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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 35, No. 1, May 1966

STUDIES IN THE TETRAARYLBORATES

PART II. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-FLUOROPHENYL)BORATE, A SELECTIVE REAGENT FOR CESIUM

Sodium tetrakis(*p*-fluorophenyl)borate has been synthesized and found to be a very selective gravimetric reagent for the determination of cesium. It formed precipitates with cesium, silver, thallium(I) and rubidium but not with potassium and ammonium ions. The cesium tetrakis(*p*-fluorophenyl)borate separated as a white crystalline compound, which was easily filterable. It achieved constant weight rapidly at 110° and showed no signs of decomposition after 18 h of drying.

C. E. MOORE, F. P. CASSARETTO, H. POSVIC AND J. J. MCLAFFERTY,
Anal. Chim. Acta, 35 (1966) 1–5

THE SPECTROPHOTOMETRIC MICRODETERMINATION OF SUBSTANCES ON PAPER DISKS

The principles and application of a method for the microdetermination of substances on small paper disks are described. Photometric measurements are made at 2 wavelengths, thus eliminating the errors due to inhomogeneity in the paper. A simple device for serial determinations that can be adapted to a common spectrophotometer is described. Microdetermination of RNA with measurement at 260 and 350 mμ is given as an example of the proposed method, and the best means of correcting the effect of paper inhomogeneity is established. Amounts of RNA in the range 0.8–4 μg can be determined with a mean error of ± 0.03 μg, using 5 μl of solution.

O. L. HÖRER AND M. POPESCU,
Anal. Chim. Acta, 35 (1966) 6–16

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM AFTER EXTRACTION OF THE CHLORO-STANNOUS COMPLEX BY TRI-*n*-OCTYLAMINE

The complex formed between palladium(II) and tin(II) in hydrochloric acid solutions, and its extractability by tri-*n*-octylamine were investigated. Two different species were obtained: one a brown-red complex and the other yellow. Both were extracted into tri-*n*-octylamine in benzene, but the yellow species which had a definite absorption maximum at 410 mμ was more suitable for the determination of palladium. A method is described for the spectrophotometric determination of palladium in the presence of many other elements. Both species are considered to be anionic and a mechanism for their extraction is proposed.

M. A. KHATTAK AND R. J. MAGEE,
Anal. Chim. Acta, 35 (1966) 17–23

COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN SELENIUM(IV) AND 2,2'-DIANTHRIMIDE

The complex formation in concentrated sulfuric acid between selenium(IV) and 2,2'-dianthrimide (Di) was studied by spectrophotometry, infrared spectroscopy and chemical analysis. The system was found to contain two species, the dimer Se_2Di_2 and the monomer SeDi complex, the dimer probably consisting of two monomers connected by hydrogen bonds. The dimer was found to predominate in solutions of low total concentration containing an excess of 2,2'-dianthrimide. By increasing the total concentration and/or decreasing the excess of 2,2'-dianthrimide, the hydrogen bonds between the two 2,2'-dianthrimide molecules are disrupted. The transformation of one of the complexes into the other results in a sudden break or discontinuity in the curves of continuous variation and the mole ratio curves. The SeDi complex was prepared in the solid state.

I. DAHL AND F. J. LANGMYHR,
Anal. Chim. Acta, 35 (1966) 24–34

THE DETERMINATION OF ANTIMONY IN NATURAL WATERS WITH PARTICULAR REFERENCE TO SEA WATER

A procedure is described for the determination of antimony in natural waters at concentrations down to 0.1 μg/l or less. The element is concentrated by coprecipitation with hydrous manganese dioxide (produced by the reaction of permanganate with ethanol). It is separated from manganese, iron and interfering elements by extraction from 5 *M* sulphuric acid, 0.01 *M* with respect to iodide, using methyl isobutyl ketone. After back-extraction with 0.4 *M* hydrochloric acid, it is determined photometrically using rhodamine B. The overall chemical yield of the process is measured radiochemically and amounts to *ca.* 80%. Sea water samples from the Irish Sea were found to contain 0.13–0.40 μg Sb/l.

J. E. PORTMANN AND J. P. RILEY,
Anal. Chim. Acta, 35 (1966) 35–41

A MODIFIED DIMETHYLGLYOXIME METHOD FOR THE DETERMINATION OF NICKEL IN SEA WATER

A colorimetric dimethylglyoxime (DMG) method for the determination of nickel in sea water was studied in detail, and improved through close control of experimental conditions. For a maximum precipitation of 90% of the nickel a minimum period of 7 days was necessary between treatment with sodium carbonate and filtration. A salt effect resulted from: (*1*) a gain in absorbance due to soluble ions not precipitated by sodium carbonate, which increased with increasing salt concentration, (*2*) an offsetting loss in absorbance due to incomplete precipitation of nickel. The transition 3d ions precipitated by sodium carbonate exerted no discernible effect on the absorbance.

A procedure is recommended by which a relative standard deviation of 0.7% was achieved. Consistent recovery yields of 97% were obtained from samples of sea water spiked with nickel collected over a period of several months.

W. FORSTER AND H. ZEITLIN,
Anal. Chim. Acta, 35 (1966) 42–53

THE DETERMINATION OF STABLE SCANDIUM IN PLANTS, ANIMALS, SEDIMENTS, SANDS, SOILS, ROCKS AND MINERALS BY NEUTRON ACTIVATION ANALYSIS

A method is described for the determination of stable scandium in samples of plants, animals, sediments, soils, rocks and minerals. The samples and comparator standards were irradiated in a neutron flux of $5 \cdot 10^{12}$ n/cm^2/sec for 4 h and dissolved and the scandium quantitatively precipitated from 2 N nitric acid as scandium phytate; contaminants were rinsed from the precipitate with nitric and hydrochloric acids. The limit of detection was 0.005 μg ($\pm 10\%$ at the 95% confidence level). The activated ^{46}Sc was counted by γ-spectrometry.

M. Miro, I. Oliver de Padovani, E. Ramos, V. Román de Vega and F. G. Lowman,
Anal. Chim. Acta, 35 (1966) 54–60

ACTIVATION ANALYSIS OF MERCURY IN HIGH PURITY BISMUTH

A neutron activation method was developed for the determination of traces of mercury in high purity bismuth. After neutron irradiation at a flux of approx. $4 \cdot 10^{11}$ n/cm^2/sec, mercury was separated from the matrix by displacement on metallic copper and subsequent distillation and amalgamation on silver foil. The γ-activity of the ^{197}Hg was counted in the 68–77 keV region. The accuracy of the procedure was tested by an addition method of analysis. Bismuth samples with a mercury content in the 10 p.p.b. region were analysed.

J. I. Kim and J. Hoste,
Anal. Chim. Acta, 35 (1966) 61–68

NEUTRON-ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION

A new approach to activation analysis is described. Chemical yield determinations are avoided by selective extraction of the required element in conjunction with the standard addition technique. The principle and its application to the determination of traces of uranium in aluminium and the standard granite (G-1) are given. The advantages of this method are its simplicity and rapidity.

A. Alian and R. Parthasarathy,
Anal. Chim. Acta, 35 (1966) 69–73

THE CONTROLLED POTENTIAL COULOMETRIC AND CONTROLLED POTENTIAL POLAROGRAPHIC DETERMINATIONS OF SUBSTITUTED NITROBENZENE COMPOUNDS IN DIMETHYLSULFOXIDE

The *n*-values for the reduction of the isomers of nitrophenol and nitrobenzoic acid and for several other nitro compounds were determined in dimethylsulfoxide by controlled potential coulometry. A procedure is given in which one μmole of nitro compound may be determined in less than 8 min with an error of approximately $\pm 1\%$. The associated background currents were quantitatively evaluated, and electrolysis conditions for their minimization were discussed. A procedure and results are given for the controlled potential polarography of these nitro compounds in dimethylsulfoxide.

M. R. Lindbeck and H. Freund,
Anal. Chim. Acta, 35 (1966) 74–84

THE POLAROGRAPHY OF MOLYBDENUM, TITANIUM AND NIOBIUM IN SOLUTIONS OF ORGANIC ACIDS

Further work on the polarographic reduction of molybdenum(VI), niobium(V) and titanium(IV) in base electrolytes containing organic acids is reported. A base electrolyte of 0.5 M citric acid $-$0.025 M sulphuric acid$-$0.05 M thorium nitrate proved suitable for the determination of molybdenum and titanium in the presence of niobium, tantalum, tungsten and zirconium. A direct polarographic method using this base electrolyte is described for the determination of molybdenum in a niobium base alloy.

J. B. Headridge and D. P. Hubbard,
Anal. Chim. Acta, 35 (1966) 85–90

ANALYSIS OF LEAD TITANATE–ZIRCONATE CERAMICS

DETERMINATION OF LEAD, TITANIUM AND NIOBIUM BY DIFFERENTIAL CATHODE-RAY POLAROGRAPHY

Differential cathode-ray polarography is applied to the direct determination of lead, titanium and niobium in lead titanate–zirconate solid–solution ceramics containing small additions of niobium pentoxide. Titanium and niobium are determined in buffered EDTA solution at pH 4.0 and lead in 1 M hydrochloric acid. With the high precision comparative technique, relative standard deviations of 0.11% and 0.31% for lead and titanium respectively are obtained. Niobium is determined by the subtractive technique.

G. C. Goode, J. Herrington and W. T. Jones,
Anal. Chim. Acta, 35 (1966) 91–95

THE USE OF ARGON AS CARRIER GAS IN THE MICRODETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS

Argon is recommended as carrier gas in order to improve the efficiency of the method for the microdetermination of oxygen in organic compounds. To demonstrate that the use of argon is advantageous, parallel determinations were performed on a series of organic and inorganic compounds to establish the maximum amounts of substance quantitatively pyrolysable under normal analytical conditions. With argon, the maximum amount of the organic compound giving correct results was usually remarkably increased at all stages of the working life of the tube. This greater efficiency of the system in the conversion to carbon monoxide leads to higher reliability, allows a substantial decrease in the analysis time, and prolongs the life of the filling. The inconvenience of positive blank values with argon can be avoided if reaction tubes of very pure quartz are used.

E. Pella,
Anal. Chim. Acta, 35 (1966) 96–108

BIS-(2,6-DIMETHYLMORPHOLINE)-THIURAM DISULFIDE AS A REAGENT FOR THE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER, AND FOR COPPER TRACES IN BIOLOGICAL MATERIALS

(Short Communication; in German)

O. Wawschinek and H. H. Tagger,
Anal. Chim. Acta, 35 (1966) 109–110

PRELIMINARY STUDIES OF PRECIPITATION TITRATIONS OF ORGANIC COMPOUNDS USING POLAROVOLTRIC END-POINT INDICATION. PART II. TITRATION OF ORGANIC ACIDS AND SALTS WITH COPPER(II)

(Short Communication)

M. R. F. Ashworth and R. Fehringer,
Anal. Chim. Acta, 35 (1966) 111–115

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM AND TELLURIUM WITH THIOGLYCOLLIC ACID

(Short Communication)

G. F. Kirkbright and W. K. Ng,
Anal. Chim. Acta, 35 (1966) 116–119

PHOSPHORIMETRIC BACKGROUND OF THE ETHER EXTRACTS OF BLOOD AND URINE AT VARIOUS pH VALUES

(Short Communication)

W. J. McCarthy and J. D. Winefordner,
Anal. Chim. Acta, 35 (1966) 120–123

THE DETERMINATION OF CADMIUM IN STAINLESS STEEL BY ATOMIC ABSORPTION SPECTROSCOPY

(Short Communication)

L. Wilson,
Anal. Chim. Acta, 35 (1966) 123–126

DETERMINATION OF FREE TUNGSTEN IN TUNGSTEN SILICIDE (WSi_2)

(Short Communication)

K. F. Sugawara,
Anal. Chim. Acta, 35 (1966) 127–131

AN INVESTIGATION OF THE COMPOSITION OF THE PRECIPITATES FORMED BY THE DECOMPOSITION OF SILICATE ROCKS IN 38–40% HYDROFLUORIC ACID

(Short Communication)

F. J. Langmyhr and K. Kringstad,
Anal. Chim. Acta, 35 (1966) 131–135

THE SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 8-QUINOLINE CARBOXYLIC ACID

(Short Communication)

J. M. Zehner and T. R. Sweet,
Anal. Chim. Acta, 35 (1966) 135–137

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STUDIES IN THE TETRAARYLBORATES

PART II. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-FLUOROPHENYL)BORATE, A SELECTIVE REAGENT FOR CESIUM

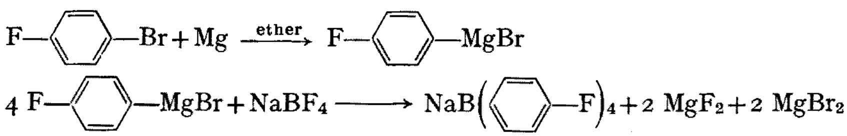
CARL E. MOORE, FRANK P. CASSARETTO, HARVEY POSVIC AND JOHN J. McLAFFERTY
Department of Chemistry, Loyola University, Chicago 26, Ill. (U.S.A.)

(Received October 9th, 1965)

In the continuation of the study of substituent effects on the reagent properties of the tetraarylborates[1], sodium tetrakis(*p*-fluorophenyl)borate has been synthesized. Substituent effects which seem analogous have been studied extensively in the arylboronic and borinic acids[2]. It has been shown that acid strengths in these can be varied over a wide range by the *ortho* or *para* substitution of electropositive and electronegative groups into the benzene ring. Thus the highly electronegative fluorine atom in the *para* position can be expected to modify the electron density in the vicinity of carbon to boron bonds. This fact can influence both the point of attack and nature of the reaction which results in the decomposition of the reagent in acidic solution. It can also modify the polarizability of the anion and indirectly affect the selectivity and solubilities of the resulting salts. However, this must be interpreted in light of the fact that the tetrakis(*p*-fluorophenyl)borate reagent is an anion which already carries a single negative charge.

EXPERIMENTAL

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



To a 500-ml 3-necked flask equipped with a stirrer, water-cooled condenser and a dropping funnel, add 9.7 g (0.4 mole) of magnesium turnings. Sweep the assembly with dry nitrogen. Add 250 ml of ether, previously dried over sodium, to the flask. Dissolve 70 g (0.4 mole) of *p*-bromofluorobenzene in 100 ml of dry ether and arrange for dropwise addition into the flask. Add approximately 10 ml of the *p*-bromofluorobenzene solution to the flask. Stir the solution and bring to reflux temperature. The reaction generally starts within 20 min. Add the remainder of the *p*-bromofluorobenzene solution dropwise over a period of 1 h. Continue the reflux and stirring for an additional hour.

To the cold solution of *p*-fluorophenyl Grignard reagent, add 11.0 g (0.1 mole) of sodium borofluoride, which has been previously dried at 110° for 1 h. Blanket with nitrogen; stir and reflux for 2 h while maintaining the blanket of nitrogen. Pour the contents of the reaction flask into 400 ml of ice-cold saturated sodium chloride solution. A white precipitate of inorganic material forms in the aqueous layer. Separate the ether layer with a separatory funnel and extract the aqueous phase three times with 100-ml portions of ether. Add these to the previously separated ether layer. The reaction mixture need not be worked up immediately. In fact, it may be left standing several days before adding it to the sodium chloride solution. Then add 300 ml of xylene and remove the ether using a rotary vacuum evaporator. Partially immerse the flask in a water bath held at 50°. As soon as nearly all the ether has been removed, the salt separates. This is usually a yellow solid. Occasionally an oil is obtained which later crystallizes. Yield: 20.8 g.

To prepare the pure sodium salt dissolve 10 g of the mixed salt in 100 ml of water; filter and pass through an ion-exchange column of Dowex 50W-X4 in its sodium form. It is best to prepare the column with 4% sodium hydroxide. The acid left on the column after the usual HCl–NaCl cycle decomposes the borate. Saturate the eluate, which amounts to 250–275 ml, with sodium chloride and extract with three 50-ml portions of ether. Combine the extracts; add 200 ml of dry xylene and evaporate the ether on a rotary vacuum evaporator. Partially immerse the flask containing the solution in a water bath held at 50°. The crystals of the white sodium salt start to appear when most of the ether has been removed. The salt separates as the dihydrate. Yield: 7.9 g.

An analysis of the hydrate yielded the following result: H_2O by Karl Fisher titration 7.85% (theor. 8.00%). An analysis* of the anhydrous salt yielded the following results (in %): C 69.55, H 3.85, F 18.54; calculated: C 69.60, H 3.89, F 18.35.

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

A 1% solution of the sodium salt was used for qualitative testing. About 2 ml of the reagent was added to 2 ml of a 0.1 *M* solution of the ion to be tested. The following ions gave precipitates: cesium, rubidium, thallous and silver. No precipitates were obtained with potassium, ammonium, cobalt, nickel, barium and copper.

The reagent was tested for its ability to precipitate quaternary ammonium compounds and other compounds containing a basic nitrogen atom which had been protonated. The nitrogen-containing compound was dissolved in dilute hydrochloric acid and a 1% solution of the reagent added. The following compounds gave precipitates: quinidine, cinchonine, di-*n*-heptylamine, tetrabutylammonium iodide, *p*-bromoaniline, aniline and brucine. These precipitates either decomposed or melted over a wide range and were judged unsuitable for derivatives.

The reagent was tested for its ability to precipitate the cesium ion by mixing 2 ml of a 0.03 *M* solution of the reagent with 2 ml of test solution. For a comparison tetraphenylborate and tetrakis(*p*-chlorophenyl)borate were used in a similar series of tests. The results are summarized in Table I.

Sodium tetrakis(p-fluorophenyl)borate as a reagent for cesium

The procedure described by GLOSS[3] in the determination of potassium by

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* The elemental analysis of this compound proved very difficult. After some method research, the Huffman Laboratories, Wheatridge, Colorado, were able to report a satisfactory method for the sodium salt.

sodium tetraphenylborate was selected for the study of the precipitation of cesium with sodium tetrakis(*p*-fluorophenyl)borate. A 2% solution of the reagent in water was used in the quantitative study. The sample containing the cesium ion was adjusted to 50 ml and brought to 70°. The reagent which usually amounted to 40 ml was added slowly from a pipet. The sample was allowed to stand at room temperature for 1 h, immersed in an ice bath for 1 h, transferred to a fine sintered glass filtering crucible and washed with three 5-ml portions of ice water. The crucible was dried for 1 h at 110°, cooled in a desiccator, weighed and the recovery of cesium was calculated using the theoretical gravimetric factor 0.2536. The results are summarised in Tables II, III and IV.

TABLE I

COMPARATIVE SENSITIVITIES OF SOME TETRAARYLBORATES AS PRECIPITANTS FOR CESIUM

Cs taken (mg)	$NaB(C_6H_5F)_4$	$NaB(C_6H_5Cl)_4$	$NaB(C_6H_5)_4$
2.0	Heavy, immed.	Heavy, immed.	Heavy, immed.
0.2	Med., immed.	Heavy, immed.	Heavy, immed.
0.1	Slow, slight ppt.	—	—
0.05	V. Slight, slow	—	—
0.02	None	Light, immed.	Light, immed.
0.01	None	Slight, immed.	Slight, immed.
0.005	None	Slight, immed.	Slight, immed.
0.002	None	None	None

TABLE II

RECOVERY OF CESIUM FROM PURE CESIUM SOLUTIONS

Cs taken (mg)	*Cs found (mg)*	*% Recovery*
65.3	64.5	98.8
65.3	64.3	98.5
32.7	32.5	99.4
32.7	32.2	98.5
32.7	32.2	98.5
32.5	32.0	98.5
32.5	31.9	98.2
32.5	31.9	98.2
32.5	31.8	97.8
16.3	16.0	98.2
16.3	16.2	99.4
16.2	16.0	98.8
16.2	15.9	98.1

As shown in Table I, the precipitate is somewhat more soluble than the cesium tetraphenylborate and tetrakis(*p*-chlorophenyl)borate. The solubility of the pure cesium salt was determined at 25° and at 0°. At 25° the solubility is essentially unaffected by pH in the range 3.3–9.5. The solubilities, which were computed from flame photometric results on the cesium ion in solution, were taken after 30 h and are listed

TABLE III

RECOVERY OF CESIUM IN THE PRESENCE OF POTASSIUM

Cs taken (mg)	*K taken (mg)*	*Cs found (mg) (gravimetric)*	*K found (mg)*	*Corrected result for Cs (mg)*
32.5	11.9	32.0	0.02	32.0
32.5	11.9	32.0	0.02	32.0
32.5	23.8	32.0	0.04	31.9
32.5	23.8	31.9	0.03	31.8
32.5	23.8	31.8	—	—
32.5	23.8	31.8	—	—
32.7	23.8	32.3	—	—
32.5	35.7	32.2	0.06	32.0
32.5	35.7	32.1	0.04	32.0

TABLE IV

RECOVERY OF CESIUM IN THE PRESENCE OF RUBIDIUM

Cs taken (mg)	*Rb taken (mg)*	*Cs found (mg) (gravimetric)*	*Rb found (mg)*	*Corrected result for Cs (mg)*
32.5	2.8	32.3	0.22	32.0
32.5	2.8	32.3	0.20	32.0
32.5	8.5	33.2	0.63	32.3
32.5	8.5	33.2	0.71	32.2
32.5	14.1	33.8	1.25	32.0
32.5	14.1	33.7	1.13	32.1
32.5	14.1	33.8	—	—

TABLE V

SOLUBILITY OF CESIUM TETRAKIS(*p*-FLUOROPHENYL)BORATE

pH	*Temperature (°)*	*Time (h)*	*g/l*
3.3	25	30	0.17
7.2	25	30	0.24
7.3	25	30	0.18
9.5	25	30	0.17
~7	0	30	0.10

in Table V. Long equilibration times were not employed because of the possible decomposition of the precipitate. Solubility results obtained shortly after precipitation were essentially the same as those in Table V.

DISCUSSION

The data in Tables III and IV indicate that the tetrakis(*p*-fluorophenyl)borate anion is remarkably selective for cesium. Previously, it has not been possible to separate cesium from rubidium and potassium satisfactorily by precipitation techniques. The extent of the coprecipitation of potassium and rubidium is shown in Tables III and IV. The precipitates which were analyzed by standard flame photometric methods show, as expected, rubidium to be more strongly co-precipitated than potassium. Under normal analytical conditions, both rubidium and potassium introduce errors which can either be tolerated or easily evaluated by analysis of the precipitates.

The cesium tetrakis(*p*-fluorophenyl)borate separates as a white crystalline compound with good analytical characteristics. It is easily filterable and achieves constant weight rapidly at 110°. A prolonged heating of 18 h caused no further weight loss or signs of decomposition. The theoretical factor for cesium is 0.2536. This value was used to compute the recovery figures in Tables II, III and IV. Most recovery values were 1–2% low. Thus an empirical factor which compensates for this error can be used to advantage.

SUMMARY

Sodium tetrakis(*p*-fluorophenyl)borate has been synthesized and found to be a very selective gravimetric reagent for the determination of cesium. It formed precipitates with cesium, silver, thallium(I) and rubidium but not with potassium and ammonium ions. The cesium tetrakis(*p*-fluorophenyl)borate separated as a white crystalline compound, which was easily filterable. It achieved constant weight rapidly at 110° and showed no signs of decomposition after 18 h of drying.

RÉSUMÉ

On a effectué la synthèse du tétra(*p*-fluorophényl)borate de sodium. Ce composé constitue un réactif gravimétrique sélectif pour le dosage du césium. Il précipite césium, argent, thallium(I) et rubidium, mais non potassium et ammonium. Le sel de césium est blanc, cristallin et se filtre facilement. Il est stable et atteint rapidement un poids constant à 110°.

ZUSAMMENFASSUNG

Natriumtetrakis(*p*-fluorophenyl)borat wurde synthetisiert und eignete sich als sehr selektives gravimetrisches Reagenz zur Bestimmung von Cäsium. Es bildet Niederschläge mit Cäsium, Silber, Thallium(I) und Rubidium, aber nicht mit Kalium- und Ammoniumionen. Das Cäsiumtetrakis(*p*-fluorophenyl)borat wurde als weisse, kristalline Verbindung, die leicht filtrierbar war, abgetrennt. Sie erreicht schnell konstantes Gewicht bei 110° und zeigt nach 18 stündigem Trocknen keine Anzeichen von Zersetzung.

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THE SPECTROPHOTOMETRIC MICRODETERMINATION OF SUBSTANCES ON PAPER DISKS

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Determination *in situ* of a substance on paper by absorption spectrophotometry is currently done by comparison with a blank control at the wavelength of maximum absorption of the substance. The limits of the precision and sensitivity of this method depend upon several factors, among which hyperchromic absorbancy due to the multiple scattering of light by paper is considered as an important source of error; making the paper translucent[1] or the use of an empirical nomogram or equation[2] has been recommended. In order to obviate the absorption fluctuations due to the lack of homogeneity of the paper, the section of the light beam that passes through the paper must be fairly large. However, a large spot of a substance on the paper presents a variable concentration from the center to the periphery, which might lead to other sources of error.

The present paper describes a spectrophotometric method that makes it possible to reduce the amount of substance necessary for the determination by limiting the area of the paper, and by compensating for the fluctuations due to the lack of homogeneity of the paper by carrying out the determinations at 2 wavelengths. The sensitivity of the method is enhanced by the hyperchromic absorption effect.

Differential spectrophotometry at 2 wavelengths

If the absolute extinctions are measured at 2 wavelengths, λ_1 and λ_2, and if the extinctions of a paper portion considered as the sample ($E_1{}^s$ and $E_2{}^s$) and of another portion considered as the control ($E_1{}^c$ and $E_2{}^c$) vary only because of the difference in the cellulose mass, then the general relationship may be expressed as follows:

$$E_1{}^s - E_1{}^c = \mathrm{f}(E_2{}^s - E_2{}^c) \tag{1}$$

Function f is fairly complicated and difficult to explain on the basis of the theory of transmission through highly turbid media with a large absorption[3].

If an arbitrary extinction, E^0, equal for both the wavelengths used, is defined by

$$E^0 = E_1{}^c - e_1 = E_2{}^c - e_2 \tag{2}$$

and if spectrophotometric compensation is done with respect to this definition, then the relative extinctions E_1 and E_2, corresponding to the sample at the two wavelengths, will be:

$$\begin{aligned} E_1 &= E_1{}^s - e_1 \\ E_2 &= E_2{}^s - e_2 \end{aligned} \tag{3}$$

In eqn. (1) a substitution of variables will result in:

$$E_1 - E^0 = f(E_2 - E^0) \qquad (4)$$

If the substance deposited on the paper in a very small amount absorbs strongly at wavelength λ_1 but neither absorbs nor modifies the absorption of the paper itself at wavelength λ_2, then it should be possible to compensate for local extinction variations at the wavelength λ_1 at which the chromophore of the analysed substance absorbs.

EXPERIMENTAL

Paper disks

In order to ensure a homogeneous spread of the substance it is necessary to delimit and saturate the entire surface of the disk with a definite amount of the solution studied. These conditions were realized by using chromatographic paper disks, 6 mm in diameter, cut out with a punch.

The paper disks were washed by repeated extractions with distilled water; strong shaking, which roughens the surface of the paper, was avoided; the disks were then dried in a current of air.

Each paper disk was placed on a clean glass slide, and 5 μl of the solution to be investigated was added by means of a capillary pipette (internal diameter 0.4 mm), divided into 5-μl units by gravimetric calibration. This amount corresponded to a layer of $1.77 \cdot 10^{-2}$ cm thickness and ensured saturation of the entire surface of the disk with solution. The solvent was evaporated within a few minutes in the air. In order to protect the paper disks, the glass slides upon which they are placed, should be covered.

Measurement device

In order to obtain sufficient sensitivity for the spectrophotometric determinations when they are done by transmission through filter paper, the paper must be as close as possible to one of the focusses of the light beam, at the input or output slit of the monochromator and not in the space in which the light beam section is constant.

The absorbance of the disks was measured with the aid of the device shown in Fig. 1a, which was adapted to the Zeiss-Jena spectrophotometer model VSU 1 (Fig. 1b). The paper disks were introduced between the plates of sample holder H and adjusted with the help of "fork" g in front of the openings d which were of 5 mm diameter. The circular slits f_1 (diam. 4 mm) and f_2 (diam. 3 mm) delimited the light beam. Pressure upon button B lifted level L, thus releasing sample holder H upon axis A and making it possible to change the paper disks easily. The holder used in this experiment allowed direct comparison of 24 paper disks, indicated on the margin of the holder.

Procedure

After the control and the sample paper disks had been placed in the holder, spectrophotometric determinations were done as follows. The holder was turned until the control paper disk was within the light beam; the monochromator was adjusted to the required wavelength λ_1, and the slit was opened to an appropriate value. The measuring compensator was adjusted to the corresponding value of extinction E^0 and

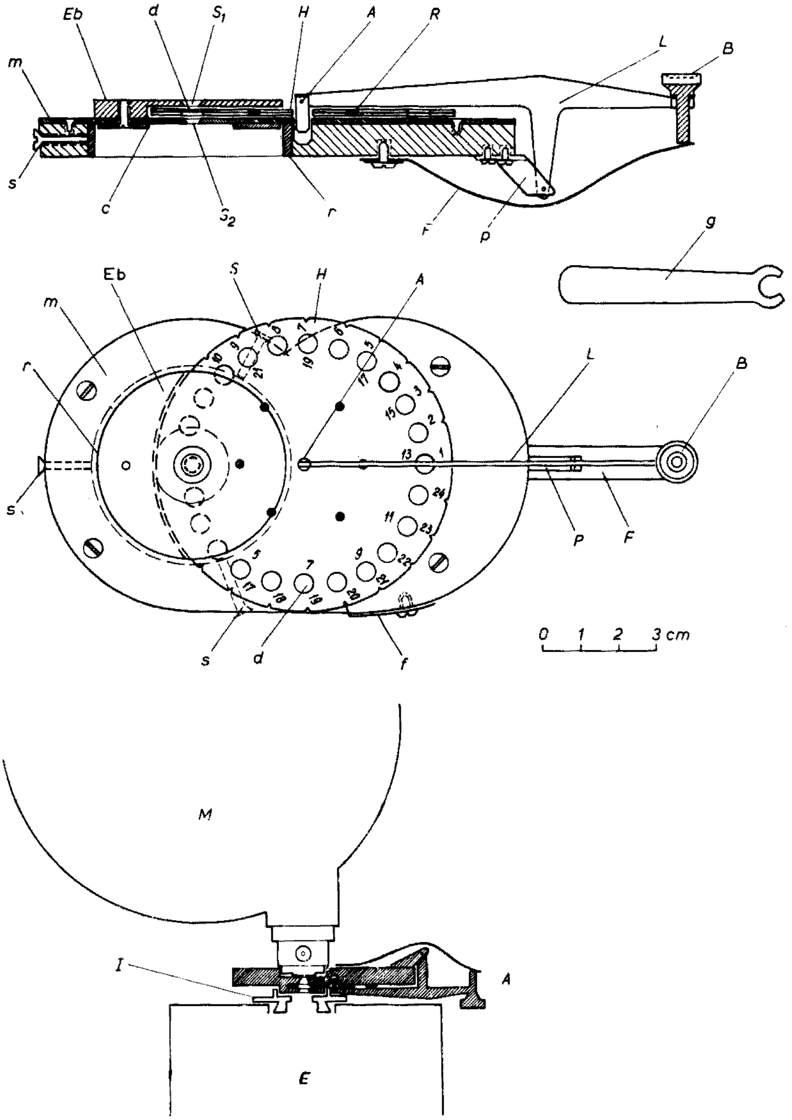


Fig. 1. (a) Device for serial spectrophotometric determinations on small paper disks. H, paper disk holder; d, openings; A, axis; L, level; B, button; p, level axis; F, fixing spring; r, centering ring; S_1 and S_2, circular slits; Eb, ebonite screen; m, metallic plate; s, screws; c, fixing ring; R, rivets; g, "fork". (b) Mounting of the spectrophotometric device in the Zeiss VSU 1 spectrophotometer. M, monochromator; I, fixing ring; E, electrometer; A, device.

the control disk absorption was compensated in the measuring position. Holder H was then turned until the required sample paper disk came into position, and was fixed by spring F. The sample absorption was compensated with the measuring compensator and extinction E_1 was read. All the paper disks were measured in turn, up to the control disk with which the series had started. The measuring compensator was maintained at E^0 and the monochromator was then adjusted to wavelength λ_2. The entire operation was repeated as above, successively determining the extinctions E_2 of the sample paper disks.

RESULTS AND DISCUSSION

Control paper disks

In order to establish the particular form of eqn. (4) in conditions corresponding to clean paper disks, the relative extinctions of 24 disks made from Schleicher-Schüll 2043a chromatographic paper were determined at 350 and 260 mμ with respect to 2 arbitrarily chosen disks (nos. 1 and 15 in Table I). The reference extinction of the controls was in both cases $E^0 = 0.300$. The monochromator slits were opened 2 mm for the wavelength 260 mμ and 1 mm for the wavelength 350 mμ. The data obtained (Table I) indicated a linear dependence between $(E_{260} - E^0)$ and $(E_{350} - E^0)$.

The equations obtained, using the method of the least squares in case both variables are affected by errors, were with respect to control no. 1:

$$(E_{260} - E^0)_1 = (0.0004 \pm 0.0018) + (1.78 \pm 0.04)(E_{350} - E^0)$$

and with respect to control no. 15:

$$(E_{260} - E^0)_{15} = (0.0002 \pm 0.0018) + (1.84 \pm 0.04)(E_{350} - E^0)_{15}$$

TABLE I

WEIGHT AND RELATIVE EXTINCTIONS AT 260 AND 350 mμ OF 24 SCHLEICHER-SCHÜLL 2043a PAPER DISKS WITH RESPECT TO CONTROL DISKS NO. 1 AND 15 WITH AN ARBITRARY EXTINCTION $E^0 = 0.300$

No. of disk	*Weight (mg)*	*Relative extinction*			
		Control disk no. 1		*Control disk no. 15*	
		E_{350}	E_{260}	E_{350}	E_{260}
1	2.40	*0.300*	*0.300*	0.274	0.256
2	2.42	0.295	0.290	0.271	0.248
3	2.48	0.296	0.294	0.274	0.251
4	2.62	0.382	0.445	0.357	0.401
5	2.53	0.335	0.365	0.312	0.322
6	2.50	0.306	0.316	0.282	0.270
7	2.54	0.338	0.367	0.316	0.324
8	2.46	0.302	0.315	0.278	0.272
9	2.60	0.318	0.341	0.294	0.299
10	2.73	0.368	0.423	0.343	0.379
11	2.53	0.303	0.304	0.280	0.262
12	2.59	0.351	0.385	0.325	0.343
13	2.60	0.328	0.355	0.306	0.310
14	2.47	0.292	0.290	0.268	0.247
15	2.52	0.325	0.345	*0.300*	*0.300*
16	2.51	0.338	0.364	0.314	0.319
17	2.58	0.315	0.318	0.291	0.276
18	2.46	0.294	0.288	0.267	0.246
19	2.54	0.323	0.343	0.299	0.300
20	2.34	0.280	0.275	0.257	0.231
21	2.48	0.290	0.271	0.266	0.228
22	2.50	0.300	0.297	0.277	0.252
23	2.56	0.328	0.346	0.304	0.301
24	2.16	0.254	0.215	0.230	0.170

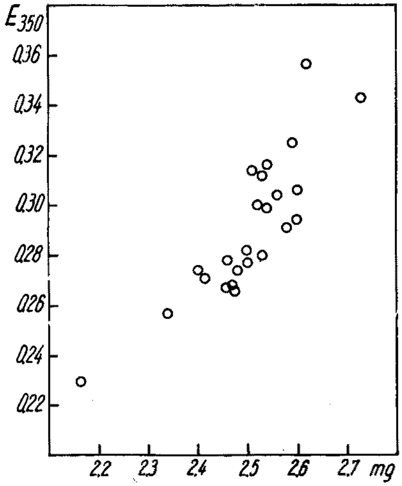
These are almost superimposable within the limits of the calculated standard deviations. This agreement results from the practically constant mean difference between the extinctions at the same wavelength with respect to both controls:

$$\Delta E_{260} = (E_{260})_1 - (E_{260})_{15} = 0.0434 \pm 0.0018 \text{ and}$$

$$\Delta E_{350} = (E_{350})_1 - (E_{350})_{15} = 0.0240 \pm 0.0018$$

The ratio of these differences is equal to the average slope of the linear function whose equations were calculated before and which pass through the origin: $\Delta E_{260}/\Delta E_{350} = 1.81 \pm 0.12$. These results prove that the determinations are independent of the control chosen.

In order to check whether the differences in extinction from one disk to another were indeed due to fluctuations in the mass of the cellulose, the correlation between the individual weight of the disks and the corresponding relative extinction at 350 mμ was analysed. Figure 2 shows the relative extinction values with respect to control disk no. 15 in terms of the disk weights given in Table I. Although the correlation is not linear, the linear correlation coefficient, calculated acording to PEARSON's equation, is $r = 0.88$, *i.e.* close to unity. Thus it is confirmed that the variations in the relative extinction between disks are due primarily to local fluctuations of the cellulose mass within the paper.



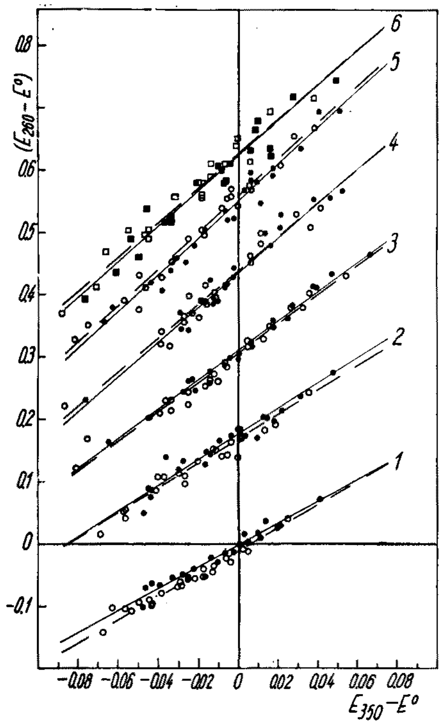


Fig. 2. The relative extinction at 350 mμ ($E_{350} - E^0$) in terms of the paper disk weight.

Fig. 3. The relative extinctions at 260 mμ ($E_{260} - E^0$) with respect to a NaCl-free control (○, □ and ---), and to a control with NaCl (●, ■ and ——) in terms of the extinctions at 350 mμ for various RNA concentrations. (1) 0 mg/ml; (2) 0.16 mg/ml; (3) 0.32 mg/ml; (4) 0.48 mg/ml; (5) 0.64 mg/ml; (6) 0.8 mg/ml.

Disks with substances

In order to establish the general conditions for the spectrophotometric determination of substances on paper disks according to the method described, a natural polymer of great biological importance, ribonucleic acid (RNA), was chosen; RNA has an absorption maximum at approximately 260 mμ and practically no absorption at 350 mμ.

Solutions in 0.14 M sodium chloride were prepared from yeast RNA (Merck) in concentrations of 0.8, 0.64, 0.48, 0.32 and 0.16 mg RNA/ml. Thus when 5 μl of these solutions was added, the disks contained from 0.8 to 4 μg of RNA and approximately 0.03 mg of sodium chloride. The optical density of the solutions was also determined at 260 mμ in quartz cells, with the aid of the VSU 1 spectrophotometer.

Schleicher-Schüll 2043a paper disks were used: 23 for the samples and the control containing only 0.14 M sodium chloride and 22 disks for each of the RNA concentrations. After 5 μl of the solutions investigated had been added, the disks were dried and weighed.

The relative extinctions, E_{260} at 260 mμ and E_{350} at 350 mμ, of each disk were determined with respect to clean disk no. 15 (see Table I) and with respect to the control disk containing only sodium chloride.

The results obtained (Fig. 3) show the differences between the relative extinctions of the samples and the extinctions of the controls at 260 mμ ($E_{260}-E^0$) in terms of those at 350 mμ ($E_{350}-E^0$), with respect to controls with and without sodium chloride. As shown in Fig. 3, the relationship between these magnitudes is linear and satisfies the particular form of eqn. (4):

$$E_{260}-E^0 = a_1 + b_1(E_{350}-E^0) \tag{5}$$

where a_1 represents the contribution of the substance on the disk to the extinction measured at 260 mμ. Constants a_1 and b_1 were calculated by the method of least squares, considering both variables as affected by errors. The standard deviations of these constants were likewise evaluated.

In order to compare the results of the differential method at 2 wavelengths with the comparative values of extinctions of samples determined at a single wavelength, the standard deviation σ of the individual values of $(E_{260}-E^0)_1$ from the intercept a_1 was calculated.

The results obtained are summarized in Table II, and show that:

(*i*) although the presence of sodium chloride had only a slight effect on the extinction of the blank paper disk, it is preferable to compare the samples with a control treated with the solvent of the substance, *i.e.* in the present case 0.14 M sodium chloride;

(*ii*) constant a_1 in eqn. (5) varies regularly with the RNA concentration, *i.e.* with the optical density of the solutions determined in cells at 260 mμ—$\varepsilon_{260}{}^c$ (Fig. 4);

(*iii*) within the concentration range 0.16–0.64 mg RNA/ml, constant b_1 is a linear function of constant a_1:

$$b_1 = 1.595 \pm 0.047 + (2.54 \pm 0.09)a_1 \tag{6}$$

Equation (6), likewise calculated by the method of least squares, fully satisfies the data calculated with respect to the control without sodium chloride, as well as those with respect to the control containing sodium chloride.

TABLE II

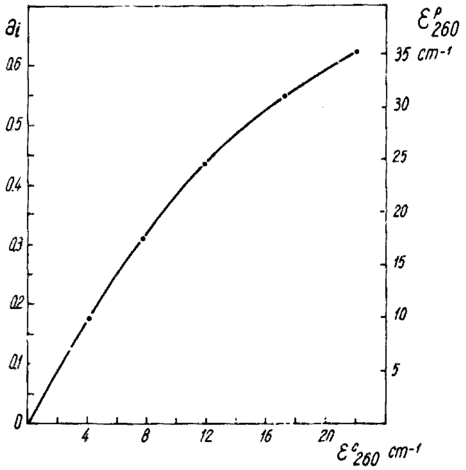
THE VALUE OF THE STANDARD DEVIATION OF a_i IN EQN. (5), b_i IN EQNS. (5) AND (6) AND $a_i^{\text{approx.}}$ IN EQN. (10)
(In terms of the solution concentration c_i and corresponding extinction coefficients ε_i^0 determined in cells at 260 mμ.(a) control disk without NaCl; (b) control disk with NaCl)

Curve no. Fig. 3	c_i *RNA (mg/ml)*	ε_i^0 *(cm^{-1})*	a_i *eqn. (5)*	$a_i^{\text{approx.}}$ *eqn. (10)*	$\pm\sigma$[a]	b_i *eqn. (5)*	*eqn. (6)*
1	0.00	0.00	−0.011 ± 0.003	—	0.095	1.85 ± 0.06	—
2	0.16	4.06	0.165 ± 0.004	0.152 ± 0.020	0.060	1.99 ± 0.10	2.00 ± 0.09
3	0.32	7.70	0.306 ± 0.004	0.298 ± 0.022	0.077	2.36 ± 0.08	2.37 ± 0.11
(a) 4	0.48	11.9	0.438 ± 0.004	0.435 ± 0.022	0.090	2.72 ± 0.10	2.71 ± 0.12
5	0.64	16.6	0.557 ± 0.005	0.544 ± 0.024	0.11	2.94 ± 0.10	3.01 ± 0.15
6	0.80	21.0	0.626 ± 0.006	0.620 ± 0.020	0.11	2.77 ± 0.10	—
1	0.00	0.00	−0.002 ± 0.003	—	0.070	1.76 ± 0.07	—
2	0.16	4.06	0.175 ± 0.004	0.171 ± 0.018	0.053	2.05 ± 0.12	2.05 ± 0.09
3	0.32	7.70	0.310 ± 0.002	0.306 ± 0.020	0.078	2.36 ± 0.07	2.38 ± 0.11
(b) 4	0.48	11.9	0.434 ± 0.004	0.429 ± 0.024	0.075	2.80 ± 0.13	2.70 ± 0.12
5	0.64	16.6	0.548 ± 0.004	0.542 ± 0.024	0.095	2.98 ± 0.11	2.99 ± 0.15
6	0.80	21.0	0.622 ± 0.004	0.620 ± 0.023	0.098	2.84 ± 0.16	—

[a] $\sigma = \sqrt{\Sigma[(E_{260} - E^0)_i - a_i]^2/n}$.

In the field of applicability of eqn. (6) a direct relationship can be expressed between extinction a_i and the relative extinctions of the disks with the investigated substances, eliminating constant b_i from eqns. (5) and (6):

$$a_i = \frac{(E_{260}-E^0)-1.6(E_{350}-E^0)}{1+2.54(E_{350}-E^0)} \tag{7}$$



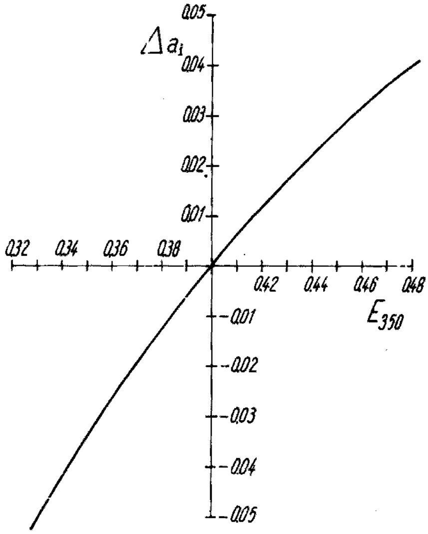


Fig. 4. The corrected extinctions a_i, calculated by eqn. (5), of the RNA-containing disks and the corresponding optical densities ($\varepsilon_{260}{}^p$) at 260 mμ in terms of the optical densities of the RNA solutions used ($\varepsilon_{260}{}^c$).

Fig. 5. The correction term $\Delta a_i = 0.24(E_{350} - 0.4)/E_{350}$ as a function of the relative extinction at 350 mμ (E_{350}).

If the value $E^0 = 0.4$ is chosen for the extinction of the control disk then eqn. (7) becomes simpler; it can be approximated and written in the form:

$$a_i = 0.4\,\frac{E_{260}-E_{350}}{E_{350}} - 0.24\,\frac{E_{350}-0.4}{E_{350}} \tag{8}$$

The second term on the right of eqn. (8) does not depend upon the chromophore of the substance investigated and does not exceed ±0.05. It may therefore be considered as a correction term that can readily be read on a graph such as that in Fig. 5.

