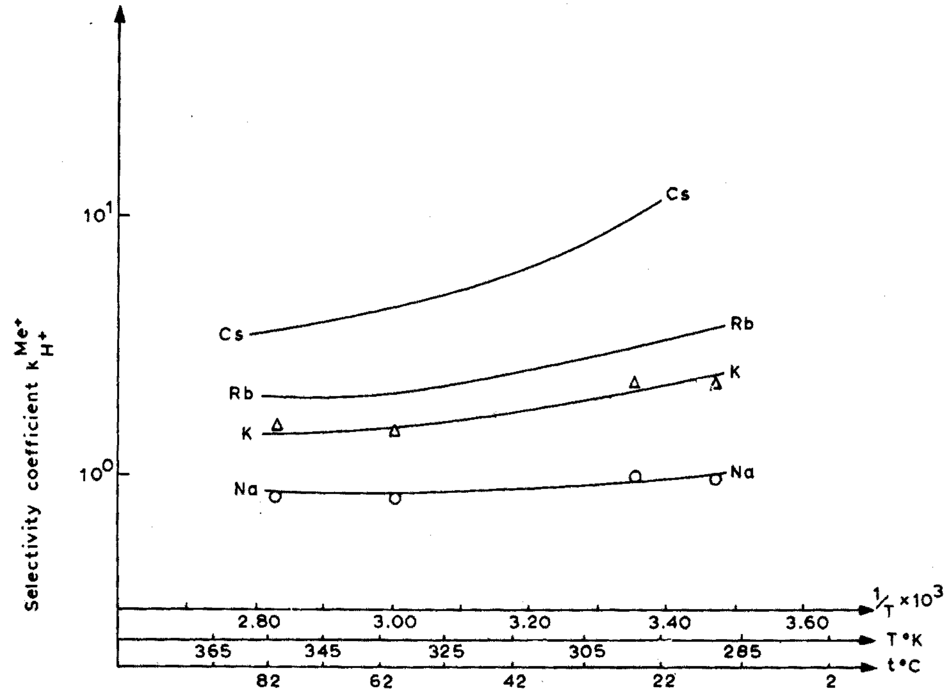

Fig. 2. Identification of traces of potassium and sodium by ion-exchange chromatography at different temperatures. System: cation exchanger MK-3 $[H^+]$–HCl aq. Solid lines = selectivity coefficients for the ion-exchange reaction: $RH + Me^+ \rightleftharpoons RMe + H^+$ as a function of temperature. Δ and ○ = experimental values for the peaks being identified.

specific test. It is hoped that this procedure may be widely applied for the purposes of qualitative analysis, especially when detection of elements and substances present in trace amounts is needed.

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Anal. Chim. Acta, 29 (1963) 369–372

An improved method for the detection and estimation of micron-sized sulfate particles

A number of laboratories have reported difficulty in applying the method of LODGE[1] for the detection and estimation of air-borne sulfate particles. This technique has worked dependably in our own hands, but requires a certain manipulative skill about which it is difficult to verbalize. Furthermore, the reaction spots are somewhat difficult to distinguish in the microscope; since barium sulfate is isotropic, the contrast between the reaction spot and its surroundings is not enhanced by the use of crossed polars. Accordingly, we have developed a new method which appears easier to use and which also gives greater sensitivity.

The fact that the membrane filters are prepared before sampling may add somewhat to the convenience of the technique. This is, however, accomplished at the cost of loss of flexibility since a single untreated membrane filter can be used to test for different species by simply cutting the filter into an appropriate number of pieces. On the other hand, a filter specifically impregnated for sulfate in advance can, of course, only be used for sulfate determination.

After several reagent combinations were tried, the barium salt of rhodizonic acid formed in the filter prior to sampling was selected for a further study[2]. This method gave reaction spots of very high contrast as seen by incident illumination.

Experimental

Millipore filters (Millipore Filter Corporation, Bedford, Mass.) were impregnated first with a saturated aqueous solution of rhodizonic acid, dipotassium salt, by floating the filter, collection side down, on the surface of the solution. The filter was thereby dyed a strong yellow.

The filter then was removed from the solution and gently pressed between two discs of blotting paper to remove the excess solution. Next, the filter was floated face down in a saturated aqueous solution of barium chloride, whereupon the filter became brownish-red. It was then placed in distilled water to remove excess soluble barium salt and finally dried. The color of the treated filter was deep red.

This filter was then used for sampling in the usual way. The filter was treated after sampling by floating it, sample side up, on a few ml of distilled water until the water had penetrated through the filter. This dissolved any solid sulfates and permitted them to complete their reaction with the barium rhodizonate. It also removed at least a portion of the liberated rhodizonic acid or soluble rhodizonate salt. The filter was dried and examined by surface illumination. The reaction spots were clearly defined white to pale yellow circles in a red background (Fig. 1).