Hence, the following expression may be defined by further approximation:

$$a_i^{\text{approx.}} = 0.4(E_{260}-E_{350})/E_{350} \tag{9}$$

It is now clearly possible to calculate a relationship equivalent to eqn. (9) for any chosen value of E^0:

$$a_i^{\text{approx.}} = 0.4(E_{260}-E_{350})/(E_{350}+0.4-E^0) \tag{10}$$

Table II also shows the mean values for $a_i^{\text{approx.}}$ with the standard deviations of the individual determinations calculated on the basis of eqn. (10).

In order to establish the optimal conditions of application of eqn. (9) or (10), by eliminating before use any paper disks giving deviations due to neglect of the correction in eqn. (8), the weights of 132 paper disks were correlated to their relative extinctions with respect to the control with sodium chloride at 350 mμ. Although the relationship between the weight of the paper disks and ($E_{350} - E^0$) was not perfectly linear, so that the calculated coefficient of linear correlation was decreased still further, a coefficient value of $r = 0.91$ was obtained.

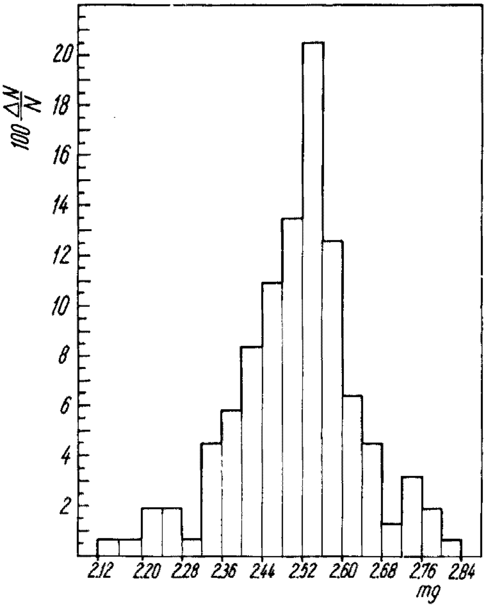


Fig. 6. The percentage weight frequency of 156 Schleicher-Schüll 2043a paper disks (diam. = 6 mm).

The weight frequency distribution of all the disks used is given in Fig. 6. As some of the disks also contained 0.03 mg of sodium chloride, the corresponding values in Fig. 6 were previously corrected. The distribution curve is close to the normal distribution curve with a slight asymmetry, so that the maximum frequency corresponds to a weight of 2.54 mg and the arithmetic average to 2.51 mg.

Therefore, it is possible to select the disks previously, so that the best control can be chosen from the maximum frequency range and any sample disks that require large corrections can be discarded; such large corrections would involve grave errors in the application of eqn. (9) or (10), particularly in the case of single determinations. However, even with unselected material, as was the case in our experiments, because of the random distribution of the variations caused by the lack of homogeneity of the cellulose content, the mean values calculated on the basis of eqn. (10) using several disks, were very close to the most accurate value corresponding to the particular eqn. (5) or the general relation (7), as shown in Table II.

Reproducibility of the method

Hyperchromic extinction amplifies the variations in the optical densities of the nucleic acid solutions because of certain factors such as temperature, ionic strength or pH; it is therefore essential to maintain certain conditions as rigorously as possible, especially when standard curves are used. It was observed that a rise in ionic strength, *i.e.* an increase in the sodium chloride concentration, improved the reproducibility of the RNA determinations, by lowering the sensitivity of the system to the action of the above-mentioned parameters.

Storage of the dry paper disks containing RNA for 2 or 3 weeks protected from dust and other polluting factors, had no effect on the extinction of the samples, within the limits of precision of the method. This stability permits accumulation within a short interval of a large amount of experimental material that may be measured photometrically in the course of a few days or weeks.

Sensitivity of the method

As shown in Fig. 4, the extinction coefficient $\varepsilon_{260}{}^{p}$, calculated from the extinction a_1, is approximately twice the extinction coefficient corresponding to solution $\varepsilon_{260}{}^{c}$, determined in the cell at 260 mμ. This hyperchromic effect[1] is one of the factors that increase the sensitivity of spectrophotometric determinations. On the other hand, 5-μl quartz microcells (for instance those supplied with the VSU spectrophotometer corresponding to a path length of 0.0050 ± 0.0001 cm) have a path length which is 3.5 times smaller than that corresponding to the same volume of solution loaded on the 6-mm disks. Hence, the sensitivity of the paper disk method is almost one order of magnitude greater than that of the current microcell method.

Precision of the method

The data in Table II permit comparative evaluation of the precision of the spectrophotometric method at 2 wavelengths on paper disks, using eqn. (5) or (10), and of extinction determinations at a single wavelength affected by the standard deviations σ. On calculating a_1 according to eqn. (5) and $a_1{}^{\text{approx.}}$ according to eqn. (10), the mean standard deviations of individual determinations, σ included, are: 0.004, 0.021 and 0.085, *i.e.* approximately a ratio of 1:5:21. It is clear that the differential method is far more precise than the current method.

The relative percentage error of the method proposed in the present paper decreases, within the range of concentrations studied, from 2.5% for a concentration of 0.16 mg RNA/ml to less than 1% for a concentration of 0.8 mg RNA/ml, corresponding to a mean absolute error of ± 0.03 μg.

CONCLUSIONS

The differential method involving 2 wavelengths, applied in the quantitative analysis of substances on paper disks, permits the determination of amounts smaller than 1 μg with a precision of 1–2.5%, using 5 μl of solution. The effect of extinction fluctuations due to the lack of homogeneity in the paper can be compensated by using the general equation:

$$\varepsilon_1{}^{p} = \frac{E_1 - E_2 - \alpha(E_2 - E^0)}{1 + \beta(E_2 - E^0)} \Big/ \frac{4v}{\pi\phi^2} \tag{11}$$

where $\varepsilon_1{}^{p}$ represents the extinction coefficient on paper at wavelength λ_1, at which the chromophore of the required substance absorbs; E_1 and E_2 represent the sample extinctions at wavelengths λ_1 and λ_2 respectively, compared to the control disk whose extinction at both wavelengths is E^0; α and β are empirical constants that characterize the paper used; and v is the volume of the solution with which the paper disk of diameter $\varnothing$ is impregnated.

A large number of determinations on dry paper disks can be carried out with the aid of a device for serial spectrophotometric determinations such as that described in Fig. 1.

The fact that the substance investigated can be pipetted on the disk, dried and stored for several weeks before the determinations is of particular importance when substances unstable in solution are used, as often occurs with biological products.

The principle of spectrophotometry at 2 wavelengths may also be applied for improving the quantitative evaluation of substances in chromatography and electrophoresis on paper.

SUMMARY

The principles and application of a method for the microdetermination of substances on small paper disks are described. Photometric measurements are made at 2 wavelengths, thus eliminating the errors due to inhomogeneity in the paper. A simple device for serial determinations that can be adapted to a common spectrophotometer is described. Microdetermination of RNA with measurement at 260 and 350 mμ is given as an example of the proposed method, and the best means of correcting the effect of paper inhomogeneity is established. Amounts of RNA in the range 0.8–4 μg can be determined with a mean error of ± 0.03 μg, using 5 μl of solution.

RÉSUMÉ

Les auteurs décrivent une méthode de microdosage spectrophotométrique sur disques de papier, utilisant 5 μl de solution pour chaque essai. La comparaison des extinctions, déterminées à deux longueurs d'onde, permet la correction des erreurs dues aux défauts du papier (non-homogène). L'acide ribonucléique a pu être dosé par cette méthode, de 0.8 à 4 μg, avec des erreurs absolues moyennes de ± 0.03 μg.

ZUSAMMENFASSUNG

Es werden die Prinzipien und die Anwendung einer Methode zur quantitativen spektralphotometrischen Mikrobestimmung von Substanzen auf kleinen Papierscheiben beschrieben. Relative Extinktionsbestimmungen bei zwei Wellenlängen gestatten, die durch die Ungleichmässigkeiten des Papiers verursachten Fehler zu korrigieren. Als Anwendungsbeispiel wurde die Bestimmung von 0.8 bis 4 μg Ribonucleinsäure bei 260 und 350 mμ durchgeführt. Die absoluten Messfehler betrugen im Durchschnitt ± 0.03 μg bei Verwendung von 5 μl Lösung.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM AFTER EXTRACTION OF THE CHLORO-STANNOUS COMPLEX BY TRI-*n*-OCTYLAMINE

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The use of high molecular weight amines (HMWA) as "liquid anion" exchangers and extractants for anionic complex metal ions has been mainly confined to the separation of specific pairs of ions[1-4] and to the extraction of uranium, thorium and plutonium[5-8]. Recently, however, an extensive investigation on the formation and extraction of Group VIII metals was carried out by GOOD *et al.*[9-12], and the present authors[13] in a study of the Pt(IV)–Sn(II) system used HMWA for the quantitative extraction of dichloro(trichlorostannatoplatinate).

However, the Pd(II)–Sn(II) chloro complex has not been previously investigated. YOUNG *et al.*[14] studied the structure of the chlorotin complexes of the platinum group metals, but omitted the palladium complex. SANDELL[15] and AYRES AND MEYER[16] both investigated the chlorotin complex of platinum and observed marked interference from palladium.

The present authors began investigations on the Pd(II)–Sn(II) system by determining the structure of the complex formed[17]. In the course of this work, it became clear that this complex under suitable conditions might form the basis of a method for the determination of palladium. Investigations in this direction were therefore carried out.

EXPERIMENTAL

Apparatus

Hilger Uvispek Spectrophotometer S.P. 700.

Reagents

Palladium chloride solution. 0.336 g of palladium chloride (Johnson and Matthey Reagent) were dissolved in 2 l of water containing 40 ml of hydrochloric acid. The concentration of palladium in the solution was checked by the dimethylglyoxime method. 1 ml of this solution contained 100 μg of palladium.

Tin(II) chloride solution. 23 g of tin(II) chloride dihydrate was dissolved in 100 ml of 3.5 *M* hydrochloric acid.

Tri-n-octylamine. A 0.2 *M* solution in thiophene-free benzene was used without additional purification.

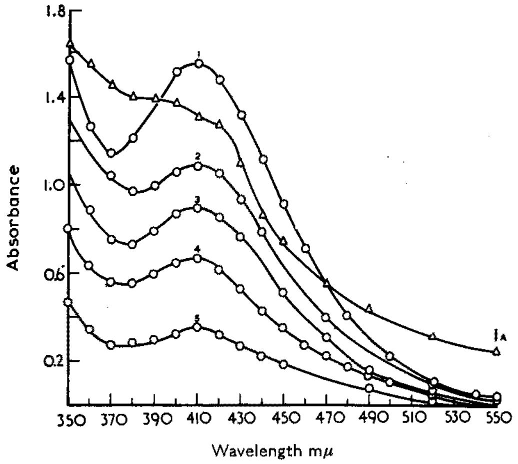
All other chemicals used were of AnalaR Grade.

Formation of the Pd(II)–Sn(II) chloride complex and extraction by tri-n-octylamine

On treatment of palladium(II) with tin(II) chloride, two different complexes are formed, depending on the experimental conditions. One of these is a brown-red species and the other a yellow species. Conditions for the formation of both are indicated below.

Formation of the brown-red species. This complex was formed by treating 250 μg of palladium(II) with 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride. A dark red colour appeared, changing to greenish-blue and finally brownish-red after heating for 30 min on a water bath.

Investigations on the extractability of the complex were carried out; the complex was quantitatively extracted by 0.2 *M* tri-*n*-octylamine in benzene on shaking for 2 min. The colour of the complex in the organic phase was brownish-red. After filtering through filter paper to remove suspended water droplets, the solution was made up to volume in a 10-ml flask with benzene and the absorption spectrum determined with respect to a "blank" containing all the reagents, but no palladium, and extracted in the same way. The spectrum obtained is shown in Fig. 1a. It will be seen that no definite maximum occurs in the range 350–550 mμ.



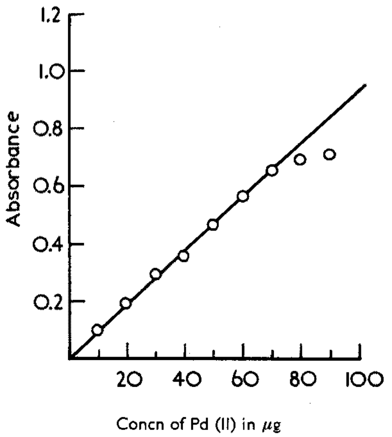


Fig. 1. The absorption spectra of palladium chlorostannate complexes after extraction by 0.2 *M* tri-*n*-octylamine in benzene. (1A) The brown-red species; (1–5) the yellow species for varying amounts of palladium.

Fig. 2. Standard curve for palladium chlorostannate complex (yellow species) extracted by 0.2 *M* tri-*n*-octylamine in benzene.

Formation of the yellow species. This complex was formed readily by treating 50–250 μg of palladium(II) with 7 ml of concentrated hydrochloric acid, diluting the solution to 50 ml with water, thus changing the acidity to 1.55 *M* in hydrochloric acid, and adding 1 ml of the tin(II) chloride reagent. On shaking, a yellow coloured complex was formed, which was easily extracted into 0.2 *M* tri-*n*-octylamine in benzene. The absorption spectrum of the complex was determined and is shown in Fig. 1 (1–5) for varying amounts of palladium(II) in the range 350–600 mμ. It can be seen from the spectrum that a maximum occurred at 410 mμ, in contrast to the absorption spectrum of the reddish-brown species. Because of this factor, the yellow-coloured complex was more suitable than the reddish-brown species. The procedure used in subsequent work is outlined below.

General procedure

To the solution containing palladium, add 7 ml of concentrated hydrochloric acid, dilute to 50 ml with water in a separatory funnel and then add 1 ml of tin(II) chloride reagent. To the separatory funnel, add 5 ml of 0.2 *M* tri-*n*-octylamine in benzene and quickly extract the yellow complex by shaking the mixture for 2 min on a mechanical shaker (Note 1). Allow the phases to separate; the yellow complex is completely transferred to the amine phase. Filter the amine phase through a small filter paper into a 10-ml flask and make up to the mark with benzene. A second extraction is unnecessary (Note 2).

Measure the absorbance at 410 mμ and compare with a calibration curve (Fig. 2) prepared by putting different amounts of palladium through the same procedure (Note 3).

Notes

(*1*) Extraction is carried out quickly as the chloro tin complex of palladium is highly unstable in aqueous phase, the colour fading. However, extraction into the amine phase within a reasonable time stabilises the complex.

(*2*) It would appear that the Pd(II)–Sn(II) complex is extracted into the amine phase as an anionic complex[14] by so-called "liquid ion-exchange" extraction; hence the great affinity of amine for the coloured species and the high efficiency of extraction.

(*3*) In the range 5–70 μg/10 ml, Beer's law is closely obeyed and a good straight line is obtained. The molar extinction coefficient was found to be $9.964 \cdot 10^3$.

Effect of hydrochloric acid concentration

To prevent precipitation of tin(II) chloride the presence of hydrochloric acid was essential. The most suitable concentration for efficient extraction was found to lie in the range 1.5–1.55 *M*, in which the extract was stable and clear. On increasing the molarity beyond these limits, the extinction coefficient decreased. Under these conditions the amount of tin(II) chloride had little effect on the intensity of the colour; 1 ml of the tin(II) chloride solution was sufficient to produce maximum colour intensity.

Extraction efficiency and stability of extract

As indicated above, the Pd(II)–Sn(II) system was unstable in the aqueous phase. In earlier work, the authors[13] used a number of different amines, including tri-*n*-octylamine in organic solvents, and achieved excellent stability and efficient extraction. This was in contrast to previous unsuccessful attempts by other workers to extract the platinum system with isoamyl acetate and ethyl acetate[16]. The instability of complexes of this type in the latter solvents is probably due to the fact that the negatively charged species is not strongly bound by the solvent and decomposes into entities of indefinite composition on standing. On the other hand there is a great affinity of HMWA for anions, as can be judged from the fact that 5 ml of tri-*n*-

octylamine in benzene extracted the complex quantitatively from 50 ml of aqueous phase in a single extraction.

The stability of the amine/organic extract was found to be dependent on two factors: (*1*) the hydrochloric acid concentration, as discussed above, and (*2*) the time of extraction.

After the addition of 1 ml of tin(II) chloride to 50 ml of the 1.5 *M* hydrochloric acid solution of palladium, a bright yellow colour developed which changed to greenish-yellow in about 1 min. The amine should, therefore, be added quickly after the tin(II) chloride. The accuracy and reproducibility of results was strongly dependent on the time of standing of the complex in the aqueous phase. Maximum absorbance of the solution was attained 15 min after extraction and, thereafter, gave constant absorbance readings for 2 h.

Interferences

Two types of interference in the determination of palladium, by the procedure outlined, are most frequently encountered: (*i*) ions which readily form an anionic complex with tin(II) chloride are extracted as the amine salt of a chlorotin complex, *e.g.*, Pt(IV), Rh(III)[13,14]; (*ii*) ions which form an anionic complex with tin(II) chloride on heating, *e.g.*, Ru(III), Ir(IV)[14].

Interference from rhodium(III) and platinum(IV) cannot be avoided without prior separation. No interference, however, arose from the presence of the other platinum group metals. It was possible to determine palladium accurately in the presence of a 5-fold excess of these metals and a 20-fold excess of other commonly

TABLE I

INTERFERENCE OF DIVERSE IONS

Palladium (μg)		*Error*	*Diverse ions*	
Present	*Found*			
50	50	0	Os	(250 μg)
50	49	—1	Ru(III)	(250 μg)
50	50.5	+0.5	Ir(III)	(250 μg)
50	50	0	Fe(III)	(1 mg)
50	50	0	Ni	(1 mg)
50	50	0	Co	(1 mg)
50	50	0	Zn	(1 mg)
50	50	0	Pb	(1 mg)
50	50	0	Cu	(1 mg)
50	50	0	Mn	(1 mg)
50	50.5	+0.5	Cr(VI)	(1 mg)
50	50.5	+0.5	Mo(VI)	(1 mg)
50	51.5	+1.5	V(V)	(1 mg)
50	51	+1	W	(1 mg)
50	52	+2	SO_4^{2-}	(1 mg)
50	49	−1	ClO_4^-	(1 mg)
50	51	+1	PO_4^{3-}	(1 mg)
50	50	0	NO_3^-	(1 mg)
50	50	0	CH_3COO^-	(1 mg)
50	10	−40	SCN^-	(1 mg)

associated elements, some of which, *e.g.*, Mo, V, W, and Cr, gave strongly coloured products with tin(II) chloride, but fortunately were not extracted into the amine phase. Thus, the presence of Os, Ir, Ru, Fe, Ni, Zn, Co, Pb, Cu, Mn, Cr, Mo, V and W caused no interference in the determination of palladium. Various anions (sulphate, phosphate, perchlorate, thiocyanate, nitrate and acetate) were examined. Only thiocyanate interfered; negative results were obtained, probably due to the formation of[18] $Pd(SCN)_4^{2-}$ which hinders the formation of the chlorotin complex of palladium. The influence of diverse cations and anions on the determination of palladium is shown in Table I.

As a final check on the method, various "unknowns" were analysed. The results are shown in Table II.

TABLE II

DETERMINATION OF PALLADIUM IN "UNKNOWN" MIXTURES

Sample no.	*Palladium (μg/ml)*		*Error (μg/ml)*	*Other elements present (μg/ml)*
	Present	*Found*		
I	5.0	5.1	+0.1	
		5.05	+0.05	Os 25
		4.95	−0.05	Ir 20
		5.0	0	Ru 25
		5.0	0	
II	10.0	9.85	−0.15	
		10.05	+0.05	Os 50
		10.00	0	Ir 25
		10.05	+0.05	Ru 50
		10.00	0	
III	—	0	0	Os 20
		0	0	Ir 20
		0	0	Ru 20

DISCUSSION

From the ease with which the complexes formed between palladium(II) and tin(II) are extracted into tri-*n*-octylamine, it is assumed that the species are anionic and that "liquid anion exchange" occurs between the complex and the amine. Confirmation of this is given by previous work[17] on the determination of the structure of tetraphenylarsonium palladium(II) trichlorostannate $[(C_6H_5)_4As]_2PdCl(SnCl_3)_2$. It is, therefore, proposed that the extraction of the anionic species may be represented by an overall reaction of the type:

$$(i)\ R_3N + H^+A_{(aq)}^- \rightleftharpoons R_3NH^+A_{(org)}^-$$

$$(ii)\ PdCl_2 + 2\ SnCl_2 \rightarrow [PdCl(SnCl_3)_2]^{2-}$$

$$(iii)\ 2\ R_3NH^+A^- + [PdCl(SnCl_3)_2]_{(aq)}^{2-} \rightleftharpoons [R_3NH^+]_2PdCl(SnCl_3)_2 + 2\ A^-$$

where $H^+A_{(aq)}^-$ represents hydrochloric acid, and R_3N represents tri-*n*-octylamine.

The fact that two different complexes exist indicates the instability of the system in the aqueous phase. The "yellow" species which possesses a definite absorption maximum at 410 mμ in the amine phase provides a further indication that the unstable complex in the aqueous phase is stabilised by extraction into the amine.

In work at present in progress in this laboratory it has been found possible to isolate the anionic species of the Pt(IV)–Sn(II), Rh(III)–Sn(II), and Au(III)–Sn(II) systems by extraction into HMWA. Results for the Pt(IV)–Sn(II) system have already been reported[13,14] and those for the last two will be reported by the present authors in a later communication.

SUMMARY

The complex formed between palladium(II) and tin(II) in hydrochloric acid solutions, and its extractability by tri-*n*-octylamine were investigated. Two different species were obtained: one a brown-red complex and the other yellow. Both were extracted into tri-*n*-octylamine in benzene, but the yellow species which had a definite absorption maximum at 410 mμ was more suitable for the determination of palladium. A method is described for the spectrophotometric determination of palladium in the presence of many other elements. Both species are considered to be anionic and a mechanism for their extraction is proposed.

RÉSUMÉ

Les auteurs ont examiné le complexe formé entre palladium(II) et étain(II), en solution chlorhydrique, et son extraction dans la tri-*n*-octylamine. On obtient deux composés: un complexe brun et un complexe jaune. Ce dernier présente un maximum d'absorption à 410 mμ; il convient mieux pour le dosage du palladium. Une méthode est décrite pour le dosage spectrophotométrique du palladium, en présence de nombreux autres éléments.

ZUSAMMENFASSUNG

Es wurde der Komplex untersucht, der zwischen Pd(II) und Zn(II) in Salzsäurelösungen gebildet wird; ferner seine Extrahierbarkeit durch Tri-*n*-octylamin. Zwei unterschiedliche Spezies wurden gefunden: ein braunroter und ein gelber Komplex. Beide wurden mit Tri-*n*-octylamin in Benzol extrahiert, jedoch war der gelbe, welcher ein definiertes Absorptionsmaximum bei 410 mμ besitzt, besser für die Bestimmung von Palladium geeignet. Es wird eine Methode beschrieben für die spektralphotometrische Bestimmung des Palladiums in Gegenwart anderer Elemente. Beide Spezies sind anionisch. Ein Mechanismus für ihre Extraktion wird vorgeschlagen.

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COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN SELENIUM(IV) AND 2,2'-DIANTHRIMIDE

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In a previous paper[1] the authors described a study of the applicability of 2,2'-dianthrimide in spectrophotometry and introduced this reagent for the determination of selenium(IV).

The present investigation was started with the general purpose of elucidating the complex formation between selenium(IV) and 2,2'-dianthrimide and the special intention of explaining the irregular calibration curve obtained in the earlier investigation.

EXPERIMENTAL

Instruments and equipment

Extinction measurements were made with a Zeiss spectrophotometer PMQ II, a Beckman DB recording spectrophotometer and 1-cm cells.

All solutions were prepared and heated in 100- or 50-ml bottles (Jena Geräteglas) with ground-glass stoppers. The solutions were heated, where required, in a thermostatically controlled drying oven of standard construction.

Reagents

2,2'-Dianthrimide was synthesized by a procedure given in DRP 257 811. The product was recrystallized twice from dimethyl phthalate. Traces of inorganic salts were finally removed by dissolution in 95.5% sulfuric acid and reprecipitation in ice water. The preparation exhibited the colour reactions specified in DRP 216 083. An infrared spectrum and quantitative elemental analysis confirmed the structure and composition of the reagent.

The spectrographically standardized selenium dioxide (Johnson, Matthey & Co., Ltd.) contained—according to the accompanying certificate—2 p.p.m. of sodium, and less than 1 p.p.m. each of copper, magnesium and silver. Other chemicals, with exception of fuming sulfuric acid, were of reagent-grade quality.

Standard solutions

A series of sulfuric acid solutions was prepared by adding fuming acid or distilled water to concentrated (95–97%) acid, the exact strength being determined by alkalimetric titration.

Different 2,2'-dianthrimide standard solutions were employed, these being prepared by dissolving the proper amounts in 96.2% sulfuric acid. The concentrations are given below.

Selenium(IV) standard solution ($25.33 \cdot 10^{-3}$ *M*). In a 100-ml volumetric flask, 0.2811 g of selenium dioxide was dissolved in 1% sodium hydroxide solution. The solution was diluted to the mark with the same solvent*. Other standard solutions (concentrations $31.66 \cdot 10^{-4}$, $25.33 \cdot 10^{-4}$, $6.33 \cdot 10^{-4}$ and $5.07 \cdot 10^{-4}$ *M*) were prepared by dilution with 1% sodium hydroxide solution.

Concentration of sulfuric acid, temperature and heating time

On the basis of previous studies[1] the concentration of acid was maintained at 95.5%, and the temperature and heating time at 90° and 5 h, respectively.

Absorption curves

In a previous paper[1] absorption curves of solutions of 2,2'-dianthrimide and of the complex were recorded. Solutions of the reagent exhibited maxima at about 340 and 660 nm. When measured against a blank solution containing the same amount of the reagent, solutions of the complex showed two small maxima at about 430 and 480 nm and one predominant maximum at 605 nm. However, in the present work, as can be seen from Fig. 1, both complexes were found to exhibit a predominant absorption maximum at 660 nm. In the previous investigation[1] higher concentrations of both selenium(IV) and 2,2'-dianthrimide were maintained, and under these conditions some oxidation of 2,2'-dianthrimide by selenium(IV) seemed to take place, this resulting in the change of maximum.

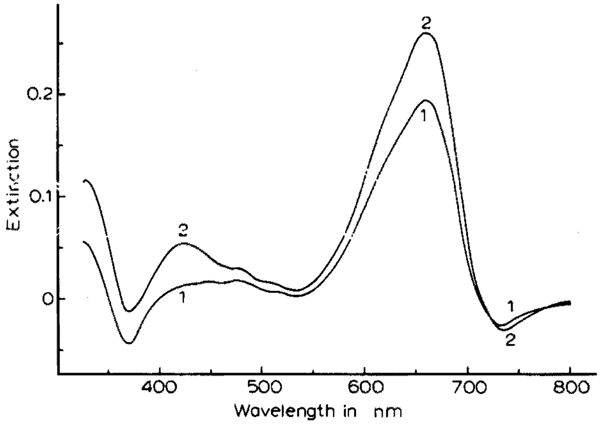

Fig. 1. Absorption curves of solutions with the same total concentration ($1.44 \cdot 10^{-4}$ *M*), but containing an excess of 2,2'-dianthrimide, $c_{Se}/c_{Di} = 1:9$ (curve 1), and an excess of selenium, $c_{Se}/c_{Di} = 9:1$ (curve 2).

Preliminary investigations on the complex formation

It was known that mixtures of the reactants had to be heated in order to obtain complex formation. The selenium(IV) reacted in the same way whether it was added

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* Standard solutions of selenium(IV) may also be prepared by dissolving selenium dioxide directly in concentrated sulfuric acid.

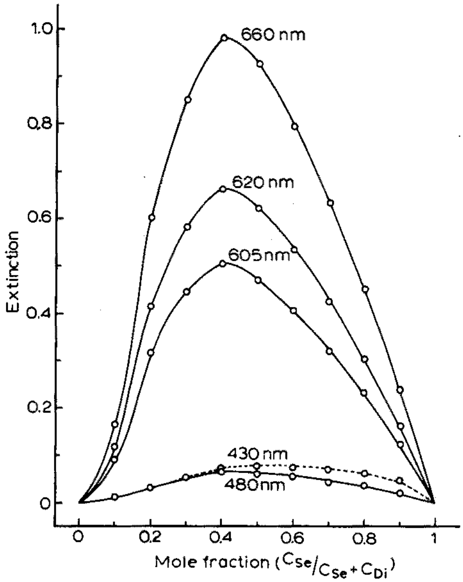
as a solution of selenium dioxide in sodium hydroxide solution, or as a solution of selenium dioxide or selenious acid in concentrated sulfuric acid*. Under the present experimental conditions no complex formation was found to take place between 2,2′-dianthrimide and elemental selenium or selenium(VI).

Preparation of solutions for the photometric measurements

In the spectrophotometric investigations described below solutions of the reactants were prepared by mixing in 50-ml bottles v_1 ml of a selenium(IV) standard solution, $(1-v_1)$ ml of 1% sodium hydroxide solution, 12 ml of 99.9% sulfuric acid, v_2 ml of 2,2′-dianthrimide solution and $(5-v_2)$ ml of 96.2% sulfuric acid. The final acid concentration was 95.5%. Because of contraction the total volume was 17.6 ml. The blank solutions were identical in composition, but did not contain selenium $(v_1=0)$.

The method of continuous variation

The concentrations of the standard solutions of selenium(IV) and 2,2′-dianthri-



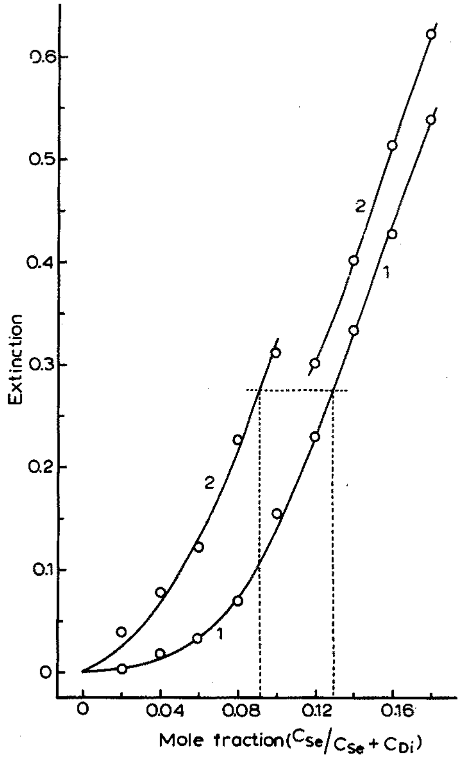


Fig. 2. Curves of continuous variation plotted at different wavelengths. Total concentration $1.44 \cdot 10^{-4}\,M$.

Fig. 3. Detailed curves of continuous variation plotted at 660 nm for low mole fractions of selenium. Total concentrations: curve 1, $1.44 \cdot 10^{-4}\,M$; curve 2, $1.80 \cdot 10^{-4}\,M$.

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* The behaviour of selenium dioxide in the sulfuric acid solvent system has been studied by FLOWERS, GILLESPIE AND ROBINSON[2].

mide employed were $25.33 \cdot 10^{-4}$ and $5.07 \cdot 10^{-4}$ M, respectively; v_1 was varied with 0.1-ml intervals between 0.1 and 0.9 ml, while v_2 was varied correspondingly with 0.5-ml intervals between 4.5 and 0.5 ml. The mole fraction x ($x = c_{Se}/(c_{Se}+c_{Di})$) varied from 0.1 to 0.9, and the constant total concentration of the reactants was $1.44 \cdot 10^{-4}$ mole. The extinctions were measured at 430, 480, 605, 620 and 660 nm. The curves are reproduced in Fig. 2.

With the exception of the curve plotted at 430 nm, the curves exhibit a maximum at the mole fraction 0.4. The curve branches for mole fractions $0 < x < x_{max}$ exhibit inversions and a parabolic approach to the end-point, while the other parts of the curves show a gradient different from zero and absence of inflections.

Detailed curves were then plotted of new mixtures with smaller mole fractions. The solutions were prepared as described above, but measurements were only made at 660 nm. Two series were prepared with the total concentrations $1.44 \cdot 10^{-4}$ and $1.80 \cdot 10^{-4}$ M. The resulting curves (Fig. 3), as well as similar curves of a series of mixtures with mole fraction near 1 (the latter curves are not reproduced), confirmed the results of the series plotted in Fig. 2. However, in Fig. 3 an unexpected break appeared in one of the curves.

The curve maxima of Fig. 2 pointed to the presence of one complex with a mole ratio of selenium(IV) to 2,2'-dianthrimide of 2 : 3. However, from the theoretical treatments of ASMUS[3] and of KLAUSEN AND LANGMYHR[4] it was concluded that the form of the present curves was not in accordance with this composition. A complex exhibiting a parabolic approach for mole fractions near zero and a gradient different from zero for the mole fraction one cannot have the composition Se_2Di_3, but must be of the form Se_mDi_n ($m > 1$; $n = 1$). For a complex of the latter type, the maximum in the curves of continuous variation can be expected somewhere in the mole fraction range $0.5 < x < 1.0$. It was concluded that the series of solutions did not contain a single, predominating species, but a mixture of two or more complexes.

Absorption curves were then recorded of two solutions representing the mole fractions 0.1 and 0.9, both belonging to the $1.44 \cdot 10^{-4}$ M series. The absorption curves are reproduced in Fig. 1; the different forms of these curves, particularly in the wavelength range 400–500 nm, seemed to indicate that they belonged to different complexes.

The mole ratio method

Two standard solutions of selenium(IV) were prepared, the first (with concentration $5.07 \cdot 10^{-4}$ M) being employed for mole ratios $c_{Se}/c_{Di} \leqq 1$, and the second (with concentration $25.33 \cdot 10^{-4}$ M) being used for mole ratios $1 < c_{Se}/c_{Di} \leqq 5$. The concentration of the standard solution of 2,2'-dianthrimide was $1.01 \cdot 10^{-4}$ M. The different solutions were prepared by varying v_1, while in all mixtures v_2 was 5.00 ml, corresponding to a constant concentration of 2,2'-dianthrimide of $2.88 \cdot 10^{-5}$ mole. The extinctions were measured at 605 and 660 nm . The form of the two curves was completely identical. The curve plotted at 660 nm is reproduced in Fig. 4.

The curve exhibits a parabolic approach to the origin and as in Fig. 3, a break. The intersection point indicated the presence of a complex with mole ratio 1 : 1.

The straight-line method

The straight-line method was introduced by ASMUS[5] and was extended by KLAUSEN AND LANGMYHR[9]. Two series of mixtures were prepared, one with a constant concentration of 2,2′-dianthrimide and varying amounts of selenium(IV), and another with a constant concentration of selenium(IV) and different amounts of the ligand. The concentrations of the standard solutions of selenium(IV) and of 2,2′-dianthrimide were $31.66 \cdot 10^{-4}\,M$ and $6.33 \cdot 10^{-4}\,M$, respectively. In the first series v_1 varied between 0.09 and 0.60 ml, while v_2 was 5 ml. The constant concentration of 2,2′-dianthrimide in the solutions was thus $1.80 \cdot 10^{-4}$ mole. The extinctions were measured at 605 nm. The resulting figure exhibited a straight line for $m=2$. Thus, in solutions containing an excess of 2,2′-dianthrimide a complex with two selenium atoms predominated.

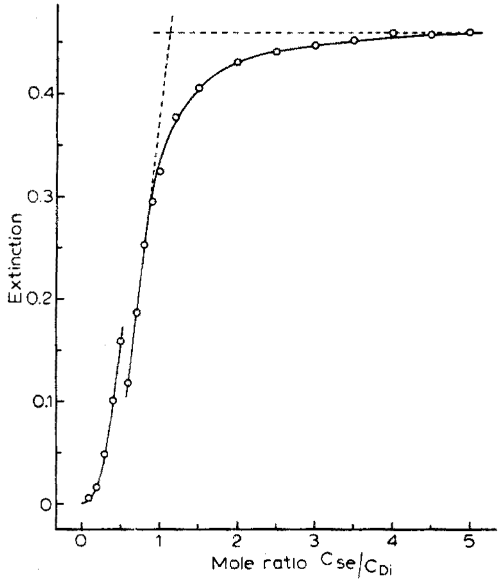

Fig. 4. Mole ratio curve recorded at 660 nm of a series of solutions containing a constan concentration ($2.88 \cdot 10^{-5}\,M$) of 2,2′-dianthrimide and varying concentrations of selenium.

In the second series v_2 was varied between 0.54 and 2.50 ml; v_1 was 1 ml, the constant concentration of selenium(IV) thus being $1.80 \cdot 10^{-4}$ mole. The extinctions were again measured at 605 nm. This time a straight line was obtained for $n=1$. Thus, in solutions having an excess of selenium(IV) the predominant complex contained one molecule of 2,2′-dianthrimide.

Preparation of the solid SeDi complex

On the basis of some preliminary experiments the following procedure was used for the preparation of the solid SeDi complex. In a 100-ml bottle 0.0500 g of 2,2′-dianthrimide and 0.1292 g of selenium dioxide were dissolved in 100 ml of 95.5% sulfuric acid, the mole ratio of selenium(IV) to 2,2′-dianthrimide corresponding to 10:1. (As apparent from the subsequent discussion, the SeDi complex was found to predominate in solutions of high total concentration containing an excess of selenium(IV).) After heating, the solution was cooled to room temperature and transferred to a dry separating funnel. The solution was then added dropwise to a 1-l beaker containing about 750 ml of a mixture of ice and water. During this addition the content of the beaker was mixed vigorously. The precipitate was allowed to settle for 24 h. The supernatant liquid was removed by decantation and the product was collected on a loose-textured filter. The preparation was washed on the filter with hot water until sulphate could no longer be detected in the wash water. The product was finally dried in a vacuum desiccator to constant weight (drying agent: phosphorus pentoxide). The product was a crystalline, dark powder which decomposed at about 335° (m.p. for 2,2'-dianthrimide: 308–310°). The yield was about 70%.

Investigations of the solid complex

A solution of the complex was prepared by transferring 0.0500 g to a 100-ml volumetric flask, dissolving the substance in 95.5% sulfuric acid and diluting to volume with acid of the same strength; 2 ml of this solution were pipetted into a 100-ml volumetric flask and diluted to volume with 95.5% sulfuric acid. In another experiment, 0.0500 g of 2,2'-dianthrimide and 0.1292 g of selenium dioxide were dissolved in 100 ml of 95.5% sulfuric acid. After heating, 2 ml of the solution were pipetted into a 100-ml volumetric flask and diluted to the mark with 95.5% sulfuric acid. The absorption curves of the two diluted solutions were recorded against a blank of 95.5% sulfuric acid. As seen from Fig. 5 the form of the curves is practically identical.

For the sake of comparison, 0.0500 g of 2,2'-dianthrimide was dissolved in 100 ml of 95.5% sulfuric acid; after heating, 2 ml were pipetted into a 100-ml volumetric flask and diluted to volume with 95.5% sulfuric acid. The absorption curve of the solution was recorded in the same way as described above. The curve is also reproduced in Fig. 5.

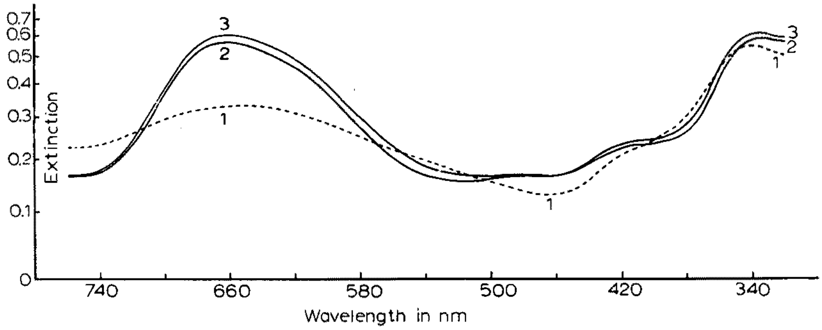

Fig. 5. Absorption curves in 95.5% sulfuric acid of solutions of 2,2'-dianthrimide (curve 1), of the solid SeDi complex (curve 2) and a mixture of selenium and 2,2'-dianthrimide in the mole ratio 10:1 (curve 3).

Infrared spectra (Nujol mull) were recorded of 2,2'-dianthrimide and of the solid complex. The spectrum of 2,2'-dianthrimide exhibited strong absorption at 1680 cm^{-1}, this being interpreted as stretching vibrations of the carbonyl groups. Three absorption bands at 1595, 1580 and 1500 cm^{-1} were believed to represent stretching frequencies typical for aromatics. An absorption at 710 cm^{-1} was found to be characteristic for anthraquinone and anthraquinone derivatives with 4 adjacent ring hydrogen atoms. The stretching frequency of the secondary amino group was expected to result in a distinct absorption somewhere in the range 3500–3300 cm^{-1}, but only a broad, indistinct band was obtained. This discrepancy could be explained by assuming that the secondary amino group participated in intra- or intermolecular hydrogen bonding.

The spectrum of the solid complex exhibited the same characteristic absorptions in the range 1600–1500 cm^{-1} and at 710 cm^{-1}. No frequency shift was registered for the absorption due to the carbonyl groups, this indicating that these groups did not participate in bonding with selenium. A weak absorption at 3340 cm^{-1} could originate either from the secondary amino group or a hydroxyl group.

The qualitative tests on the solid complex confirmed the presence of nitrogen and selenium, while tests for halogen and sulfur were negative. Quantitative elemental analysis gave the following results (in per cent): C 65.14; H 3.17; N 2.84; Se 14.48 (theor. for $C_{28}H_{15}NO_6Se$: C 62.24; H 2.80; N 2.59; Se 14.61). The high analytical results for carbon and hydrogen were believed to be caused by the presence of 2,2'-dianthrimide which is also insoluble in water. Selenium was determined gravimetrically on a weighed portion decomposed by fusion with a mixture of potassium nitrate and sodium carbonate. The melt was dissolved in hot water, the selenium was reduced by addition of concentrated hydrochloric acid saturated with sulfur dioxide and finally weighed as elemental selenium.

Attempts at a determination of the molecular weight by an ebullioscopic method failed for the lack of a suitable solvent.

RESULTS AND DISCUSSION

The experimental results can be explained by assuming the presence of two complexes with the composition SeDi and Se_2Di_2. The monomer predominated in solutions of relatively high total concentration or in solutions of lower total concentration containing the reactants either in equimolar amounts or an excess of selenium(IV). The dimer predominated in solutions of low total concentration containing an excess of 2,2'-dianthrimide.

It is thus possible to explain the irregular calibration curve for selenium(IV) obtained in the previous investigation[1]. The initial part of any calibration curve corresponds to parts of curves of continuous variation and of mole ratio curves. As seen from the Figs. 3 and 4, these curves exhibited parabolically formed end branches. Consequently, the calibration curve previously plotted[1] should not cut the vertical axis below the origin, but approach this point parabolically. The parabolic part of the curves corresponds to experimental conditions (mixtures with low total concentrations containing an excess of 2,2'-dianthrimide) under which the dimer predominates. In the previous investigation mixtures with a sufficiently low content of selenium(IV) were not prepared and the parabolic approach was thus not detected.

Both curves in Fig. 3 (in curve 1 the break lies just outside the figure — in the mole fraction range $0.18 < x < 0.20$) and the curve in Fig. 4 exhibit a break or discontinuity which was explained by assuming a sudden transformation of one of the two complexes into the other*. In these Figures the initial left branches again correspond to conditions under which the dimer predominates. By increasing the total concentration of the reactants and/or decreasing the excess of 2,2'-dianthrimide, a sudden monomerization takes place, the discontinuity resulting from a difference in the absorbing properties of the two species. To the authors' knowledge, a discontinuity of this type has not been reported before.

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* A similar transformation and corresponding discontinuity in the curves of continuous variation has been observed in the system selenium(IV)–1,1'-dianthrimide[6].

The dissolution of 2,2'-dianthrimide (Di) in concentrated sulfuric acid can be assumed to result in the following equilibrium

$$\mathrm{Di} + x\,\mathrm{H_2SO_4} \rightleftharpoons \mathrm{DiH}_x^{x+} + x\,\mathrm{HSO_4^-}$$

For solutions of 1,1'-dianthrimide in 100% sulfuric acid ARNESEN AND LANGMYHR[7] found the value of x to be 3.

The results of the infrared investigations of the solid 2,2'-dianthrimide indicated that the secondary amino group participated in intra- or intermolecular hydrogen bonding. In 2,2'-dianthrimide the steric conditions were found not to favour intramolecular hydrogen bonding, whereas an intermolecular bonding between two molecules, as suggested in Fig. 6, was more probable.

On the basis of the investigations of FLOWERS, GILLESPIE AND ROBINSON[2] it was assumed that under the present experimental conditions the selenium(IV) participated in the reactions as the ion $\mathrm{HSeO_2^+}$.

As stated above, the dimer predominated in solutions of low total concentration containing 2,2'-dianthrimide in excess. A possible structural formula for the dimer is shown in Fig. 6.

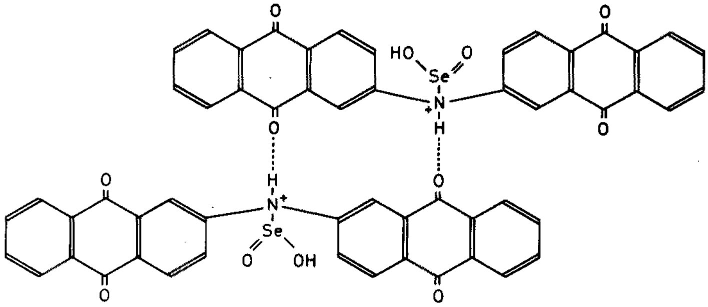

Fig. 6. Possible structural formula of the dimer $\mathrm{Se_2Di_2}$ complex.

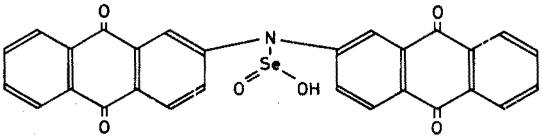

Fig. 7. Probable structural formula of the solid SeDi complex.

By increasing the total concentration and/or decreasing the excess of 2,2'-dianthrimide, the hydrogen bonds between the two 2,2'-dianthrimide molecules are disrupted, this resulting in the formation of two monomers. A probable structural formula of the solid SeDi complex prepared by precipitation in water is shown in Fig.7.

On the basis of the experimental data from the plotting of the mole ratio curve (Fig. 4), the curves of continuous variation (Fig. 3) and new calibration data for small amounts of selenium, the survey in Table I was worked out. The Table gives the concentrations and total concentrations of the reactants, as well as the mole fractions and the mole ratios for the range of transformation.

For values of the mole fraction or the mole ratio below those given in Table I, the dimer predominates, while values above those tabulated correspond to conditions under which the monomer predominates. It is seen, that at high total concentrations, such as those existing under the previous conditions for the calibration curve[1], the dimer is only stable in the presence of large excesses of 2,2'-dianthrimide.

TABLE I

THE CONCENTRATIONS AND TOTAL CONCENTRATION (C) OF THE REACTANTS, THE MOLE FRACTIONS ($x = c_{Se}/C$) AND MOLE RATIOS (c_{Se}/c_{Di}) FOR THE RANGE OF THE TRANSFORMATION

Data calculated from	$c_{Se} \cdot 10^5\ M$	$c_{Di} \cdot 10^5\ M$	$C \cdot 10^5\ M$	$x = c_{Se}/C$	c_{Se}/c_{Di}
The mole ratio curve	1.44–1.73	2.88	3.32–3.61	~ 0.46	~ 1 : 2
Curve of continuous variation	2.6–2.9	11.8–11.5	14.4	~ 0.19	~ 1 : 4
Curve of continuous variation	1.8–2.2	16.2–15.8	18.0	~ 0.11	~ 1 : 8
New calibration curve	~ 0.7	33.1	~ 33.8	~ 0.02	~ 1 : 47

TABLE II

DATA RELATING TO THE STABILITY CONSTANT OF THE Se_2Di_2 COMPLEX

Total concentration of reactants $C \cdot 10^5\ M$	*Mole fraction* $x = c_{Se}/C$	$a \cdot 10^5\ M$	$b \cdot 10^5\ M$	$y \cdot 10^5\ M$	$k_{2,2}$
18.0	0.090	1.62	16.38	0.433	$3.2 \cdot 10^{12}$
14.4	0.130	1.87	12.53		

TABLE III

DATA RELATING TO THE STABILITY CONSTANT OF THE SeDi COMPLEX

Total concentration of reactants $C \cdot 10^4\ M$	*Gradient* (α)	*Mole fraction* $x = c_{Se}/C_{Di}$	*Extinction* (E_x)	$\varepsilon \cdot 10^{-4}$ ($M^{-1}\ cm^{-1}$)	$k_{1,1}$
1.80	−3.25	0.80	0.552	3.07	$7.7 \cdot 10^3$
1.44	−2.70	0.80	0.453	3.58	$7.7 \cdot 10^3$

Stability constants

From the curves of continuous variation (Fig. 3) and by following the directions of FOLEY AND ANDERSON[8] the data in Table II for the stability constant of the dimer Se_2Di_2 were calculated.

On the basis of the papers of ASMUS[5] and of KLAUSEN AND LANGMYHR[9] the stability constant of the dimer was also calculated from the expression:

$$k_{2,2} = \frac{V^3 N}{4 a_0 v_0 b_0^2}$$

the experimental data (taken from a straight-line curve not reproduced) being $N = 31\ \text{ml}^{-2}$, $a_0 = 6.33 \cdot 10^{-4}\ M$, $b_0 = 31.66 \cdot 10^{-4}\ M$, $v_0 = 5.0$ ml and $V = 17.6$ ml. The constant was found to be $1.3 \cdot 10^{12}$.

Similarly, the stability constant of the monomer may be derived from the use of the method of continuous variation and the straight-line method. Curves of continuous variation were plotted of mixtures with mole fractions near 1 (in these solutions the monomer predominated). The stability constant was calculated according to a method described by SCHWARZENBACH[10], the data being given in Table III. As above, the experimental data from the straight-line curve were used to calculate the stability constant of the monomer from the equation:

$$k_{1,1} = \frac{V \cdot N}{b_0}$$

By introducing $N = 0.24$ ml^{-1}, $b_0 = 6.33 \cdot 10^{-4}$ M and $V = 17.6$ ml, the stability constant $6.7 \cdot 10^3$ was calculated.

SUMMARY

The complex formation in concentrated sulfuric acid between selenium(IV) and 2,2'-dianthrimide (Di) was studied by spectrophotometry, infrared spectroscopy and chemical analysis. The system was found to contain two species, the dimer Se_2Di_2 and the monomer SeDi complex, the dimer probably consisting of two monomers connected by hydrogen bonds. The dimer was found to predominate in solutions of low total concentration containing an excess of 2,2'-dianthrimide. By increasing the total concentration and/or decreasing the excess of 2,2'-dianthrimide, the hydrogen bonds between the two 2,2'-dianthrimide molecules are disrupted. The transformation of one of the complexes into the other results in a sudden break or discontinuity in the curves of continuous variation and the mole ratio curves. The SeDi complex was prepared in the solid state.

RÉSUMÉ

On a examiné la formation des complexes entre sélénium(IV) et 2,2'-dianthrimide (Di), en milieu acide sulfurique concentré, par spectrophotométrie, spectroscopie infrarouge et analyse chimique. Il se forme un dimère Se_2Di_2 et un monomère SeDi. Le dimère semble être formé de deux monomères, liés par des liaisons hydrogène. Il est prédominant en solution de faible concentration totale, renfermant un excès de 2,2'-dianthrimide. Le complexe SeDi a pu être préparé à l'état solide.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen Selen(IV) und 2,2'-Dianthrimid (Di) in konz. Schwefelsäure wurde spektralphotometrisch, mit der Infrarotspektroskopie und chemisch untersucht. Es wurden im System 2 Spezies gefunden: das dimere Se_2Di_2 und das monomere SeDi. Das Dimere besteht wahrscheinlich aus 2 Monomeren, die durch eine Wasserstoffbindung verbunden sind. In Lösungen mit niedriger Gesamtkonzentration, die einen Überschuss an 2,2'-Dianthrimid enthalten, liegt überwiegend das Dimere vor. Erhöht man die Gesamtkonzentration und/oder verringert man den Überschuss des Komplexbildners, so werden die Wasserstoffbindungen zwischen den beiden 2,2'-Dianthrimidmolekülen gelöst. Der Übergang vom einen zum anderen Komplex zeigt sich in einem plötzlichen Bruch oder einem Diskontinuum der entsprechenden graphischen Kurven. Der SeDi-Komplex wurde in festem Zustande hergestellt.

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THE DETERMINATION OF ANTIMONY IN NATURAL WATERS WITH PARTICULAR REFERENCE TO SEA WATER

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Few attempts have been made to determine antimony in sea water, and as a consequence very little is known about the marine geochemical balance of this element. NODDACK AND NODDACK[1] detected 0.2 μg Sb/l in the water of Gullmar fjord spectrographically after a preliminary concentration by coprecipitation with copper sulphide. More recently, SCHUTZ[2] has analysed 75 samples of water mostly from the Atlantic Ocean by a neutron activation method, and found that the antimony concentration ranged from 0.11 to 0.58 μg/l with an average of 0.33 μg/l. However, the uranium present in sea water (*ca.* 4 μg) will yield by neutron irradiation a wide range of fission radio-nuclides including some of those of antimony, which may interfere in the analytical method by augmenting the induced antimony activity. Since the range of antimony concentration reported by SCHUTZ was considerable, it was thought desirable to obtain independent information about the occurrence of the element in the sea. This paper describes the development of a 3-stage procedure for the determination of antimony in natural waters; the element is concentrated from a large volume of sample by coprecipitation with hydrous manganese dioxide, separated from interfering elements by solvent extraction, and determined spectrophotometrically.

Concentration of antimony

Owing to its very low abundance in sea water it is necessary to concentrate antimony from bulk samples before it can be determined by most physico-chemical methods. Only comparatively few concentration techniques could be easily adapted to deal with the large volume of sea water (*ca.* 10 l) which is necessary to obtain the 1–2 μg of the element required for accurate photometric analysis. Anion exchange of the chloro-anions of antimony from hydrochloric acid solution[3] was first considered, but was rejected since effective uptake of antimony(III) by De-Acidite FF did not take place from sea water at any practicable hydrochloric acid concentration. Coprecipitation seemed to offer greater prospects of success; although coprecipitation with sulphides[1,4] has been used for concentration of antimony, coprecipitation with hydrous manganese dioxide has been more generally employed for this purpose and MATSUURA AND KOJIMA[5] have claimed antimony recoveries of 100%. The disproportionation reaction between manganese(II) and permanganate ion in a boiling acidic medium has been commonly employed for the precipitation of hydrous manganese dioxide[6–8]. When applied to sea water this method suffers from the drawback that if the precipitate is allowed to settle, the acidic chloride solution will reduce and dissolve part of it; immediate filtration is therefore necessary. When this procedure was applied to the removal of 3 μg of antimony containing ^{125}Sb from 5 l of sea water (0.025 *N* with respect to hydrochloric acid) using 5 ml of 1 *N* permanganate and excess manganese(II) ion, it was found that if the precipitate of manganese dioxide was allowed to settle it contained only *ca.* 40% of the antimony. Neutralization of the solution after the metathesis reaction raised the recovery to *ca.* 60%. According to KOVALENKO[9], the efficiency of coprecipitation of antimony is dependent on the way in which manganese dioxide is precipitated and he recommends the reaction between permanganate and hydrogen peroxide. When this reaction was investigated using 5 l of sea water containing 3 μg of antimony(III) and added ^{125}Sb tracer it was found that 90% of the added antimony was coprecipitated. The reaction between ethanol and permanganate will take place in sea water and yields a highly adsorptive precipitate of manganese dioxide. In order to investigate its efficiency for the coprecipitation of antimony, 5 l of faintly acidified sea water (pH 4–5) was enriched with 3 μg of antimony and ^{125}Sb tracer, and 10 ml of 1 *N* permanganate and 10 ml of ethanol were added. After the precipitate had settled (4 days) it was filtered off and dissolved in sulphur dioxide solution. Radiometric examination of the solution showed that it contained 95.1% of the antimony which had been present in the sea water. On account of its simplicity the permanganate–alcohol method of coprecipitation was selected for further study.

The hydrous manganese dioxide precipitate produced by the permanganate–alcohol reaction is fairly coarse and settles within 2 days. It may be separated either by centrifugation or, more rapidly and only slightly less efficiently, by filtration using a Whatman GF/A glass-fibre filter. The precipitate can be removed from the filter with 15 ml of a solution of sulphur dioxide in 2 *M* sulphuric acid, when only *ca.* 0.5% of the coprecipitated antimony is retained by the filter; however, over 2.5% is retained if a thicker filter (Whatman GF/B) is used for the filtration.

Tests carried out on 5-l aliquots of sea water containing *ca.* 0.2 μc of carrier-free ^{125}Sb showed that optimum recoveries of antimony were obtained in the presence of 0.7 ml of concentrated hydrochloric acid with 11 ml of 1 *N* potassium permanganate and 11 ml of ethanol. After filtration of the precipitate and dissolution in 20 ml of a solution of sulphur dioxide in 2 *N* sulphuric acid, the solution was found to contain an average of 100±1% of the ^{125}Sb originally added to the sea water. Satisfactory recoveries (95±2%) of carrier-free ^{125}Sb from distilled water were also obtained under the same conditions.

Separation of antimony from iron and other elements

Since several elements are also coprecipitated by manganese dioxide it is essential to separate them, and traces of iron derived from reagents, before antimony can be determined photometrically. RAMETTE[10] has described a convenient and very selective solvent extraction method in which antimony is extracted as triiodide from a 0.1 *M* solution of iodide in 5 *M* sulphuric acid, by means of benzene. Experiments confirmed RAMETTE's findings, but suggested that the extraction of antimony would be more efficient from 6 or 7 *M* sulphuric acid medium. In view of the unpleasant physiological properties of benzene, the extraction of antimony triiodide by a number of other organic solvents was investigated.

Aliquots (35 ml) of 5 *M* sulphuric acid, 0.01 *N* with respect to iodide, each of which contained 1 μg of antimony and *ca.* 0.2 μc of antimony-125, were extracted by shaking for 5 min with two 20-ml portions of various solvents. Each of the organic extracts was diluted to 25 ml and its ^{125}Sb activity was measured by γ-spectrometry. The results of these experiments (Table I) indicate that antimony is efficiently extracted from a dilute acidic iodide solution by a considerable range of solvents. Since the highest recovery was given by methyl isobutyl ketone, this solvent was selected for further investigation.

In order to ascertain the optimum acidity for the extraction of antimony, 35-ml aliquots of sulphuric acid of various molarities, 0.01 *M* with respect of iodide, and containing 3 μg of antimony and ^{125}Sb tracer were extracted with 20-ml portions of methyl isobutyl ketone. After extraction, the organic phase was separated, diluted to 25 ml, and its ^{125}Sb content was estimated by γ-spectrometry. The results of these extractions (Table II) indicate that extraction is complete at molarities of 5–6.

TABLE I

PERCENTAGE EXTRACTION OF 1 μg OF ANTIMONY FROM 5 *M* SULPHURIC ACID MEDIUM 0.01 *M* WITH RESPECT TO IODIDE, BY VARIOUS ORGANIC SOLVENTS

Solvent	*First extn.*	*Second extn.*	*Total*
Benzene	97.7	1.6	99.3
Carbon tetrachloride	46.6	—	—
Chloroform	74.1	—	—
Diethyl ether	93.6	5.6	90.0
Di-isopropyl ether	89.8	7.0	96.5
Methyl isobutyl ketone	99.3	0.4	99.7
Toluene	94.4	4.6	99.0

TABLE II

EXTRACTION OF ANTIMONY AT VARIOUS SULPHURIC ACID MOLARITIES, IN PRESENCE OF 0.01 *M* IODIDE

Sulphuric acid *(M)*	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Sb extracted (%)	76.6	82.6	93.1	96.1	99.8	100.2	73.2

Similar experiments carried out using 5 *M* sulphuric acid, but varying the iodide content of the acid showed that the extraction was complete from solutions having iodide molarities of 0.003–0.04 *M*; below 0.003 *M* the efficiency of extraction decreased rapidly. In all subsequent work an iodide concentration of 0.01 *M* was employed.

Two methods are available for the recovery of antimony from the methyl isobutyl ketone extracts—evaporation and back-extraction. Evaporation was not satisfactory since the solvent tended to creep; furthermore, the residue left on evaporation was only partially soluble in hydrochloric acid and contained iodine which would interfere in the photometric determination of antimony. Preliminary experiments showed that antimony could be back-extracted from the ketone phase with dilute hydrochloric acid. In a study of the optimum acid concentration for the back-extraction, antimony (1 μg) spiked with ^{125}Sb tracer was extracted from aliquots of 5 *M* sulphuric acid (which were 0.01 *M* with respect to iodide) using 25-ml portions of methyl isobutyl ketone. The ketone extracts were back-extracted with 20-ml aliquots of hydrochloric acid of various molarities. The acid extracts were diluted to 25 ml and their ^{125}Sb content was assessed by scintillometry. The efficiency of back-extraction increased as the molarity of the hydrochloric acid decreased (Table III); however, below 0.4 *M* emulsification occurred, and all subsequent work was carried out using 0.4 *M* acid. Consecutive extractions using 10-ml aliquots of 0.4 *M* acid extracted 76.2, 16.7 and 3.1% (total 96.0%) of the antimony present in the ketone phase.

The hydrochloric acid back-extract contains some of the iodide ion present in the original extraction; this would interfere in the photometric determination. Its removal can be achieved by treating the back-extract with an excess of hydrogen peroxide and extracting the liberated iodine with chloroform. Experiments using ^{125}Sb showed that no antimony was lost during this extraction.

TABLE III

BACK-EXTRACTION OF ANTIMONY FROM METHYL ISOBUTYL KETONE AS A FUNCTION OF HYDROCHLORIC ACID MOLARITY

Hydrochloric acid (*M*)	0.2	0.4	0.6	0.8	1.0	2.0	4.0	6.0	8.0
Sb back-extracted (%)	—[a]	85.3	79.6	66.7	59.4	43.6	24.5	24.6	24.9

[a] Emulsified.

The rhodamine B procedure which is used in the photometric determination of antimony requires that the element is present in a minimal volume of 4.2 *N* hydrochloric acid and it is therefore necessary to evaporate the back-extract. It was found by tracer techniques that variable amounts of antimony are lost if the 0.4 *N* hydrochloric acid solution is evaporated to dryness even on the waterbath. However, if the evaporation was allowed to proceed until about 2 ml of solution remained, no antimony was lost. Decomposition of any hydrogen peroxide present could be effected by carrying out the evaporation in the presence of a piece of platinum foil plated with platinum black.

The efficiency of the extraction procedure for the separation of antimony from manganese and iron was tested radiochemically and it was found that 1 μg of antimony could be completely separated from at least 400 mg of manganese and 50 mg of iron(III).

In view of the considerable number of stages in the analytical process, the overall recovery of the element is likely to fall short of 100%. It is advisable therefore to assess the chemical yield radiochemically. In the present work, antimony-125 was used as a tracer since this isotope could be obtained in a carrier-free condition. This isotope is not ideal for the purpose since it decays to tellurium-125 which is also a γ-ray emitter (half-life, 60 days); this necessitates the use of a γ-spectrometer for the measurement of the activity of ^{125}Sb alone. As a tracer, antimony-124 would be preferable since it decays to a stable daughter and could therefore be counted with a scintillation counter; however, the supplies of this radio-nuclide currently available from the Radiochemical Centre at Amersham contain considerable amounts of inert antimony as carrier. The radiochemically determined chemical yield of the whole analytical process was found to be somewhat variable but averaged *ca.* 80%.

Photometric determination of antimony with rhodamine B

GREENHALGH AND RILEY's modification of the photometric rhodamine B procedure was selected for the determination of antimony because of its very high sensitivity (0.002 μg/cm^2). In this method, antimony is allowed to react in strong hydrochloric acid medium with a mixed reagent containing nitrite and rhodamine B. It is conjectured that the nitrite ion oxidizes the antimony to the 5+ oxidation state in which form it reacts with rhodamine B; the pink reaction product is extracted with a mixture of chlorobenzene and carbon tetrachloride and determined photometrically. Since the original publication of this method, it had become apparent that a wrong assumption had been made about the strength of the hydrochloric acid used in this work. A reinvestigation of this factor was therefore made and it was found that the optimum hydrochloric acid molarity for the extraction was *ca.* 4.5 *M* and not 5–6 *M* as was originally thought.

Since the highest possible sensitivity for antimony was required, the method of GREENHALGH AND RILEY was further modified firstly by decreasing the amount of rhodamine B to one quarter of that originally used; this reduced the reagent blank from *ca.* 0.300 to 0.075 optical density units without affecting the sensitivity. Secondly, the extraction was carried out with 5 ml of the extraction solvent instead of 10 ml; this approximately doubled the sensitivity, but resulted in a deviation from Beer's law at levels of less than 1.5 μg of antimony, necessitating the use of a calibration curve in this range. In the range 1.5–3 μg of antimony, Beer's law was obeyed and an optical density increment of 0.310/μg Sb was found (4-cm cuvettes); this corresponds to a sensitivity of 0.002 μg/cm^2. Under these conditions a coefficient of variation of $\pm 2\%$ was found for the photometric procedure at the 1.0-μg level provided that the stopcock of the separating funnel used for the extraction of the rhodamine B complex was ungreased. Greasing of the stopcock increased the coefficient of variation to *ca.* 5%.

EXPERIMENTAL

Reagents

Methyl isobutyl ketone. Redistil before use.

Rhodamine B solution. Dissolve 0.05 g of rhodamine B in 100 ml of water, and filter the solution before use.

Mixed rhodamine B reagent. Mix 9.2 ml of rhodamine B solution with 0.8 ml of 0.2 *M* sodium nitrite solution. Prepare the reagent as required.

Extraction solvent. Dilute 125 ml of carbon tetrachloride to 500 ml with chlorobenzene.

Standard antimony solution. Prepare a working standard solution containing 2.74 g of potassium antimonyl tartrate/l. This solution contains 1 mg of antimony/ml and should be used for the preparation of working standard solutions; these should be made 4 *M* with respect to hydrochloric acid and prepared as required.

Determination of antimony in natural waters

Filter the water through an acid-washed glass-fibre filter (Whatman GF/B) and place 5 l of it in a 5-l conical flask. Add 0.7 ml of concentrated hydrochloric acid and *ca.* 0.1 μc of carrier-free ^{125}Sb tracer, 11 ml of 1 *N* potassium permanganate and 11 ml of ethanol. Stir the solution well and allow it to stand until the precipitate of hydrous manganese dioxide which forms has settled (*ca.* 3 days). Suck off the supernatant liquid through a Whatman GF/A glass-fibre filter and then transfer the bulk of the precipitate to the filter. Wash the precipitate with a little water and then dissolve it *in situ* using successive small volumes of a saturated solution of sulphur dioxide in 2 *M* sulphuric acid. Collect the solution which drips through the filter in a beaker until its volume reaches *ca.* 22 ml. Quantitatively transfer the solution to a 50-ml separating funnel using not more than 6 ml of the sulphur dioxide solution for washing the beaker. Add to the solution 1 ml of 5.8% (w/v) potassium iodide solution and 5.8 ml of concentrated sulphuric acid, mix well and allow to cool. Shake the cold solution with 25 ml of methyl isobutyl ketone for 2 min, run off and discard the aqueous layer. Extract the ketone phase by shaking with three 10-ml portions of 0.4 *M* hydrochloric acid and combine the three extracts.

To the combined extracts add *ca.* 0.8 ml of 30% hydrogen peroxide solution and extract the liberated iodine with four 10-ml aliquots of chloroform allowing 10-min intervals between each extraction. Transfer the aqueous phase to a 50-ml conical flask, add a small piece of platinum foil coated with platinum black and evaporate to *ca.* 2 ml. Dilute the residue to 30 ml with 4 *M* hydrochloric acid. Remove 5 ml of the solution and using a γ-ray spectrometer compare its ^{125}Sb activity with that of 1/6 of the ^{125}Sb added at the commencement of the analysis, in order to assess the chemical yield of the analytical process.

Transfer the remaining 25 ml of solution to a separating funnel, with an ungreased stopcock, add 1 ml of the mixed rhodamine B reagent and allow to stand. After 25 min shake the solution with 5 ml of the extraction solvent for 2 min. Run off the lower layer into a centrifuge tube and centrifuge it for a few minutes. Measure the optical density of the extract at 565 mμ in a 4-cm micro-cell against a reference cell containing the extraction solvent. Determine the reagent blank using 28 ml of the saturated solution of sulphur dioxide in 2 *M* sulphuric acid as if this were the solution of the hydrous manganese dioxide precipitate from sea water. Subtract the optical density thus found from that found for the sample; evaluate the weight of antimony from a calibration curve prepared using known amounts of antimony in the photometric rhodamine B procedure. Multiply the amount of antimony thus found by 6/5 (to take account of the fact that only 25 ml of the original 30 ml was used in the photometric analysis), and by the inverse of the relative chemical yield and thus obtain the weight of antimony in the 5-l sample of water taken for analysis.

TABLE IV

ANALYSES OF SURFACE WATER SAMPLES FROM IRISH SEA BOTH ALONE AND SPIKED WITH 1.0 μg Sb/5 l

Sample no.	*Chemical yield*		*Corrected µg of Sb found per 5 l*		*Recovery of added Sb (µg)*	*Sb concn. (µg/l)*
	Unspiked	*Spiked*	*Unspiked*	*Spiked*		
1	75.6	—	1.11	—	—	0.22
	82.3	—	1.03	—	—	0.21
2	81.6	—	1.23	—	—	0.25
3	80.1	—	0.89	—	—	0.18
4	71.0	67.6	0.63	1.57	0.94	0.13
5	74.7	82.3	2.00	2.97	0.97	0.40
6	76.2	78.1	1.41	2.37	0.96	0.28
		75.2		2.33	0.92	
		80.3		2.44	1.03	
		81.0		2.41	1.00	

RESULTS

As a test of the method a number of samples of the surface waters of the Irish Sea were analysed both alone, and spiked with 1.0 μg of antimony/5 l. The results (Table IV) indicate that the antimony content of the samples ranged from 0.13–0.40 μg Sb/l and that the recovery of antimony was satisfactory.

SUMMARY

A procedure is described for the determination of antimony in natural waters at concentrations down to 0.1 μg/l or less. The element is concentrated by coprecipitation with hydrous manganese dioxide (produced by the reaction of permanganate with ethanol). It is separated from manganese, iron and interfering elements by extraction from 5 *M* sulphuric acid, 0.01 *M* with respect to iodide, using methyl isobutyl ketone. After back-extraction with 0.4 *M* hydrochloric acid, it is determined photometrically using rhodamine B. The overall chemical yield of the process is measured radiochemically and amounts to *ca.* 80%. Sea water samples from the Irish Sea were found to contain 0.13–0.40 μg Sb/l.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'antimoine dans l'eau (0.1 μg/l ou moins). L'antimoine est concentré par coprécipitation avec du dioxyde de manganèse (produit par la réaction permanganate-éthanol). Il est ensuite séparé du manganèse, du fer et d'autres éléments gênants par extraction en solution acide sulfurique 5 *M*, au moyen de méthylisobutylcétone. On effectue finalement un dosage photométrique à l'aide de rhodamine B.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Bestimmung von Antimon in natürlichen Wässern bei Konzentrationen bis hinab zu 0.1 μg/l oder weniger beschrieben. Das Element wird durch Mitfällung mit wasserhaltigem Mangandioxid angereichert. Vom Mangan, Eisen und störenden Elementen wird es durch Extraktion mit Isobutylketon aus 5 *M* Schwefelsäure, die 0.01 *M* an Jodid ist, abgetrennt. Nach der Rückextraktion mit 0.4 *M* Salzsäure wird das Antimon photometrisch mit Rhodamin B bestimmt. Die Gesamtausbeute des Verfahrens wurde radiochemisch gemessen und beträgt etwa 80%. In Seewasserproben aus der irischen See wurden 0.13–0.40 μg Antimon/l gefunden.

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A MODIFIED DIMETHYLGLYOXIME METHOD FOR THE DETERMINATION OF NICKEL IN SEA WATER*

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In a study of the bio-geochemical circulation of cobalt and the related transition element, nickel, in Hawaiian waters it was decided to employ the colorimetric methods described by THOMPSON AND LAEVASTU[1] for the determination of trace quantities of both elements. In the case of cobalt the nitroso-R method, found to be extremely sensitive to slight modifications in the procedure, was studied in detail, modified and improved[2]. A 5-fold increase in sensitivity was achieved in the measurement of the nitroso-R complex by careful control of pH, development time of complex, conditions for decomposition of excess reagent, and choice of wavelength. For optimum recovery it was necessary for a minimum period of 7 days to elapse following precipitation with sodium carbonate before filtration and analysis. A previously unreported but significant salt effect was found which requires either construction of a calibration curve prepared from sea water or correction in use of standards in distilled water.

The decision to analyze for nickel colorimetrically with dimethylglyoxime following precipitation with sodium carbonate suggested the strong possibility that this method might also be dependent upon the variables found crucial in the cobalt study. Consequently, it seemed logical to subject the nickel procedures described by THOMPSON AND LAEVASTU[3] to a similar critical study as was accorded cobalt.

The most sensitive as well as selective colorimetric reagent that has been used in the determination of nickel in silicate rocks[4–6], steels[7], bronzes[8], dust particles[9], and biological materials[10,11] has been dimethylglyoxime (DMG). Its employment in sea water[12–18] possesses certain advantages since the reagent is sufficiently specific to detect without appreciable interference, one part of nickel in 400,000 parts of water containing 50 parts of cobalt. Iron and aluminum may be rendered optically nonabsorbing by complexation with citrate or tartrate. Copper, the sole remaining major transition ion which may affect the absorbance of the Ni–DMG complex, can be removed successfully by washing the chloroform extract with dilute ammonia.

Relatively few studies, however, have been carried out on the distribution of nickel in the oceans, possibly because there is divided opinion on the biological role of this species in sea water. Many examples of specific species of both plants and animals are known which are able to concentrate nickel to 100 to 100,000 times the concentration found in the immediate environment[19]. Other authors, however, claim no biological significance to this element since no metabolic proteins are known which complex with the nickel ion[20].

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A study of existing nickel data from the oceans (Table I) reveals a 50-fold range in values, covering a low of 0.12 p.p.b. (parts per billion) to a high of 6.0 p.p.b., which appears to be dependent upon the technique used. The highest values were obtained by emission spectroscopy, the medium values by absorption spectroscopy and the low concentrations by atomic absorption, the latter being a recent but potentially powerful and, as yet, unproven tool for use in sea water. The results leave the definite impression that a pressing need exists for a critical evaluation of existing methods to establish their validity and usefulness.

TABLE I

PREVIOUS NICKEL CONCENTRATIONS FOUND IN SEA WATER

Site of collection	*Date*	*Concentration (p.p.b.)*	*Form: Soluble(S) Particulate(P) Total(T)*	*Method of det.: Emission(E) Absorption(A) Atomic absorption(AA)*
North Sea	1936	0.12	T[12]	—
Gullmarfjord	1939	0.5	T[13]	E
Black Sea	1942	6.0	T[14]	—
Avg. Bk. Sea	1945	3.4	T[14]	—
W. Atlantic	1952	5.5	T[15]	E
W. Atlantic	1952	1.5	T[15]	E
W. Pacific	1953	0.75	T[16]	A
E. Pacific	1956	2.0	S[3]	A
W. Atlantic	1962	0.25	T[17]	AA
Florida Gulf	1964	2.0	S[18]	A
		0.1	T[18]	

TABLE II

SPECIES THAT COPRECIPITATE WITH NICKEL HYDROXIDE FROM SEA WATER WITH SODIUM CARBONATE[22]

Ion	*Precipitated as*	$K_{s.p.}$*(18°)*	*Ion/nickel ratio in sea water*
Fe^{3+}, Fe^{2+}	OH^-	10^{-36}, 10^{-14}[a]	5
Zn^{2+}	CO_3^{2-}	10^{-10}	5
Cu^{2+}	CO_3^{2-}	10^{-10}	2
Cd^{2+}	$(OH)(Cl)^{2-}$	10^{-11}	0.05
Ba^{2+}	SO_4^{2-}	10^{-10}	15
Pb^{2+}	CO_3^{2-}	10^{-13}	0.01
Co^{2+}	CO_3^{2-}	10^{-13}	0.25
Ca^{2+}	CO_3^{2-}	10^{-9}	200,000
Mg^{2+}	CO_3^{2-}	10^{-5}	600,000
Sr^{2+}	CO_3^{2-}	10^{-10}	1,500

[a] *Handbook of Chemistry and Physics*, 42nd Ed., Chem. Rubber Co., Cleveland, Ohio, 1961.

The present report is concerned with the modification and improvement of the DMG method for the determination of nickel described by THOMPSON AND LAEVASTU[3].

The basic procedure in the analysis, as with cobalt, is a modified SANDELL[21] technique and involves a combined separation and concentration of nickel with sodium carbonate from a 2-l sample of sea water. The nickel is coprecipitated quantitatively as the hydroxide ($K_{s.p.} = 10^{-16}$) together with various other species[22] (Table II).

A 100-fold increase in the concentration of nickel over that in sea water is achieved by filtration, after 8 h, through a HA millipore filter and then dissolving the precipitate with 20 ml of hydrochloric acid. The nickel is separated from other coprecipitated ions by extraction with dimethylglyoxime–chloroform solution at a pH of 8.0 according to the SANDELL procedure. The extracted acid solution containing the nickel(II) is oxidized with bromine water to nickel(IV) and analyzed colorimetrically as the nickel dimethylglyoximate complex. The absorbance is read at 450 mμ and the concentration of nickel determined from a standard calibration curve. The calibration curve had been constructed previously by dissolving appropriate concentrations of nickel in distilled water, extraction with DMG in chloroform and subsequent color development as above omitting, however, precipitation with sodium carbonate.

Erratic results were obtained, in the use of the above procedures, in 3 main phases of the determination: precipitation, extraction, and color development. The results were influenced markedly by ageing time of the precipitate following treatment with sodium carbonate, minor changes in extraction procedures and reagent volume, time and temperature of the oxidation with bromine water, effect of time on the stability of complex, pH of complex formation, and wavelength at which the complex is read. These factors were studied in detail with the hope that through proper control the difficulties could be eliminated or reduced.

EXPERIMENTAL

Apparatus

Spectrophotometer. Beckman DU with matched quartz cells of 10.0 cm light path.

pH Meter. Beckman Model H2, with glass indicating and calomel reference electrodes. The meter and electrodes were checked with buffer standards.

Filters. Millipore, HA (0.45 μ) with diameter of 47 mm.

Glassware. 150-ml pyrex beakers were used for evaporation of the acid solution used in dissolving the precipitate. Extractions were carried out in 125-ml pyrex Squibb separatory funnels. All glassware was cleaned with 6 *N* nitric acid followed by thorough rinsing with distilled water and finally with deionized doubly distilled water from an all-glass still.

Reagents

All reagents were made from analytical grade chemicals dissolved in doubly distilled, deionized water. The chloroform used was reagent grade.

Standard nickel solutions. A solution containing 0.85 μg-at/ml (53.5 p.p.m.) was prepared by weighing 0.3365 g of nickel ammonium sulfate hexahydrate and diluting to a liter with water. A solution of this concentration remained stable for months.

For use in preparing standards, 5.0 ml of the above solution was pipetted into a 100-ml volumetric flask and diluted to the mark with water. The resulting solution A had a concentration of 0.0425 μg-at/ml (2.4 p.p.m.), was unstable and had to be made up every 48 h. Solution A constituted the stock solution from which appropriate aliquots (1.0–10.0 ml) were taken to prepare standards for use in preparation of all calibration curves. These aliquots, when diluted with water to 50 ml as suggested in the recommended procedure, provided concentrations of nickel ranging from 0.85 μg-at/l (53.5 p.p.b.) to 8.5 μg-at/l (535 p.p.b.).

Selection of wavelength and stability of complex

The transmittance spectrum of nickel dimethylglyoxime (Ni–DMG) (Fig. 1) shows maximum light absorption at 442 mμ, a wavelength which would provide the highest sensitivity. The use of this wavelength with increased sensitivity, twice that which is obtained at 550 mμ, has the disadvantage of greater instability. Two additional factors were considered in the selection of conditions for measuring the absorbance of the complex which are based on an early observation that the stability of the complex is dependent both on the alcohol concentration of the final medium and on time. The former was tested by measuring out identical aliquots of stock solution A and carrying through the color development step first in distilled water and then in a solvent in which the concentration of alcohol was varied in the final dilution step.

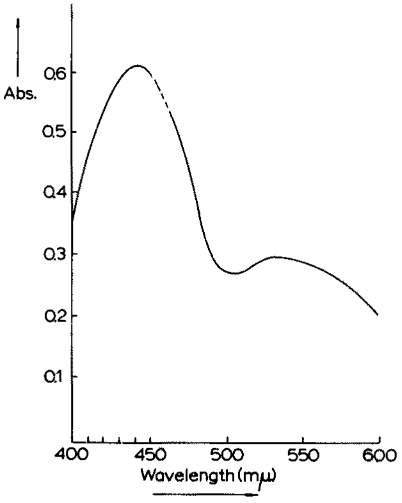


Fig. 1. Absorption spectrum of the nickel dimethylglyoxymate complex measured in 2% alcohol.

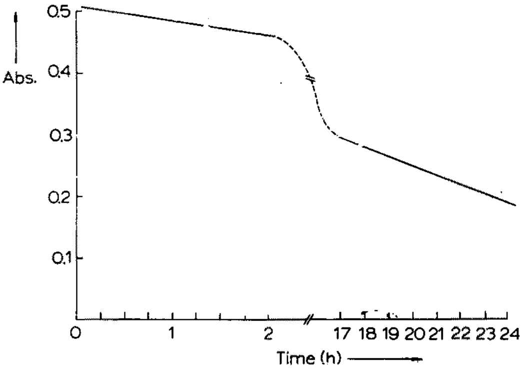


Fig. 2. Stability of Ni–DMG complex as a function of time at 442 mμ.

The absorbances from samples with the highest alcohol content (50%) were most stable as measured by the rate of change (0.001 absorbance units/15 min) while those with the least alcohol (2% due to the DMG reagent) were the least stable (0.003 absorbance units/15 min). The rate of loss in a solution containing 2% alcohol was not so great as to rule out the employment of this concentration since reproducible and satisfactory readings could be obtained under these conditions. Moreover, it was found that despite an increased stability as shown by a one-third reduction in rate of loss of absorbance in 50% alcohol, the accompanying experimental difficulties did not warrant the change to this concentration. The reading of the Ni–DMG complex at the alternative 550 mμ wavelength did not result in sufficient increase in stability to compensate for the loss in sensitivity.

The effect of time on the stability of the complex was studied with complexes formed from 5.0-ml aliquots of stock solution A. Initial readings were commenced 5 min after addition of the DMG reagent. The results are shown in Fig. 2; each point is the average of 2 readings on 2 separate solutions treated identically. It was observed that maximum intensity of the color was obtained almost immediately upon addition of DMG. The constant loss in color as shown by a decrease of 0.003 absorbance units/15 min showed the apparent advantage of making a reading as soon after dilution as possible, in order to obtain maximum values. Under routine conditions which may involve the analysis of a relatively large number of samples, each of which is performed in duplicate, the experimental manipulations required make it impractical to make the readings so soon after the addition of the DMG reagent. Excellent results were obtained by reading the absorbance of the complex 60 min after addition of the reagent; notwithstanding the loss in absorbance, this period is recommended in the procedure.

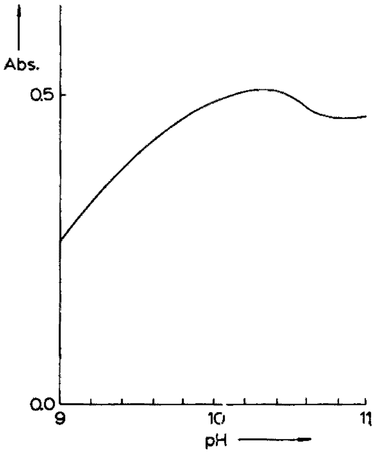
Effect of pH on complex formation

For the maximum development of color of the Ni–DMG complex most workers recommend addition of 1 ml of concentrated ammonia in excess[20] after discharge of the color of the bromine water with the base. The pH of the solution at this point is 10.4. In order to demonstrate the effect of pH on the absorbance of the Ni–DMG complex, eighteen 5.0-ml aliquots of stock solution A were measured to provide 9 pairs of duplicates.

The recommended procedure was used to develop the color except that the amount of ammonia added in excess was varied from 0.1 to 10 ml. The results (Fig. 3) showed that control of the pH is critical. Satisfactory and reproducible results were obtained by adding exactly 1.0 ml of ammonia in excess to a pH 10.4 following disappearance of the bromine color, as recommended by SANDELL[21].

Precipitation time vs. amount precipitated

In the cobalt study[2] it was found most difficult to filter the gelatinous precipitate immediately after treatment with sodium carbonate. Tests revealed that precipitation of the cobalt was incomplete unless the mixture was allowed to stand for a period of 7 days.



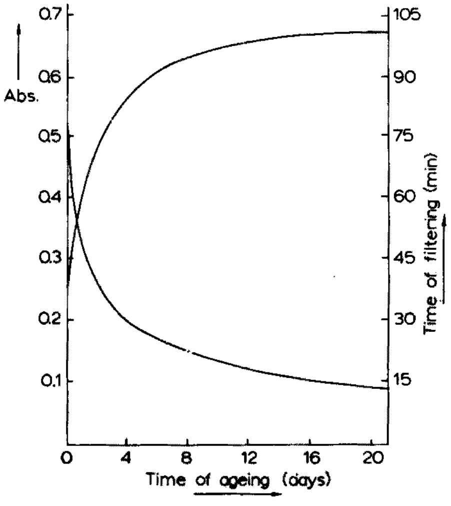


Fig. 3. Effect of pH on absorbance of Ni–DMG complex.

Fig. 4. Effect of ageing of precipitate on yield of nickel.

A similar study on the completeness of precipitation of nickel also brought down with sodium carbonate was carried out by spiking 21 duplicate 2-l sea water samples each containing 12.5 p.p.b. of stock solution A. Precipitation was started with 100 ml of sodium carbonate solution. In succession each pair of duplicates was filtered daily and analyzed for nickel by the recommended procedure over a period of 21 days. The results are compiled in Fig. 4 and Table III..

TABLE III

PRECIPITATION TIME AND YIELD OF NICKEL FROM SPIKED SEA WATER SAMPLES

Ni solution (p.p.b.)	*Time of precipitation (days)*	$A_{442\ m\mu}$	*Yield of nickel (p.p.b.)*	*% Yield*
12.5	1	0.380	6.4	51
12.5	2	0.485	8.1	65
12.5	3	0.525	8.9	71
12.5	4	0.560	9.5	76
12.5	5	0.595	10.0	80
12.5	6	0.615	10.4	83
12.5	7	0.625	10.5	84
12.5	8	0.630	10.6	85
12.5	9	0.640	10.7	86
12.5	10	0.650	11.0	88
12.5	11	0.665	11.4	91
12.5	12	0.643	11.0	88
12.5	13	0.673	11.5	92
12.5	14	0.658	11.2	90
12.5	15	0.658	11.2	90
12.5	16	0.650	11.1	89
12.5	17	0.628	10.7	86
12.5	18	0.643	11.0	88
12.5	19	0.658	11.2	90
12.5	20	0.658	11.2	90
12.5	21	0.650	11.1	89

The reciprocal curves demonstrate the inverse relationship between ease of filtration as noted by the time required to filter a sample and the completeness of precipitation as measured by an increase in absorbance. The two curves, as was the case for cobalt, reached their maximum and minimum at about the same time (one week) although unlike cobalt[2], nickel was never precipitated quantitatively. The results showed that when the precipitate had been aged to the point that it could be collected easily and quickly a maximum of 90% of the nickel had coprecipitated (Fig. 4 and Table III). In actual practice the 10% loss, assuming it is constant throughout the concentration range of nickel encountered in sea water, was compensated for by use of a calibration curve constructed from sea water or by application of a factor if distilled water was used for calibration purposes.

Salt error

The two assumptions implied in the papers of THOMPSON AND LAEVASTU were found to be unwarranted: (*1*) cobalt and nickel are precipitated quantitatively with sodium carbonate, (*2*) the absorbance of the complex is independent of the medium in which it is developed. The salt error or effect is the difference between the absorbance of the complex in distilled water compared to that formed in sea water, and may result in positive or negative errors. In order to determine both the amount of effect and its direction, varying volumes of stock solution A ranging from 0 to 10.0 ml were added to 4 series of sea water samples (i.e., 1 l, 2 l, 3 l and 4 l) obtained from a common source. Each series had similar volumes of sodium carbonate added, precipitation times and the identical subsequent treatment. The results (Fig. 5) showed that the blank, which increased regularly in the order 1 l < 2 l < 3 l < 4 l, was an index of the nickel content of the sea water before spiking. Each series gave a Beer's law plot since the absorbance varied linearly with concentration. The curves had slopes which increased with increasing salt concentrations with the blanks incorporated. If the blanks were subtracted, the curves passed through the origin showing a progressive increase in slope (0.095 absorbance units/ml to 0.100 absorbance units/ml) which accompanied the increase in the concentration of salt present. This increase, diametrically opposite in trend to that found previously for cobalt[2] for a similar series, demonstrated what may be termed a positive salt error since an increase in salt concentration resulted in a regular and definite increase in absorbance. If the salt error factor for Ni–DMG, as measured by the slope, were dependent on the presence of the dissolved salt alone which is responsible for the gain in absorbance, its value would be less than unity. The situation is complicated by the fact that in the total process the precipitation loss of 10% more than offsets the gain in absorbance from the salt effect. For this reason the salt error curves (Fig. 5) with blanks subtracted lie below instead of above the distilled water curve resulting in a net salt factor of 1.10 (calculated on the basis of a salinity of $35\,^0/_{00}$). This value will increase or decrease slightly varying inversely with salinity. This work would suggest that whenever an analysis for nickel in sea water is to be carried out, the standard calibration curve should be prepared from sea water of similar salinity.

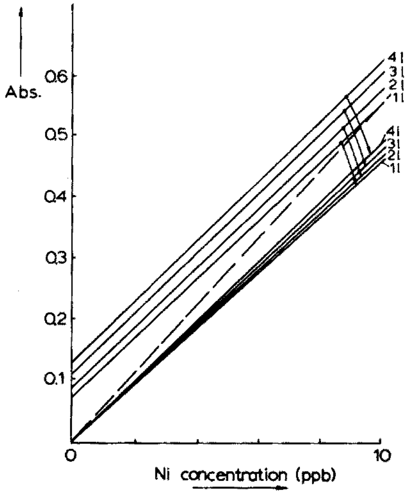


Fig. 5. Salt error in the DMG determination of nickel as a function of the concentration of dissolved salts.

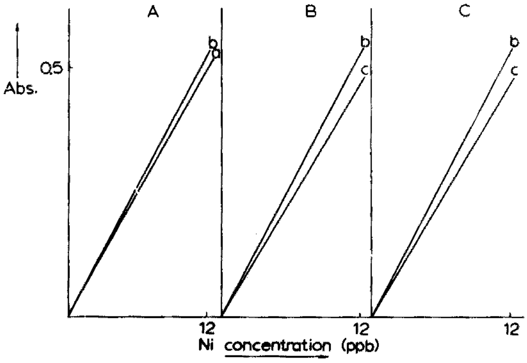


Fig. 6. Calibration curves run in different media for the DMG complex measured at 442 $m\mu$. All blanks subtracted from all absorbance values. a, color development, b, extraction and color development, c, precipitation, extraction and color development.

In order to clarify the gain in absorbance of the Ni–DMG complex with increase of salt concentration, a series of standard nickel solutions was prepared in duplicate in 3 media: (*1*) distilled water, (*2*) sea water, (*3*) sea water minus miscellaneous ions (*i.e.*, sea water from which cobalt, nickel, and other metallic ionic species were removed by precipitation with sodium carbonate). Separate calibration curves were prepared where possible, using the recommended procedure for various combinations of the major steps in the total process: (*1*) color development, (*2*) extraction and color development, (*3*) precipitation, extraction and color development. The linear plots obtained in all cases (Fig. 6, curves a, b, c) when absorbance was plotted *vs.* concentration were quite different from those found in similar studies with the cobalt nitroso-R complex in the same media. The curves prepared in distilled water (Fig. 6, curve a) had different slopes. The slope of the standard curve after extraction and color development was higher (0.0020 absorbance units/p.p.b.) than that for the standard curve with only color developed (0.0019 absorbance units/p.p.b.). The entire process of precipitation, extraction, and color development could not be carried out successfully in distilled water. The results revealed an increase in slope in both raw sea water and sea water less miscellaneous ions as neither medium would permit the development of the color alone. However, in all 3 media, the extraction and color development procedures gave linear plots with identical slopes (0.0020 absorbance units/p.p.b.). The precipitation loss remained constant since the same amount of nickel hydroxide was brought down in both sea water and in sea water from which ions that precipitate with sodium carbonate were removed. The precipitated species which include, in addition to nickel and cobalt, iron, zinc, cadmium, copper, etc. apparently play no important role in the mechanism by which nickel is removed from solution. In the past, questions have been raised as to whether nickel is precipitated by itself or is coprecipitated or adsorbed on iron(III) and/or magnesium hydroxide[3]. In addition, the identical slopes and curves obtained from both sea water and sea water pretreated with sodium carbonate lend support to the conclusion that the 3d transition metal ions such as iron, cobalt, copper, etc. removed by the treatment with sodium carbonate are not responsible for the salt error since no effect on the absorbance of the Ni–DMG complex was observed throughout the various stages of the total process in their presence or absence (Fig. 6, curves b, c). On the other hand, the evidence points to the conclusion that those species which remain in solution upon addition of sodium carbonate such as ions in Group I A and II A are indeed responsible to a substantial degree for the salt effect since with an increase in concentration of these ions in sea water, an increase in the slope of the curves is observed (Fig. 5).