The relation between the measured size of the reaction spot and the initial size of the sulfate particle was determined by the statistical technique of LODGE[3]. Sodium sulfate was used as the test material. Reaction spot size was found to be approximately ten times the diameter of the initial particle. Higher precision did not appear warranted in view of the uncertainty concerning the hydration state of the sodium sulfate. If the latter is assumed to be present as the decahydrate, and if it is assumed that the smallest reaction spot which can be clearly identified is 2 μ, then the lower limit of the method is approximately $2 \cdot 10^{-15}$ g of sulfate.

A number of simultaneous determinations of atmospheric sulfate in Boulder, Colorado by this method and by the previous method of LODGE produced results identical within the normal variability of atmospheric concentrations. Contemporaneous determination of sulfate by this method and of chloride by the method of LODGE gave concentrations and size distributions which were similar for the two species,

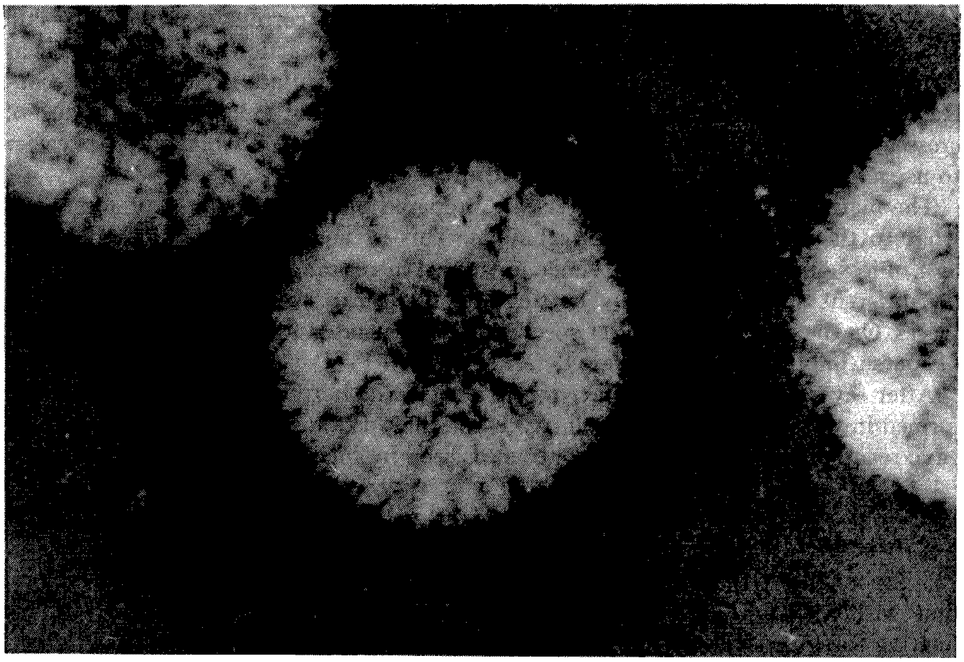

Fig. 1. Photomicrograph of a single, large (50 μ) reaction spot.

as would be expected for this portion of the continent. It is thus concluded that the technique gives valid results under field conditions.

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(Received April 2nd, 1963)

Book Reviews

D. J. CRAM, G. S. HAMMOND UND W. LWOWSKI, *Die Reaktionsmechanismen in der organischen Chemie*, S. Hirzel Verlag, Stuttgart, 1962, xii + 355 S., Ganzleinen DM 38.—.

Es gibt Menschen, die den besten Witz durch die Art, wie sie ihn erzählen, wirkungslos machen, indem sie entweder die Pointe unter der Tisch fallen lassen, den Sachverhalt falsch wiedergeben oder gewisse Details, auf die es ankommt, weglassen. Für den Zuhörer, der den Witz kennt, ist das peinlich. Ein solcher "Witzmörder" ist offenbar

W. LWOWSKI, der das schöne Lehrbuch "Organic Chemistry" von Cram und Hammond ins Deutsche übersetzt hat.

Die "Pointe" beim Cram–Hammond ist, dass es ein Anfängerbuch ist, in welchem die theoretische Bindungs- und Reaktivitätslehre zur Grundlage der Stoffeinteilung gemacht wurde. Die Theorie stellt sozusagen dass Gerüst dar, an welchem der wichtigste fundamentale Wissensstoff der organischen Chemie befestigt werden kann, um im Gedächtnis Gestalt anzunehmen. So gelingt es auch meist ohne allzu grossen Zwang, eine Reihe wichtiger Reaktionen, die früher einfach gelernt werden mussten, wobei i.A. nur der Name des Entdeckers als Erinnerungsmerkmal diente, in diesem System zu placieren. Mit dem Titel "Reaktionsmechanismen" wird wesentlich mehr beansprucht, durch Weglassen vieler Kapitel des Originaltextes aber erheblich weniger geliefert. Damit fällt die Pointe des Buches, Anfängerlehrbuch zu sein, unter den Tisch, und sein Inhalt wird weit überfordert.