RECOMMENDED PROCEDURE

Collection

The sea water samples were collected with 4-l ASLO (American Society of Limnology and Oceanography) plastic samplers. The water was divided into two 2-l portions in order to provide duplicates. The water samples were transferred to plastic bottles (gallon chlorox jugs were found suitable) and charged with 100 ml of 5% (w/v) sodium carbonate solution in order to concentrate and prevent changes in the nickel content of the water. This process may be conveniently carried out at sea. The precipitate was allowed to settle for a minimum of 7 days. The rolling of a ship was an ideal agitator. On shore the precipitate was filtered through the Millipore filter, washed twice with distilled water and dissolved with a minimum volume of 1:1 hydrochloric acid (*ca.* 20 ml). Sodium citrate (15 ml of aqueous 10% solution) was added to the acid solution and the solution evaporated on a low temperature hot plate to a volume of approximately 30 ml.

Separation

Adjust the pH of the above solution to 8.0 with 1:1 ammonia solution. (The heat of neutralization raised the temperature so a correction was applied with use of the pH meter.) Add 2 ml of 1% (w/v) dimethylglyoxime solution in ethanol, mix well, and cool in the refrigerator to room temperature. Add 3 ml of chloroform, shake in a separatory funnel and repeat the above process with an additional 3-ml portion of chloroform. This treatment separates nickel and copper from the other ions which remain soluble in the basic solution. Wash the combined portions of chloroform with 5 ml of dilute ammonia by shaking for 1 min. Allow the mixture to stand, shake for 1 min, allow to stand and drain off the bottom chloroform layer into another separatory funnel. This mild basic washing should remove the copper. To insure complete separation of the nickel, extract the ammonia solution with 3 ml of chloroform and combine with the previously separated chloroform solution extracts yielding a total of 9 ml of solution. To remove the nickel from the organic phase, extract twice with two 5-ml portions of hydrochloric acid. In all separations an effort should be made to avoid the white foam material at interphase of the two layers.

Color development

To the above solution add exactly 1.0 ml of saturated bromine water, mix thoroughly, and allow to stand for 15 min to permit the complete oxidation of Ni(II) to Ni(IV). Neutralize the excess bromine as shown by the disappearance of the bromine color by dropwise addition of 1:1 ammonia solution, then add exactly 1.0 ml in excess (final pH = 10.4). The color develops immediately upon the addition of 1.0 ml of alcoholic 1% dimethylgloxime but after dilution to 50.0 ml readings are taken, as explained above, at 442 mμ 60 min after the addition of the DMG. After subtraction of the blank, the concentration of the nickel is obtained from the calibration curve (below).

Sea water calibration curve

The construction of a calibration curve prepared from sea water avoids both the need for a salt error factor which is salinity-dependent and any changes in the absorbance of the nickel complex due to reagents used in the precipitation and extraction processes. Prepare the curve by spiking 2-l sea water samples with aliquots of standard nickel solution A ranging from 0 through 5.0 ml (0–12 p.p.b. Ni), and carry the spiked samples through the total process of precipitation with sodium carbonate, ageing of the precipitate for the same length of time accorded the samples to be analyzed, filtration, extraction and color development as detailed above.

When the absorbance minus the blank is plotted against concentration of nickel, a linear plot with a slope of 0.0020 absorbance units/p.p.b. nickel is obtained passing through the origin. A typical plot is shown in Fig. 7. Each value plotted is the mean of 3 determinations. If the blank is included the concentration of the nickel originally present in the sea water may be obtained from the intercept of the ordinate.

Distilled water calibration curve

Measure aliquots of 1–5.0 ml of nickel stock solution A into beakers, dilute with distilled water and carry through the regular process, omitting the precipitation and filtration steps. In order to use the resulting distilled water calibration curve for Hawaiian water with salinity of *ca.* 35‰, a salt factor of 1.10 (see Fig. 7) is applied.

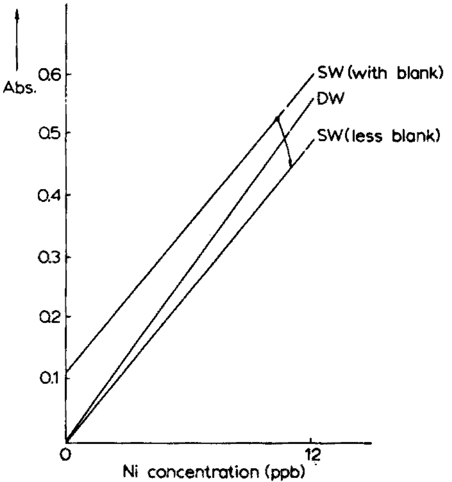


Fig. 7. Calibration curves in the DMG determination of nickel in sea water (SW) and distilled water (DW).

This factor when multiplied by the absorbance determined on a sea water sample should give the comparable absorbance in distilled water. Thus a distilled water calibration curve can be used if desired, provided that the salinity and the subsequent salt factor are known.

RECOVERY OF NICKEL FROM SEA WATER

The previously constructed sea water calibration plot (Fig. 7) prepared from water from Koko Head on the northeast shore of Oahu (May 11/65) was used as the reference in order to determine the effectiveness of the procedure in terms of the recovery of nickel from sea water. Freshly collected sea water samples (May 31/65) were spiked with varying aliquots of standard nickel solution (0–5.0 ml). These were carried through the total process, the absorbances measured and the nickel concentrations read from this curve. The results are shown in Table IV. The blank (2.4 p.p.b.) is due to the nickel present in the sea water. The results gave a recovery of 97% over the range of concentrations used. This same figure (97%) could be obtained by comparing the slope of the newly collected sea water (0.096 absorbance units/5 ml) with that of the standard curve (0.098 absorbance units/5 ml).

Precision

Six replicate determinations of the color development with various amounts

TABLE IV

RECOVERY OF NICKEL FROM SPIKED SEA WATER

Stock solution A added to 2 l of sea water (ml)	*Absorbance at 442 mμ*	*Concentration of nickel (p.p.b.)*		*% Yield*
		Calculated	*Found*	
Blank	0.090	2.40	—	—
1.0	0.180	4.96	4.75	96
2.5	0.330	8.78	8.60	98
5.0	0.572	15.20	15.10	99

TABLE V

PRECISION[a] OF THE DIMETHYLGLYOXIME DETERMINATION OF NICKEL IN 3.5% SALT SOLUTION AND DISTILLED WATER AT 442 mμ

Solution	*Nickel concentration (p.p.b.)*	*Mean absorbance*[b]	*Relative standard deviation (%)*
Distilled water	12.5	0.517 ± 0.003	0.7
3.5% Salt solution	12.5	0.686 ± 0.008	0.9

[a] Precision calculated on the basis of $\sigma = \left[\frac{\Sigma(x - \bar{x})^2}{n}\right]^{\frac{1}{2}}$.

[b] Absorbance values minus blank.

(1.0–5.0 ml) of nickel stock solution A with the dimethylglyoxime were carried out in both distilled water and 3.5% salt solution. The results are shown in Table V.

Examination of the absorbances after the blanks have been subtracted shows that the precision for the colorimetric determination of nickel with DMG in distilled water, calculated on the basis of relative standard deviation is 2.1% at a concentration of 2.0 p.p.b., which is about the concentration of nickel in the Hawaiian water. The precision increases 3-fold to 0.7% as the concentration rises to 12 p.p.b.

SUMMARY

A colorimetric dimethylglyoxime (DMG) method for the determination of nickel in sea water was studied in detail, and improved through close control of experimental conditions. For a maximum precipitation of 90% of the nickel a minimum period of 7 days was necessary between treatment with sodium carbonate and filtration. A salt effect resulted from: (*1*) a gain in absorbance due to soluble ions not precipitated by sodium carbonate, which increased with increasing salt concentration, (*2*) an offsetting loss in absorbance due to incomplete precipitation of nickel. The transition 3d ions precipitated by sodium carbonate exerted no discernible effect on the absorbance.

A procedure is recommended by which a relative standard deviation of 0.7% was achieved. Consistent recovery yields of 97% were obtained from samples of sea water spiked with nickel collected over a period of several months.

RÉSUMÉ

Une méthode pour le dosage colorimétrique du nickel dans l'eau de mer, au moyen de diméthylglyoxime a été étudiée en détail et perfectionnée. Pour une précipitation maximum de 90% de nickel, une durée de 7 jours est nécessaire entre le traitement au carbonate de sodium et la filtration.

Un effet salin provient (*1*) de l'augmentation du pouvoir absorbant dû à la présence d'ions solubles qui ne sont pas précipités par le carbonate de sodium, ce gain augmente avec la concentration du sel; (*2*) une diminution du pouvoir absorbant, provenant de l'incomplète précipitation du nickel. Les ions de transition 3d, précipités par le carbonate de sodium, n'ont pas d'effet sensible sur le pouvoir absorbant.

On recommande une façon d'opérer qui donne une déviation standard relative de 0.7%. Après plusieurs mois de travail un rendement de 97% de nickel a été obtenu.

ZUSAMMENFASSUNG

Eine kolorimetrische Methode zur Bestimmung von Nickel in Seewasser mit Dimethylglyoxim wurde im einzelnen untersucht und durch genaue Kontrolle der experimentellen Bedingungen verbessert. Für eine maximale Fällung von 90% des Nickels waren zwischen der Behandlung mit Natriumcarbonat und der Filtration mindestens 7 Tage nötig. Es wird ein Salzeffekt beschrieben, der hervorgerufen wurde durch: (*1*) Einen Gewinn in der Absorption, der durch die löslichen Ionen, die nicht durch Natriumcarbonat gefällt werden, verursacht wird, und der mit steigender Salzkonzentration anwächst. (*2*) Einen Verlust in der Absorption durch unvollständige Fällung des Nickels. Die Übergangs-3d-Ionen, die durch Natriumcarbonat gefällt wurden, zeigten keinen erkennbaren Effekt auf die Absorption. Es wird ein Verfahren mit einer relativen Standardabweichung von 0.7% empfohlen. Die Rückgewinnung des Nickels betrugt 97%.

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THE DETERMINATION OF STABLE SCANDIUM IN PLANTS, ANIMALS, SEDIMENTS, SANDS, SOILS, ROCKS AND MINERALS BY NEUTRON-ACTIVATION ANALYSIS

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The distribution of scandium in the lithosphere has been studied by several workers[1-3] but little is known of its biogeochemistry in the ocean. The scarcity of information concerning the distribution of this element in the marine environment is due partly to the lack of accurate and reproducible techniques for separating and measuring submicrogram amounts of scandium from samples containing large amounts of other elements.

The measurements of scandium in samples of terrestrial origin have been obtained almost entirely by optical spectrographic or, more recently, by colorimetric methods. The limit of detection usually attained with the optical spectrograph is about 2 p.p.m. with precisions of 12–30%[3-11] although limits of detection of 1 p.p.m. with a precision of 8% may be realized[4]. Colorimetric methods for the determination of scandium have been reported which provide limits of detection from 1 μg[5-8] to as little as 0.01–0.04 μg[9,10] with precisions of about 15%.

Neither the spectrographic nor the colorimetric method provides the sensitivity or the precision required to determine the scandium content of many marine samples of interest in biogeochemical considerations. In addition, both methods are subject to contamination of the samples by scandium in the preparative techniques or by contaminated reagents.

Recently scandium has been measured in meteorites and rocks[1,2,11,12] by neutron activation analysis with limits of detection of the order of 1–10 ng. Results obtained utilized chemical separation of the elements after neutron irradiation with yields of 60–90%. The gravimetric determination of yield provided an avoidable source of error in the analyses. A separation procedure, done after neutron irradiation, which would produce quantitative yield relatively free from other radioisotopes, would provide a method sensitive enough to measure scandium accurately in samples containing low but variable amounts.

VICKERY[13] has reviewed quantitative methods of scandium precipitation but, of the precipitants reviewed, only disodium hydrogen phosphate and sodium phytate resulted in 99–100% yields for concentrations less than 10 mg/ml. BECK[14] worked with biological samples and reported that solutions of scandium sulphate treated with inositol hexaphosphoric acid (phytic acid) produced a white, flocculant precipitate

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insoluble in concentrated hydrochloric or nitric acid, aqua regia, hydrogen peroxide, oxalic acid, and alkali fluorides. In addition, he reported that titanium, zirconium, hafnium, and thorium produced acid-insoluble phytates although zirconium and hafnium phytates were partially dissolved in oxalic acid and titanium phytate in alkali fluorides.

Because of the high cost of scandium carrier, the possibility of using zirconium phytate as a carrier for neutron-activated scandium was investigated with ^{95}Zr and ^{46}Sc tracers in the present work. When 30 mg of sodium phytate were added to 50 ml of 2 N nitric acid solution containing 30 mg of tagged zirconium, and the suspension was filtered 3 times through glass filter papers, all of the ^{95}Zr was removed from the filtrate. Although the filter paper was then washed with 200 ml of 4 N nitric acid and the same volume of 0.2 N hydrochloric acid, the ^{95}Zr activity remained on the filter. The precipitation of tagged zirconium was repeated with 0.5 mg of biological ash dissolved in 2 N nitric acid. Quantitative yields of zirconium were retained by the filter papers when the samples were filtered.

Samples of biological ash were tagged with high-specific-activity ^{46}Sc, dried, and subjected to the zirconium–sodium phytate precipitation procedure described above. Approximately 80% of the ^{46}Sc remained on the filter. Two additional precipitations from the filtrate with added zirconium carrier resulted in a precipitation yield greater than 99% for the scandium. Fifteen samples of biological ash, ranging in weight from 0.1 to 1.0 g were tagged with high-specific-activity ^{46}Sc and coprecipitated, as described above, with zirconium phytate. The average chemical yield for scandium was $99.8 \pm 2.7\%$ (95% confidence level).

EXPERIMENTAL

Nuclear data

The determination of stable scandium by neutron activation analysis depends upon the reaction ^{45}Sc (n, r) ^{46}Sc. The reaction is efficient because of the 100% isotopic abundance of ^{45}Sc and its relatively high neutron cross-section of 22.3 ± 2.2 barns.

Scandium-46, with a half-life of 85 days, decays by the emission of β-particles ($E_{max} = 0.36$ MeV) followed by the emission of two γ-photons in cascade (0.89 and 1.12 MeV) which results in a sum-peak of 2.01 MeV. Both γ-rays are emitted at the rate of 100 photons per 100 disintegrations of ^{46}Sc.

Reagents

All materials used in the work were of reagent grade.

Zirconium carrier. Zirconyl nitrate (7.6 g) was dissolved in 100 ml of distilled water to provide a solution of 3% zirconium carrier.

Sodium phytate solution. Sodium phytate (Nutritional Biochemical Corporation (30 g) was dissolved in 100 ml of distilled water.

Scandium standard. Comparator standards of scandium were prepared from 99.9% scandium chloride (K and K Laboratories Incorporated) dissolved in 0.2 N hydrochloric acid to a concentration of 2 mg of scandium per ml of solution.

Ion-exchange resin. Dowex 50 W-X8 resin was placed in plastic chromatographic columns 0.8 × 20 cm. The resin was rinsed with 60 ml of 6 N hydrochloric acid and 200 ml of distilled water.

Preparation of comparator standards

Standards of scandium were prepared by pipetting 1- and 5-μl aliquots of a 2% scandium chloride solution (in 0.2 N hydrochloric acid) onto strips of Whatman #40 low-ash-content filter paper (maximum ash per cm^2 0.926 μg). The paper strips were dried under cover and were used as comparator standards. One or more standards were irradiated along with the samples in the reactor. Variability in the comparator standards resulting from pipetting and other errors was estimated by preparing several of the standards in the manner described above and comparing the γ-activity after neutron activation with that of standards prepared by diluting 1 ml of a 0.20% scandium solution irradiated at the same time. The differences in γ-activity between the 1- and 5-μl standards and the diluted standards were occasionally as high as 5% but were usually 2% or less. In most cases the standards did not differ significantly (95% confidence level).

Tests were also made to determine which contaminants were present in the filter paper strips used for the comparator standards. Strips of filter paper of the same dimensions used for the standards were placed in a neutron flux of $5 \cdot 10^{12}$ n/cm^2/sec for 4 h and subjected to γ-spectrometry. The only γ-emitting radioisotope detected was ^{24}Na ($T_{\frac{1}{2}} = 15$ h). The amounts of sodium were sufficiently small that the photopeaks of ^{24}Na could not be detected in the paper strips which were counted one week after irradiation. No other γ-emitters, including ^{46}Sc, were detected.

Procedure

Preliminary treatments. Samples of biological specimens were dried at 95° for 24 h, weighed and ashed at 450° for the same length of time. Aliquots of 0.2 g of each sample were sealed in hard glass ampoules and irradiated for 4 h in a thermal flux of $2.5 \cdot 10^{12}$ n/cm^2/sec. Comparator standards were also sealed in glass ampoules and irradiated with the samples.

Samples of marine sediments, beach sands, soils, rocks and minerals were dried for 24 h at 95°. The samples were broken up and ground to a powder with an agate mortar and pestle. Aliquots of 0.1–0.2 g were sealed in glass ampoules and irradiated under the same conditions as described above.

After irradiation the ampoules were placed in a lead shield for 2–7 days to allow decay of the short-lived radioactivity before the separations were started.

Some samples of marine plankton, sponges, sediments, soils, rocks and minerals contained large amounts of silica. After the decay of the short-lived activity the ampoules were broken and each sample mixed with 7 g of sodium peroxide in a crucible. A lid was placed over the crucible and heat was applied with a flame until fusion was complete. The crucible was placed in a 250-ml beaker and the melt was dissolved by slow and careful addition of 5 ml of 4 N nitric acid with one or two drops of 2 N hydrochloric acid. The remaining contents of the crucible were rinsed into the beaker with an additional 10 ml of heated 4 N nitric acid followed by 10 ml of distilled water. Thirty ml of 6 N nitric acid were added to the dissolved sample in the beaker. The solution was retained for separation of scandium.

Samples which did not contain silica were dissolved in 10 ml of 4 N nitric acid. Individual solutions were filtered through glass filters and the filters were rinsed with 20 ml of 2 N nitric acid in small aliquots. The filtrate of each sample was combined with the acid rinse and retained for separation of scandium. The filters were counted in a multichannel γ-spectrometer to be certain that none of the activated scandium remained on the filter.

Many of the samples contained large amounts of neutron-induced ^{32}P. The acid solutions of the samples were taken almost to dryness and redissolved in 60 ml of 0.1 *N* hydrochloric acid. The solution of each sample was added to an ion-exchange column (0.8 × 20 cm) of Dowex-50 (H-form) at a flow rate of 10–15 drops/min. The column was rinsed with 20 ml of 0.2 *N* hydrochloric acid at the same flow rate. The rinse was added to the sample eluate. (This fraction contained ^{32}P and ^{124}Sb and may be used to determine the amounts of these two elements if desired.) The ion-exchange column was eluted with 200 ml of 2 *N* nitric acid at a rate of 10–15 drops/min. This fraction contained the scandium and was retained for phytate separation.

Zirconium phytate coprecipitation of scandium. The dissolved sample, in 2 *N* nitric acid, was placed on a magnetic mixer and a teflon-coated stirring bar was placed in the solution. Zirconium carrier (1 ml; 30 mg Zr/ml) was thoroughly mixed with the dissolved sample, and 1 ml of 30% sodium phytate was added. The sample was stirred for 20 min and filtered twice under suction, through 2 layers of glass filter paper in a porcelain buchner funnel. The precipitate was not taken to dryness. Another 1 ml of zirconium carrier was added to the filtrate and the suspension was stirred for 20 min. The sample was filtered twice through the original 2-layer filter, with care being taken not to allow the precipitate on the filter to become dry. A further 1 ml of zirconium carrier was added to the filtrate and the sample was again stirred and filtered as described above. When a depth of *ca.* 1 mm of liquid remained above the precipitate on the filter, the suction was removed and the filtrate was discarded into the hot waste. The filter paper was rinsed, under suction, with 100 ml of 2 *N* nitric acid in 10-ml aliquots. With each wash of 10 ml of acid, the liquid was allowed to drain to a depth of about 1 mm over the precipitate before the next aliquot was added. The nitric acid filtrate was discarded and the washing procedure was repeated with 100 ml of 0.2 *N* hydrochloric acid in 10-ml aliquots*. After the final rinse the vacuum was left on for 15 min. The precipitate was dried in an oven for 30 min at 80° and placed in a polyethylene bag. The plastic bag and the sample were folded into a constant configuration, which provided the same geometry as that used for the comparator standards.

The precipitates were counted by two methods: (*1*) by γ-spectrometry with data reduction and, (*2*) by coincidence γ-spectrometry. NaI (Tl) detectors (3 × 3 in.) were used in both methods. Those samples which were counted by ordinary γ-spectrometry were centered over the detector on top of a β-filter of aluminum 4.8 mm thick. The sample was counted for 10–60 min (live-time) and the spectrum was stored in the first half of the 512-channel magnetic memory. The sample was then replaced by the comparator standard which was counted for an equal length of live-time. The counts from the standard were stored in the second half of the memory. The standard curve was progressively subtracted from the sample curve, by means of the data reduction system, until the photopeaks of 0.89 and 1.12 MeV and the sum peak of 2.01 MeV could no longer be detected in the γ-spectrum of the sample. The weight of the scandium in the comparator standard was then multiplied by the data reduction factor to determine the amount of scandium in the sample.

Samples which were counted by coincidence γ-spectrometry were placed be-

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* The decontamination factor for ^{24}Na and ^{38}Cl was greater than 10^9.

tween two 3×3-in. detectors without β-absorbers. The detectors were connected to 2 single-channel analyzers, one of which was adjusted to accept the counts from the 0.89 MeV photopeak and the other, the 1.12 photopeak of ^{46}Sc. The outputs of the analyzers were introduced into a coincidence analyzer set for a resolving time of 0.5 μsec. The counts from the coincidence analyzer were recorded with a scaler. Only small amounts of ^{124}Sb and ^{59}Fe were found as contaminants in the phytate precipitates for scandium. The discrimination factors against ^{59}Fe and ^{124}Sb in the coincidence spectrometer were 113 and 63 respectively. Background activity was 4 counts per 24 h. Corrections for interference by ^{59}Fe and ^{124}Sb were calculated from spectra made with regular γ-spectrometry. Only those samples with small amounts of scandium (<0.01 μg/sample) were counted by coincidence γ-spectrometry.

DISCUSSION

Neutron activation analysis is one of the most sensitive methods reported for the determination of stable scandium[1,2,11,12]. LEDDICOTTE *et al.*[15] reported a sensitivity for scandium of $5 \cdot 10^{-5}$ μg, based on a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec and an irradiation time of one week. FUKAI AND MEINKE[16] calculated an approximate detection limit for scandium in marine organisms of $3 \cdot 10^{-2}$ μg for a flux of 10^{12} n/cm²/sec and an irradiation time of 10 h.

A comparison of the experimental values assumed by FUKAI AND MEINKE with those used in the present work is shown below.

	I *Fukai and Meinke*	*II* *Present work*	*III* *Ratio II/I*
Neutron flux	10^{12}	$5 \cdot 10^{12}$	5
Irradiation time (h)	10	4	0.4
Chemical yield	50%	100%	2
	Combined ratio II/I = 4		

The experimental conditions used in the present work should result in a 4-fold increase in sensitivity over that calculated by FUKAI AND MEINKE. A further increase could be realized by increasing duration of neutron irradiation. The time of 4 h was selected because the polyethylene sample containers maintain their physical integrity in the neutron and gamma fluxes for about twice this length of time and polyethylene containers are convenient to use.

An increase in sensitivity of 4 times that calculated by FUKAI AND MEINKE results in a theoretical limit of detection of $7.5 \cdot 10^{-3}$ μg of scandium*. The limit found in the present work was $5 \cdot 10^{-3}$ μg and was within the error of sensitivity of ±50% estimated by FUKAI AND MEINKE.

Although neutron activation affords a sensitive method for the determination

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* The term 'limit of detection' used in the present work is defined as that amount of stable scandium which may be measured by counting the γ-radiation from purified ^{46}Sc, with a maximum error of ± 10% at the 95% confidence level. The definition is based upon irradiation time of 4 h, a neutron flux of $5 \cdot 10^{12}$ n/cm²/sec, quantitative chemical yield and the use of a 3×3″ NaI (Tl) detector.

of stable scandium and is free of the errors introduced by reagent contamination, it may be subject to intrinsic sample errors in some types of samples. Possible sources of error for the determination of scandium by this method may result from differential shielding of the sample and the comparator standard during neutron irradiation or by interfering neutron reactions with other elements in the specimen.

Some samples contain appreciable amounts of elements which have large neutron cross-sections. In many marine samples a high percentage of the material is sodium chloride. One of the stable isotopes of chlorine, ^{35}Cl, has a large neutron cross-section (44 barns) and comprises 75% of the total element. Neutron shielding by ^{35}Cl must therefore be taken into consideration in comparisons of the neutron-induced ^{46}Sc radioactivity in the sample with that induced in the scandium comparator standard. GUINN AND WAGNER[17] found that the shielding effect of chlorine was negligible in samples containing up to 1 g of chlorine. Thus, the sample size of 0.2 g used in the present work is within the range of negligible neutron shielding by this element.

Scandium-46, in addition to the desired reaction (^{45}Sc(n, r)^{46}Sc), may be formed by the reaction, ^{46}Ti(n, p)^{46}Sc, in the presence of high energy neutrons. However, the neutron cross-section for the latter reaction is only 4.1 mb. KEMP AND SMALES[2] calculated that the error introduced by this reaction would be significant only in samples with titanium/scandium ratios greater than 50,000/1 and demonstrated that the reaction did not occur in a purely thermal neutron flux. Titanium/scandium ratios of this magnitude are not common except in some geological samples.

Thus, the method described in this report is free of the problems of reagent contamination or intrinsic sample error, provides sufficient sensitivity for most samples of terrestrial or marine origin, results in quantitative yield with adequate decontamination factors for interfering radioisotopes and is relatively simple in execution. The determination of scandium by this method may be applied to large numbers of samples with a high degree of reproducibility. As many as 5 samples of diverse composition may be completed by a technician in one day. During the past 2 years a total of 300 samples have been analyzed by this method as part of a marine biogeochemical program on the west coast of Puerto Rico.

This work was performed under Contract AT(40-1)-1833 with the U.S. Atomic Energy Commission.

SUMMARY

A method is described for the determination of stable scandium in samples of plants, animals, sediments, soils, rocks and minerals. The samples and comparator standards were irradiated in a neutron flux of $5 \cdot 10^{12}$ n/cm^2/sec for 4 h and dissolved and the scandium quantitatively precipitated from 2 N nitric acid as scandium phytate; contaminants were rinsed from the precipitate with nitric and hydrochloric acids. The limit of detection was 0.005 μg ($\pm$10% at the 95% confidence level). The activated ^{46}Sc was counted by γ-spectrometry.

RÉSUMÉ

Une méthode est décrite pour le dosage de scandium stable dans les plantes, les animaux, les sédiments, les sols, les roches et minéraux. Les échantillons et les étalons sont irradiés dans un flux de neutrons de $5 \cdot 10^{12}$ n/cm²/sec pendant 4 heures; le scandium est précipité quantitativement, en milieu acide nitrique 2 *N*, sous forme de phytate. Limite de détection: 0.005 μg. ^{46}Sc activé est compté par spectrométrie-γ.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung stabilen Scandiums in Proben von Pflanzen, Tieren, Sedimenten, Böden, Gesteinen und Mineralien beschrieben. Die Probe und der Vergleichsstandard werden mit einem Neutronenfluss von $5 \cdot 10^{12}$ n/cm²/sec 4 Std. lang bestrahlt, gelöst und das Scandium quantitativ aus 2 *N* Salpetersäure als Scandiumphytat gefällt. Verunreinigungen werden aus dem Niederschlag mit Salz- und Salpetersäure herausgespült. Die Nachweisgrenze betrug 0.005 μg ($\pm 10\%$ bei einem Vertrauensbereich von 95%). Das aktivierte ^{46}Sc wurde mit der γ-Spektrometrie bestimmt.

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ACTIVATION ANALYSIS OF MERCURY IN HIGH PURITY BISMUTH

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WESTERMARK *et al.*[1,2] have determined mercury in biological materials by direct γ-spectrometry, with a sensitivity of 0.1 p.p.m. The same method was applied by CHOI AND TUCK[3] to study the solubility of mercury; SJÖSTRAND[4] further improved the sensitivity down to 0.5 p.p.b. by introducing a chemical separation, *i.e.* distillation as mercuric chloride and electrolytic deposition on a gold foil.

Many different methods of chemical separation for mercury have been applied, *e.g.* precipitation as sulfide, periodate[5,6], chloride[7], bichromate[8], precipitation by organic reagents[7,9], extraction by organic solvents[7,10,11], electrolytic deposition[4,6,12] and steam distillation of the metal[13]. However, owing to the chemical properties of the sample, these separations do not always give satisfaction, and they are often tedious as several steps must be combined in order to obtain a satisfying radiochemical purity.

As appears from Bock-Werthmann[14-16], the determination of mercury in various samples has been studied by many authors, but up to now no paper has appeared dealing with the determination of mercury in bismuth.

In the present work mercury was determined in high purity bismuth using a chemical separation based on the deposition of mercury on coarse metallic copper powder, followed by a distillation of metallic mercury and amalgamation on a silver foil. This method was found to be highly satisfactory because of the high radiochemical purity of the produced mercury, the high chemical yield which can be determined with good accuracy and the short time required.

NUCLEAR DATA

When mercury is activated by neutron irradiation in a reactor, 5 active nuclides are obtained, whose nuclear data are given in Table I. The short-lived ^{199m}Hg and ^{205}Hg could not be used in our case because of the long time required to transfer the samples from the reactor to the laboratory. Moreover the relatively low cross-section for the formation of these nuclides does not allow a high sensitivity.

It can be seen that the activation cross-section for the production of ^{203}Hg is 1.1 barns and for ^{197}Hg, together with ^{197m}Hg, it is 1.9 barns. As ^{203}Hg requires a long irradiation period to obtain a comparable degree of saturation ^{197}Hg was preferred.

From the decay scheme it appears that 97% of ^{197m}Hg undergoes an isomeric transition to ^{197}Hg, emitting 0.134 MeV and 0.164 MeV γ-quanta which are internally converted, to the extents of 66% and 92.5% respectively[17]. As the result of this internal conversion the 71-keV Hg K-X ray (average energy) is emitted. The excited state of ^{197}Au, the result of a 99% electron capture of ^{197}Hg, gives a strong γ-ray of 77 keV, a 68-keV Au K-X ray following the electron capture, and a weaker γ-ray of 191 keV. The 68-keV Au K-X ray occurs to an extent of 95%[4]. The 77 keV is strongly converted and only 20%[17] of the disintegrations yield γ-rays. Therefore the 68–77 keV region was chosen for counting.

TABLE I

NUCLEAR DATA [17, 22–24]

Target nuclide	*% Abundance*	σ_{act} *(b)*	*Isotope produced*	*Half life*	*Radiation and energy (MeV)*
^{196}Hg	0.146	880[a]	^{197}Hg	65 h	γ: 0.077 (20%), 0.19 (0.5%) 0.068 Au K-X ray
		420[a]	^{197m}Hg	24 h	γ: 1.33 (31%), 1.64 (4.5%) 0.071 Hg K-X ray
^{198}Hg	10.02	0.018[a]	^{199m}Hg	42 m	γ: 0.159, 0.368
^{202}Hg	29.80	3.8	^{203}Hg	46.9 d	β^-: 0.208 γ : 0.279 (83%) Tl K-X ray (0.073)
^{204}Hg	6.8	0.43	^{205}Hg	5.5 m	β^-: 1.8 γ : 0.203

[a] Quoted from[25].

SEPARATION TECHNIQUE

Deposition on copper powder

Displacement of mercury ions by more electro-negative metals has been applied by several authors[5,12,18]. With regard to the composition of the sample solution, copper was chosen, since the bismuth matrix may contain impurities which are more electro-negative than copper. With the latter, only the more electro-positive elements can be deposited, such as mercury, silver, gold, platinum, etc.

The deposition can be performed in hydrochloric[5] or nitric acid solution[12,18], the latter being preferable as the former is rather time-consuming for a complete deposition. With nitric acid, good results are obtained in the concentration range of 0.01–1.5 N. An acid concentration lower than 1 N favors the deposition of undesirable elements such as antimony and bismuth itself, whereas a concentration higher than 1.5 N causes a quick dissolution of the copper. Therefore the use of 1.0–1.5 N nitric acid is believed to be appropriate.

Preference was given to copper powder (200 mesh) over metal foils as the surface is larger. The copper powder was placed on a microfiltering unit, and the sample solution sucked through the copper powder at a rate of 2–3 ml/min. It was found that one passage gave a complete deposition of up to 100 mg of mercury on 1 g of copper. This procedure was still insufficiently selective for the separation of mercury from other interfering species as gold, silver, etc. The obtained metallic mercury was therefore further purified by distillation, the distillate being collected on a silver foil.

Distillation

For the recovery of mercury, amalgamation with gold[5] or silver[6,12] foil is often used in conventional analytical procedures.

Accordingly, after the previous separation technique, the copper powder was transferred to a nickel crucible, inserted in the circular opening of an iron plate placed on an asbestos board, just large enough for the crucible to fit snugly and protrude by about half its height. This prevented the flame from heating the upper portion. The disc of the silver foil was cooled by contact with a cylindrical brass condenser, through which cold water circulated, as shown in Fig. 1. The bottom of the crucible was gradually heated with a small Bunsen burner, being careful not to overheat. To avoid the escape of mercury vapour, which might be due to overheating as well as to leakage between the silver foil and the crucible, a circular incision was made on the bottom surface of the condenser, to the edge of which the crucible could be matched, thus making a tight joint. All portions of the crucible were readily brought above the boiling point of mercury (375°) while the silver foil was kept at 10–50°. Heating for 30 min was sufficient to distill all the mercury deposited on the copper powder. The

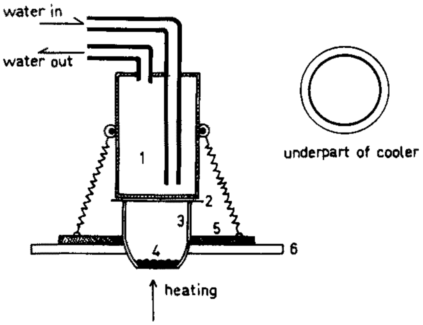

Fig. 1. Apparatus for Hg distillation. 1, cooler: made of brass (o.d. ~ 3 cm, o.h. ~ 5 cm); 2, Ag plate (thickness ~ 0.05 mm, diam. ~ 3 cm); 3, nickel crucible (i.d. ~ 2.7 cm, height ~ 2.5 cm); 4, sample deposited on copper powder (Cu ~ 1 g); 5, iron crucible-supporter; 6, asbestos.

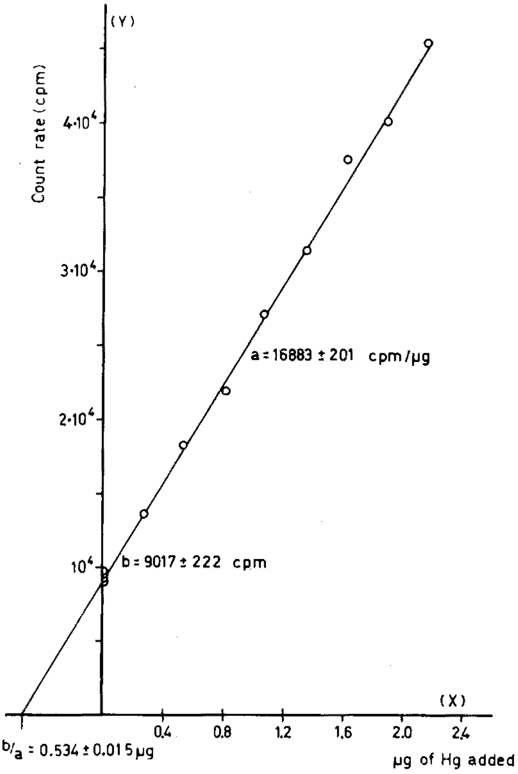

Fig. 2. Calibration curve of ^{197}Hg.

apparatus was then allowed to cool for 10 min without disconnecting the condenser. The increase in weight of the foil was due to mercury.

Before starting this procedure, the sample containing the mercury deposited on the copper grains should be washed with alcohol and ether, otherwise the moisture in the copper grains will condense on the foil and cause a poor amalgamation.

The results of this procedure were found to be satisfactory in accuracy and reliability. Gold and silver, deposited together with mercury on the copper grains, did not interfere. The results of tracer techniques and gravimetric determinations for the whole procedure are shown in Table II. For these determinations ^{203}Hg tracer, 18.5 mg of mercury carrier and 1 g of non-active bismuth were used.

TABLE II

CHEMICAL RECOVERY OF MERCURY

Number of experiment	*Chemical recovery(%)*	
	Gravimetry	*Isotope technique*
1	96.00	93.30
2	102.01	99.21
3	98.75	98.30
4	92.54	93.25
5	97.03	97.50
6	95.61	96.01
7	95.70	95.65
8	98.50	98.05
Mean value	97.02±2.62	96.41±2.26

EXPERIMENTAL

Sampling and irradiation

Approximately 1-g samples were taken from 3 different kinds of matrices: certified purity of 99.999% (B-1), of unknown but high purity (B-2) and of certified purity of 99.9999% (B-3). The samples were washed with dilute nitric acid and packed in sealed quartz ampoules. The insides of the quartz ampoules were also thoroughly washed with concentrated nitric acid, water and alcohol, then dried, as they might contain mercury impurities[19]. The mercury contained in the quartz would not be removed by this procedure; the washing of the inner surface was only intended to avoid any accidental contamination.

For the standard, high purity mercuric oxide was used, dissolved in 6 *N* nitric acid and diluted to a 10 μg/ml; 100 μl were taken and sealed in a quartz ampoule.

The samples were irradiated for 3 days in the BR-1 reactor at a flux of $4 \cdot 10^{11}$ n/cm^2/sec. The quartz ampoules were placed in liquid air before opening to condense any mercury vapour that might be formed during irradiation.

Radiochemical separation

Place the irradiated sample in a 150-ml beaker together with the open quartz ampoule. Add 18.5 mg of mercury carrier (18.5 mg/ml) and 5 ml of 7 *N* nitric acid. Cover with a watch glass and dissolve on a hot plate by gentle heating.

Dilute to 30 ml with cold water and transfer to the reducing apparatus, in which about 1 g of copper powder is placed. Wash the beaker with 1.4 *N* nitric acid and add to the sample solution. Pass the solution at a rate of 2–3 ml/min through the copper powder and repeat this step. Wash the copper powder under suction, with water, alcohol and ether and carefully transfer to a nickel crucible set in the distillation apparatus. Insert a silver foil between the nickel crucible and the brass condenser, adjust the crucible and condenser together in the circular incision on the bottom surface of the condenser, and tighten with spring holders. Apply increasing heat to the bottom of the crucible during 30 min, taking care not to overheat. Allow to cool for 10 min without disconnecting the condenser.

Remove the silver foil, wash successively with alcohol and ether and dry in a desiccator. Weigh the foil and pack in a thin plastic bag for counting.

Standard samples are processed by the same technique.

Counting

Counting was performed with a γ-scintillation spectrometer (3″×3″ NaI(Tl) crystal coupled to a 400-channel analyzer). For the quantitative measurements the photopeak in the 68–77 keV region was selected and counted for 5 min, starting 1.5 days after the end of the irradiation. When mounting the sample on the scintillation detector, the silver foil, packed in the plastic bag, was placed flatly, the amalgamated side toward the detector. It is obvious that this way of mounting gave rise to a somewhat better counting efficiency, since the silver foil absorbed the weak-energy γ-rays, *i.e.* ±15% of the 68–77 keV region by 0.05-mm silver foil.

All the samples and standards were counted alternately and results were calculated by comparison of the obtained data.

ACCURACY OF THE METHOD AND RESULTS

The accuracy of the analytical procedure was tested by the addition method. As a large variation in the distribution of mercury in the samples was found (Table V),

TABLE III

ADDITION METHOD (B-1)

Number of experiment	*Sample weight (mg)*	*Hg added (µg) (X)*	*Activity*[a] *measured (counts/min) (Y)*	*Remarks*
1	124.814	0	8848	
2	124.814	0	8946	
3	124.814	0	9479	a = 16883 ± 201 counts/min/µg
4	124.814	0	9166	
5	124.814	0.268	13608	
6	124.814	0.536	18013	b = 9017 ± 222 counts/min
7	124.814	0.804	21897	
8	124.814	1.073	27019	
9	124.814	1.341	31306	b/a = 0.534 ± 0.015 µg
10	124.814	1.609	37419	
11	124.814	1.877	40131	
12	124.814	2.145	45352	

[a] Values corrected for chemical yield (to 100% yield).

it was of course necessary, before carrying out the experiments, to dissolve the sample in order to obtain a homogeneous mercury distribution.

For checking, 12.481 g of sample B-1 were dissolved in 7 N nitric acid and made up to 50 ml. From this solution 0.5 ml was transferred to a quartz ampoule. In this way 12 samples were prepared, to which 0.268, 0.536, 0.804, 1.073, 1.341, 1.609, 1.877 and 2.145 μg of mercury were added. To the remaining samples no mercury was added. Two blank solutions of the same volume were prepared.

All samples were irradiated and submitted to the chemical separation already described. The results, which were corrected for the reagent blank ($9 \cdot 10^{-3}$ μg of mercury in 0.5 ml of solution), were calculated by the least squares method[20,21]. The slope a of the obtained straight line gave the specific activity of the mercury whereas its intercept b with the ordinate was due to the activity of the mercury originally present. Therefore the original concentration of the component to be determined could be calculated from b/a. The results are shown in Table III and Fig. 2.

Results of 4 analyses by comparison with a mercury standard are given in Table IV. It appears that these results are in good agreement with the addition procedure.

TABLE IV

STANDARD METHOD (B-1)

Number of experiment	*Sample weight (mg)*	*Chem. yield (%)*	*Hg found (μg)*	*Activity of STD (counts/min/μg)*
1	124.814	95.59	0.515	
2	124.814	93.52	0.520	
3	124.814	97.77	0.551	16948 ± 918
4	124.814	96.26	0.533	
Mean value			0.530 ± 0.016	

TABLE V

ACTIVATION ANALYSIS OF MERCURY

Sample	*Sample weight (g)*	*Chemical yield (%)*	*Hg found (p.p.m.)*	*Sample*	*Sample weight (g)*	*Chemical yield (%)*	*Hg found (p.p.m.)*
B-1	1.1290	96.36	3.542	B-2	1.2738	95.90	0.014
	1.1121	97.85	3.044		1.1478	99.80	0.010
	1.3815	98.50	2.953		1.1298	94.96	0.008
	1.0791	88.59	5.033		1.0759	96.27	0.014
	1.0262	93.00	5.956		1.0606	98.34	0.011
	0.8725	97.29	2.572		1.9962	98.10	0.014
	0.8918	95.88	1.802				
	0.8750	97.62	2.090	B-3	1.6277	93.16	0.029
	0.9595	98.56	1.905		1.8139	90.84	0.049
	0.9860	98.91	1.672		1.6153	92.11	0.030
	1.0305	99.10	2.353		1.8082	99.52	0.033
	1.1658	95.58	1.539		1.5496	99.44	0.032
	0.8643	97.40	2.476		1.9678	97.23	0.031
	0.9427	99.30	2.210		1.5161	98.91	0.117
	0.6997	98.39	1.991		1.0773	97.23	0.045

Results of analyses of samples B-1, B-2 and B-3 are given in Table V. The B-1 samples show a large variation in mercury content whereas the other samples show little fluctuation. It is obvious that this variation is mainly due to the inhomogeneous distribution of mercury in the samples.

SUMMARY

A neutron activation method was developed for the determination of traces of mercury in high purity bismuth. After neutron irradiation at a flux of approx. $4 \cdot 10^{11}$ n/cm^2/sec, mercury was separated from the matrix by displacement on metallic copper and subsequent distillation and amalgamation on silver foil. The γ-activity of the ^{197}Hg was counted in the 68–77 keV region. The accuracy of the procedure was tested by an addition method of analysis. Bismuth samples with a mercury content in the 10 p.p.b. region were analysed.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est développée pour le dosage de traces de mercure dans du bismuth de haute pureté. Après irradiation avec un flux d'environ $4 \cdot 10^{11}$ n/cm^2/sec, le mercure est séparé de la matrice par déplacement sur cuivre métallique, distillation et amalgamation sur feuille d'argent. L'activité gamma de ^{197}Hg est comptée dans la région 68–77 keV. On a analysé ainsi des échantillons de bismuth renfermant des quantités de mercure de l'ordre de 10 p.p.b.

ZUSAMMENFASSUNG

Zur Bestimmung von Spuren Quecksilber in hochreinem Wismut wurde eine Neutronenaktivierungsmethode entwickelt. Nach der Bestrahlung mit einem Fluss von $4 \cdot 10^{11}$ n/cm^2/sec wurde das Quecksilber von der Matrix durch Abscheiden auf metallischem Kupfer getrennt, darauf destilliert und auf einer Silberfolie amalgamiert. Die γ-Aktivität des ^{197}Hg wurde im Bereich von 68–77 keV gezählt. Die Genauigkeit des Verfahrens wurde mit der Additionsmethode geprüft. Wismutproben mit einem Quecksilbergehalt im Bereich von 10 p.p.b. wurden analysiert.

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NEUTRON-ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION

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In neutron-activation analysis, the determination of chemical yield is necessary when losses in the different steps of chemical separation are significant. When the chemical yield correction cannot be made owing to a lack of suitable carriers, the yields from standards and samples must be quantitative or equal. A selective and quantitative procedure of this type for the determination of uranium in aluminium and lead was developed in an earlier study[1]. In some cases however, the recovery from the sample was different from that from the standard, owing to the presence of relatively large amounts of cations and anions in the solution obtained by dissolving the sample. In order to take care of such situations, a new method was developed, in which the problem of chemical yield determination is avoided by selective extraction of the element under study coupled with the application of the method of standard addition[2]. In the present paper the principle of this new approach is discussed and data obtained in the application of the method to the determination of uranium are presented.