Auch der zweiten Sünde des Witzmörders macht sich der Übersetzer wieder und wieder schuldig. An einem Beispiel wird das am besten klar.

Im amerikanischen Original wird der Unterschied zwischen einer gleichgewichts- und einer kinetisch kontrollierten Reaktion am Beispiel der Bildung von *cis*- und *trans*-2-Phenyl-2-buten einerseits durch Solvolyse von 2-Phenyl-2-butylacetat mittels Eisessig, andererseits durch protonenkatalysierte Equilibrierung der Phenylbutene dargestellt. Der Witz der Geschichte ist, dass im ersten Fall bei 26-stündiger Reaktionszeit und 75° das Endprodukt der Reaktion überwiegend aus dem an sich weniger stabilen *trans*-Produkt besteht, während im zweiten Fall durch Zufüger von ein wenig *p*-Toluolsulfonsäure bei gleicher Temperatur und gleichem Lösungsmittel trotz kürzerer Reaktionszeit über das Carbonium-ion die beiden Butene ins Gleichgewicht gesetzt werden und die thermodynamisch stabilere *cis*-Verbindung zum Hauptprodukt wird.

In der "Übersetzung" wird das Experiment in der Weise reduziert, dass in beiden Fällen unter denselben Reaktionsbedingungen gearbeitet wird (Eisessig, *p*-Toluolsulfonsäure, Raumptemperatur), nur erfolgt die Aufarbeitung einmal nach 1, das andere Mal nach 48 Stunden. Dies besagt aber nicht mehr, als dass eine Reaktion solange kinetisch mitkontrolliert ist, als die Gleichgewichtseinstellung noch nicht erfolgt ist. Aus dem einleuchtenden Beispiel wurde also eine Banalität. Ins Groteske gesteigert erscheint dies, wenn man liest: "Anilin ist um 6 Grössenordnungen schwächer basisch als die aliphatischen Amine, ein Unterschied, der grösstenteils von der Energiedifferenz zwischen Anilin und dem Anilinium-ion herrührt" (S. 60), während es im Originaltext heisst: . . . "is due largely to the delocalization energy of aniline, which is lost when a proton is added to the nitrogen". Dass die fundamentele sterische Formulierung der S_N2-Reaktion im Kapitel 5 *ohne* Inversion der Substitutenten erfolgt, überschreitet den Rahmen der Unexaktheit in Details bereits erheblich.

Soll ich nun noch eine Liste anfügen dessen, wass einfach falsch ist: Falsch verstanden, falsch gedacht und falsch gedruckt? Man könnte damit Seiten füllen. Aber das lohnt wohl nicht. Insgesamt: Ein peinliches Buch.

K. WALLENFELS (Freiburg i. Br.)

Anal. Chim. Acta, 29 (1963) 374–375

H. V. MALMSTADT AND C. O. ENKE with the assistance of E. C. TOREN, JR., *Electronics for Scientists, Principles and Experiments for those who use Instruments*, W. A. Benjamin, New York, 1962, xi + 619 p., price US $11. 85 (clothbound).

This book is written for chemists, physicists, engineers, medical research workers and biologists, and is based on several years of experience in training students and graduate scientists. The text begins with the principal electrical measurements (Chapter 1), where voltage and current measurements, as well as the oscilloscope, are discussed. Chapter 2 on power supplies includes transformers, rectifiers, regulators and batteries, while amplification by vacuum tubes and transistors (Chapter 3), and amplifier circuits (Chapter 4), are treated in separate chapters. A detailed description of oscillators (Chapter 5), including oscillator stabilisation and modulation and demodulation follows; then under the heading "Comparison Measurements" (Chapter 6), various topics (based on analogy to weight measurement) such as voltage, current, resistance, impedancy and frequency measurements are presented. The next chapter (7) deals with servo systems, introducing operational amplifiers for measuring and control (Chapter 8), electronic switching and timing, and digital counting systems (Chapter 9), which represent the highest level in electronics needed for non-electronic scientists. There are three supplements, with descriptions of apparatus needed for the experiments, as well as fundamental electrical laws and phenomena for those who have no previous knowledge of electronics. Useful electronic data and tables are collected in an appendix, while an index supplements the book.

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CONTENTS

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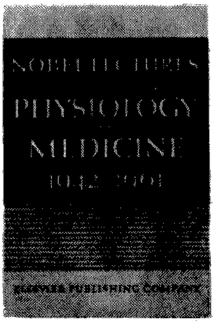
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