PRINCIPLE OF THE METHOD

In conventional comparative activation analysis, the amount of the required element (X) originally present in the sample is calculated from the activity induced by irradiation

$$X = X_s \frac{A}{A_s} \tag{1}$$

where X_s is the amount of the element in the standard, A is the activity of the recovered isotope from the sample and A_s is the activity of the recovered isotope from the standard. The above relation is valid, however, only when the overall recovery from the sample and standard is quantitative or when the chemical yields in both cases are normalized.

When chemical yield corrections cannot be made because of a lack of suitable carriers, and when the yields are neither quantitative nor equal from both the sample and standard as discussed above, the following variations in the experimental procedure can be adopted; from the measured activities an accurate value of X can be calculated as explained below.

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(*1*) Known amounts of the sample and standard are irradiated under the same conditions and then completely dissolved.

(*2*) An aliquot of the sample solution is adjusted to suitable conditions for extraction, the active isotope under study is selectively extracted in a single stage and the activity of the extract is measured.

(*3*) A suitable amount of the standard solution is added to another aliquot of the sample solution, which is then extracted and the activity of the extract measured under the same conditions as in step (*2*).

It can be shown that the amount of the required element (X) originally present in the sample is given by the following simple equation

$$X = \frac{X_s A}{A_m - A} \tag{2}$$

where A_m is the activity of the fraction recovered from the mixture containing the same amount of sample and an amount of standard originally containing X_s of the element to be determined. The other values in eqn. (2) are the same as in eqn. (1). It is evident that the value of $A_m - A$ corresponds to the fraction extracted from the standard under the same conditions as the extraction from the sample solution. This value will obviously be different from the value of A_s in eqn. (1). It is also clear that $(A_m - A)/A_s$ is equal to the ratio of the chemical yields in the case of extraction from solutions of sample and pure standard respectively.

Application of the method to the determination of uranium

The (n,γ) reaction on ^{238}U has been employed indirectly by isolating and counting ^{239}Np. The advantages and limitations of this reaction have already been discussed. ^{239}Np is extracted selectively with 2-thenoyltrifluoroacetone[3] and assayed by counting the 0.103-MeV photopeak.

EXPERIMENTAL

Apparatus

A single-channel medical spectrometer (manufactured by the Electronics Division, Atomic Energy Establishment Trombay) connected to a scintillation head consisting of a 1.5″ × 1″ NaI(Tl) crystal, an E.M.I. 9536 photomultiplier tube and cathode follower, was used to measure the γ-ray activities and spectra of ^{239}Np.

Uranium standard solution

100 mg of uranium metal was dissolved in nitric acid and then made up to 100 ml. 5 ml of this solution was further diluted to 100 ml to give a concentration of 50 μg/ml.

Irradiations

The uranium standard (5 μg of uranium) was prepared by evaporating 100 μl of the working solution of uranium in a quartz tube (0.5 cm diameter × 3 cm height) and sealing the tube. About 300 mg of the standard granite G-1 was sealed in a similar quartz tube. About 1 g of S$_2$-grade aluminium was wrapped in an aluminium foil and the standard and samples were placed in an aluminium can (4.5 cm in height × 2 cm in diameter) for irradiation in the Canada India Reactor (a natural uranium, heavy water-moderated reactor of the NRX type). Irradiations were carried out in one of the self-serve positions at a flux of 10^{13} n cm^{-2} sec^{-1} for 48 h. After irradiation, the can was cooled for 2 days before the samples were removed for analysis.

Processing of the irradiated standards and samples

The tube containing the standard was crushed in a polythene sheet, transferred to a 100-ml beaker, boiled with 3 *M* hydrochloric acid and filtered; the solution was diluted to 25 ml. The aluminium sample was etched with dilute nitric acid, washed with water and dried; a known weight was dissolved in 3 *M* hydrochloric acid and diluted to 50 ml.

A weighed amount of the granite sample (about 200 mg) was placed in a platinum crucible, heated with a few drops of a mixture of hydrofluoric acid and hydrochloric acid in order to expel silica, and then evaporated repeatedly with hydrochloric acid. The residue was then carefully fused with about 1 g of sodium carbonate. The fused mass was taken up in 3 *M* hydrochloric acid and diluted to 50 ml.

Two equal aliquots of the sample solutions were taken in 100-ml beakers, and to one of these an amount of standard similar to the amount of the required element present in the sample solution was also added. The solutions were evaporated to dryness and 5 ml of 3 *M* hydrochloric acid, 5 ml of 3 *M* hydroxylammonium hydrochloride, and 5 ml of 6 *M* potassium iodide were added to reduce the neptunium. The solutions were heated on a water bath for 20 min, allowed to cool for 5 min and transferred to separating funnels. Then 10 ml of 0.5 *M* thenoyltrifluoroacetone (TTA) were added to the beaker and transferred to the separating funnel; the neptunium was extracted for 10 min. The organic phase was then scrubbed with 10 ml of 1 *M* hydrochloric acid and neptunium was finally stripped with 10 ml of 10 *M* nitric acid. The stripped solution was re-extracted with 10 ml of 0.5 *M* TTA to remove any traces of zirconium.

Measurement of radioactivity and calculation of results

The aqueous phase containing ^{239}Np (10 ml) was transferred to a stoppered glass counting vial, and the γ-activity was measured at constant geometry. The photopeak activities at 0.103 MeV of ^{239}Np were measured for the sample, and for the mixture of sample and standard, and the decay followed. The observed half-life was always between 2.25 and 2.40 days ($T_{\frac{1}{2}}$ of $^{239}\text{Np}=2.35$ days). The amount of uranium in the sample was calculated by means of eqn. (2).

RESULTS AND DISCUSSION

The results obtained in the analysis of the standard granite G-1 and S2-grade aluminium are presented in Table I; for comparison, the values reported for G-1 by previous workers are included. The results show that the method gives satisfactory precision and accuracy in the determination of uranium. That a complex mineral like granite could be analysed satisfactorily indicates the general applicability of the method. The decay of the 0.103-MeV photopeak activity (Fig. 1) shows that the purity of neptunium is satisfactory for γ-spectrometric determinations.

TABLE I

ANALYSIS OF STANDARD GRANITE AND THE S_2-GRADE ALUMINIUM

Wt. of sample (g)	*Amount of U added (μg)*	*A*[a] *(counts/min)*	*A_m*[b] *(counts/min)*	*U found (p.p.m.)*	*Previous reported values (by activation)*	*Ref.*
G-1						
0.0397	0.10	644	1190	3.0	3.55 (mean of 2)	4
0.0316	0.08	587	1037	2.7	3.46 ± 0.47 (mean of 9)	5
					2.7 (mean of 2)	6
0.0199	0.06	550	1150	2.8	3.10 ± 0.08	7
			Mean	2.8		
Al						
0.1089	0.2	1526	3212	1.7		
0.1089	0.2	1523	2900	2.0	2.1 (mean of 3)	1
0.1089	0.3	1609	4245	1.7		
			Mean	1.8		

[a] *A* = Photopeak activity of ^{239}Np from sample.

[b] *A_m* = Photopeak activity of ^{239}Np from sample and standard.

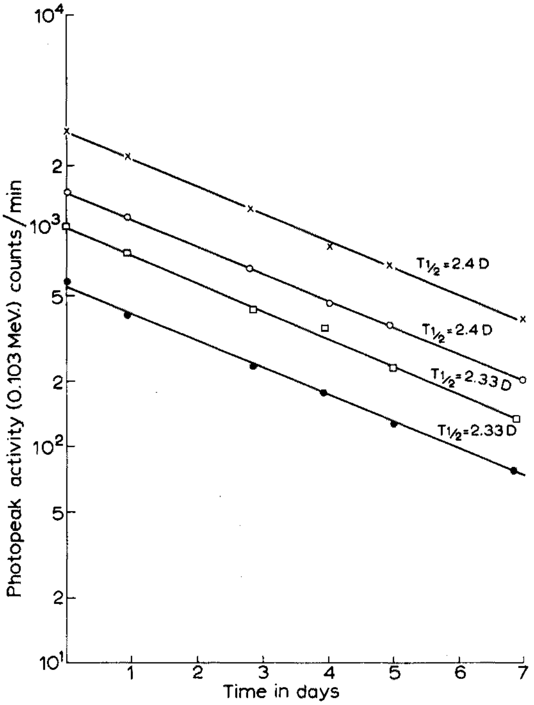

Fig. 1. Decay of ^{239}Np isolated from samples and standards. ○, Al sample; ×, Al sample + standard; ●, standard granite; □, standard granite + std.

The simplicity and rapidity of the present method provide advantages over other methods of activation analysis for uranium.

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SUMMARY

A new approach to activation analysis is described. Chemical yield determinations are avoided by selective extraction of the required element in conjunction with the standard addition technique. The principle and its application to the determination of traces of uranium in aluminium and the standard granite (G-1) are given. The advantages of this method are its simplicity and rapidity.

RÉSUMÉ

Un nouveau procédé est décrit pour l'analyse par activation. Le principe est donné, ainsi qu'une application au dosage de traces d'uranium dans l'aluminium et le granite standard (G-1). Les avantages de cette méthode sont: simplicité et rapidité.

ZUSAMMENFASSUNG

Es wird ein neues Verfahren für die Aktivierungsanalyse beschrieben. Dabei wurden die Bestimmungen der chemischen Ausbeute vermieden, indem das betreffende Element in Verbindung mit der Standardzugabetechnik selektiv extrahiert wurde. Das Prinzip und seine Anwendung bei der Bestimmung von Spuren Uran in Aluminium und dem Standardgranit G-1 werden beschrieben. Die Vorteile der Methode liegen in ihrer Einfachheit und Schnelligkeit.

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THE CONTROLLED POTENTIAL COULOMETRIC AND CONTROLLED POTENTIAL POLAROGRAPHIC DETERMINATIONS OF SUBSTITUTED NITROBENZENE COMPOUNDS IN DIMETHYLSULFOXIDE

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Only a few applications of controlled potential coulometry have been reported for the determination of aromatic nitro compounds. These include the determination of aromatic nitro compounds in methanol–water[1] or absolute methanol[2], picric acid in aqueous media[3], and nitric acid oxidation products of humic acid employing dimethylsulfoxide as the solvent[4]. The latter paper emphasized the need for additional studies of electrochemistry in dimethylsulfoxide.

The polarography of aromatic nitro compounds in non-aqueous media has been limited to a few organic solvents, and usually is employed for the investigation of the first one-electron reduction. Polarographic studies have been made in dimethylformamide[5,6], acetonitrile[5,7,8], and methanesulfonic acid[9].

Controlled potential coulometry and controlled potential polarography have not, as yet, been used for the electroanalysis of aromatic nitro compounds in dimethylsulfoxide. This investigation is concerned with the use of these methods for the determination of the electrochemical processes involved in the reduction of several substituted nitrobenzene compounds, including the isomers of nitrophenol and nitrobenzoic acid at a mercury electrode, using dimethylsulfoxide as a solvent. The paper includes the use of this information in the development of a controlled potential coulometric procedure for the determination of these nitro compounds and a quantitative evaluation of the background currents associated with the determinations.

EXPERIMENTAL

Apparatus

Cell design. The cell used for controlled potential coulometry and controlled potential polarography is shown schematically in Fig. 1. The working electrode compartment is constructed from a 50-ml glass-stoppered Erlenmeyer. The counter and reference electrode side-cells are made from 14/20 standard taper ground joint units, which are sealed at the bottom. The side-cells are connected to the center compartment by fine porosity frits. Nitrogen deaeration tubes are provided in each side-cell compartment for removal of dissolved oxygen. The mercury level of the working electrode is determined by the connection height of the capillary deaeration side-arm; any excess mercury is removed by vacuum.

Electrodes. The dropping mercury electrode (D.M.E.) is sealed into a standard taper polyethylene stopper which is designed to replace the glass stopper in the Erlenmeyer compartment of the cell in Fig. 1. Typical capillary characteristics at open circuit in 0.5 *M* LiCl solution in dimethylsulfoxide (DMSO–electrolyte solvent) with 27.5 cm mercury are: $m = 0.820$ mg/sec and $t = 8.35$ sec.

The working electrode consists of 12.3 ml of distilled mercury.

The mercury pool reference electrode in DMSO–electrolyte solvent (see Fig. 1) is used for both controlled potential coulometry and controlled potential polarography.

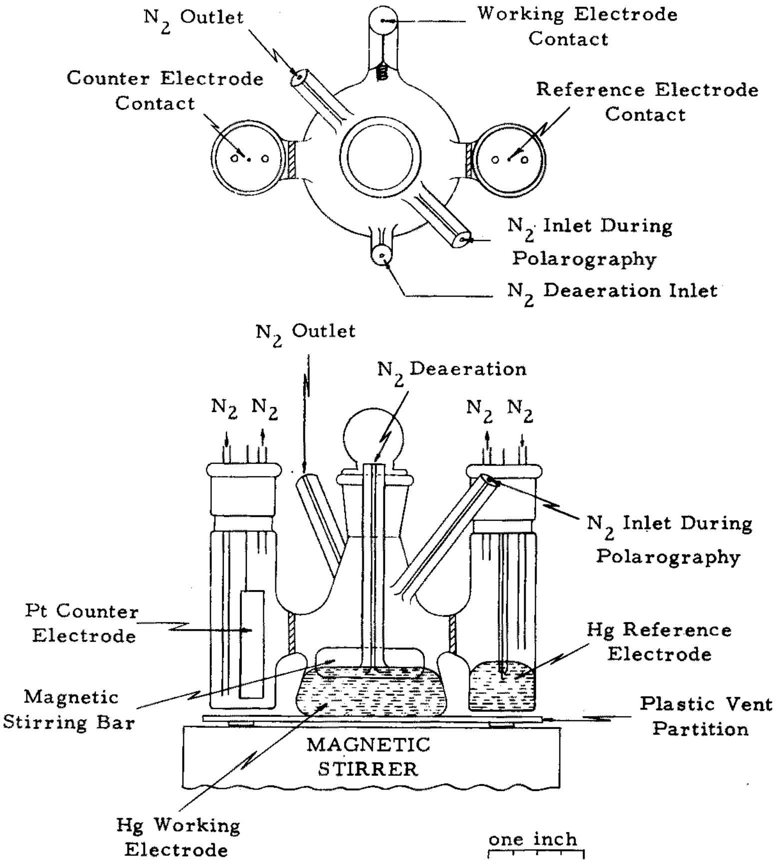


Fig. 1. Cell for controlled potential coulometry and polarography.

The potential of the mercury pool is measured against an aqueous saturated calomel electrode by means of an agar–KCl salt bridge. The mercury pool reference is used during the determinations in order to prevent water contamination of the DMSO–electrolyte solvent.

The counter electrode is made of heavy gauge platinum foil. The dimensions of the counter electrode are not important as long as the area is sufficient to carry the current.

Instruments. The controlled potential coulometer used is essentially the same as that described by SCOTT AND PEEKEMA[10]. The instrument's electronic current integrator was continuously monitored by a 50-mV recorder.

The controlled potential polarograph used is essentially the same as that described by ENKE AND BAXTER[11].

Reagents

Lithium chloride (Baker and Adams, reagent grade) dried at 160° for 48 h.

Dimethylsulfoxide (Crown Zellerbach Chemical Products Division, spectro grade 40823) water content less than 0.02%.

Nitrogen (Matheson Co., Inc., prepurified) passed through Anhydrone drying trains before entering the electrolysis cell.

o-*Nitrophenol,* p-*nitrophenol, and* p-*nitrobenzoic acid* (Matheson, Coleman and Bell Division, The Matheson Co., Inc., one degree melting point range).

o-*Nitrobenzoic acid,* m-*nitrophenol,* m-*nitrobenzoic acid,* p-*nitroanisole,* p-*nitrobenzaldehyde, 3-nitrophthalic acid, and nitroterephthalic acid* (Eastman Kodak Co., white label). Where necessary these compounds were recrystallized from ethanol–water mixtures until the nitro compounds gave approximately a one-degree melting point range.

m-*Nitrobenzoic acid sodium salt and* p-*nitrophenol sodium salt* (Eastman Kodak Co., white label) used without further purification.

Procedure for controlled potential coulometry

At the beginning of a series of determinations, the counter and reference electrode side-cells of the electrolysis cell (Fig. 1) were charged with fresh DMSO–electrolyte solvent. The solution level of the side-cells was maintained just above the level of the solution in the working compartment. Both side-cells were deaerated for 10 min with nitrogen. DMSO–electrolyte solvent (8 ml) was added to the working electrode compartment. The magnetic stirrer was activated and the solution was deaerated with nitrogen for 5 min. The faradaic reducible impurities in the 8.0 ml of DMSO–electrolyte solvent were determined coulometrically. The controlled potential

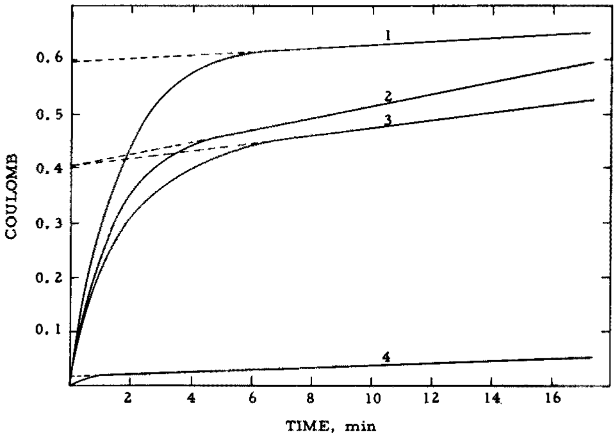


Fig. 2. Typical chronocoulograms. The results represent the determination of 1.00 μmole of the nitro compound in 8.0 ml of dimethylsulfoxide containing 0.5 *M* lithium chloride at an applied potential of −1.6 V *vs.* S.C.E. 1, *o*-nitrophenol; 2, *p*-nitrophenol; 3, *p*-nitrobenzoic acid; 4, solvent system.

coulometric reduction was made at the same applied potential as that required for the nitro compound which was to be determined. An example of a chronocoulogram obtained from the recorder readout of the instrument integrated current is given in Fig. 2, curve 4. The extrapolation back to zero time gives the quantity of electricity due to the solvent impurities that are reducible at this applied potential. The DMSO–electrolyte solvent was removed from the electrolysis cell by means of a vacuum liquid trap which was attached to the nitrogen deaeration capillary side-arm. This capillary was attached at the bottom of the cell so that the solution was removed, leaving the mercury electrode in the cell. An 8.0-ml DMSO–electrolyte solvent sample which contained 1.00 μmole of the nitro compound was then added to the working compartment, and the solution was deaerated for 5 min. After deaeration, the nitro compound was determined coulometrically at the same applied potential as the solvent faradaic reducible impurities. Examples of chronocoulograms obtained for the reduction of some of the nitro compounds are given in Fig. 2. The quantity of electricity given by the reduction of the nitro compound was determined by extrapolating back to zero time and subtracting from this value the value found for the faradaic reducible impurities in 8.0 ml of DMSO–electrolyte solvent.

Pre-electrolysis is required for n-value determinations. This eliminates the necessity of correcting for the quantity of electricity due to the solvent faradaic reducible impurities. After deaeration, the 8.0 ml of DMSO–electrolyte solvent was pre-electrolyzed at the applied potential required for determination of the nitro compound until a continuous faradaic background current was obtained. This continuous faradaic current corresponds to the final slope of curve 4 in Fig. 2. After the pre-electrolysis, a 0.100-ml sample of DMSO–electrolyte solvent containing 1.00 μmole of the nitro compound was added by syringe. This was achieved by placing the needle of the syringe through one of the nitrogen outlet capillaries. One minute was allowed for nitrogen deaeration, and then the nitro compound was determined at the same applied potential as the pre-electrolysis. The quantity of electricity necessary for the reduction of the nitro compound was obtained from the resulting chronocoulogram by extrapolation to zero time. The DMSO–electrolyte solvent containing the reduced species was then removed by vacuum and the cell rinsed with two 10-ml volumes of fresh solvent.

Procedure for controlled potential polarography

The polarographic determinations were made in the same cell, used for the controlled potential coulometric determinations. The only changes were that the magnetic stirring bar was removed and the glass stopper of the working cell was replaced with the DME assembly. The side-cells were filled to just above the frits with DMSO–electrolyte solvent, and deaerated with nitrogen for 10 min. Approximately 10 ml of the sample solution was added to the working cell from a 10-ml syringe by placing the needle through one of the nitrogen capillary outlets. The sample solution was deaerated for 15 min with nitrogen which had previously passed through DMSO–electrolyte solvent. During the determination, the nitrogen stream was passed over the sample by means of the upper capillary nitrogen inlet. The 12.3 ml of mercury comprising the coulometric working electrode was left in the cell so that the sample solution could be removed by vacuum through the nitrogen deaeration capillary side-arm after completion of the determination. The cell was rinsed with 2 consecutive 10-ml portions of DMSO–electrolyte solvent.

RESULTS AND DISCUSSION

Controlled potential polarography

The results from the controlled potential polarographic determinations of several substituted nitrobenzene compounds in DMSO are shown in Figs. 3–5. The polarograms were determined from millimolar solutions of the nitro compounds. The supporting electrolyte consisted of 0.5 *M* LiCl. The polarograms were taken as the envelope of the maximum current. A polarogram of the residual current given by the DMSO–electrolyte solvent is shown in Fig. 4, curve 5.

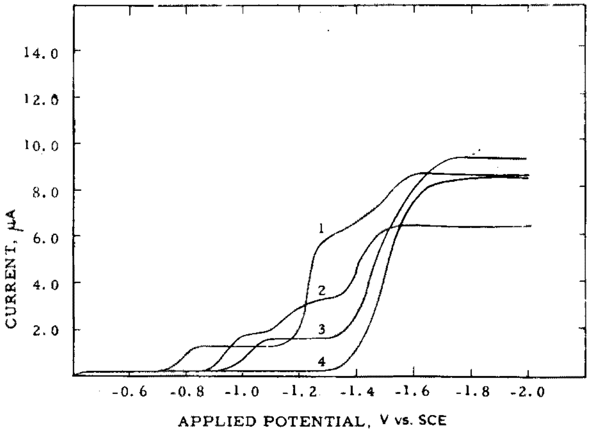


Fig. 3. Polarograms of dimethylsulfoxide solutions, which are 1.0 m*M* in nitrophenol and 0.5 *M* in lithium chloride. 1, *o*-nitrophenol; 2, *m*-nitrophenol; 3, *p*-nitrophenol; 4, *p*-nitrophenol sodium salt.

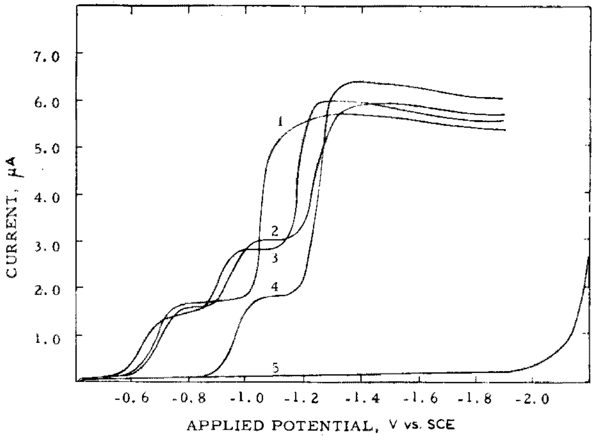


Fig. 4. Polarograms of dimethylsulfoxide solutions, which are 1.0 m*M* in nitrobenzoic acid and 0.5 *M* in lithium chloride. 1, *o*-nitrobenzoic acid; 2, *m*-nitrobenzoic acid; 3, *p*-nitrobenzoic acid; 4, *m*-nitrobenzoic acid sodium salt; 5, residual.

It was found experimentally that the rate of scan, the concentration of the electroactive species, and the drop time are significant factors in obtaining well-defined polarograms in DMSO. If the scan rate is greater than 0.1 V/min, large maxima are observed. Quite often these maxima appear on the rising portion of the wave. Very erratic drop times and drop growths are observed when the concentration of the nitro compound exceeds $5 \cdot 10^{-3}$ *M*. The drop time of 8.35 sec at open circuit, which is somewhat longer than employed in aqueous systems, is necessary because of the rapid rate at which the drop time decreases during the polarographic determination. Erratic drop times are observed when the drop time is less than about 4 sec.

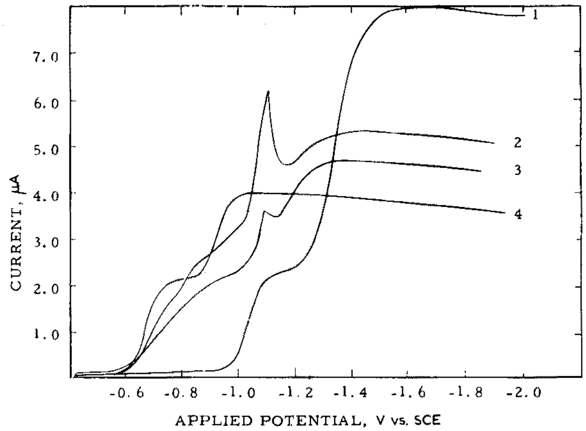


Fig. 5. Polarograms of dimethylsulfoxide solutions, which are 1.0 m*M* in nitro compound and 0.5 *M* in lithium chloride. 1, *p*-nitroanisole; 2, 3-nitrophthalic acid; 3, nitroterephthalic acid; 4, *p*-nitrobenzaldehyde.

TABLE I

COULOMETRIC *n*-VALUES FOR THE REDUCTION OF SUBSTITUTED NITROBENZENE COMPOUNDS IN DIMETHYLSULFOXIDE

Nitro compound	*Experimental n-value*	*Average deviation*[a]	*Applied potential (V) vs. S.C.E.*
o-Nitrophenol	5.97	±0.02	−1.6
m-Nitrophenol	4.01	±0.04	−1.6
p-Nitrophenol	6.06	±0.06	−1.8
p-Nitrophenol, sodium salt	6.09	±0.10	−1.8
p-Nitroanisole	4.02	±0.04	−1.6
o-Nitrobenzoic acid	3.99	±0.04	—1.4
p-Nitrobenzoic acid	4.12	±0.04	—1.4
m-Nitrobenzoic acid	3.97	±0.05	—1.4
m-Nitrobenzoic acid, sodium salt	4.08	±0.05	−1.4
Nitroterephthalic acid	3.97	±0.05	—1.4
3-Nitrophthalic acid	4.01	±0.05	−1.4

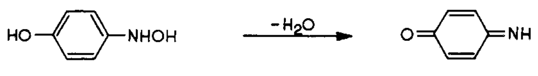
[a] The average deviations are based on at least 6 *n*-value determinations.

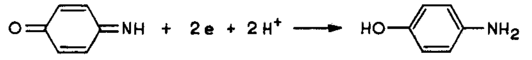
Controlled potential coulometry

n-Value determinations. The results for the controlled potential coulometric determination of the *n*-values for the reduction of several substituted nitrobenzenes are given in Table I. The determinations were made from the reduction of 1.00 μmole of the nitro compound in 8.0 ml of DMSO–electrolyte solvent. The choice of applied potential was made on the basis of the polarogram produced by the nitro compound (see Figs. 3–5). The n-values were calculated by the use of the following equation

$$n = \frac{\text{coulombs found}}{\text{moles taken} \cdot 96493 \text{ coul./eq.}} \tag{1}$$

The reduction of 3-nitrophthalic acid, nitroterephthalic acid, the isomers of nitrobenzoic acid, *p*-nitroanisole, and *m*-nitrophenol yields n-values of 4, indicating that these nitro compounds are reduced to the corresponding hydroxylamine compounds; *o*- and *p*-nitrophenol yield n-values of 6, indicating that these nitrophenols are reduced to the corresponding aminophenols. This further 2-electron reduction is probably due to a chemical reaction which produces the corresponding benzoquinoneimine, which in turn is reduced to the corresponding aminophenol.


(2)


(3)

o-Nitrophenol probably follows the same reduction process, and involves the formation of *o*-benzoquinoneimine. The n-values for the reduction of the sodium salts of *m*-nitrobenzoic acid and *p*-nitrophenol are 4 and 6, respectively, which agree with the n-values given for the reduction of the corresponding acids. *p*-Nitrobenzaldehyde gave what appeared to be a n-value of 2, but a quantitative determination was considered questionable because of a large background current which slowly decreased with time.

The analytical significance of the results given in Table I is that integral values of 4 or 6, depending on the nitro compound being determined, can be used for n in eqn. (1). The precision in the measurement would then apply to the determination of the quantity of the nitro compound. This means that under these conditions 1 μmole of the nitro compound can be determined with an approximate precision of $\pm 1\%$.

Background. The background quantity of electricity consumed in a controlled potential coulometric analysis may be defined as the difference between the theoretical and the actual quantity consumed. This difference is considered to arise from the passage of currents that can be classified as charging, impurity faradaic, continuous faradaic, kinetic, and induced. These phenomena are discussed in detail by MEITES AND MOROS[12]. All 5 types of background quantities of electricity are observed in the controlled potential coulometric reduction of substituted nitrobenzene compounds in DMSO–electrolyte solvent.

For the cell and conditions used in this work, the charging background current is insignificant.

The impurity faradaic quantity of electricity is consumed by the reduction of trace impurities. It is determined by the extrapolation to zero time of a chronocoulogram of the DMSO–electrolyte solvent. An example of this determination is shown by chronocoulogram 4 in Fig. 2. Eight milliliters of DMSO–electrolyte solvent typically gave impurity faradaic backgrounds of from 0.01 to 0.02 coulomb, depending on the applied potential.

The continuous faradaic quantity of electricity is consumed continuously by the reduction of lithium ions. The continuous faradaic current is determined from the slope of the plateau of a chronocoulogram of the DMSO–electrolyte solvent (see Fig. 2, chronocoulogram 4). This background is dependent on the area of the working electrode and the applied potential. Typical values were 17.7 and 42.5 μA at applied potentials of -1.4 and -1.8 V, respectively.

The kinetic quantity of electricity is consumed by the reduction of an electroactive species which is produced by a slow chemical reaction of the reduced product with the solvent or some constituent in the solvent. The kinetic background current is dependent on the concentration of the reduced product and increases during the reduction. The continuous kinetic current, after complete reduction of the nitro compound, is determined by the increase in slope of the plateau of a chronocoulogram of the nitro compound compared to a chronocoulogram of the DMSO–electrolyte solvent, all other parameters being the same. It was found that the continuous kinetic background for the nitro compounds is independent of applied potential and stirring rate. The process that occurs probably involves the followings steps:

$$\mathrm{O} + \mathrm{ne} \rightarrow \mathrm{R} \tag{1}$$

$$\mathrm{R} + \mathrm{mS} \rightarrow \mathrm{O'} + \mathrm{mS'} \tag{2}$$

$$\mathrm{O'} + \mathrm{me} \rightarrow \mathrm{R} \tag{3}$$

where (2) is the rate-determining step, O is the nitro compound, and R is the corresponding reduced compound. O may or may not be the original oxidized state, and S may be DMSO or hydrogen ion.

The magnitude of the continuous kinetic current is different for different substituted nitrobenzenes, and also varies among different isomers. This variation and the increase in continuous kinetic current with increase in the cell concentration of the reduced product is given in Table II. The cell concentration of the reduced product is assumed to correspond to the initial cell concentration of the nitro compound. The *ortho* isomers of nitrophenol and nitrobenzoic acid give smaller continuous kinetic background currents than those given by the corresponding *p*- and *m*- nitro compounds.

TABLE II

EFFECT OF THE INITIAL CELL CONCENTRATION ON THE CONTINUOUS KINETIC BACKGROUND CURRENT

Nitro compound	*Background current (µA)* *Initial cell concentration*			
	0.125 mM	*0.250 mM*	*0.375 mM*	*0.500 mM*
o-Nitrophenol	12	12	12	19
m-Nitrophenol	23	38	49	60
p-Nitrophenol	20	50	79	162
p-Nitrophenol, sodium salt	15	42	57	84
p-Nitroanisole	135	195	212	227
o-Nitrobenzoic acid	19	27	38	42
p-Nitrobenzoic acid	88	110	125	144
m-Nitrobenzoic acid	79	105	124	143
m-Nitrobenzoic acid, sodium salt	76	121	140	162
Nitroterephthalic acid	27	34	56	68
3-Nitrophthalic acid	27	42	53	68

This may be caused by a steric hindrance in the case of the *ortho* isomers, which causes a slower chemical regeneration of the electroactive species.

The induced quantity of electricity is consumed by a secondary reduction which is induced by the reduction of the nitro compound, and is dependent on the rate of the latter. It is determined by the increase in total quantity of electricity consumed over the theoretical quantity required for reduction of the nitro compound after the other background quantities of electricity have been accounted for. The effect of rate of reduction of different nitro compounds on the induced background is given in Table III. The increase in rate of reduction is achieved by increase in initial cell concentration, all other parameters being the same. Different values of induced background are found for different nitro compounds and, in the case of nitrobenzoic acid and of nitrophenol, the *ortho* isomers show the smallest and the *para* isomers the largest effect. The most important observation, however, is that no induced background is found at the lower rates of reduction.

TABLE III

EFFECT OF THE INITIAL CELL CONCENTRATION ON THE INDUCED BACKGROUND

Nitro compound	*Induced background (coulomb)* *Initial cell concentration*[a]			
	0.125 mM	*0.250 mM*	*0.375 mM*	*0.500 mM*
o-Nitrophenol			0.017	0.069
m-Nitrophenol	0.003	0.014	0.027	0.139
p-Nitrophenol		0.127	0.266	0.428
p-Nitrophenol, sodium salt	0.004	0.062	0.054	0.135
p-Nitroanisole		0.007	0.031	0.101
o-Nitrobenzoic acid				0.019
p-Nitrobenzoic acid	0.007	0.019	0.073	0.134
m-Nitrobenzoic acid		0.007	0.042	0.116
m-Nitrobenzoic acid, sodium salt		0.023	0.104	0.205
Nitroterephthalic acid			0.024	0.069
3-Nitrophthalic acid		0.024	0.062	0.093

[a] Cell solution volumes are 8.00 ml.

The kinetic and induced backgrounds cannot be completely corrected for by extrapolation of the chronocoulograms to zero time, which gives an overcorrection in the case of the kinetic background and an undercorrection in the case of the induced background. These errors were, however, decreased by careful choice of electrolysis conditions. The electrolysis cell parameters were adjusted so that the time necessary for complete reduction was as short as possible. This shortened the extrapolation and thus decreased the error due to the kinetic background. The initial cell concentration of the nitro compound was kept low enough to avoid any detectable induced background. The lower initial cell concentration also decreased the error from kinetic background.

CONCLUSIONS

It is possible to obtain well-defined controlled potential polarograms of the isomers of nitrophenol and nitrobenzoic acid in dimethylsulfoxide, provided that the scan rate is not greater than 0.1 V/min, the concentration of the nitro compound is less than $5 \cdot 10^{-3}$ M, and the initial drop time is not less than 8 sec.

One μmole of nitro compound can be determined by controlled potential coulometry from cell concentrations of approximately 10^{-4} M in nitro compound in dimethylsulfoxide solution, with an error of approximately ±1%. The nitrobenzoic acids and *m*-nitrophenol give a 4-electron reduction, which indicates that these compounds are reduced to the corresponding hydroxylaminobenzoic acids; *o*- and *p*-nitrophenol both give a 6-electron reduction, which indicates that the corresponding hydroxylaminophenol undergoes a chemical reaction to give the corresponding benzoquinoneimine which in turn is reduced to the aminophenol.

The nitrophenols and nitrobenzoic acids give both kinetic and induced backgrounds when determined by controlled potential coulometry. The *ortho* isomers give smaller backgrounds than do the *meta* and *para* isomers. This may be caused by a steric hindrance in the case of the *ortho* isomers. The backgrounds can be decreased to insignificant values by proper choice of the electrolysis conditions, of which the most important are a shorter electrolysis time and lower initial cell concentrations.

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SUMMARY

The *n*-values for the reduction of the isomers of nitrophenol and nitrobenzoic acid and for several other nitro compounds were determined in dimethylsulfoxide by controlled potential coulometry. A procedure is given in which one μmole of nitro compound may be determined in less than 8 min with an error of approximately ±1%. The associated background currents were quantitatively evaluated, and electrolysis conditions for their minimization were discussed. A procedure and results are given for the controlled potential polarography of these nitro compounds in dimethylsulfoxide.

RÉSUMÉ

Les valeurs *n* de réduction des isomères du nitrophénol, de l'acide nitrobenzoïque et de plusieurs autres nitrocomposés ont été déterminées dans la diméthylsulfoxide, par coulométrie à potentiel contrôlé. Un procédé est décrit, permettant de doser une μmole de nitrocomposé, en moins de 8 min avec une erreur d'environ ±1%. Une méthode polarographique à potentiel contrôlé est également décrite pour le dosage de ces nitrocomposés.

ZUSAMMENFASSUNG

Die *n*-Werte für die Reduktion der Isomeren des Nitrobenzols, der Nitrobenzosäure und verschiedener anderer Nitroverbindungen wurden in Dimethylsulfoxid mit der Coulometrie mit kontrolliertem Potential bestimmt. Es wird ein

Verfahren angegeben, in der ein μMol Nitroverbindung in weniger als 8 Min mit einem Fehler von etwa ±1% bestimmt werden kann. Die Untergrundströme wurden quantitativ ermittelt und die Elektrolysebedingungen für deren Verringerung diskutiert.

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THE POLAROGRAPHY OF MOLYBDENUM, TITANIUM AND NIOBIUM IN SOLUTIONS OF ORGANIC ACIDS

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Polarography is an attractive analytical technique if it can be applied without any preliminary separations. With this in mind, it was decided to investigate further the polarographic reduction of molybdenum(VI), titanium(IV) and niobium(V) in order to develop rapid polarographic methods for the determination of these elements in niobium, tantalum and tungsten base alloys.

Recently HEADRIDGE AND HUBBARD[1] reported that molybdenum can be determined in certain niobium base alloys by a simple polarographic method using 0.5 M hydrofluoric acid–0.5 M sulphuric acid as base electrolyte. That method does, however, require a Teflon dropping mercury electrode and these are not commercially available. In addition it would be advantageous to determine not only molybdenum but also titanium and niobium in such high-temperature alloys, and this is not possible with the fluoride base electrolyte. It was proposed to dissolve the alloys in a mixture of hydrofluoric and nitric acids, add sulphuric acid, heat to fumes of sulphur trioxide, and then dilute with a solution of an organic acid to give the base electrolyte for polarography, since the organic acids form soluble complexes with niobium, tungsten, etc.

Previous polarographic investigations on niobium(V) in solutions of citric acid[2,3], EDTA[2,3], and tartaric, oxalic, lactic, malic and gluconic acids[2] have been reported, and the polarography of titanium(IV) in EDTA solution has been studied[4]. However, in these papers, little information is given on interfering elements and further investigations on these organic acid supporting electrolytes are reported in this paper.

EXPERIMENTAL

Apparatus

A Sargent model XV polarograph was used. A Meites-type H-cell was employed with a solution compartment for *ca.* 40 ml of solution. This compartment was connected to a saturated calomel electrode by means of an agar-saturated potassium chloride bridge.

Reagents

Citric, lactic, hydrofluoric, nitric and sulphuric acids, sodium hydroxide, thorium nitrate and the disodium salt of EDTA were all of analytical reagent grade. Other organic acids were of the purest grade available.

Standard molybdenum(VI) solution. A suitable weight of Specpure molybdenum trioxide (Johnson, Matthey and Co. Ltd.) was dissolved in boiling ammonia solution, s.g. 0.88, the solution was evaporated to dryness, and the residue dissolved in a citric–sulphuric acid mixture such that, on dilution, the final concentrations were 1 *M* citric acid and 0.1 *M* sulphuric acid. Less concentrated solutions of molybdenum were prepared from this solution.

Standard niobium(V) solution. A suitable weight of Specpure niobium pentoxide was dissolved in hot concentrated hydrofluoric acid. A calculated volume of concentrated sulphuric acid was added and the solution heated to fumes of sulphur trioxide. The cooled solution was added to an aqueous solution of citric acid, such that, on dilution, the final concentrations were 1 *M* citric acid and 0.5 *M* sulphuric acid.

Standard titanium(IV) solution. This was prepared from Specpure titanium metal in a similar manner to that used for the niobium(V) solution, except that a hot mixture of concentrated hydrofluoric and nitric acids was used to dissolve the metal.

Standard tungsten(VI) solution. This was prepared from Specpure tungsten trioxide in a similar manner to that used for niobium(V) solution, except that the tungsten trioxide was first dissolved in boiling ammonia solution, the solution evaporated to dryness and the residue dissolved in hot concentrated hydrofluoric acid before the addition of concentrated sulphuric acid.

Solutions of molybdenum, niobium and titanium in other organic acids were prepared in a similar manner.

RESULTS AND DISCUSSION

EDTA

A base electrolyte containing 0.05 *M* EDTA and 0.25–0.5 *M* sulphuric acid adjusted to pH 3.6 was found to be satisfactory for the determination of both titanium(IV) and niobium(V). At this pH the half-wave potentials are respectively −0.32 V and −0.65 V *vs.* S.C.E., which is in good agreement with previous studies[2,4]. Unfortunately, at this pH, molybdenum(VI) interferes by producing 2 waves covering the range of −0.34 V to −0.85 V *vs.* S.C.E. This is in accord with the findings of PECSOK AND SAWYER[5]. No EDTA base electrolyte could be found for the analysis of a mixture of molybdenum, titanium and niobium.

Citric acid

Investigations made for molybdenum(VI) and niobium(V) in various base electrolytes containing citric and sulphuric acids and their salts, in conjunction with the information given by KENNEDY[3], indicate that a mixture of molybdenum(VI) and niobium(V) is best determined in a citric acid base electrolyte of pH 2.4–3.6. The polarography of titanium(IV) in citric acid base electrolytes has been studied by PECSOK[6] and VANDERBOSCH[7] and their results combined with those above, would suggest that a mixture of molybdenum(VI), titanium(IV) and niobium(V) could be determined polarographically with 0.5 *M* citric acid in the pH range 2.4–3.6, the first wave being due to the reduction of molybdenum(VI) to molybdenum(V), the second to molybdenum(V) to molybdenum(III) plus titanium(IV) to titanium(III), and the third to niobium(V) to niobium(IV). The titanium would be determined by subtracting $2 \times \mathrm{Mo}(6 \rightarrow 5)$ from $\mathrm{Mo}(5 \rightarrow 3) + \mathrm{Ti}(4 \rightarrow 3)$.

In practice, however, no satisfactory wave could be obtained for titanium(IV) at pH 2.4–3.6 in the presence of citric and sulphuric acids. The sulphate ion was obviously interfering. For example, at pH 2.45 (1 *M* citric acid–0.5 *M* sulphuric acid) the titanium wave started at -0.60 V *vs.* S.C.E. with the diffusion current increasing rapidly as for a reversible reduction wave. But, then, the slope decreased and the plateau was not reached until the potential was -1.15 V *vs.* S.C.E. The wave probably consisted of 2 waves, a reversible reduction wave for a titanium–citrate complex surmounted by an irreversible wave for a titanium–sulphate complex.

It was, therefore, decided to try to suppress the interfering effect of sulphate ions by adding an excess of thorium nitrate to the solution. Thorium nitrate is a suitable complexing agent for sulphate[8] and good titanium reduction waves were found in base electrolytes consisting of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate in the pH range 2.0–3.5. The effect of thorium nitrate on the titanium wave is illustrated in Fig. 1 where 2 polarograms are recorded for solutions of pH 2.0. Polarographic data for molybdenum(VI), titanium(IV) and niobium(V) in the above base electrolyte adjusted to pH 3.5 are given in Table I.

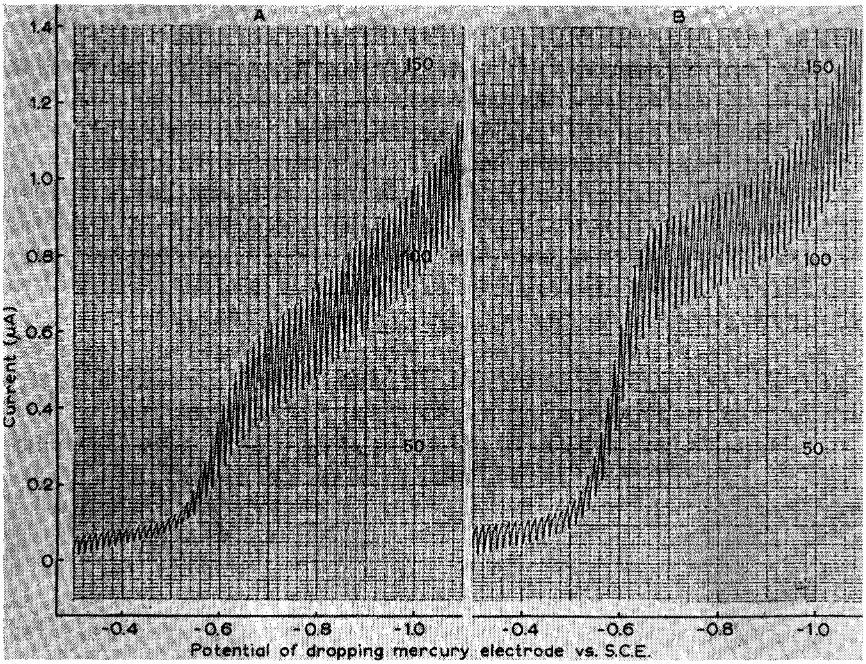

Fig. 1. Polarograms for $2.5 \cdot 10^{-4}$ *M* solutions of titanium(IV) in base electrolytes of (A) 0.5 *M* citric acid—0.025 *M* sulphuric acid adjusted to pH 2.0, and (B) 0.5 *M* citric acid—0.025 *M* sulphuric acid—0.05 *M* thorium nitrate adjusted to pH 2.0.

Unfortunately, the addition of thorium nitrate to the base electrolyte caused the hydrogen ion wave to occur earlier to the extent of about 0.1 V and the niobium(V) wave was no longer separated sufficiently from the hydrogen ion wave to allow a precise determination of niobium by d.c. polarography. The thorium nitrate had no effect on the molybdenum waves.

A method is, however, available for the determination of molybdenum and titanium in the presence of niobium.

In 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5, the diffusion current was directly proportional to the molybdenum(VI) concentration in the range $1.5 \cdot 10^{-5}$–$1.5 \cdot 10^{-4}$ *M*. In this range the standard deviation of the error in the diffusion current was 0.0025 μA, which corresponds to a relative standard deviation of 0.6% at a molybdenum concentration of $1.5 \cdot 10^{-4}$ *M*.

TABLE I

POLAROGRAPHIC DATA FOR MOLYBDENUM(VI), TITANIUM(IV) AND NIOBIUM(V) IN 0.5 *M* CITRIC ACID —0.025 *M* SULPHURIC ACID—0.05 *M* THORIUM NITRATE ADJUSTED TO pH 3.5

Species	$E_{\frac{1}{2}}$ *vs. S.C.E.* *(V)*	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ *(mV)*
Molybdenum(VI)	−0.273	96
	−0.635	72
Titanium(IV)	−0.698	69
Niobium(V)	Approx. −1.00	Approx. 80

Diffusion currents were measured on the plateau of the first molybdenum wave at a potential of −0.48 V *vs.* S.C.E. The error in diffusion current is expressed by i_d (measured)−i_d (calculated) where the values of i_d (calculated) are points exactly on the straight line calibration graph of diffusion current *vs.* concentration.

With regard to titanium(IV) in the same base electrolyte, the diffusion current was again directly proportional to titanium concentration in the range $5 \cdot 10^{-5}$–$5 \cdot 10^{-4}$ *M*. In this range the standard deviation of the error in the diffusion current was 0.0095 μA, which corresponds to a relative standard deviation of 0.9% at a titanium concentration of $5 \cdot 10^{-4}$ *M*. Diffusion currents were measured on the plateau of the titanium wave at a potential of −0.85 V *vs.* S.C.E.

The diffusion current constant for molybdenum(VI) in the above base electrolyte was 1.21, the rate of flow of mercury (*m*) being 2.309 mg/sec and the drop time (*t*) being 3.871 sec. The diffusion constant for titanium(IV) was 0.97 with *m* at 2.310 mg/sec and *t* at 3.798 sec. Maximum currents were used in these calculations.

A method involving the base electrolyte 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5 was then developed and applied to the determination of molybdenum in a niobium base alloy, which contained no titanium. The method is outlined below. The molybdenum content of the alloy (nominal composition 15% tungsten, 5% molybdenum and 1% zirconium) was found by the polarographic method to be 4.63% with a standard deviation of 0.09%. The molybdenum content of the alloy determined spectrophotometrically using thiocyanate[9] was 4.65%.

The precision of this determination is satisfactory but would have been even better with a more sensitive polarograph. It was not possible to acquire suitable alloys for evaluating the method for the determination of titanium, and molybdenum plus titanium in niobium base alloys, but there seems no reason why titanium could not be determined. With molybdenum present, titanium could not, of course, be determined as precisely as in its absence, since for solutions containing both molybdenum and titanium, the diffusion current for titanium is obtained by subtraction.

Tungsten(VI), tantalum and zirconium are reduced well after the titanium wave and do not interfere with the determination of molybdenum and titanium. More than trace amounts of iron(III) interfere with the determination of molybdenum(VI) using the first wave. The reduction wave for chromium(III) occurs well after the first molybdenum wave but interferes with the determination of titanium(IV). There is no interference from nickel.

Method for the determination of molybdenum in niobium base alloys

Dissolve about 200 mg of alloy, accurately weighed, in 5 ml of concentrated nitric acid plus 10 ml of concentrated hydrofluoric acid in a platinum crucible. Add 2.77 ml of concentrated sulphuric acid from a burette and heat the solution to fumes of sulphur trioxide. Add the contents of the crucible to *ca.* 50 ml of water containing 21.02 g of citric acid monohydrate crystals in a beaker and dilute the solution to 100 ml in a graduated flask.

Pipette 5 ml of the solution into a beaker and add 45 ml of 1 *M* citric acid solution and 30 ml of water. Adjust the pH to within the range 2.0–3.0 with 10 *M* sodium hydroxide solution and add 2.94 g of thorium nitrate hexahydrate crystals. Stir to dissolve the crystals, add sodium hydroxide solution until the pH is exactly 3.5 and dilute the solution to 100 ml in a graduated flask.

Place approximately 40 ml of this solution in the polarographic cell and deoxygenate by bubbling oxygen-free nitrogen through it for 10 min. Record a polarogram from 0 to -1.0 V *vs.* S.C.E. Measure the diffusion current for the first molybdenum wave at an applied potential of -0.48 V *vs.* S.C.E. and read the concentration of molybdenum in the solution from a calibration graph prepared with standard solutions of molybdenum examined polarographically under the same conditions as for the alloy.

(For the alloy, the calibration graph mentioned above, for verification that the diffusion current was directly proportional to concentration, was used.)

Other organic acids

Polarograms for base electrolytes containing lactic or glycollic acid were un satisfactory since both acids obviously contained reducible impurities. No further work was done with these.

With gluconic acid, a good reduction wave for niobium(V), $E_{\frac{1}{2}} = -1.04$ V *vs.* S.C.E., was obtained in the base electrolyte, 0.3 *M* gluconic acid–0.5 *M* sulphuric acid adjusted to pH 4.3. In this base electrolyte, titanium(IV) produced a wave, $E_{\frac{1}{2}} = -0.99$ V *vs.* S.C.E., but the upper part of the wave was drawn out, indicating that sulphate was again having an undesirable effect. Under the same conditions, molybdenum(VI) produced 3 overlapping reduction waves with half-wave potentials of approximately -0.47, -0.60 and -0.80 V *vs.* S.C.E.

It was therefore concluded that none of the other organic acids which were examined, was likely to be as satisfactory as citric acid as base electrolyte for the polarographic determination of molybdenum and titanium in the presence of niobium.

CONCLUSIONS

Although the object of this study, namely the development of a polarographic method for the simultaneous determination of molybdenum, titanium and niobium in alloys containing these elements and zirconium, tantalum and tungsten was not achieved, it was shown that a base electrolyte of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate adjusted to pH 3.5 should be suitable for the determination of molybdenum and titanium in niobium base alloys. This base electrolyte should also be satisfactory for the determination of molybdenum and titanium in tungsten base and tantalum base alloys. In the absence of titanium, the thorium nitrate can be omitted and a base electrolyte of 1 *M* citric acid–0.5 *M* sulphuric acid adjusted to pH 2.4–3.6 is suitable for the determination of both molybdenum and niobium.

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SUMMARY

Further work on the polarographic reduction of molybdenum(VI), niobium(V) and titanium(IV) in base electrolytes containing organic acids is reported. A base electrolyte of 0.5 *M* citric acid–0.025 *M* sulphuric acid–0.05 *M* thorium nitrate proved suitable for the determination of molybdenum and titanium in the presence of niobium, tantalum, tungsten and zirconium. A direct polarographic method using this base electrolyte is described for the determination of molybdenum in a niobium base alloy.

RÉSUMÉ

Les auteurs ont examiné la réduction polarographique du molybdène(VI), du niobium(V) et du titane(IV) dans des électrolytes de base renfermant des acides organiques. Le mélange acide citrique 0.5 *M*, acide sulfurique 0.025 *M* et nitrate de thorium 0.05 *M* convient au dosage du molybdène et du titane, en présence de niobium, tantale, tungstène et zirconium. Une méthode est proposée pour le dosage du molybdène dans un alliage à base de niobium.

ZUSAMMENFASSUNG

Über die polarographische Reduktion von Molybdän(VI), Niob(V) und Titan(IV) in Grundelektrolyten, die organische Säuren enthalten, wird berichtet. Ein Grundelektrolyt mit 0.5 *M* Citronensäure, 0.025 *M* Schwefelsäure und 0.05 *M* Thoriumnitrat ist für die Bestimmung von Molybdän und Titan in Gegenwart von Niob, Tantal, Wolfram und Zirkonium geeignet. Es wird eine direkte polarographische Methode, die diesen Grundelektrolyten verwendet, für die Bestimmung von Molybdän in einer Nioblegierung beschrieben.

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ANALYSIS OF LEAD TITANATE–ZIRCONATE CERAMICS
DETERMINATION OF LEAD, TITANIUM AND NIOBIUM BY DIFFERENTIAL CATHODE-RAY POLAROGRAPHY

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The piezo-electric properties of lead titanate–lead zirconate solid–solution ceramics (P.Z.T.) have been studied by a number of workers[1,2], and it has been shown that improved electrical properties result from the addition of small amounts of tri- or pentavalent atoms[3] *e.g.* Nb or Nd.

In the past, the composition and reproducibility of such preparations have been assessed mainly by the measurement of physical and electrical properties. Other somewhat empirical, chemical tests have been applied to indicate the presence of uncombined constituents[4], *e.g.* uncombined lead oxide soluble in EDTA solutions and zirconium oxide insoluble in concentrated hydrochloric acid. In addition, however, precise determinations of total metal constituents are useful and analytical methods for lead, titanium, zirconium and niobium have been considered.

ROBINSON AND JOYCE[4] have applied spectrophotometric methods for the determination of lead and titanium in such materials and recently, a cation-exchange separation of zirconium and titanium followed by gravimetric analysis, has been described by DOSCH AND CONRAD[5].

High precision comparative polarography using the Differential Cathode-Ray Polarograph, as described by DAVIS AND SEABORN[6], and applied by SHALGOSKY AND WATLING[7] and others, appeared to provide a more direct and precise technique for such analyses. This paper describes the development of polarographic methods for the determination of lead, titanium and niobium in P.Z.T. ceramics; the determination of zirconium will be described later.

EXPERIMENTAL

In polarographic measurements all potentials are referred to the mercury pool anode.

In preliminary work aimed at the simultaneous determination of lead and titanium in P.Z.T. ceramics, 0.5 *M* oxalic acid supporting electrolyte was investigated. In this medium resolution of the two polarographic peaks was possible (peak potentials −0.55 and −0.72 V for titanium and lead respectively); using the comparative technique with suitable standards, a satisfactory precision was obtained. For lead–titanium ratios of greater than about 1:1, however, interference from lead in the determination of titanium became apparent, resulting in a considerable lowering in precision. Since this ratio is approximately 12:1 in P.Z.T. ceramics, this electrolyte was not investigated further. Clearly lead could be determined satisfactorily in this medium but the method offers no advantage over direct polarography in the hydrochloric acid solution used for dissolution of the ceramic. The determination of titanium in the presence of a large excess of lead thus necessitated either the application of a suitable separation technique or selection of a complexing electrolyte giving improved resolution of polarographic peaks. In a search for the latter it was found that EDTA solutions at pH 2–6 had been used both for the determination of titanium and niobium[7–10] and that the lead half-wave potential was considerably more negative than in oxalate solutions. Polarographic peaks for titanium, niobium and lead reductions were measured by cathode-ray polarography in acetate-buffered EDTA solutions and it was found that the peak potentials were pH dependent, at pH 4.0 being −0.44, −0.77 and −1.15 V respectively. While titanium and niobium could be determined satisfactorily in this medium, precise determination of lead using the comparative technique was precluded by the close proximity of the hydrogen ion reduction potential. Attempts to shift the lead potential to a more positive value by lowering the pH were unsuccessful since free EDTA precipitated below pH 2.5. Lead was therefore determined separately in 1 M hydrochloric acid. In this medium, although the half-wave potentials for lead and titanium were separated by 450 mV, some distortion of the lead peak resulted from the irreversibility of the titanium reduction. In order to obtain precise results by the comparative technique, it was necessary to compensate for this effect by addition of an equal quantity of titanium to the standard cell. A similar problem arose in the determination of niobium in EDTA at pH 4.0, where the 330-mV separation of the lead and niobium peaks was insufficient to resolve a satisfactory niobium wave in the presence of the 70-fold excess of lead. Compensation by the subtractive technique eliminated this problem; the comparative method was not applied in this case since high precision was not required at the levels of niobium present.

EXPERIMENTAL

Apparatus

Davis Differential Cathode-Ray Polarograph type A 1660, supplied by Southern Analytical Ltd., Camberley.

Reagents and standard solutions

All reagents used were Analytical Reagent grade. The nitrogen used contained less than 10 p.p.m. of oxygen.

Acetate buffer solution. Adjust the pH of a 2 M sodium acetate solution to 4.0 by addition of 6 M hydrochloric acid.

Standard lead solution (approx. 10 mg/g). Weigh out 1 g of "Specpure" lead, and dissolve in 6 M nitric acid. Add 10 ml of 72% perchloric acid, fume to remove the last traces of nitric acid, cool and dilute to approximately 100 g, weighed to 0.01 g, with water.

Standard titanium solution (approx. 2.5 mg/g). Weigh out 250 mg of "Specpure" titanium sponge and dissolve in 20 ml of 8 M hydrochloric acid adding concentrated nitric acid dropwise to obtain a clear titanium(IV) solution. Dilute to about 100 g with 4 M hydrochloric acid containing 2% (w/v) of sulphamic acid and weigh the solution to 0.01 g.

Standard niobium solution (approx. 400 µg/ml). Fuse 286 mg of "Specpure" niobium pentoxide with 10 g of fusion mixture in a platinum basin, dissolve the melt in hot water and dilute to 500 ml in a volumetric flask.

Lead solution for subtractive niobium determination (approx. 500 µg/ml). Dissolve 135 mg of lead oxide in 5 ml of concentrated hydrochloric acid and transfer to a 250-ml beaker, using 125 ml of 0.2 *M* EDTA (disodium salt) solution. Adjust the pH of the solution to 4.0 by dropwise addition of 7 *M* ammonia solution and add 10 ml of acetate buffer. Dilute to 250 ml with water.

Procedure

Grind the ceramic material finely in an agate mortar. Weigh accurately about 200 mg of the finely ground sample into a 5-ml glass centrifuge tube and add 4 ml of concentrated hydrochloric acid. Place the tube in a beaker of nearly boiling water and stir with a glass rod until no more solid dissolves. Material of near stoichiometric composition is freely soluble but a residue remains if uncombined oxides are present. Centrifuge and remove the supernate using a weighed 7-ml polythene ampoule with finely drawn-out tip. Add a further 1 ml of acid and repeat the extraction of the residue. Transfer the residue with the minimum of concentrated hydrochloric acid containing 2 drops of 40% hydrofluoric acid, to a small platinum dish. Add 1 ml of 72% perchloric acid, fume gently to half the initial volume and combine this solution with the original supernate in the polythene ampoule.

Determination of lead. Dispense a weighed portion of the above solution, containing about 5 mg of lead, into a 50-ml volumetric flask and dilute to volume with 1 *M* hydrochloric acid. Transfer about 3 ml of this solution to the left-hand polarographic cell and a portion of lead standard, containing an equal amount of titanium solution to that present in the sample, to the other cell. Arrange for the differential lead concentration to be not more than 5%. Deoxygenate by passing nitrogen through both solutions for at least 10 min and determine the lead concentration by the comparative technique using a starting potential of −0.20 V (peak potential −0.44 V).

Determination of titanium and niobium. Dispense a weighed portion of sample solution containing about 1 mg of titanium into a 50-ml beaker. Add 25 ml of 0.2 *M* EDTA (disodium salt) solution and without delay adjust the pH to 4.0 by dropwise addition of 7 *M* ammonium hydroxide. Some EDTA may precipitate at this stage but will redissolve later. Add 5 ml of 2 *M* acetate buffer, heat in a boiling water bath for 30 min, cool, and transfer to a 50-ml volumetric flask. Dilute to 50 ml with water.

To determine titanium, transfer about 3 ml of this solution to one polarographic cell, and a suitable quantity of titanium standard similarly treated to the other, and determine the titanium concentration by the comparative technique using a starting potential of −0.15 V (peak potential −0.44 V).

To determine niobium, use 3.0 ml of the above sample solution and determine the peak height for lead at −1.15 V by single cell measurement. Prepare a solution calculated to give the same lead peak height as the sample by suitable dilution of the 500-µg lead stock. Use 3.0 ml of this solution in the second polarographic cell for the subtractive determination of niobium using a starting potential of −0.50 V (peak potential −0.77 V) after refilling the first cell with sample solution. Some adjustment of the potential balance control is necessary in order to obtain a well defined peak. Determine the niobium concentration by the standard addition technique using

0.1 ml of a 100 μg/ml niobium solution prepared from the 500 μg/ml stock solution by dilution with EDTA, etc. as for the sample solution. Maintain equal lead concentrations in both cells by addition of 0.1 ml of 0.2 *M* EDTA to the compensating cell.

RESULTS

The overall precision of the methods described was assessed by carrying out 10 determinations of lead and titanium using separately dispensed weights of a stock solution prepared from a P.Z.T. ceramic material. Relative standard deviations of 0.11 and 0.31% respectively were obtained. The poorer precision for the titanium determination is due to the irreversibility of this reduction and the problems associated with applying the comparative technique to broad polarographic peaks. A precision of about 5% for the niobium determination is of the order expected for normal subtractive polarography corresponding to an overall precision of 0.05%.

TABLE I

ANALYSIS OF P.Z.T. CERAMICS

Sample	*Weight (%)*					
	PbO		TiO_2	ZrO_2	Nb_2O_5	*Total*
	Polarography	*C.P. coulometry*				
A	66.74		8.09	23.92	0.89	
	66.84		8.14	24.03	0.90	
			8.24	24.08		
	Mean 66.79	66.76	8.16	24.01	0.90	99.83
B	66.83		8.16	24.04	0.87	
	66.60		8.16	23.98	0.86	
			8.16		0.93	
	Mean 66.77	66.74	8.16	24.01	0.89	99.83
C	66.88		8.16	23.87	0.87	
	66.79		8.16	23.83	0.93	
			8.14		1.00	
	Mean 66.83	66.74	8.16	23.85	0.93	99.68

Table I shows typical results, expressed as percentages of oxides obtained on separate portions of P.Z.T. ceramics calcined at 900°. Also included are results for zirconium determinations by EDTA titration following separation of lead by mercury cathode electrolysis[11], and for lead by controlled potential coulometric reduction in 1 *M* perchloric acid at a mercury cathode[12].

It can be seen that results obtained for lead are in good agreement with those obtained by the more precise controlled potential coulometric technique (relative standard deviation 0.08%). The total summation of oxide constituents, although low by 0.2–0.3% is considered satisfactory in view of the complexity of the system and the likely contamination by variable quantities of silica during grinding operations.

SUMMARY

Differential cathode-ray polarography is applied to the direct determination of lead, titanium and niobium in lead titanate–zirconate solid–solution ceramics containing small additions of niobium pentoxide. Titanium and niobium are determined in buffered EDTA solution at pH 4.0 and lead in 1 *M* hydrochloric acid. With the high precision comparative technique, relative standard deviations of 0.11 % and 0.31% for lead and titanium respectively are obtained. Niobium is determined by the subtractive technique.

RÉSUMÉ

La polarographie différentielle à rayons cathodiques a été appliquée au dosage direct du plomb, du titane et du niobium dans des céramiques titanate–zirconate de plomb renfermant un peu de pentoxyde de niobium. Titane et niobium sont dosés en solution EDTA, tamponnée au pH 4; le plomb est dosé en milieu acide chlorhydrique 1 *M*.

ZUSAMMENFASSUNG

Die Differential-Kathodenstrahlpolarographie wird für die direkte Bestimmung von Blei, Titan und Niob in speziellen Keramiken verwendet, die kleine Zusätze von Niobpentoxid enthalten. Titan und Niob werden in gepufferter AeDTE-Lösung beim pH 4.0 und Blei in 1 *M* Salzsäure bestimmt. Bei der hohen Genauigkeit der Vergleichstechnik werden relative Standardabweichungen von 0.11% und 0.31% für Blei bzw. Titan erhalten. Niob wird mit der Subtraktionstechnik bestimmt.

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THE USE OF ARGON AS CARRIER GAS IN THE MICRODETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS

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The basic requirement of the conventional method for the direct microdetermination of oxygen in organic compounds[1,2] is the quantitative conversion into carbon monoxide of the oxygen-containing gases produced by the thermal decomposition of the sample. Incomplete conversion leads to low results for oxygen. Quantitative conversion depends on several factors, such as the temperature of the carbon layer, the activity of the carbon used, the sojourn time of the pyrolysis gases in the reaction zone, the nature of the pyrolysed compound and the type of the carrier gas employed. The temperature of the carbon layer must be kept constant at 1120°[2]. The carbon must have an amorphous structure and low ash content for a good reducing activity[3]. A suitable contact time is ensured by a sufficient volume of carbon and by a not too high flow rate of the carrier gas[4]. Several gaseous products result from the pyrolysis, each of which follows a different reduction scheme[4]. The conversion to carbon monoxide may be improved by some expedients, *e.g.* recycling the pyrolysis gases over the heated carbon[5], use of a prepyrolysis technique[6], mixing the sample with powdered carbon[1] or with cleaving agents[2,7-9], increase in the volume of the carbon layer[10,11]. The same results may be achieved by the replacement of the carrier gas, generally nitrogen, by argon[12].

Little information is available on the relationship between the nature of the carrier gas and the efficiency of the conversion to carbon monoxide. According to KIRSTEN[13], nitrogen physically hinders the contact between the pyrolysis gases and the carbon; this author carried out the reaction between the pyrolysis gases and the carbon *in vacuo* and found that the absence of nitrogen could be a determining factor in increasing the activity of the carbon. According to other authors[11,14], the nitrogen reacts with carbon and organic hydrogen, giving appreciable amounts of hydrogen cyanide. In SALZER's opinion[11], this reaction is favoured by high temperatures. BLOM AND KRAUS[12] stress the negative influence of this reaction on the carbon activity; the reaction appears to lead to a marked reduction of the number of active spots in the carbon. Replacement of nitrogen by argon, suggested by BLOM, would result in a lengthening of the period in which the carbon shows sufficient activity, but would also lead to unacceptable high blank values. Other authors have already used argon as carrier gas in the determination of oxygen in steel[15,16], of total inorganic oxygen[17] and of oxygen in organic compounds[18]. The interferences indicated by BLOM have also been reported by 2 of these authors[15,18].

The purposes of the present work were to determine the correct conditions, which would give freedom from blank values with argon as carrier gas, and to evaluate quantitatively any increase in the reductive power of the system *vs.* the oxygen-containing gases; a more rapid and reliable method of analysis might be based on these studies.

CORRECT OPERATING CONDITIONS

In order to use argon in the oxygen determination, 2 conditions are required: the argon must be purified so as to be completely oxygen-free, and side reactions between the pyrolysis products and the quartz of the tube must be avoided.

Commercially available argon (*e.g.* for welding) containing 10 p.p.m. of oxygen, was used. This gas was made completely oxygen-free by passing it through a layer of activated BTS catalyst (copper–magnesium silicate), at room temperature.

To detect the presence of oxygen in the effluent gas in blank tests, a titrimetric measurement was used, as described by UNTERZAUCHER[2], in which the blank is evaluated by the delay in appearance of free iodine in an aqueous solution of iodide. When the argon was purified with BTS catalyst, the blank test solution (boat without sample) remained colorless for a surprising length of time. Under these conditions a positive blank value was obtained only when determinations were prolonged for several hours. After 14 h during which 12.6 l of argon were passed over the heated carbon layer, the total amount of oxygen detected was only 0.008 mg (Table I).

TABLE I

DEPENDENCE OF BLANK VALUES ON THE TUBE LIFE

(Conditions: argon as carrier gas at flow rate of 15 ml/min; anhydroiodic acid at 116° and iodimetric measurement)

Duration of a determination	*Working life of the filling at 1120° (h)*	*Blank values (oxygen in mg)*
15 min	2	0.013
15 min	5	0.004
15 min	18	0.003
15 min	24	— (solution colorless for 2 min)
15 min	72	— (solution colorless for 15 min)
15 min	120	— (solution colorless for 7 min)
14 h	200	0.007
14 h	300	0.008
15 min	450	— (solution colorless for 22 min)
15 min	600	— (solution colorless for 6 min)
15 min	850	— (solution colorless for 10 min)

A variety of metallic substances, such as titanium sponge at 850°[19], uranium turnings at 620°[16], powdered magnesium at 600° and others, may be employed for the removal of oxygen from argon, but in order to avoid the formation of nitrides, the argon must then have a very small nitrogen content. Moreover, in our opinion a slight nitrogen content is harmless when argon is employed as the carrier gas and the use of BTS catalyst, which eliminates the oxygen alone without the need of heating devices, is more advantageous.

The pyrolysis of organic compounds in argon presents, according to BLOM

AND KRAUS[12], different characteristics from those obtained in nitrogen; the more reactive pyrolysis products attack the quartz liberating oxygen, which accounts for the positive blank values reported.

The quality of the quartz of the reaction tube appears to be a determining factor for the occurrence of this reaction. We used reaction tubes of extremely pure quartz, obtained directly by blowing from quartz crystals without the addition of flux. After an initial adjustment period, the quartz tube no longer showed any reactivity with the pyrolysis products; the blank value was zero even in the last hours of operation (see Table I). The quartz wool plug, placed in the reaction-zone inlet to hold the filling in place and acting also as graphite filter[11], was responsible for the initial low blank values; when the wool became impregnated with carbon coming from the decomposition of the first samples, its effect on the blank value rapidly disappeared.

In conclusion, zero blank values can be obtained as easily, and perhaps more easily, with argon as with nitrogen; the time in which a blank solution remains colorless corresponds to the normal stability to oxidation of the solution itself.

COMPARISON BETWEEN ARGON AND NITROGEN

The use of argon as carrier gas instead of nitrogen, leads to a greater efficiency of the system for conversion to carbon monoxide of the oxygen-containing pyrolytic gases.

An attempt was made quantitatively to estimate the influence of either argon or nitrogen on the yield, by measuring the reducing power of the system towards the oxygen-containing pyrolytic gases, using argon or nitrogen under the same experimental conditions. The literature does not report any measurements of this kind.

After several attempts, satisfactory results were obtained by the following procedure: several oxygen-containing substances (as shown in Table IV) were chosen and a series of analyses with increasing amounts of sample was carried out until the oxygen percentage became lower than the theoretical. It was thus possible to determine the maximum amount of substance quantitatively pyrolysable under normal conditions. The maximum amount still giving correct results could be calculated from the experimental data. For example, a series of analyses to ascertain the maximum amount of oxalic acid with argon as carrier gas is shown in Table II.

The following linear function $y = 107.3 - 1.8638x$, was obtained by plotting the percentage conversion of oxygen to carbon monoxide against the mg of substance. For $y = 100$, $x = 3.92$ (the standard error being 0.517), and the maximum determinable amount of oxalic acid was thus 3.92 mg.

The method is not suitable for substances with a low oxygen content because the necessity of employing relatively large amounts of organic compounds (>40 mg) leads to excessive deposition of carbon in the reaction tube; moreover volatile hydrocarbons are formed, which interfere by giving high oxygen values.

The gravimetric procedure had to be used in these tests; this assured quantitative results for the carbon dioxide formed from the oxidation of carbon monoxide, even in considerable amounts. The carbon monoxide was oxidised over a layer of commercial copper oxide, heated at 400°. Owing to its low oxidising power[20], copper oxide is most suitable for the selective oxidation of the carbon monoxide present in

TABLE II

EXAMPLE OF DETERMINATION OF MAXIMUM PYROLYSABLE AMOUNT GIVING QUANTITATIVE YIELD OF CO

Compound	*Sample weight (mg)*	*Conversion of oxygen to CO (%)*	*Oxygen (mg)*	
			Recovery	*Loss*
Oxalic acid, anhydrous (71.08 % oxygen)	2.175	100.2		
	3.217	99.8		
	3.710	100.1		
	3.934	99.60	2.785	0.011
	4.360	99.38	3.080	0.019
	4.572	99.07	3.220	0.030
	4.639	98.67	3.253	0.044
	5.005	98.26	3.492	0.062
	5.390	98.04	3.756	0.075
	6.098	95.52	4.140	0.194
	6.691	93.85	4.464	0.292
	7.056	93.76	4.702	0.313
	8.952	91.26	5.807	0.556

TABLE III

BLANK VALUES FROM OXYGEN-FREE SUBSTANCES

(Conditions: argon as carrier gas at flow rate of 15 ml/min; gravimetric measurement)

Compound	*Approx. weight of sample (mg)*	*Apparent oxygen amount (mg) Catalyst used*	
		CuO[a]	*Körbl catalyst*[a]
Anthracene	21.0	—	0.147
Anthracene	20.2	0.011	—
Indole	18.4	—	0.123
Indole	20.6	0.013	—
Stearyl chloride	19.5	—	0.380
Stearyl chloride	21.4	0.032	—
Hexachlorbenzene	20.05	—	0.095
Hexachlorbenzene	19.7	0.026	—
Hydrogen	0.320	—	0.071
Hydrogen	0.650	—	0.112
Hydrogen	1.700	—	0.302
Hydrogen	2.440	0.028	
Hydrogen	4.880	0.035	

[a] At 400°.

the effluent gases of the reaction tube. In Table III are shown the blank values obtained from combustion of significant amounts of substances not containing oxygen, using commercial copper oxide and Körbl catalyst[21] at 400°. The use of the latter catalyst led to exaggerated blank values, because of the high oxidising power. The copper oxide was daily activated with oxygen at 700° in order to reduce to a minimum the interference from metallic copper[13] on the effluent gases.

The maximum amounts of pyrolysable substances giving quantitative yields of carbon monoxide were determined on a group of compounds of various type — both organic and inorganic — which are listed in Table IV. A series of tests with argon

TABLE IV

SUMMARY OF ANALYTICAL DATA

Compound	*% Oxygen*	*Maximum amount giving correct results*				*Ratio*
		sample (mg)		*oxygen (mg)*		
		in nitrogen	*in argon*	*in nitrogen*	*in argon*	
Oxalic acid	71.08	1.7	3.9	1.208	2.772	1 : 2.29
$Pb(NO_3)_2$[a]	28.98	12	12	3.480	3.480	1 : 1
$CaCO_3$	31.97[b]	12.2	12.2	3.900	3.900	1 : 1
PtO_2[c]	13.98	32.8	32.8	4.590	4.590	1 : 1
Glycollic acid	63.12	4.8	8.6	3.030	5.428	1 : 1.78
Benzoic acid	26.20	13	22.8	3.406	5.973	1 : 1.75
Picric acid	48.91	2.4	13	1.174	6.358	1 : 5.42
H_2O	88.81	2.7	8.7	2.398	7.726	1 : 3.22
Succinic acid	54.20	10.1	14.7	5.474	7.967	1 : 1.46
Mannitol	52.70	9.5	17.4	5.007	9.170	1 : 1.83
Phenacetin	17.86		> 30			
Acetanilide	11.84		> 40			
Hydroxyquinoline	11.02		> 40			

[a] All the oxygen can be recovered by mixing the sample with 20–25 mg of carbon.
[b] Calculated for two atoms of oxygen, according to the reaction: $CaCO_3 \rightarrow CaO + CO_2$.
[c] Adams' catalyst, dried *in vacuo* 12 h at 130°. Oxygen found 13.98%, calculated 14.08%.

as carrier gas was performed, followed under the same experimental conditions by another series in which the argon was replaced by nitrogen. The method used is described on p. 102. The results are tabulated in the 3rd and 4th columns of Table IV. The substances are arranged in the Table according to the increasing order of the maximum determinable amount, expressed in mg of oxygen, using argon as carrier gas. The organic compounds examined were all of the highest purity and of high oxygen content, and it is known that these compounds are analysed only infrequently and with difficulty.

The last column of the Table gives the ratio between the maximum amounts determinable in argon and in nitrogen. This ratio represents the gain in power of the system to convert the oxygen-containing gases into carbon monoxide, when argon is used as carrier gas. Particularly high increases were observed in the case of picric acid and water. The adoption of argon by Blom[12], as carrier gas in the determination of water by conversion to carbon monoxide over heated carbon, is therefore fully justified. In the case of other substances such as oxalic acid, mannitol, glycollic and benzoic acids, the increases were of a lower order in magnitude and still lower for succinic acid.

Some inorganic compounds are also listed in Table IV. These were chosen for the purpose of obtaining pure oxygen-containing gases without tarry pyrolysis products. Calcium carbonate on heating gives a molecule of carbon dioxide, lead nitrate 2 molecules of NO with free oxygen, and PtO_2 one molecule of oxygen. For these substances the maximum amount determinable was the same both for argon and nitrogen. Using argon as carrier gas, no increase in efficiency was observed in the case of pure oxygen-containing gases.

This fact can explain the different behaviour of argon and nitrogen as carrier gas in the analysis of organic compounds. As no difference exists in the case of pure gases, it may be definitely stated that the use of either gas causes no change in the activity of the carbon. The different behaviour of the 2 gases when used as carriers in the thermal decomposition of organic compounds remains a matter of hypothesis. Nitrogen acts as an hindering agent in the thermal decomposition by reacting with the pyrolysis products, with formation of hydrogen cyanide. In contrast, argon is completely inert towards the pyrolysis products and so allows a greater interaction between the latter, thus leading to a greater carbon monoxide yield from the very start. It may also be stated that argon allows an apparent activation of the thermal decomposition.

The noticeable increase in the case of picric acid may be precisely explained through a more efficient reduction of the nitrogen oxides, in presence of argon, carried out by the carbon formed *in situ* from degradation of the benzene ring. It has recently been found[22] that even combustion in oxygen does not give rise to nitrogen oxides if the precombustion technique is used.

It was impossible to confirm BLOM's hypothesis[12] that the activity of the carbon depends on the content of absorbed hydrogen. A filling used for 400 analyses in argon, and then treated for several hours with hydrogen at 1120° showed no positive variation after treatment, as far as the maximum amount of substance pyrolysable with quantitative yield of carbon monoxide was concerned.

Other conclusions can be drawn from Table IV. With a layer of active carbon at a constant temperature of 1120° for reducing pure oxygen-containing gases to carbon monoxide, the ease with which the gases can be converted can be roughly established as follows: $NO < CO_2 < O_2 < H_2O$. This classification explains why nitroderivatives are unanimously agreed to be the most difficult to analyse for their oxygen content. By contrast, the carbohydrates are the easiest to analyse because on heating they supply their oxygen in the form of water.

Other deductions can be made by considering the column in which the maximum amounts expressed in mg of oxygen are shown. The maximum quantity of organic oxygen convertible to carbon monoxide is extremely variable from compound to compound. It varies not only according to the nature of the oxygen-containing gases produced, but also as a function of the amount of carbon present in the molecule. The carbon of an organic compound released at the moment of the thermal decomposition exerts on the oxygen-containing gases an action which supplements that of the carbon of the filling, thus increasing the initial yield of carbon monoxide. Precisely because of the fact that oxalic acid gives rise only to gaseous products, free from tarry matter, this compound presents the smallest quantity of oxygen that can be converted quantitatively. By contrast, glycollic and succinic acids show a distinctly larger quantity of determinable oxygen.

The above work justifies experimentally: (1) the ease of analysing compounds with low oxygen and high carbon contents, (2) the application of the pre-pyrolysis technique[6], and (3) the addition of an oxygen-free substance as a donor of active carbon, at the moment of gasification of the sample[9].

FURTHER TESTS ON AGED PACKINGS

The measurements shown in Table IV were always carried out with new active carbon fillings; under these conditions the carbon shows its maximum activity. Measurements of surface area were performed by the BET method[23] with suitable equipment (Sorptomat, Scientific Instruments Division of Carlo Erba, Milan, Italy); for fresh carbon the surface area was found to be 920 m²/g.

It must be pointed out that the values for the maximum amount of substance reported in Table IV, progressively decreased with use of the filling. Accordingly, we investigated, for 4 substances only, the maximum amount giving quantitative pyrolysis with a filling which was almost exhausted, having been utilized for *ca.* 800 analyses in argon. The argon was replaced by nitrogen and the maximum amount determinations were repeated for the 4 substances. The results are given in Table V. The ratios between the maximum amounts in argon and those in nitrogen still appear to favour argon. The decrease in the efficiency of the system in this case is greater than the increase shown in Table IV. Moreover, with argon as carrier gas, the results were still within the confidence limits, even when these limits had been already surpassed with nitrogen. In fact, with nitrogen as carrier gas such a filling of carbon must be considered as exhausted because of the danger of negative errors in the results.

TABLE V

DETERMINATION WITH USED CARBON FILLING

Compound	*Maximum amount of sample giving correct results (mg)*		*Ratio*
	in argon	*in nitrogen*	
Picric acid	3.2	0.9	3.55 : 1
H_2O	2.8	1.1	2.54 : 1
Succinic acid	4.6	1.9	2.42 : 1
Benzoic acid	7.4	2.6	2.84 : 1

The surface area was determined for the carbon of this filling, with the precaution of sampling material from the half of the filling farther from the inlet zone. A value of 770 m²/g was obtained. The slight decrease in the surface area does not explain the large decrease in the activity of the carbon filling. According to KAINZ AND SCHEIDL[4], the deposition of graphitic carbon on the inlet layer is responsible for the ageing of the filling rather than a reduction in the surface area of the carbon. This confirms the utility of the quartz wool placed at the inlet of the main furnace, as a graphite filter[11].

REPLACEMENT OF NITROGEN BY ARGON

In the above work, the different behaviour of argon and nitrogen with fresh fillings of carbon, and the fall in the activity of the system when argon was replaced by nitrogen with an old filling, were observed. Only the variation in the reducing power occurring with the abrupt replacement of nitrogen by argon remained to be studied. For these tests, a carbon filling already half way towards exhaustion in a nitrogen stream was chosen. It was to be expected, even in the case of such a filling, that the abrupt replacement of nitrogen by argon would lead to increased activity. Therefore the maximum amount of substance was determined with this filling in the nitrogen stream and then the same determinations were repeated 24 h later in an argon stream. The results are given in Table VI.

Increases in activity were still observed, except for benzoic and succinic acid. The increases were smaller but proportional to those indicated in Table IV. Replacement of the nitrogen with argon is therefore advantageous even in these conditions. However, it is obvious that it is best to use argon from the start. The fact that the desired increase did not occur for all the substances may be explained by the more marked graphitization occurring with nitrogen at the packing inlet zone. This agrees with the observation that a carbon filling associated with prolonged use in argon showed much less marked graphitization than that observed when nitrogen was used.

TABLE VI

DETERMINATION AFTER ABRUPT REPLACEMENT OF NITROGEN BY ARGON

Compound	*Maximum amount of sample giving correct results (mg)*		*Ratio*
	in nitrogen	*in argon*	
Picric acid	1.8	8.4	1 : 4.67
H_2O	2.4	7	1 : 2.92
Mannitol	8.9	14.7	1 : 1.65
Succinic acid	7.5	7.5	1 : 1
Benzoic acid	11.2	11.2	1 : 1

CONCLUSIONS

Replacement of nitrogen by argon as carrier gas in the method for the microdetermination of oxygen is justified primarily by the increased reducing power of the system, but also by the lengthening of the useful life of the filling. Finally, the results are free from blank values.

The increased reducing power allows pyrolysis of amounts of substances much larger than the normal microamounts and therefore the micromethod can be considered perfectly reliable, even when compounds with high oxygen contents are analysed. Furthermore, it is possible to increase the rate of flow of the carrier gas, thus shortening the time of analysis. A flow rate of 15 ml/min is considered satisfactory and this can be maintained in all stages of the analysis. Even flow rates of 20 ml/min and higher can be used, but these are less reliable because of the low reactivity of the anhydroiodic acid[24].

The gasification of the sample must also be considered in the light of the above discussion. There is no reason to perform slow and gradual gasification, except in the case of an exhausted carbon filling. It is convenient instead, to carry out gasification by allowing the pyrolytic oxygen-containing gaseous products to remain in contact with the tarry products of thermal decomposition of the sample.

Increase in the flow rate of the carrier gas and the greater speed of gasification lead to substantial shortening of the time required for analysis. The overall time for analysis, previously 30 min, can be reduced to only 15 min. Thus, one aim of the present work — speeding up the slow conventional method — was successful. Further improvements based on deductions from the above results may be possible.

EXPERIMENTAL

Apparatus

The apparatus is shown diagrammatically in Fig. 1. The flow of carrier gas is finely adjusted with a needle valve (1). The gas reaches the deoxidation tube through a 3-way stopcock. The deoxidation tube (2) consists of a Pyrex glass tube, 16 mm diameter and 400 mm effective length, provided with B10 socket joint, and filled with active BTS catalyst (65 ml). It is connected through a glass joint with 2 ground tapered connections, to the vertical drying tube (3) (16 mm diameter and 140 mm effective height, fitted with a B14 socket at the top and a 2/12 joint at the bottom) containing 80 mm of granular soda asbestos and 60 mm of phosphorus pentoxide on pumice. The drying tube is connected to the rotameter by means of a 2/12 cup joint. The conical ground joints are sealed with Krönig cement and the spherical ones lubricated with vaseline.

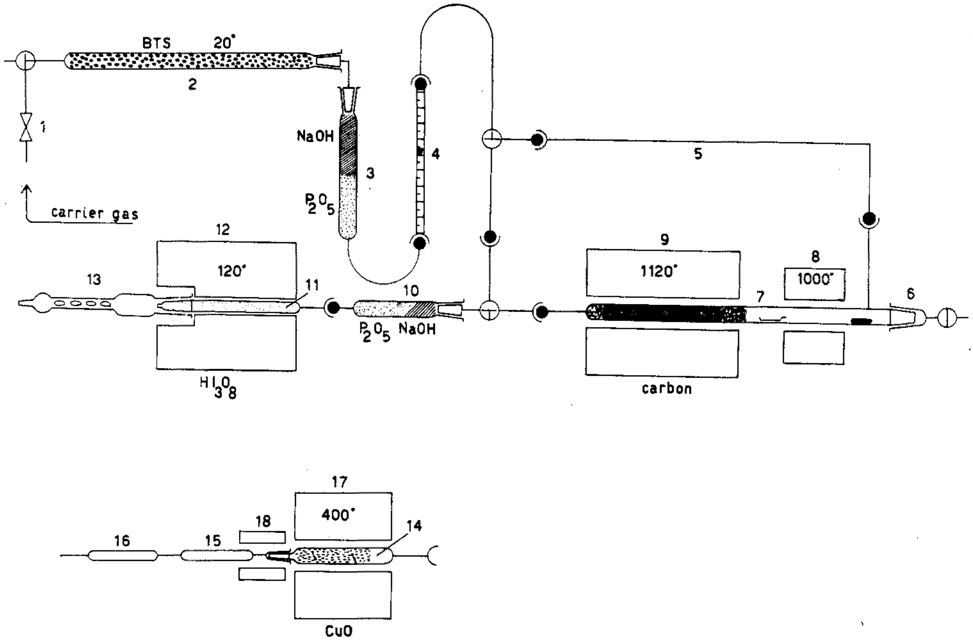

Fig. 1. Schematical diagram of the apparatus. (1) Needle valve; (2) Deoxidation tube; (3) Drying tube; (4) Rotameter; (5) Reverse-flow circuit; (6) Glass stopper with stopcock; (7) Reaction tube; (8) Movable furnace; (9) Main furnace; (10) Purifying tube; (11) Anhydroiodic acid tube; (12) Heating block; (13) Absorber; (14) CuO tube; (15) H_2O-absorption tube; (16) CO_2-absorption tube; (17) Oxidation furnace; (18) Heater.

The rotameter (4) measures 0–25 ml/min of air at 15° and 760 mm pressure, and is fitted with 2/12 ball and cup joints at both ends. It is attached to the reverse-flow circuit (5), which is regulated by two 3-way stopcocks and is assembled, but not rigidly, with glass connections provided with spherical ground joints.

The reaction tube (7) is provided with a 2/12 cup joint at the side arm, a 2/12 ball joint at the beak end and a B14 inlet cone closed by a glass socket with stopcock. The reaction tube, of extremely pure blown quartz (ing. ANDREINI, via Martini 8, Milan, Italy), has an internal diameter of 10 mm with a wall thickness of 1.5 mm; the electric furnace (9) is 210 mm long and is capable of maintaining a constant temperature of 1120° ± 5° in a central zone of 130 mm. The tube filling starting from the entrance of the gas flow, is as follows: 40 mm of quartz wool, of which 10 mm protrude from the furnace, 160 mm of pelleted carbon, 5 mm of quartz wool and 25 mm of quartz chips. The volume of the carbon is 13 ml.

An glass-enclosed iron rod is placed in the empty portion of the tube and is used to push the boat into the desired position with a magnet. The movable furnace (8), 80 mm long, is capable of reaching 1100° and can be advanced at a variable rate of 7–10 mm/min.

The pyrolysis section is followed by a purifying tube (10), 16 mm diameter and 120 mm effective length, provided with B14 socket and 2/12 ball joints and filled with 80 mm of soda asbestos and 40 mm of phosphorus pentoxide on pumice.

Two different units can be connected to the apparatus, as shown in Fig. 1, for the titrimetric or gravimetric procedure. In the first case, an oxidation tube and a Vigreux absorption tube (13) as described in the literature are used. The oxidation tube contains anhydroiodic acid (11) (15 ml), heated to a constant temperature of 116° by the heating block, 210 mm long (12).

The oxidation tube (14) for the gravimetric procedure is made of Supremax glass, 11 mm diameter and 120 mm effective length, provided with 2/12 cup and B5 conical joints. It is filled with a layer of copper oxide, 80 mm long, before sealing, and heated to 400° by small furnace 110 mm long (17). The absorption train consists of a water-absorption tube (15) without diaphragm provided with a B5 socket joint for greaseless connection to the copper oxide tube; 40 mm of this tube is heated to 100° with a small electric heater (18). The carbon dioxide-absorption tube (16) contains 70 mm of a soda asbestos–dehydrite mixture (8 : 1) and 30 mm of dehydrite. It is connected by means of a silicone rubber tubing.

Reagents

Nitrogen, research grade. Less than 10 p.p.m. of oxygen (Bonizzoni, Crema, Italy).

Argon, for welding. Less than 250 p.p.m. of nitrogen and 10 p.p.m. of oxygen. From the same manufacturer.

BTS catalyst (B.A.S.F., Ludwigshafen/Rhein, Germany), 7–35 mesh. This is activated with hydrogen diluted with nitrogen at 120° and then stored in glass ampoules sealed under nitrogen. It is used at room temperature for the removal of oxygen from both nitrogen and argon.

Granular soda asbestos, 12–25 mesh. It is advisable to allow this reagent to stand for a few minutes in the air, before introduction into the purifying tube. The soda asbestos must be renewed frequently.

Phosphorus pentoxide on pumice. 1 : 1 by volume on pumice of 18–40 mesh.

Carbon, pelleted (type CK3 from Degussa, Frankfurt, Germany), 25–50 mesh. It is heated at 1100° in hydrogen for 6–8 h, and allowed to cool in hydrogen before use.

Anhydroiodic acid. Prepared according to UNTERZAUCHER[2] (30–50 mesh). It is used at 116° and always kept at this temperature to avoid loss of activity.

Copper oxide, wire form, 18–35 mesh. The copper oxide filling is treated daily with oxygen at 700° to reoxidise the copper formed.

All unspecified analytical reagents were obtained from Carlo Erba, Milan, Italy.

Distilled water. A solution of 100 ml of twice-distilled water with all the necessary reagents for volumetric analysis must remain colorless at least 20 min.

Method related to Tables II and IV

The new reaction tube, thoroughly washed and treated with 40% hydrofluoric acid for 1 h, was packed with the fresh carbon, and then flushed with carrier gas for 2–3 h and heated at 1120° for 48 h. A few pyrolyses of material such as liquid paraffin were carried out, in order to cover the inlet quartz wool layer with carbon. The tube was then ready for analysis.

A carbon filling was used for 10 days and then discarded, the same tube being filled with a fresh packing. One reaction tube was used for the determinations in argon and another new tube was used for the parallel determinations in nitrogen, again with fresh filling after 10 days.

For these tests the oxidation and absorption sections of the gravimetric procedure were used (Fig. 1). The flow rate of the gas was always 15 ml/min. Since the rotameter was calibrated with air, a correction factor was necessary when argon or nitrogen was employed.

The platinum boat with the weighed substance was introduced about 30 mm into the reaction tube during reversal of the gas stream and the tube was swept out for a few minutes before the boat was magnetically pushed to 20–30 mm in front of the main furnace. After the direct gas flow had been reestablished, the sample furnace at 700–800° was placed 40 mm in front of the main furnace. The gasification lasted about 4 min, at the end of which the temperature of the movable furnace was 1000°. The furnace was removed after 10 min. The average duration of the analysis was 15 min, and 20 min when large amounts of carbon dioxide were produced. The carbon dioxide-absorption tube was then removed with gloved hands and weighed at the 4th min; during weighing the capillaries were closed with 0.30-mm Ni–Cr wires.

Method related to Tables V and VI

In this case the same reaction tube and the same filling were always used, with a change only in the carrier gas. The oxygen present was again measured by the gravimetric determination. The analytical conditions were as described above.

General analytical method

The titrimetric procedure was used, based on the measurement of the iodine produced by the reaction between carbon monoxide and anhydroiodic acid. In this case the upper oxidation and absorption section shown in Fig. 1 was used. The carrier gas was argon, at a constant rate of 15 ml/min.

The platinum boats were heated twice daily in hydrogen to red heat. A backsweeping time for the boats and capillaries of 3 min was required. In the case of substances containing water of crystallization, the boat was introduced 80 mm into the reaction tube in a zone previously cooled with solid carbon dioxide. In order to analyse liquid substances, quartz capillaries containing an iron rod, 6 mm long and 1 mm diameter welded at the bottom, were used. The position of the boat in the tube and the method of pyrolysis were as described before.

In our tests, all the iodine corresponding to the carbon monoxide produced was absorbed after 7–8 min. The absorption tube was then disconnected between the 10th and 12th min. The washing and titration were performed as in the conventional method[2].

The reaction tube was never cleaned from the deposited carbon in the gasification zone. After 400 analyses, the quartz wool plug at the inlet was replaced.

SUMMARY

Argon is recommended as carrier gas in order to improve the efficiency of the method for the microdetermination of oxygen in organic compounds. To demonstrate that the use of argon is advantageous, parallel determinations were performed on a series of organic and inorganic compounds to establish the maximum amounts of substance quantitatively pyrolysable under normal analytical conditions. With argon, the maximum amount of the organic compound giving correct results was usually remarkably increased at all stages of the working life of the tube. This greater efficiency of the system in the conversion to carbon monoxide leads to higher reliability, allows a substantial decrease in the analysis time, and prolongs the life of the filling. The inconvenience of positive blank values with argon can be avoided if reaction tubes of very pure quartz are used.

RÉSUMÉ

L'argon est recommandé comme gaz entraîneur pour le microdosage de l'oxygène dans les composés organiques. Des essais parallèles avec composés organiques et inorganiques ont été effectués afin de montrer les avantages de l'argon et déterminer les quantités de substances quantitativement pyrolysables dans les conditions analytiques normales. Il est nécessaire d'utiliser des tubes à réaction en quartz très pur.

ZUSAMMENFASSUNG

Argon wird als Trägergas empfohlen, um die Wirksamkeit der Methode zur Mikrobestimmung von Sauerstoff in organischen Verbindungen zu prüfen. Um zu zeigen, dass der Gebrauch von Argon vorteilhaft ist, wurden an einer Reihe von organischen und anorganischen Verbindungen Parallelbestimmungen durchgeführt, um die maximalen Beiträge einer Substanz festzusetzen, die unter normalen analytischen Bedingungen quantitativ pyrolisierbar ist. Mit Argon stieg im allgemeinen der maximale Betrag der organischen Verbindung, der korrekte Ergebnisse liefert, bei allen Stufen mit der Betriebszeit der Röhre bemerkenswert an. Diese grössere Wirksamkeit des Systems bei der Umwandlung zu Kohlenstoffmonoxid führt zu höherer Zuverlässigkeit, gestattet eine Verminderung der Analysenzeit und verlängert die Lebenszeit der Füllung. Positive Blindwerte mit Argon können vermieden werden, wenn Reaktionsröhren aus sehr reinem Quartz verwendet werden.

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SHORT COMMUNICATIONS

Bis-(2,6-dimethylmorpholin)-thiuramdisulfid als Reagens für die photometrische Extraktionsbestimmung kleiner Kupfergehalte und von Kupferspuren in biologischem Material

Wie in früheren Arbeiten gezeigt wurde[1,2], eignen sich die Thiuramdisulfide auf Grund ihrer hohen Empfindlichkeit und Spezifität gut als Nachweisreagentien für geringe Kupfermengen. In der vorliegenden Arbeit wird ein Thiuramdisulfid beschrieben, das es gestattet, Kupferspuren durch Extraktion anzureichern und spektralphotometrisch zu bestimmen. Das als Lösungsmittel für das Reagens und als Extraktionsmittel für die mit Kupfer-Ionen entstehende Gelbfärbung dienende Tri-*n*-butylphosphat ist schon wiederholt als Extraktionsmittel für Kationen[3–5] beschrieben worden.

Herstellung des Reagens

Man mischt Lösungen von 2.3 g 2,6-Dimethylmorpholin (2 Mol) und 0.76 g Schwefelkohlenstoff (1 Mol) in Tetrachlorkohlenstoff. Nach dem Einengen fällt das 2,6-Dimethylmorpholin-N-dithiokarbonsaure-2,6-Dimethylmorpholinium[6] als weisser, kristalliner Niederschlag aus. Der Niederschlag wird abgenutscht, an der Luft getrocknet und in 500 ml Wasser unter Rühren gelöst. Jetzt wird eine 20%ige, wässrige Lösung von Kaliumferricyanid unter heftigem Turbinieren zugetropft. Wenn keine Abscheidung von Bis-(2,6-dimethylmorpholin)-thiuramdisulfid mehr auftritt, ist die Reaktion beendet. Das Produkt wird abgenutscht und aus wenig 96%igem Äthanol umkristallisiert: gelblich-weisse Nadeln vom Schmelzpunkt Fp 123°. Die Struktur des Reagens als Thiuramdisulfid wurde durch Bestimmung des Kohlenstoff-, Wasserstoff-, Stickstoff- und Schwefelgehaltes, sowie durch U.V. und I.R. Spektren gesichert.

Zur Feststellung des qualitativen Verhaltens des Bis-(2,6-dimethylmorpholin)-thiuramdisulfides (BDMTD) gegenüber Metallkationen wurde eine 0.001 M methanolische Lösung des Reagens verwendet. Die Metallionen lagen in einer Konzentration von 0.5 mg/ml bzw. bei gelbgefärbten Lösungen 0.05 mg/ml in 6 N Salzsäure vor. Als einziges Kation zeigte das Kupfer(II)-Ion eine starke Gelbfärbung mit dem Reagens. Das Reagens ist auch in Tri-*n*-butylphosphat löslich.

Für den Kupfernachweis mit BDMTD beträgt der pD-Wert bei Extraktion aus 6 N Salzsäure mit 0.001 M tri-*n*-butylphosphatischer Reagenslösung 6.7.

Das Absorptionsmaximum der Gelbfärbung liegt bei 430 mμ. Die von uns ausgearbeitete Extraktionsbestimmung mit einer 0.001 M Lösung von BDMTD in Tri-*n*-butylphosphat ergibt eine Spurenelementausbeute R (recovery factor)[7] von 0.84. Üblicherweise multipliziert man diesen Wert mit 100, dann ergibt sich, wieviel Prozent des betreffenden Spurenelementes im angereicherten Zustand wiedergefunden werden ($R \cdot 100 = 84$); also 84%. Diese Spurenelementausbeute ist bei der vorliegenden Arbeitsvorschrift (dreimaliges Ausschütteln) und dem Bereich von 0.5 μg Cu/ml bis 5.0 μg Cu/ml ausreichend. Bei dieser Extraktionsmethode stören naturgemäss alle mit Tri-*n*-butylphosphat extrahierbaren Metallkationen, soweit sie bei hoher Konzentration eine störende Färbung bewirken. Bei Analyse in biologischem Material stört nur das Eisen(III)-Ion. Um diese störende Färbung zu beseitigen, kann man das Eisen(III)-Ion mit Ascorbinsäure reduzieren. In hundertfachem Überschuss stören folgende Anionen nicht: Sulfat, Chlorid, Azetat, Phosphat, Oxalat, Borat, Tartrat, Rhodanid und Fluorid. Es stört lediglich Nitrat. Diese Störung kann durch Abrauchen der Probe mit Schwefelsäure umgangen werden.

Aufstellung der Eichkurve

Es werden 10 ml einer 6 *N* Salzsäurelösung, die eine definierte Menge Kupfer enthält, vorgelegt, und mit 2 ml 0.001 *M* Lösung von BDMTD in Tri-*n*-butylphosphat extrahiert. Man lässt die wässrige Schicht in einen zweiten Schütteltrichter ab und füllt die gelbgefärbte Tri-*n*-butylphosphatschichte in einen 10-ml Kolben. Es wird noch zweimal mit 2 ml Reagenslösung extrahiert und der Kolben mit Methanol aufgefüllt. Die Extinktion der Gelbfärbung wird bei 430 mμ in 5-cm Küvetten gemessen. Das Lambert–Beer'sche Gesetz ist im Bereich von 0.5 bis 5 μg Cu/ml erfüllt. Eine Messung der Zeitabhängigkeit ergab, dass die Färbung 25 Minuten konstant bleibt.

Als Beleganalysen wurde Kupfer in Reinaluminium und im menschlichen Gehirn bestimmt. 50 mg Reinaluminium wurden eingewogen, in 50 ml conc. Salzsäure gelöst und mit Wasser auf 100 ml aufgefüllt. 10 ml davon wurden herauspipettiert und dann wie bei Aufstellung der Eichkurve verfahren.

Der angegebene Gehalt von 0.46% Kupfer konnte bestätigt werden. Die bei 105° getrocknete und bei 650° geglühte Hirnsubstanz[8] wurde mit 1 ml 6 *N* Salzsäure in Lösung gebracht und mit destilliertem Wasser in einen 10-ml Kolben gespült. Es wurden 3 ml aus dem Kolben pipettiert, mit etwas Ascorbinsäure versetzt und das gleiche Volumen conc. Salzsäure zugegeben. Dann wurde dreimal mit 2 ml einer 0.001 *M* Lösung von BDMTD in Tri-*n*-butylphosphat extrahiert und mit Methanol auf 10 ml aufgefüllt. Gemessen wurde bei 430 mμ in 5-cm Küvetten.

Die nach der Methode von HAAS UND WINTERSTEIN[9] durchgeführte Kupferbestimmung in Zentren des menschlichen Gehirnes ergab die gleichen Werte wie unsere Methode.

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Preliminary studies of precipitation titrations of organic compounds using polarovoltric end-point indication.
Part II. Titration of organic acids and salts with copper(II)

Copper(II) has been quite extensively used as a direct titrant in organic analysis. Most determinations have, however, been based on its oxidising properties; the determination of reducing sugars accounts for a good three-quarters of the published applications. End-point determination in other titrations with copper(II) has usually depended on indication of excess copper(II), such as the first appearance of blue or the response of an external indicator like sulphide, ferrocyanide, cyanide, iodide/acid or iron(II) thiocyanate. Instrumental end-point indication has been comparatively little used. Since copper(II) yields a fairly good polarovoltric electrode response over a wide pH range, it was thought of interest to investigate titrations using this method of indication.

The principal compounds and compound classes previously determined by direct precipitation with copper(II) have been mercaptans, xanthates, uric acid, picric acid and pyridine. The titration of the first three is accompanied by precipitation of copper(I) compounds, following initial oxidation of the organic compound. Pyridine can be directly determined[1] in the presence of thiocyanate, yielding a complex, $[Cu(C_5H_5N)_2]\,[SCN]_2$ (the method, also for other bases like quinoline and aniline, is perhaps better known as an indirect titration using excess thiocyanate). Picric acid can be determined[2] in ammoniacal solution, with precipitation of $[Cu(NH_3)_4]\,[C_6H_2(NO_2)_3O]_2$. It was decided to limit the present work to precipitation reactions in which no oxidation occurs. Primarily carboxylic acids were studied, since their direct titration with copper(II) appears not to have been reported. The aim of the work, as in Part I[3], was to establish the conditions under which polarovoltric end-point indication is possible and then briefly to study the influence of conditions (notably pH) on the stoichiometry of the reactions.

Reagents and solutions

Sulphuric and acetic acid solutions. 0.1 *N* and *N*.

Acetate buffers. pH 3.6, 4.6 and 5.6, *ca.* 0.1 *M* and *M*.

Phosphate buffers. pH 6.3, 7.2 and 8.1, *ca. M*.

Ammonium hydroxide/chloride buffers. pH 8.4, 9.4 and 10.4, *ca.* 0.1 *M* and *M*.

Aqueous 1% solution of electrolyte-free colloid stabiliser polyvinylpyrrolidone.

Copper sulphate and copper acetate aqueous solutions. Stabilised with a few drops sulphuric and acetic acid respectively, per litre of stock solution; 0.1 *N* and 0.05 *N*.

The acids and salts were either commercial pure materials or were purified by distillation or crystallisation, mostly from ethanol or carbon tetrachloride. Stock solutions, 0.1 *M* or 0.05 *M*, were made up in water, ethanol or acetone.

Apparatus and procedure

These were the same as described briefly in Part I[3]. *Ca.* 20 ml buffer, acid or ammonium hydroxide solution were used. After the initial blank titration, 0.1 mmol of the studied compound was added (1 ml aliquot of a 0.1 *M* solution or 2 ml of 0.05 *M* solution) and the titration carried out. Where possible, further additions were made to the titrated solution and further end-points located. Stabiliser solution was usually added (4 drops; 2 or 6 drops were found to have essentially the same effect as 4). Omission of stabiliser did not appear to influence the position of the end-point but tended to slow up titration. The electrodes then had to be cleaned from adhering precipitate at frequent intervals during titration.

The titration medium chosen (solvent + buffer or other electrolyte solution) had to fulfil 4 conditions:

(*i*) permit a reasonably sensitive indication of added copper(II),
(*ii*) maintain the added acid or salt sample in solution,
(*iii*) not precipitate the copper(II),
(*iv*) permit precipitation of a copper(II) derivative of the compound studied.

These conditions were fulfilled mostly in ammonium buffers or ammonium hydroxide solutions (pH 8.4–11.2). Ammonium acetate had to be added to the phosphate buffers to inhibit precipitation of the copper(II) reagent. Aqueous acid medium could be used only with water-soluble samples.

Results

Sensitivity of end-point indication. The values in Table I, although averages of rather widely fluctuating readings (dependent on the previous electrode treatment), show certain tendencies. The response was highest in the acetate buffers with the ammonium hydroxide and acetic acid solutions next. It was consistently less in the more concentrated buffer solutions. In all solutions the response was adequate for satisfactory end-point indication, although markedly less than that given by ferrocyanide (Part I).

It was noticeable that in acid solution, the jump in potential difference was greatest with the first added drop, then falling off sharply. In alkaline solution the response was more extended and often reached its maximum with the second or even third drop containing 2.5 μeq. of copper(II); the Table quotes averages for the first 2 or 3 drops in these cases.

Titration of carboxylic acids. The lower aliphatic carboxylic acids yield copper(II) salts too soluble for an end-point to be obtained in the concentration range studied.

TABLE I

SENSITIVITY OF END-POINT INDICATION

(*Ca.* 20 ml solution. Speed of stirring *ca.* 500 rev./min; electrode response given as change in p.d. (mV) caused by addition of 2.5 μeq. of Cu(II))

pH (approx.)	*Electrode response*	*pH (approx.)*	*Electrode response*
0.1 (N H_2SO_4)	30	6.3	65
1.1 (0.1 N H_2SO_4)	40	7.2	70
2.2 (N CH_3COOH)	100	8.1	60
2.8 (0.1 N CH_3COOH)	120	8.4 (*ca.* 0.1 *M*)	95
3.6 (*ca.* 0.1 *M*)	160	8.4 (*ca. M*)	60
3.6 (*ca. M*)	90	9.4 (*ca.* 0.1 *M*)	90
4.6 (*ca.* 0.1 *M*)	130	9.4 (*ca. M*)	40
4.6 (*ca. M*)	85	10.4 (*ca.* 0.1 *M*)	50
5.6 (*ca.* 0.1 *M*)	150	10.4 (*ca. M*)	40
5.6 (*ca. M*)	95	11.2 (0.1 N NH_4OH)	135
		11.8 (M NH_4OH)	110

Lauric acid was the first which gave a detectable end-point. Data are given in Table II for 4 saturated acids.

The low values for lauric and myristic acids are probably related to the slightly greater solubility of their copper(II) salts. The concentration of copper(II) in the solution near which the maximum electrode response occurred (*i.e.* where the end-point was taken) was then attained too soon. The use of smaller electrodes and faster stirring rates effected little improvement. In the same way, the lower results in more concentrated ammonium hydroxide are probably also due to increased solubility of the precipitate in this medium.

TABLE II

TITRATION OF SATURATED FATTY ACIDS

pH	*Percentage of acid titrated*					
	Lauric	*Myristic*	*Palmitic*		*Stearic*	
	0.1 mmol	*0.1 mmol*	*0.1 mmol*	*0.2 mmol*	*0.1 mmol*	*0.2 mmol*
8.4					96	
9.4		91	98	99	94	94
10.4		90	94	94	96	97
11.2	79	94	94	95	100	101
11.8			91	92	92	93

TABLE III

TITRATION OF ELAIDIC ACID

(0.1 mmol in *ca.* 20 ml solution)

Initial NH_4OH (*N*)	*Equivalent titrated*	*Initial* NH_4OH (*N*)	*Equivalent titrated*
0.7	0.98; 0.97; 1.00	0.25	1.35; 1.31
0.6	0.95; 0.96	0.2	1.36; 1.38
0.5	0.93	0.175	1.41; 1.35
0.45	0.94; 0.99; 0.96	0.15	1.43
0.4	0.94	0.1	1.44; 1.44; 1.44
0.35	0.96; 0.95; 0.94; 0.96	0.075	1.45
0.3	1.41; 1.39; 0.95; 0.97	0.05	1.50; 1.49
0.27	1.38; 1.36; 0.97	0.025	1.50
0.263	1.33; 1.35		

Some results for elaidic acid (Table III) are remarkable for the variation of stoichiometry with pH, or at least with initial concentration of ammonium hydroxide. The results were reproducible and the end-points well defined, although slow titration was necessary. Only in the region of 0.3 *N* solution, where the sudden change in stoichiometry occurred, were fluctuations of the titration value observed. It is interesting that oleic acid behaved differently. It could be titrated only in dilute ammonium hydroxide solution (0.025 *N* to 0.1 *N*) giving values ranging between 1.37 and 1.5 eq. of copper reagent per equivalent of acid. The titrations were exceedingly slow. End-points were sometimes obtained in 0.015 *N* and 0.2 *N* ammonium hydroxide, giving *ca.* 1.5 and 1.8 eq. of copper(II) respectively, but were not properly reproducible. No satisfactory end-points could be obtained with some other unsaturated acids like undecylenic, linoleic and linolenic acids. The titration of a few other assorted carboxylic acids (dodecanedicarboxylic, α-naphthoic, hydrocinnamic, hippuric and chelidonic) was similarly unsuccessful. The solubility of the copper(II) salts was evidently too high and no precipitation occurred under the conditions used.

TABLE IV

TITRATION OF 1:1 FATTY ACID MIXTURES

Acid titrated	*pH*	*Percentage titrated in presence of*		
		No addition	*Decanoic acid*	*Undecylenic acid*
0.1 mmol lauric	11.2	79	94	76
0.1 mmol palmitic	9.4	98	100	97
0.2 mmol palmitic	9.4	99	—	99
0.1 mmol palmitic	10.4	94	101	96
0.2 mmol palmitic	10.4	94	99	98
0.1 mmol palmitic	11.2	94	102	100
0.2 mmol palmitic	11.2	95	100	99
0.1 mmol stearic	9.4	94	—	99
0.2 mmol stearic	9.4	94	—	103
0.1 mmol stearic	10.4	96	97	97
0.1 mmol stearic	11.2	100	102	100

TABLE V

TITRATION OF PHENOLS AND SODIUM LAURYL SULPHATE

pH	*% Oxine titrated*			*pH*	*% Oxine titrated*		*% Picric acid titrated*			*% Lauryl sulphate titrated*		
	0.1 mmol	*0.2 mmol*	*0.3 mmol*		*0.1 mmol*	*0.2 mmol*	*0.1 mmol*	*0.2 mmol*	*0.3 mmol*	*0.1 mmol*	*0.2 mmol*	*0.3 mmol*
2.8	99			8.4	99							
3.6	98	101	102	9.2	100	101						
4.6	99			9.4	102		94	92		78	77	
5.6	100			10.4	99		95	97		78	79	80
6.3	102	100		11.0	102	101						
7.2	100	102		11.2	102		99	99	99	70	72	
8.1	99	102		11.8			87			70	73	

Some 1:1 mixtures of lower fatty acids with higher, titratable members of the series were titrated. Table IV contains a summary of the data. There is an evident slight tendency for the decanoic acid to raise the titration percentage of the higher acid, probably through co-precipitation. Undecylenic acid has a less marked effect and the higher acids could be titrated fairly accurately with copper(II) in the presence of at least approximately equal amounts of the undecylenic acid. Fatty acids below decanoic acid appeared, at least in 1:1 mixtures, to have no perceptible influence on the titration of the higher acids.

Titration of other compounds. Satisfactory results with good end-points were obtained with sodium lauryl sulphate, picric acid and 8-hydroxyquinoline (Table V). The last named could be titrated to within about 2% at any pH value from 2.8 to 11.2. Picric acid could be titrated reasonably precisely at pH 11.2 and reproducibly, although no longer stoichiometrically, at the other alkaline pH values. The lauryl sulphate could be titrated reproducibly at the 4 alkaline pH values quoted. It may be mentioned that the same lauryl sulphate sample gave a purity value of *ca.* 88% by polarovoltric titration with cetyl trimethylammonium chloride, using methylene blue as "electro-indicator"[4]. The values from the copper(II) titrations were appreciably lower. As in the fatty acid titrations, lower results were obtained in the more strongly basic solutions.

TABLE VI

TITRATION OF 1:1 PHENOL MIXTURES

pH	*Percentage of picric acid titrated in presence of*					
	No addition		*2,4-Dinitrophenol*		*2,4,6-Tribromophenol*	
	0.1 mmol	*0.2 mmol*	*0.1 mmol*	*0.2 mmol*	*0.1 mmol*	*0.2 mmol*
9.4	94	92	93	97	99	100
10.4	95	97	91	96	97	98
11.2	99	99	97	100	100	100

Other phenols examined were 2,4-dinitrophenol, 2,4,6-trinitroresorcinol, picramic acid and 2,4,6-tribromophenol. The first two gave no precipitates with copper(II) under the conditions used. The other two yielded a precipitate but of evidently too high solubility to permit polarovoltric end-point indication. Some approximately 1:1 mixtures of picric acid with other phenols were titrated. The results, summarised in Table VI, show that neither 2,4-dinitrophenol nor 2,4,6-tribromophenol would seriously interfere in a picric acid titration under the conditions used. No end-point could be attained in titrations of mixtures of picric and picramic acids.

Conclusions

The potentialities of the copper(II) reagent lie in its comparatively specific precipitating power. This is demonstrated in Tables IV and VI. It is thus possible for higher fatty acids to be precipitated and hence titrated with at least fair accuracy in the presence of lower acids; and picric acid in the presence of some other substituted phenols. The basic reagents commonly used to titrate acids would not distinguish between the different acids. In comparison, other possible inorganic precipitating agents are less suitable. Lead(II) and zinc(II) cannot be used in basic or neutral solution and their salts with organic acids are often soluble in acid. Silver(I), although giving an excellent electrode response, is less specific and has a greater tendency to oxidise than copper(II).

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Spectrophotometric determination of selenium and tellurium with thioglycollic acid

Thioglycollic acid (TGA) forms soluble complexes with many metal ions, and has been used for the spectrophotometric determination of iron[1,2], molybdenum[3,4], uranium(VI)[5] and nickel[6]. The complexes formed between TGA and Bi, Cd, Pb, In, Hg(II), Ag, Tl, Sn and Zn in alkaline solution are more stable than the corresponding EDTA complexes[7]; CABRERA AND WEST[8] have investigated TGA as a compleximetric titrant. In the present work, TGA was shown to react with selenium(IV) and tellurium(IV) to form soluble yellow complexes over a wide range of hydrochloric acid concentrations; in neutral solution selenous and tellurous acids were reduced to the elements by TGA. The yellow selenium and tellurium–TGA complexes could be extracted into oxygen-donor solvents such as diethyl ether, *n*-butanol, ethyl acetate, amyl acetate and butyl methyl ketone, but were not soluble in chloroform, carbon tetrachloride or benzene. Ethyl acetate was chosen as the most convenient solvent for extraction.

This paper reports the use of TGA for the spectrophotometric determination of selenium and tellurium by direct measurement of the extract; a method for determination of selenium in presence of tellurium is also described.

Apparatus

Hilger and Watts H999 ultrascan Mark II spectrophotometer.

Reagents

Thioglycollic acid solution ($10^{-1}M$). The solution was prepared fresh as required. Weigh 2.303 g of thioglycollic acid (98%, G.P.R. grade), transfer to a 250-ml volumetric flask, and dilute to volume with distilled water.

Tellurium(IV) solution ($10^{-2}M$). Dissolve 1.276 g of chemically refined tellurium powder (Johnson, Matthey and Co., Ltd.) in 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid. Warm gently to aid dissolution and heat to expel brown fumes. Cool the solution, transfer to a 1-l volumetric flask and add sufficient concentrated hydrochloric acid to make the final acidity approximately 1 *M* with respect to acid. Dilute to volume with distilled water.

Selenium(IV) solution (10^{-2} M). Dissolve 0.789 g of chemically refined selenium shot (Johnson, Matthey and Co., Ltd.) in the same way as for the tellurium solution, warming gently to aid dissolution. Cool the solution and dilute to volume in a 1-l volumetric flask with distilled water.

Diverse ions. Reagent-grade salts were used to prepare 10^{-1} *M* solutions of diverse ions. All other reagents were analytical reagent grade.

Preparation of calibration curves

Tellurium(IV). Add 2 ml of concentrated hydrochloric acid and 2 ml of 10^{-1} *M* TGA solution to a series of 100-ml separating funnels. Dilute to *ca.* 20 ml and add 1, 2, 3, 4, 5 and 6 ml of 10^{-3} *M* tellurium(IV) solution. Add 25 ml of ethyl acetate and shake vigorously for 1 min. Measure the absorbance of the ethyl acetate phase at 260 mμ in a 1-cm silica cell against a reagent blank prepared similarly.

Selenium(IV). Proceed as described for tellurium(IV), but use only 1 ml of 10^{-1}

M TGA solution and 2-, 4-, 6-, 8- and 10-ml aliquots of 10^{-3} M selenium(IV) solution.

Determination of selenium in the presence of tellurium. Transfer the solution containing selenium(IV) and tellurium(IV) to a 100-ml beaker. Add 2 ml of 10^{-1} M potassium dichromate solution and sufficient hydrochloric acid to make the solution approximately 1 M. Warm the solution to 50°, cool, and transfer to a 100-ml separating funnel. Add 10^{-1} M TGA solution until the yellow dichromate colour can no longer be detected, and then add 1 ml of 10^{-1} M TGA in excess. Extract the selenium thioglycollate into 25 ml of ethyl acetate and measure its absorbance at 360 mμ against a reagent blank. Construct a calibration curve for selenium thioglycollate at 360 mμ.

Results

Spectral characteristics. The selenium and tellurium thioglycollates formed in 1 M hydrochloric acid medium, were extracted into an equal volume of ethyl acetate and their absorption spectra recorded. The selenium and tellurium complexes both exhibited maximum absorbance at 260 mμ (Fig. 1). The thioglycollic acid reagent showed appreciable absorption at 260 mμ and this necessitated the use of reagent blanks throughout the work.

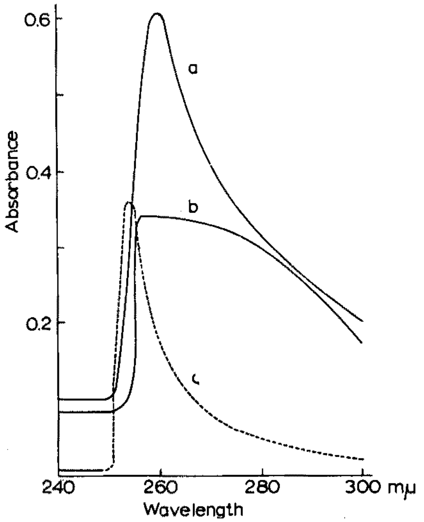

Fig. 1. Absorption spectra of TGA and its selenium and tellurium complexes in ethyl acetate. (a) 5 ml 10^{-3} M Te(IV) + 10 ml 10^{-2} M TGA against reagent blank. (b) 5 ml 10^{-3} M Se(IV) + 10 ml 10^{-2} M TGA against reagent blank. (c) 10 ml 10^{-2} M TGA extracted from 1 M HCl into ethyl acetate recorded against ethyl acetate equilibrated with 1 M HCl.

Effect of acidity. Selenium and tellurium solutions containing 1–5 M hydrochloric acid were prepared; a 50-fold molar excess of TGA was added and each solution was extracted with an equal volume of ethyl acetate. No appreciable variation in the absorbance of the organic phase at 260 mμ with hydrochloric acid concentration was noted; extraction from 1 M hydrochloric acid was adopted because this acidity should minimize interference from elements which form extractable chloro complexes in more concentrated hydrochloric acid medium.

Effect of time on colour development. The absorbances of the selenium and tellurium complexes reached a maximum in aqueous solution within 1 min of addition of the TGA, and then remained constant in the ethyl acetate phase, after extraction for at least 2 h.

Effect of reagent concentration. In 1 *M* hydrochloric acid medium, a 5-fold molar excess of TGA was required for maximum absorbance of tellurium thioglycollate at 260 mμ; the presence of a 150-fold molar excess of reagent had no effect on the absorbance. A 4-fold molar excess of TGA was required for maximum absorbance of the selenium thioglycollate, and the presence of a 50-fold molar excess of reagent had no further effect.

Beer's law and sensitivity. The calibration curves at 260 mμ for selenium and tellurium followed Beer's law in the range 6–34 p.p.m. and 5–36 p.p.m. respectively. The optimum ranges for quantitative measurements were 10–34 p.p.m. for selenium and 8–27 p.p.m. for tellurium. The molar absorptivity of selenium thioglycollate in ethyl acetate was $\varepsilon_{260\ \mathrm{m}\mu} = 1660$ and for tellurium thioglycollate $\varepsilon_{260\ \mathrm{m}\mu} = 3330$.

Interferences. Solutions were prepared containing 15 p.p.m. tellurium(IV) or 14 p.p.m. selenium(IV) and a 100-fold amount of each ion to be tested. The selenium and tellurium TGA complexes were then formed and the total absorbance at 260 mμ was measured. The presence of a 100-fold amount of the following ions caused less than 3% error in the absorbance: Al, Ca, Cd, Co(II), Fe(II), K, Mg, Mn(II), Na, Ni, Se(VI), Te(VI) and Zn. However, Au(III), Cr(III), Cu, Fe(III), Ge, Hg(II) and V(V) caused low results either by consumption of reagent to form non-extractable TGA complexes or through oxidation by the metal ion. As(III), As(V), Bi(III), Mo(VI) and Sb(III) caused high results owing to the formation of extractable TGA complexes or extractable chloride ion-association complexes.

Determination of selenium and tellurium in the presence of each other

The reactions of both selenium(IV) and tellurium(IV) with TGA are similar, and it was not possible to determine these ions in the presence of each other at 260 mμ. Tellurium(VI), however, did not interfere with the determination of selenium(IV), hence it was possible to determine selenium(IV) in the presence of tellurium(IV) by selective oxidation to tellurium(VI) with dichromate[9]. The excess dichromate was destroyed by the addition of sufficient TGA to reduce Cr(VI) to Cr(III) and provide a large enough excess for formation of the selenium(IV) thioglycollate complex. The chromium(III) interfered with the determination of selenium(IV) at 260 mμ, but not at 360 mμ. The tellurium content of a mixture of selenium(IV) and tellurium(IV) could be determined by subtraction of the absorbance of selenium(IV) thioglycollate, determined as above at 360 mμ, from the total absorbance obtained at 360 mμ when the selenium(IV) and tellurium(IV) TGA complexes were both formed and extracted. The difference was then expressed in terms of tellurium(IV) content from a calibration curve prepared from tellurium(IV) under the same conditions.

The sensitivity of this procedure for the determination of both elements at 360 mμ was very much less than that for the separate elements at 260 mμ; for selenium $\varepsilon_{360\ \mathrm{m}\mu} = 94$, and for tellurium $\varepsilon_{360\ \mathrm{m}\mu} = 240$. For milligram amounts of selenium and tellurium the method is more convenient and less time-consuming, however, than methods which require an initial separation of selenium from tellurium by reduction or distillation. The results in Table I show that the method is applicable to relatively large amounts of selenium and tellurium alone and in admixture.

Composition of complexes. The constitution of the selenium and tellurium thioglycollate complexes was studied by the methods of continuous variations, mole ratio and slope ratio. The presence of a 1:4 tellurium–TGA complex and a 1:3 selenium–TGA complex was clearly revealed by each method. It is not possible to assign any definite structure to the complexes without further evidence; however, the sulphur of the reagent molecules is probably coordinated to the tellurium and selenium, and the carboxyl groupings remain undissociated and are not bonded to the cation. Calculations of the degree of dissociation (α) of the 2 complexes from the continuous variations studies gave conditional stability constants of $2.2 \cdot 10^{18}$ for the 1:4 tellurium complex and $9.0 \cdot 10^{15}$ for the 1:3 selenium complex.

TABLE I

DETERMINATION OF SELENIUM AND TELLURIUM IN SYNTHETIC MIXTURES

Se taken (mg)	*Se found (mg)*	*Te taken (mg)*	*Te found (mg)*	*Error (%)*	
				Se	*Te*
		0·57	0·57		0
		0.64	0.63		−1.7
		0·95	0.98		+3.1
0.27	0.25			− 7.3	
0·35	0.34			− 2.8	
0·47	0.49			+ 3.8	
0·71	0·74			+ 3.9	
1.58	1.54	0.63	0.65	− 2.5	+3.2
1.42	1.41	1.28	1.23	− 0.7	−3.9
0.24	0.27	3.06	2.95	+12.5	−3.6
0·40	0.41	3.06	2.91	− 2.5	−4.9

Extraction of complexes. Under the recommended conditions quantitative extraction of selenium and tellurium was achieved; no selenium(IV) or tellurium(IV) was detectable in the residual aqueous phase. Only 80–90% extraction was achieved, however, when large amounts of selenium (80 mg) and tellurium (120 mg) were extracted using a 50- and 30-fold excess of TGA respectively from both 1 and 5 *M* hydrochloric acid.

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Phosphorimetric background of the ether extracts of blood and urine at various pH values*

Phosphorimetry has recently been used for the trace analysis of drugs[1,2] and metabolites of pesticide residues[3] in blood and urine. In all of these studies, the compound of interest was extracted from blood or urine in a somewhat arbitrary manner with regard to the pH of the sample. It was felt that a thorough and systematic study of the phosphorescent characteristics of an ether extract of the 2 body fluids would aid in the judicious choice of a pH for performing the extraction (where more than one pH range will yield a good recovery of the compound of interest, of course). Such a study would allow analysts to decide whether phosphorimetry will provide a convenient means of analysis. Because phosphorimetric measurements must be made[4] in a solvent which forms a clear, rigid glass when rapidly cooled to 77°K (liquid nitrogen temperature), the phosphorescence of the compound of interest cannot be easily and accurately measured directly in the body fluid. Also the presence of relatively high concentrations of phosphorescent substances in these fluids normally eliminates possibilities for measurement of the compound of interest which is often present in relatively small concentrations. Hence, suitable separation methods must generally be used. Usually the initial separation technique, which is used before chromatographic separation and phosphorimetric measurement, is simple extraction with an immiscible solvent such as ether. The solvent used, of course, depends on the solubility characteristics of the compound. After appropriate adjustment of the pH, the extraction is carried out.

Because of the complex nature of blood and urine, the phosphorimetric background of an ether extract varies with pH. Therefore, in order to choose judiciously the pH for an extraction in which phosphorimetry is the measurement technique, the analyst should be aware of the phosphorimetric background which may be expected. With these considerations in mind, the variation of ether-extractable phosphorescence background with pH of blood or urine was determined.

Apparatus

An Aminco-Bowman Spectrofluorimeter with an Aminco-Keirs phosphoroscope attachment (manufactured by American Instrument Company, Inc., Silver Spring, Maryland), a 150-W xenon arc lamp, a potted R.C.A. 1P28 photomultiplier tube and an Electro Instruments model 1620-814 X-Y recorder (manufactured for American Instrument Company, Inc., by Electro-Instruments, Inc., San Diego, California), were used for all phosphorimetric measurements and for obtaining excitation and emission spectra. All quantitative data were obtained with slit arrangement number 3 (American Instrument Company, Inc., Silver Spring, Maryland, Instruction Manual No. 838).

Procedure

Whole blood (1 ml) was pipetted into a centrifuge tube. A protein-free filtrate was prepared by adding 6 ml of 5% trichloroacetic acid (w/w). The mixture was shaken vigorously and centrifuged for 5 min. The protein-free filtrate was decanted into a vial, and the pH was adjusted to the desired value with acid or base. The filtrate was then quantitatively transferred to a 10-ml volumetric flask and diluted to volume.

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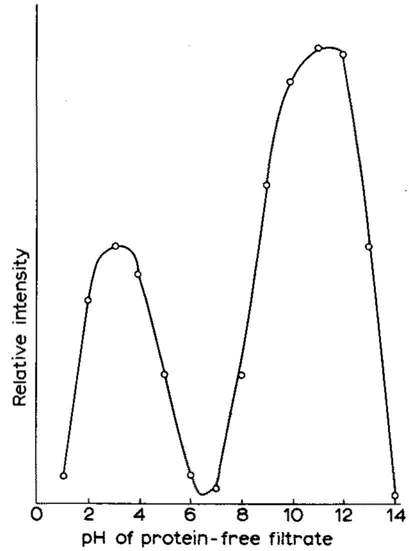
* This work was carried out as part of a study of the phosphorimetric analyses of drugs in blood and urine, supported by a grant from the U.S. Public Health Service (GM-11373-02).

The extraction was performed with one 10-ml portion of ethyl ether. Five ml of the ether extract were decanted with the aid of a hypodermic syringe into a vial. To this extract, 7 ml of a previously made mixture of 2-methylbutane and ethyl alcohol (5:2, v/v) were added. This combination makes an excellent solvent for quantitative phosphorimetric analysis[4]. This mixture is known as EPA. The phosphorescence intensity of the EPA solution was measured, and spectra were recorded[1].

Fresh urine (1 ml) was adjusted to the desired pH and diluted to 10 ml as above. Before extracting any urine sample, it was checked for the presence of protein by performing parallel analyses with and without deproteinization by trichloroacetic acid. In all of the urine samples measured, there was no significant difference in the 2 determinations, and hence the protein which might have been present was regarded as negligible. This solution was extracted with 10 ml of ether and diluted as above. The phosphorescence intensity was measured, and spectra were recorded[1].

Results and discussion

Figure 1 shows the variation in phosphorescence intensity with pH for blood extracted by the above procedure. Each plotted point represents the average of 4 replicate determinations. The emission spectrum (uncorrected for instrumental characteristics) for all pH values was a broad structureless band. The excitation spectrum



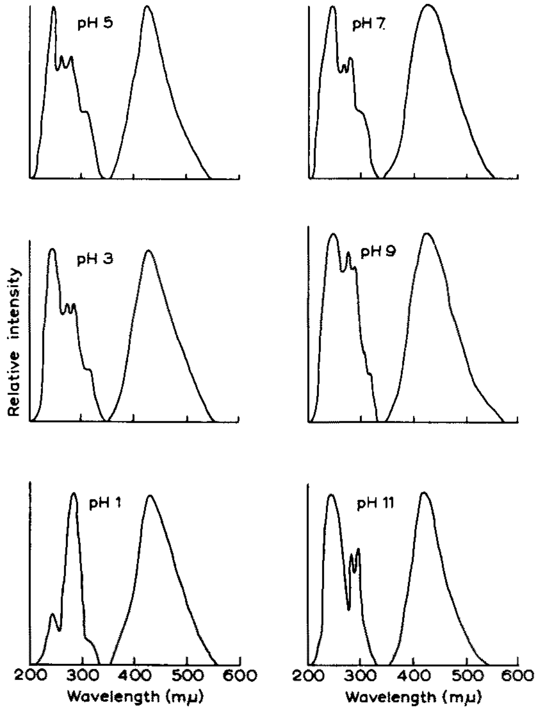
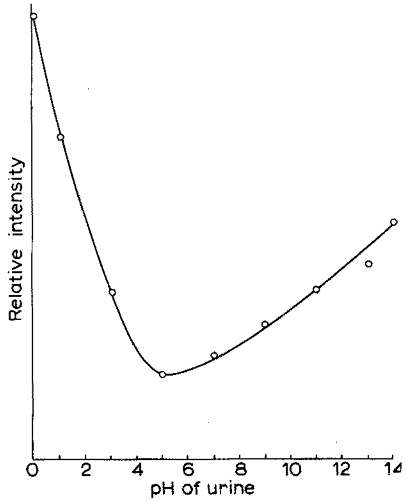


Fig. 1. Variation of ether-extractable phosphorescent background of a protein-free filtrate of whole blood as a function of pH.

Fig. 2. Phosphorescence excitation and emission spectra of the ether extract of a protein-free filtrate of whole blood at various pH values. In each plot, the excitation spectrum is at lower wavelengths than the emission spectrum.

(uncorrected for instrumental characteristics[5]) showed 2 major peaks at 235 and 265 mμ. Figure 2 shows the variation in the phosphorescence excitation and emission spectra for blood extracted at different pH values.



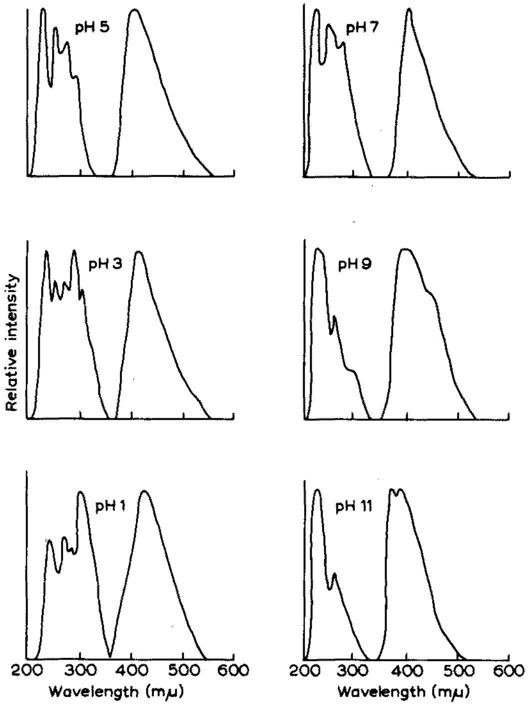


Fig. 3. Variation of ether-extractable phosphorescent background of urine as a function of pH.

Fig. 4. Phosphorescence excitation and emission spectra of the ether extract of urine at various pH values. In each plot the excitation spectrum is at lower wavelengths than the emission spectrum.

Figure 3 shows the variation in phosphorescence intensity with pH for urine extracted at different pH values. Eight different urine samples were run with a duplication at alternate pH units from 1 to 13 and at 0 and 14. Wide variations in the phosphorescence intensity at any given pH and for any given wavelength were found in the relative intensities of different urine samples, but the shape of the curve in Fig. 3 was reproduced for each specimen. Figure 4 shows the variation in the excitation and emission phosphorescence spectra of the urine extract at different pH values. The emission spectrum was in all cases a broad structureless band; the maximum shifted from 425 to 385 mμ from pH 0 to pH 14. The excitation spectrum showed wide variation with pH as can be seen in Fig. 4.

It should be noted that all intensities were recorded on the most sensitive scale of the meter (with the exception of urine backgrounds at pH less than 1). This indicates that great sensitivities should be obtained even for weakly phosphorescent substances. In all cases the backgound of the EPA was small and constant as has been previously observed[1,2,6].

With the information given in this communication, the analyst can more knowledgeably plan the procedure for the phosphorimetric determination of a compound in blood or urine. Ideally, of course, one would choose a pH for extraction where a low background would be encountered because this would allow a more sensitive analysis to be performed. In addition, one would not choose a pH where the background changes rapidly with a small change in pH. It should be pointed out that the phosphorescence background of the specific biological fluid in concern should always be measured. The studies performed here only give the analyst a general look at the phosphorescence background of blood and urine.

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The determination of cadmium in stainless steel by atomic absorption spectroscopy

Polarography is the technique most commonly used for determining cadmium in metals and alloys; this nearly always involves time-consuming prior separations[1–3]. Atomic absorption spectroscopy, which is noted for its relative freedom from interference, was considered worth investigating when a need arose for determining cadmium in some stainless steel. The technique has been successfully applied to the determination of cadmium in urine[4].

Apparatus

An atomic absorption spectrophotometer, similar to that described by Box and Walsh[5], was modified by equipping it with a 10-cm stainless steel tubular burner and a scale expansion unit, both of which were obtained from Techtron Pty. Ltd., Melbourne, Australia.

The cadmium hollow-cathode tube was supplied by Atomic Spectral Lamps Pty. Ltd., Melbourne, Australia.

Reagents

Hydrochloric acid (s.g. 1.18) and nitric acid (s.g. 1.42) were Standard Laboratories Pty. Ltd. Analytical Reagents. Orthophosphoric acid (s.g. 1.75) was Hopkins and Williams AnalaR Grade. High-purity iron powder was obtained from Hilger.

Standard cadmium solutions. (*1*) 0.500 g of spectrographically pure cadmium was dissolved in 20 ml of 50% (v/v) hydrochloric acid by boiling; the solution was cooled and diluted to 500 ml with distilled water. (*2*) 10.0 ml of standard cadmium solution (*1*) were diluted to 1 l with distilled water; 1 ml of this solution contained 0.00001 g of cadmium.

Optimum instrument settings

GATEHOUSE AND WILLIS[6] have listed the cadmium lines at 2288 Å and 3261 Å as the most suitable for atomic absorption measurements. The sensitivities, defined as the concentrations of cadmium required to give 1% absorption, were given as 0.03 p.p.m. and 20 p.p.m. respectively. The use of the 3261-Å line for a 1-g sample diluted to 100 ml corresponds to 0.2% cadmium, which is obviously too insensitive for the determination of cadmium in stainless steel, where the concentration of cadmium is in the range 0–0.01%.

Plots of absorbance *vs.* concentration over the range 0 to 3 p.p.m. of cadmium using air–coal gas or air–acetylene flames at a wavelength of 2288 Å showed that cadmium produced higher absorption in the air–coal gas flame than in the air–acetylene flame. The production of a satisfactory signal-to-noise ratio necessitated operating the hollow-cathode tube at 7 mA, since scale expansion of up to 5 times was used in the lower (<0.5 p.p.m.) concentration ranges. The optimum slit width under these conditions was found to be 0.1 mm. The sensitivity for the air–coal gas flame was checked to be 0.03 p.p.m. of cadmium; this corresponds to a concentration of 0.0003% for a 1-g sample diluted to 100 ml.

TABLE I

THE EFFECT OF ACIDS AND IRON ON THE ABSORBANCE OF CADMIUM

Solvent	*Absorbance*					
	0 p.p.m. Cd		*0.5 p.p.m. Cd*		*1.0 p.p.m. Cd*	
	0 p.p.m. Fe	*10,000 p.p.m. Fe*	*0 p.p.m. Fe*	*10,000 p.p.m. Fe*	*0 p.p.m. Fe*	*10,000 p.p.m. Fe*
Aqueous	0	—	0.097	—	0.201	—
10% HCl	0	0.018	0.100	0.119	0.201	0.208
10% HNO_3	0	0.018	0.097	0.119	0.208	0.215
10% H_3PO_4	0.031	0.031	0.131	0.131	0.215	0.222
10% HCl–2% HNO_3	0	0.018	0.091	0.119	0.205	0.215
10% HCl–2% HNO_3–10% H_3PO_4	0.033	0.031	0.125	0.125	0.222	0.222

Tests for interference

The effect of solvents and matrix elements. The dissolution of stainless steel was best accomplished by heating the sample with concentrated hydrochloric acid. After the initial reaction had ceased, 1–2 ml of concentrated nitric acid was added and the solution boiled until clear. For steels containing tungsten, phosphoric acid was also added to prevent precipitation of tungstic acid. The effect of these acids and iron on the absorbance of cadmium at the 0, 0.5, and 1.0 p.p.m. levels is shown in Table I. It can be seen that phosphoric acid and iron both produced a small "blank effect" which was significant at the lower concentrations of cadmium.

It was necessary to ascertain whether this absorption was due to the presence of cadmium as an impurity in the iron and/or phosphoric acid, or to the effect noted by other workers[7–9] whereby solutions containing dissolved solids caused unreal absorptions at short wavelengths—the so-called "salt effect". Measurements of the solutions were made at a cadmium line which had previously been found to be non-absorbing, *viz.* 2321.2 Å. All the solutions containing iron and/or phosphoric acid produced an absorbance of 0.018 at this wavelength, which could not be due to the presence of cadmium. It was apparent, therefore, that although the iron powder used was quite free from cadmium, the phosphoric acid contained a trace (*ca.* 0.00005%) of this impurity. Thus both the "salt effect" and the presence of cadmium in the phosphoric acid had to be considered in the final procedure.

The effect of alloying elements. Interference studies were carried out at the 0, 0.005, and 0.01% cadmium levels by adding the appropriate quantities of spectrographically pure metal to 1-g samples of H.H.P. iron powder dissolved in 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid. It was found that the presence of 20% chromium, 20% nickel, 20% manganese, 10% cobalt, 10% copper, 5% molybdenum, 5% titanium, 5% vanadium, 5% lead, or 5% aluminium had no effect on the absorbance obtained in the presence of the iron alone. Tests were also carried out by dissolving 1-g samples of National Bureau of Standards (N.B.S.) samples 123 and 50a in a mixture of 10 ml of hydrochloric and 10 ml of phosphoric acids, oxidising with 2 ml of nitric acid and adding 0, 5, and 10 ml of standard cadmium solution (*2*) before dilution to 100 ml. These tests showed that niobium and tungsten, in concentrations of 0.4 and 18% respectively, also did not affect the cadmium absorption observed in solutions made from pure iron.

Recommended procedure

Preparation of working curves. Dilute 1.0-, 5.0-, 10.0-, 15.0- and 20.0-ml portions of standard cadmium solution (*2*) to 100 ml with distilled water. Measure the absorbance of each solution using a cadmium hollow-cathode tube operated at 7 mA with the monochromator set to pass the cadmium resonance line at 2288 Å using a slit width of 0.1 mm, and an air–coal gas flame of 10-cm length.

Analysis of stainless steel. Weigh out 1 g of sample, add 10 ml of concentrated hydrochloric acid (Note 1) and warm until no further reaction occurs. Add 2 ml of concentrated nitric acid and boil until the solution is clear. Dilute to 100 ml with distilled water and measure the absorbance due to cadmium as described in the preparation of the working curve. Adjust the monochromator to pass the cadmium line at 2321 Å and again measure the "absorbance". Subtract this value from that obtained at 2288 Å and read off the percentage of cadmium from the working curve.

Note 1. If the sample contains tungsten, add 10 ml of phosphoric acid also, and run a blank determination on the phosphoric acid. Subtract the value obtained from the final result.

Results and conclusion

Known amounts of cadmium were added to N.B.S. standard steels 101a, 123, and 50a to give samples corresponding to a range of cadmium concentrations from 0

TABLE II

RECOVERY OF ADDED CADMIUM FROM STANDARD STEEL SAMPLES

Stainless Steel	*% Cadmium added*	*% Cadmium recovered*	*% Error*
N.B.S. 101a	0	0	0
18Cr–9Ni	0.001	0.0010	0
	0.005	0.0052	+4
	0.010	0.0100	0
	0.020	0.0190	−5
N.B.S. 123	0	0	0
18Cr–11Ni–0.4Nb–0.03Ta	0.001	0.0009	−10
	0.005	0.0050	0
	0.010	0.0104	+4
	0.020	0.0200	0
N.B.S. 50a	0	0	
18W–3.5Cr–1.0V	0.001	0.0009	−10
	0.005	0.0052	+4
	0.010	0.0104	+4
	0.020	0.0205	+2.5

to 0.02%. These were carried through the developed procedure alongside two actual stainless steel samples. The unknown samples were also analysed by the polarographic method of KARP AND KRAPF[3]. The results obtained on the synthetic samples showed that the method is at least as accurate as the polarographic procedure[3] since recoveries were within ±5% of the amount added except at the 0.001% cadmium level (Table II). For the two stainless steel samples, cadmium values of 0.0005% were found by the recommended method, and values of 0.0005% and 0.0006% by the polarographic method.

The procedure was found to be accurate, rapid, and free from interference. The lower limit of detection of cadmium was 0.0003%.

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Determination of free tungsten in tungsten silicide (WSi_2)

Tungsten silicide is one of numerous important refractory compounds currently being studied experimentally for utilization as a high temperature material in the space program. Thus far, there has been no known report in the literature on the determination of free tungsten in tungsten silicide. When the concentration of free tungsten is within the range of 1–2% or lower, analysis of this material through X-ray diffraction is not feasible. This paper describes a simple chemical procedure whereby small amounts of free tungsten, incorporated in a tungsten silicide matrix, can be determined. Other techniques of analysis do not appear to be capable of quantitatively differentiating between the two phases.

In order to determine free tungsten, it was necessary to use a reagent that attacked free tungsten[1] without attacking tungsten silicide. Hydrogen peroxide solution (30%) was shown to satisfy this requirement (see below). The dithiol spectrophotometric extraction procedure[2] was utilized to determine tungsten in the hydrogen peroxide extract. The quantity of tungsten in this extract included not only free tungsten but also much smaller amounts of tungsten combined as the silicide which were dissolved by the hydrogen peroxide. However, dissolution of the silicide was shown to be very slight; the amount of tungsten silicide calculated to have been dissolved by the hydrogen peroxide was less than 1% of the total silicide present. In order to calculate the amount of free tungsten in the WSi_2 matrix, it was first necessary to determine the concentration of silicon in the peroxide fraction. Based on this value, the amount of tungsten (originally combined as the silicide) in the peroxide solution was calculated asuming that the tungsten was combined as WSi_2. Thus, the free tungsten was equivalent to the difference between the total tungsten in the peroxide fraction and the tungsten originally combined as silicide.

The silicon content in the hydrogen peroxide fraction was determined experimentally by applying the spectrophotometric silicomolybdate (yellow) procedure[3], after removal of hydrogen peroxide.

Determinations of material balance can yield important conclusions about the homogeneity of samples, as well as proving the validity of the method. In an attempt to obtain a material balance, it was necessary to analyze both the tungsten silicide residue remaining after the hydrogen peroxide extraction, and the peroxide fraction, for tungsten and silicon. For this purpose, a 100.0-mg sample was extracted in a plastic beaker with 20 ml of hydrogen peroxide solution (30%) at 60–70° for 1 h. After centrifuging, the supernatant liquid was diluted to volume and analyzed for tungsten and silicon, and the tungsten silicide residue was also analyzed. A plastic, rather than a pyrex, beaker was used for the extraction because the silicide had less tendency to creep on the wall of the plastic beaker.

Preparation of standard stock solution

Standard silicon solution (0.100 mg/ml). Fuse 0.1067 g of ignited SiO_2 in a platinum crucible with 3 g of sodium carbonate. Cool and dissolve the melt in 150 ml of distilled water using a plastic beaker heated on a steam bath. Cool the solution and dilute to 500.0 ml using a pyrex volumetric flask. Store the solution immediately in a plastic container.

Procedure for the determination of free tungsten

Prepare the sample by grinding with a clean steel mortar and pestle. Add 20 ml of hydrogen peroxide solution (30%) to a 100.0-mg sample in a 100-ml plastic beaker. Place a polyethylene sheet over the beaker and secure with a rubber band. Heat the peroxide solution on a water bath at 60–70° for 1 h. After cooling in a cold water bath, transfer the liquid to a centrifuge tube. Centrifuge until clear, and then carefully siphon the supernatant liquid into a 100.0-ml volumetric flask using Tygon tubing (1/16 inch i.d.). Particular care is needed to insure that only the clear supernatant liquid is siphoned. Rinse the residue in the tube with dilute hydrogen peroxide solution (1:20), centrifuge and again siphon into the flask. Dilute to volume with distilled water, and reserve this stock solution for the determination of tungsten and silicon.

Transfer an aliquot of the above stock solution containing 40–100 μg of tungsten to a platinum crucible. Add 5 ml of sulfuric acid to the crucible and evaporate the solution to fumes. After cooling and rinsing the side of the crucible with distilled water, fume the solution again. Apply the dithiol extraction procedure of HOBART AND HURLEY[2] for the determination of tungsten. Take a reagent blank through the complete procedure.

Silicon is determined in the hydrogen peroxide fraction using the silicomolybdate (yellow) spectrophotometric procedure. Transfer a 50.0-ml aliquot of the stock solution to a platinum crucible in a cold water bath. The platinum must remain cool, otherwise the decomposition of hydrogen peroxide in contact with the platinum becomes exceedingly vigorous. When the initial effervescence subsides, warm the solution slightly to continue the decomposition. When the effervescence ceases, add 10 drops of silicon-free sodium hydroxide solution (1:2) and evaporate to dryness. Rinse the wall of the crucible with distilled water and again evaporate to dryness. Dissolve the alkaline residue in 25 ml of distilled water by heating and then cool. Make slightly acidic with dilute sulfuric acid, using pH indicator paper, and then adjust the pH to 1.4 using a pH meter. Add 2 ml of ammonium molybdate solution (10%), allow the color to develop for 5 min, and dilute to 50.0 ml. Using 1-cm cells, read the absorbance at 410 mμ. Take a reagent blank through the procedure and subtract its absorbance from that of the sample. Derive the result from a calibration curve prepared in a similar manner.

Based on the concentration of silicon in the hydrogen peroxide fraction, the amount of free tungsten in the original silicide can be calculated. Free tungsten is equivalent to the total tungsten in the hydrogen peroxide fraction minus the quantity of tungsten that is combined originally as the silicide (WSi_2).

Analysis of the tungsten silicide residue

As part of the material balance study, the tungsten silicide residue remaining after the hydrogen peroxide extraction was analyzed for tungsten and silicon. The following is a summary of the method which was applied.

Fuse the residue remaining after the hydrogen peroxide extraction with sodium carbonate in a platinum crucible, dissolve in hot distilled water, and dilute to 100.0 ml. Transfer a 50.0-ml aliquot of this solution to a 400-ml beaker, heat on a hot plate, and then hydrolyze the tungstic acid from solution by addition of 10 ml of nitric and 5 ml of hydrochloric acid. After digesting for 30 min, add 150 ml of distilled water plus 10 ml of cinchonine solution (60 g per 500 ml of 1:1 HCl solution). Continue the digestion for a few hours until the supernatant liquid is clear. Using a small amount of filter paper pulp, filter the precipitate and ignite to the oxide using a Bunsen burner and a tared platinum crucible. Dilute the filtrate to 500.0 ml and subsequently analyze spectrophotometrically for tungsten using the dithiol extraction procedure. Add several drops of sulfuric acid (1:1) plus 5 ml of hydrofluoric acid to the platinum crucible. Carefully evaporate to dryness on a hot plate volatilizing the silica. Rinse the wall of the crucible with dilute nitric acid (1:98) and re-evaporate to dryness. Ignite to constant weight with a Bunsen burner. The conversion factor (W/WO_3) is 0.793. Tungstic oxide should not be ignited above 850° because of its volatility.

From the 500.0-ml volumetric flask containing the filtrate, transfer a 15.0-ml aliquot to a 50-ml beaker. Add 5 ml of sulfuric acid and cool in a cold water bath. Add 15 ml of HNO_3–HCl (1:1) solution, digest for several hours and evaporate to 7–10 ml. Add 10 ml of nitric acid plus 1 ml of perchloric acid. Digest the resulting solution for another hour and then slowly evaporate to fumes of sulfuric acid. When the organic matter is destroyed, the solution remains clear. Rinse the wall of the beaker with distilled water and evaporate to strong sulfur trioxide fumes to destroy the last traces of organic matter to volatilize the perchloric acid. Then continue as in the dithiol procedure for tungsten.

Determine silicon in the sodium carbonate melt by transferring a 10.0-ml aliquot to a 50.0-ml volumetric flask and diluting to volume. Analyze a 10.0-ml aliquot spectrophotometrically for silicon by following the procedure for the determination of silicon.

Discussion and results

A primary concern was to ascertain whether hydrogen peroxide solution (30%) could selectively and quantitatively separate free tungsten from tungsten silicide; accordingly, it was necessary to determine whether low levels of tungsten (10–12 mg) could be quantitatively recovered from spiked tungsten silicide samples. The tungsten powder used as a spike was weighed out on a Gramatic balance sensitive to 0.03 mg, the accuracy of which was checked in the 5.00–12.00 mg range; the maximum error, 1.3%, was within the range of experimental errors for the procedure. It was shown that quantitative recoveries from spiked samples by the recommended procedure were possible (Table I). No difficulty was experienced in dissolving the free tungsten within 1 h. A tungsten silicide sample containing low levels of free tungsten was chosen

TABLE I

RECOVERY OF TUNGSTEN FROM TUNGSTEN SILICIDE

Weight (mg)	*Tungsten (spike) (mg)*	*Tungsten (extracted) (mg)*	*Blank (free tungsten as part of matrix) (mg)*	*Recovery (mg)*	*% Recovery*
100.0	11.50	11.5	0.28	11.2	97.3
100.0	11.30	11.5	0.28	11.2	99.0
100.0	10.30	10.5	0.28	10.2	99.2

so that the blank would be at a minimum. As noted in Table I, the free tungsten in the matrix material amounted to only 0.28%. The average recovery was approximately 98% of the amount added.

When 100 ml of 30% hydrogen peroxide was placed in contact with 100 mg of tungsten silicide at 60–70° for periods of 1, 2, 3, and 4 h in order to study its reaction with the silicide, the results for the determination of tungsten and silicon indicated that the concentration of tungsten in the extract attained a maximum value within 1 h and then remained essentially constant. Thus, the hydrogen peroxide readily dissolved the small amount of free tungsten, without attacking the tungsten silicide significantly. If the tungsten silicide itself had been attacked, the concentration of tungsten in the extract would have increased with time.

Since the silicomolybdate procedure was used to determine silicon in the hydrogen peroxide fraction as well as in the sodium carbonate melt, it was necessary to test the possible interferences from tungsten and peroxide. With platinum crucibles, an amount of tungsten corresponding to a sample with 2% of free tungsten, was added to a reagent blank and also to an aliquot from a standard solution of silicon. After adding 20 ml of hydrogen peroxide (30%), the solutions were carried through the procedure for the determination of silicon in the hydrogen peroxide extract. The results showed that tungsten and hydrogen peroxide did not interfere at all. The peroxide was effectively destroyed by the platinum crucible acting as a catalyst[4].

A simple test indicated that silicon itself was insoluble in hydrogen peroxide at 60–70°. Although the physical state of silicon changed partially from a black metallic to a brownish amorphous condition, a test of the extract was negative for the presence of significant amounts of silicon.

The material balance study was greatly dependent on the analysis of the WSi_2 residue following the extraction of free tungsten with hydrogen peroxide. The gravimetric method of analysis used for the determination of tungsten lacked precision; however, the average values were significant in that the distribution of tungsten, both in its free and combined state, relative to the two samples was clearly evident (Tables II and III).

TABLE II

MATERIAL BALANCE STUDY

Sample type	*Powder*	*Powder*	*Powder*	*Powder*	*Powder*	*Average*
Sample size (mg)	100.0	100.0	100.0	100.0	100.0	100.0
Tungsten, residue[a] (mg)	77.3	77.2	76.8	75.6	77.7	76.9
Tungsten, H_2O_2[b] (mg)	0.29	0.27	0.28	0.27	0.27	0.28
Silicon, residue[a] (mg)	22.0	23.2	23.2	23.2	23.3	23.0
Silicon, H_2O_2[b] (mg)	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Material balance (mg)	99.6	100.7	100.3	99.1	101.3	100.2
% Free tungsten	0.29	0.27	0.28	0.27	0.27	0.28

[a] The tungsten silicide residue remaining after the extraction.
[b] The peroxide extract.

TABLE III

MATERIAL BALANCE STUDY

Sample type	*Single crystal*	*Single crystal*	*Single crystal*	*Single crystal*	*Average*
Sample size (mg)	100.0	100.0	100.0	100.0	100.0
Tungsten, residue (mg)	74.5	76.6	74.8	75.9	75.4
Tungsten, H_2O_2 (mg)	2.54	2.24	2.26	2.38	2.35
Silicon, residue (mg)	22.0	22.4	22.5	22.2	22.3
Silicon, H_2O_2 (mg)	0.22	0.20	0.20	0.21	0.21
Material balance (mg)	99.3	101.4	99.8	100.7	100.3
% Free tungsten	1.82	1.58	1.60	1.69	1.67

Spectrographic analysis showed that the total impurity was approximately 1250 p.p.m. The major impurities, molybdenum and iron, were each in the approximate concentration range 500 p.p.m. Since the recommended procedure requires only 100 mg of sample, complete extraction of the molybdenum and iron by hydrogen peroxide would yield about 50 µg of each. Tests with the dithiol extraction spectrophotometric method[2] for molybdenum showed that no molybdenum was in fact extracted. Therefore, molybdenum was probably present as the silicide and not as free molybdenum. By means of the *o*-phenanthroline method, the level of iron in the hydrogen peroxide fraction was found to be insignificant.

X-Ray diffraction analysis indicated that free tungsten, if present, was less than 5%. Reportedly, this technique is not sensitive enough to determine free tungsten in the 1–2% concentration range.

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An investigation of the composition of the precipitates formed by the decomposition of silicate rocks in 38–40% hydrofluoric acid

The decomposition of silicate minerals and rocks in 38–40% hydrofluoric acid usually results in the formation of slightly soluble compounds. According to one author[1] the precipitate consists of fluorides and fluorosilicates, while another author[2] assumes the presence of calcium fluoride and magnesium fluoride. Recent investigations[3,4] have demonstrated that the precipitates usually do not contain silicon, and that, in addition to calcium and magnesium, appreciable amounts of aluminium, sodium and iron are present. These results led the present authors to assume that fluorosilicates are not formed, and that, in addition to the simple fluorides, such as calcium and magnesium fluorides, other more complex fluorides are likely to occur. In the literature no data were found on the solubility of fluorides in the 38–40% hydrofluoric acid normally used for analytical purposes.

On the basis of previous qualitative analyses[3,4] of precipitates resulting from the decomposition of silicate minerals in hydrofluoric acid, it was considered of interest to synthesize some fluorides that are likely to be formed, and to examine, by means of X-ray diffraction technique, whether or not the synthesized compounds are present in the precipitates from silicate rocks.

EXPERIMENTAL

Equipment

For the syntheses and analyses plastic equipment was used. Filter crucibles made from polytetrafluoroethylene (PTFE) were constructed; the porous bottom (produced by Gachot, France; porosity 5–10 μ) was made of the same material. The rock samples were decomposed in a specially made PTFE vessel equipped with a tightly fitting stopper. During heating the vessel was placed in an aluminium block.

Reagents

Most of the chemicals were of reagent-grade quality. Chemicals of technical-grade quality were sodium fluoride and iron(II) carbonate. The following acids were used: hydrofluoric 38–40%, hydrochloric about 37% and sulfuric 95–97%.

Synthesis and analysis

Table I gives a survey of the systems studied and the composition of the precipitates that were formed.

In the synthesis the procedure was as follows: 0.500 ± 0.005 g of the solid substance or a mixture (in most cases corresponding to equimolar amounts of the two metals) of the solid substances listed in Table I were weighed out and transferred to a 100-ml plastic beaker; 11.5 ± 0.2 ml of hydrofluoric acid* were added cautiously and the beaker was covered with a plastic watch glass. In most cases the substances dissolved rapidly. After dissolution the beaker was kept on the boiling water bath for 1 h and then cooled to room temperature. In case of precipitation, the solid phase was filtered off, washed with chloroform and dried to constant weight at 105–110°.

The precipitates were then analyzed chemically. With the exception of the samples used for the determination of iron(II) and fluorine, the weighed samples were brought into solution by adding sulfuric acid and evaporating twice to dryness. The residue was dissolved in water. Iron(II) was determined on a weighed sample dissolved in a saturated solution of boric acid. The samples weighed out for the determination of fluorine were brought into solution by fusion with sodium carbonate.

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* The ratio between the volume of hydrofluoric acid added and the amount of rock sample corresponds to the ratio recommended in a scheme of silicate rock analysis[5].

Standards methods were used for the determination of magnesium, aluminium, iron(III), iron(II), sodium and fluorine. Magnesium was determined by precipitation with 8-hydroxyquinoline and drying at 105°. Where required, aluminium was removed by a double precipitation with ammonia solution; iron was removed by a chloroform extraction of the cupferrate. Aluminium was precipitated twice as the hydrous oxide and ignited at 1100°. Where required, iron was separated as described above. The total content of iron was determined either gravimetrically or by titration with a standard solution of potassium permanganate. The latter method was also used for iron(II). Sodium was determined gravimetrically as the sulphate. Fluorine was determined gravimetrically according to a slightly modified Berzelius' method. The latter method was tested using known amounts of fluorine and was found, as expected, to give results 0.8–1.0% (relative) too low. The content of water was found by difference.

TABLE I

A SURVEY OF THE SYSTEMS INVESTIGATED AND THE COMPOSITION OF THE SOLID COMPOUNDS FORMED

System no.	*System*	*Composition of the precipitate*
1	Na_2CO_3–HF	No ppt.
2	$CaCO_3$–HF	CaF_2
3	MgO–HF	MgF_2
4	Al–HF	No ppt.
5	$FeCO_3$–HF[a]	No ppt.
6	Fe_2O_3–HF	No ppt.
7	Al–Na_2CO_3–HF	$NaAlF_4 \cdot 1.3H_2O$
8	Al–MgO–HF	$MgAlF_5 \cdot 2.7H_2O$
9	Al–$CaCO_3$–HF	CaF_2
10	Al–$FeCO_3$–HF[a]	$Fe(II)\,(Al, Fe(III))F_5 \cdot 3.7H_2O$
11	Fe_2O_3–Na_2CO_3–HF	No ppt.
12	Fe_2O_3–MgO–HF	MgF_2
13	Fe_2O_3–$CaCO_3$–HF	CaF_2
14	Fe_2O_3–$FeCO_3$–HF[a]	No ppt.
15	$FeCO_3$–Na_2CO_3–HF[a]	An amount — too small for quant. analysis — was formed. Na and Fe(II) detected.
16	$FeCO_3$–MgO–HF[a]	MgF_2

[a] No precautions were taken to avoid oxidation of iron(II), and consequently appreciable amounts were oxidized during the syntheses.

Preparation of precipitates from rocks

Three rocks were selected for the preparation of precipitates; two were granites and the third a diabase (the reference sample W-1 issued by the U.S. Geological Survey). The chemical composition of these samples is given in Table II. In the PTFE decomposition vessel 0.500 ± 0.005 g of the sample were decomposed in 11.5 ± 0.2 ml of hydrofluoric acid. After attack for 1 h at 110 ± 2° the sample was treated as described above for the synthesis. All samples gave precipitates. The amounts of precipitate are given in Table II.

The precipitates were examined by emission spectrography. The result of this qualitative analysis is given in Table II.

TABLE II

THE CHEMICAL COMPOSITION (IN PER CENT) OF THE ROCKS DECOMPOSED BY HYDROFLUORIC ACID

Constituent	*W-1 diabase*	*Granite*	*Granite*
SiO_2	52.40	62.50	70.00
Al_2O_3	15.11	18.88	14.74
Fe_2O_3	1.62	1.43	0.40
FeO	8.63	3.54	3.08
MgO	6.58	1.22	0.07
CaO	10.97	4.10	2.97
Na_2O	2.07	5.34	3.12
K_2O	0.67	0.97	1.44
TiO_2	1.07	0.92	0.60
Amount (in g) of precipitate after drying	0.274	0.108	0.064
Constituents detected by emission spectrography:			
Main constituents	Ca, Mg, Al, Fe, Na	Ca, Mg, Al, Fe, Na	Ca, Mg, Al, Fe, Na
Minor constituents	Ti, Mn	Ti, Mn	Ti, Mn
Trace constituents	Cu, Si	Zr, Cu	Zr, Cu

X-ray investigations

X-ray powder photographs were taken of the products from the syntheses and of the precipitates from the rock samples. A Guinier-type focusing camera, $CuK\alpha_1$-radiation and a calibrating standard of potassium chloride were employed. The photographs were of varying quality; those of the precipitate from W-1 and of the synthesized magnesium and calcium fluorides were less satisfactory because of broad and diffuse lines. The X-ray photographs of the precipitates from the three rocks were very much alike with regard to the position of the lines and the intensities. The photographs from the two series were compared both directly and on the basis of the *d*-values and intensities.

RESULTS AND DISCUSSION

The investigation indicated that the decomposition of a variety of ordinary silicate rocks in 38–40% hydrofluoric acid results in the formation of the same main compounds which were found to be CaF_2; $MgAlF_5 \cdot xH_2O$; $NaAlF_4 \cdot xH_2O$ and, probably, Fe(II) (Al,Fe(III))$F_5 \cdot xH_2O$.

It is interesting to note that magnesium is not precipitated as magnesium fluoride, but as the apparently less soluble $MgAlF_5 \cdot xH_2O$.

Silicon and potassium do not seem to form slightly soluble compounds, as apparent from the absence of these constituents in the precipitates.

As previously pointed out[4], a slightly soluble iron(II) compound containing fluoride is likely to be formed. The probable composition is Fe(II)(Al,Fe(III))$F_5 \cdot xH_2O$, aluminium and iron(III) replacing each other in the lattice. The possibility of obtaining a precipitate containing iron(II) should be considered when the conventional method for the determination of iron(II) in rocks is used.

Table II indicates that the amount of precipitate increases as the rock becomes more basic. This observation was also made by WILSON[2].

It may finally be mentioned that highly acidic rocks low in calcium and magnesium* may be decomposed without the formation of a precipitate.

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1 W. F. HILLEBRAND, *U.S. Geol. Surv. Bull.*, 700 (1919) 201.
2 A. D. WILSON, *Analyst*, 85 (1960) 823.
3 F. J. LANGMYHR AND P. R. GRAFF, unpublished results.
4 F. J. LANGMYHR AND S. SVEEN, *Anal. Chim. Acta*, 32 (1965) 1.
5 F. J. LANGMYHR, in press.

(Received August 28th, 1965)

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* Such as the reference rock R 117 (SiO_2, 77.06; Al_2O_3, 12.13; total content of iron, 1.27; MgO, 0.08; CaO, 0.29; Na_2O, 3.94 and K_2O, 4.57) issued by Dr. P. G. JEFFERY, Department of Scientific and Industrial Research, Warren Spring Laboratory, Great Britain.

The spectrophotometric determination of iron with 8-quinoline carboxylic acid*

MAJUMDAR[1] reported that a red precipitate with the formula $Fe(C_{10}H_6O_2N)_2 \cdot H_2O$ was formed by the reaction of iron(II) with 8-quinoline carboxylic acid. It has been found that this red precipitate can be extracted into a mixture of pyridine and chloroform and the iron determined by measuring the absorbance at 530 mμ.

Apparatus

Absorbance curves were obtained on a Cary Model 14 recording spectrophotometer. All other absorbance measurements were made on a Beckman D. U. spectrophotometer equipped with a photomultiplier attachment; 1-cm silica absorption cells were used.

Measurements of pH were made with a Beckman Model G pH meter equipped with a Beckman no. 40495 glass electrode and a saturated calomel electrode.

Reagents

8-Quinoline carboxylic acid solution. A solution was prepared by dissolving 0.8 g of reagent in sodium hydroxide and diluting to 100 ml. Nitrogen was bubbled through the solution to remove oxygen.

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* From a portion of the Ph.D. Dissertation of JAMES M. ZEHNER, Ohio State University, December, 1964.

Standard iron solution. 0.3659 g of iron wire was dissolved in 20 ml of 1:1 hydrochloric acid. The yellow color of iron(III) was removed with a few crystals of tin(II) chloride and the solution was diluted to 1 l with oxygen-free water. By diluting 50.0 ml of this solution to 1 l a solution containing 18.29 p.p.m. of iron was prepared.

Procedure

To a 12.5-ml Squibb separatory funnel with a teflon stopper, through which nitrogen has been passed to remove oxygen, add 25.0 ml of iron sample (containing 0.01–0.25 mg of iron), 1 ml of 0.18%(w/v) tin(II) chloride in 0.1 *M* hydrochloric acid, and 3 ml of 8-quinoline carboxylic acid solution. Adjust the pH to 3–6. Dilute to *ca.* 30 ml with oxygen-free water, add 5 ml of 1:9 pyridine–chloroform mixture, and shake vigorously. Allow the phases to separate and transfer the pyridine–chloroform layer to the absorption cell. Measure the absorbance at 530 mμ.

Discussion and results

The red complex dissolved in chloroform had absorbance maxima at 385 mμ and 530 mμ (Fig. 1). The maximum at 385 mμ did not obey Beer's law; at 530 mμ Beer's law was obeyed over the range 0.03–0.23 mg of iron per 5 ml of organic phase.

Studies of pH, volume of reagent, and volume of pyridine were conducted to determine the optimum conditions for the determination.

The absorbance was constant when the aqueous layer was in the pH range 6.5–7.3. This condition was satisfied when the pH of the solution before the addition of the pyridine–chloroform mixture was between 3 and 6. The final pH range was narrow but both the reagent and pyridine were good buffers in this range.

The absorbance was constant if more than 0.3 ml of pyridine was added to the solution and extracted into 5 ml of chloroform. In the final procedure approximately 0.5 ml of pyridine was used. The absorbance was also found to be constant with the addition of 2 or more ml of reagent solution.

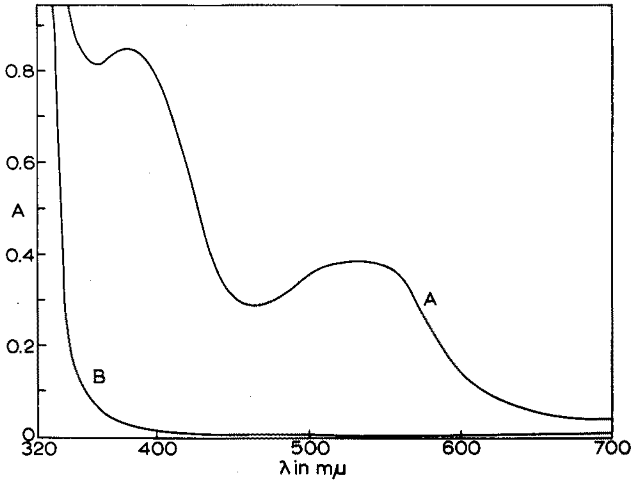

Fig. 1. Absorption spectra of iron(II) 8-quinoline carboxylic acid (A) and reagent blank (B) in chloroform–pyridine mixture. Weight of Fe(II) = 91.5 μg.

By means of Job's method the ratio of reagent to iron was confirmed as 2:1. An attempt was made to determine the ratio of pyridine molecules to iron by Job's method but it was unsuccessful. A large excess of pyridine was necessary to extract the complex. It is felt that 2 pyridine molecules fill the remaining two coordination positions of the iron.

TABLE I

TOLERANCE FOR METAL IONS

Metal tested	*Tolerable amount (mg)*	*Metal tested*	*Tolerable amount (mg)*
Copper	0.2	Zinc	1.0
Nickel	1.3	Aluminum	0.04
Cobalt	0.36	Manganese	14.0

Interferences

Table I shows the amount of interfering metal ion which will cause a relative error of 1–2% when measuring 0.10 mg of iron. Chloride, nitrate and sulfate ions did not interfere up to a concentration of 0.05 *M*.

The interference of copper was greater than that expected from the removal of reagent by precipitation; this was probably caused by adsorption of iron complex on the precipitate. Aluminum interference is explained by the adsorption of iron on aluminum hydroxide.

Tin(II) chloride was chosen to reduce the iron. However, the addition of 2 ml of this reagent caused a decrease in absorbance as a result of the adsorption of the red complex on the tin hydroxide formed; 1 ml of reducing solution did not interfere and was 5 times the amount needed to reduce the quantity of iron which gave an absorbance of 0.8.

All interferences caused a decrease in absorbance except cobalt which caused an increase when small amounts were present and a decrease in high concentrations.

The sensitivity of the method expressed as the weight of iron corresponding to an absorbance of 0.010 at 530 mμ is 2.4 μg. This is a sensitivity of 0.1 p.p.m. if a 25-ml sample of unknown iron is used.

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James M. Zehner*
Thomas R. Sweet

1 A. K. Majumdar, *J. Indian Chem. Soc.*, 22 (1945) 309.

(Received October 11th, 1965)

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* Present address: E. I. du Pont de Nemours & Co., Wilmington, Del.

BOOK REVIEWS

R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley & Sons Inc., New York–London, 1965, 721 pp., 12″ × 9¼″, price £ 15/15/—.

This is an excellent text-book on the whole subject of flame spectroscopy and its application to chemical analysis, not, as the authors are at pains to point out, a 'cook-book' of specific analytical applications of flame photometry. It is a serious and readable combination of basic theory and practical know-how. No other book provides such a comprehensive assemblage of data on the basic phenomena involved. The excellence of the work is marred almost solely by its high cost, consequent on an excessively high standard of book production with lavish illustration in colour and in black and white.

Part I contains 14 chapters on the analysis of flame properties and on the construction and functioning of flame sources, with a very good comprehensive historical introduction to flame spectroscopy. Throughout the book, prime attention is paid to acetylene flames, as the most important for analytical work, but other sources of current interest such as the cyanogen/oxygen flame and the plasma-jet flame are dealt with. The acetylene/nitrous oxide flame, however, is not treated. A good chapter on the principles of the atomic absorption method is also included.

Part II is devoted to the mechanism of the production of spectra, and to reactions and species occurring in acetylene flames. Much of the theory is available elsewhere, but its inclusion is perhaps justified for completeness. As in Part I, numerous references are given at the end of each chapter.

Parts I and II are based on the 'French Edition', *l'Analyse Spectrale Quantitative par la Flamme*, published by Masson in 1954, expanded with new material (up to about 1963) to more than twice its original size. The translation generally is very good indeed, and only occasionally do we find transliterative errors such as "enounced" for enunciated (p. 5) and the quaint chapter heading "Notions on the Theory of Atomic Spectra".

Part III consists entirely of valuable reproductions of flame spectrograms for acetylene flames, wavelength tables for lines, band-heads and continua, together with bibliographies. Ease of reference to the spectrograms could have been improved by more adequate legends.

The authors are to be congratulated on producing an important text-book and reference manual. It provides much of the background for, and leads up to, the several other books on flame photometry which are more concerned with specific analytical applications of the technique. This would be a valuable addition to the libraries of most practising analytical spectroscopists. The poor student must however wait for a cheap reprint.

A. M. Ure (Aberdeen)

E. L. ELIEL, N. L. ALLINGER, S. J. ANGYAL AND G. A. MORRISON, *Conformational Analysis*, J. Wiley and Sons, Inc., New York, 1965, xiii + 524 pp., price 113 s.

It is indeed fitting that this book should be dedicated to Professor D. H. R. BARTON, the father of conformational analysis. Although Professor BARTON's classic conceptual paper was published some 15 years ago, the continued extensive interest and activity in conformational analysis is reflected by the fact that certain sections of the book, especially the chapter on medium rings, are now sadly out of date. Nevertheless, the authors are to be complimented for their joint preparation which is likely to become the "bible" of this field.

The book contains 6 anonymous chapters but individual styles and interests are not difficult to discern. The first 4 chapters are concerned with principles and their development and with the methodology of conformational analysis. Acyclic compounds are first treated briefly followed by a more extended account of cyclohexane chemistry. There follows a comprehensive survey of physical methods. It is the chapter on small and medium rings which may at present be regarded as embryonic. The latter part of the book is concerned with the application of the principles to steroids, triterpenoids, alkaloids, and carbohydrates and the fruits of the conceptual paper are clear to be seen.

This book will remain of undoubted value for years to come both to the aspiring student and to the professional chemist.

A. B. FOSTER (Birmingham)

ANNOUNCEMENTS

EUCHEM-CONFERENCES IN 1966 — EUCHEM-KONFERENZEN IM JAHR 1966

8–13 May: *Stereochemistry*, Burgenstock (Switzerland). Organised by: Prof. D. ARIGONI, Organic Chemistry Lab., Technical High School, Zürich (Switzerland).

10–13 May: *Chemistry in Molten Salts*, Ulvik, Hardanger (Norway). Organised by: Prof. H. FLOOD, Inorganic Chemistry Dept., Technical University, Trondheim (Norway).

In September: *Far Infrared Spectroscopy*, in Great Britain. Organised by: Prof. H. W. THOMPSON, St. John's College, Oxford (Great Britain).

12–17 September: *Chemistry of Insects*, Villa Monastero, Varenna (Italy). Organised by: Prof. A. QUILICO, Politechnico di Milano, Istituto di Chimica Milano, Milano (Italy).

24–28 October: *Synthesis and Characterisation of Organic Radicals*, Schloss Elmau b. Mittenwald (Germany). Organised by: Prof. K. DIMROTH, Chemical Institute of the University, 355 Marburg, Bahnhofstr. 7 (Germany).

General enquiries and suggestions for future conferences should be sent to Prof. H. W. THOMPSON, St. John's College, Oxford (Great Britain).

INTERNATIONAL SYMPOSIUM ON PHYSICAL SEPARATION METHODS IN CHEMICAL ANALYSIS

An International Symposium on Physical Separation Methods in Chemical Analysis is being organized by the Analytical Chemistry Section of the Koninklijke Nederlandse Chemische Vereniging, and will be held in the Congres-centrum, RAI, Amsterdam, from April 10th to 14th, 1967.

Scientific programme

The scientific programme will consist of invited and submitted papers. Invited papers will be presented in four morning sessions. Submitted papers will be presented and discussed in two parallel sessions on four afternoons. On April 12th there will be excursions to the research laboratories of some large industries, or to places of interest to tourists. All papers will be published in the May/June (1967) issue of *Anal. Chim. Acta*, and this issue will be sent to the participants about two weeks before the symposium. Discussions will be published later in a supplement and forwarded to the participants.

The subjects of the invited papers and the names of the lecturers are as follows:

1. Chromatography; G. W. A. RIJNDERS (Koninklijke Shell-Laboratorium, Amsterdam).
2. Gel permeation and molecular sieve effects in chromatography (lecturer to be announced).
3. Ion exchange chromatography; O. SAMUELSON (Technical University, Göteborg).
4. Zone melting; H. SCHILDKNECHT (University of Heidelberg).
5. Ultracentrifugation of synthetic polymers; H. BENOIT (Centre de recherches sur les macromolécules, Strasbourg).
6 Macromolecular interactions in gel permeation, electrophoresis and ultracentrifugation; G. A. GILBERT (University of Birmingham).
7. Electrophoresis; H. BLOEMENDAL (University of Nijmegen).

Intending authors

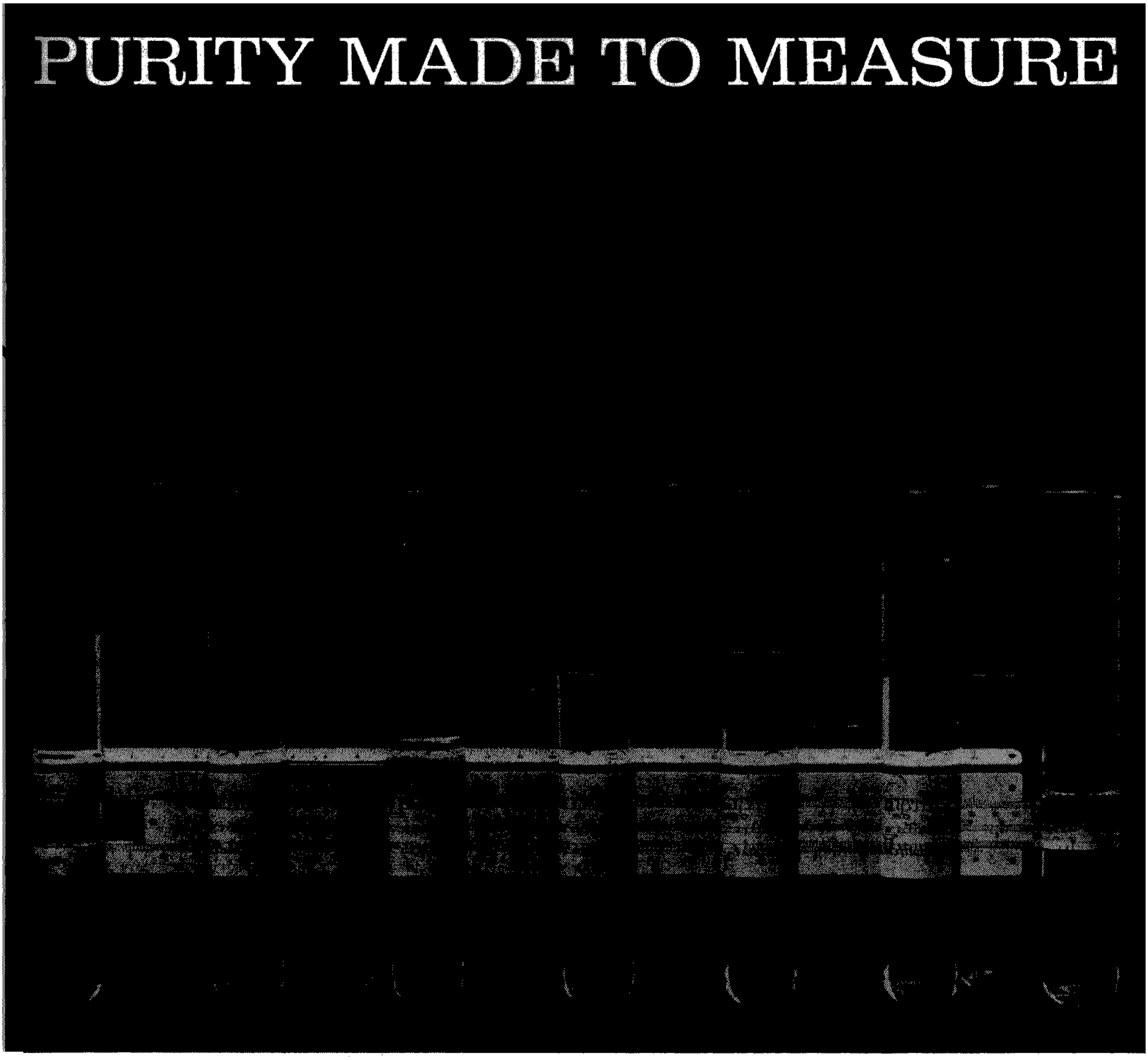
Those wishing to submit papers for consideration for the afternoon sessions should send an abstract of about 300 words (2 copies) to the secretary (C. L. DE LIGNY, c/o Analytisch Chemisch Laboratorium, State University, Utrecht, Netherlands) not later than August 1st 1966. In the course of August the abstracts will be screened by an international committee and the authors will be informed whether or not the papers are suitable for inclusion. In order that the proceedings may be prepared in time, the complete texts of accepted papers (about 2000 words, 3 copies) must be received before October 1st 1966. The papers should be of an original character. They can be read in French, German or (preferably) English and should have an English summary. For each paper 30 minutes will be reserved, including discussion. There will be facilities for projecting slides and films.

Social programme

An attractive social programme has been planned, including a visit to the Rijksmuseum and trips to the Keukenhof with its magnificent flowers and to the hydraulic engineering projects of the Delta works.

Registration

Intending participants can obtain further information and application forms from the Congress Bureau, St. Agnietenstraat 4, Amsterdam, Netherlands. The registration fee for delegates will be fl. 125, including proceedings and printed discussions (fl. 35 for non-participating members). The final date for registration is 31.12.1966.


PURITY MADE TO MEASURE

JUST PUBLISHED

Hermann Schildknecht

Zone Melting

Zone melting has within recent years achieved great technical importance. It is the only economic process for producing semiconductors pure enough for the manufacture of transistors, diodes, rectifiers, and solar batteries. For the physicist and chemist it very often presents the ideal method for the production of pure fractions by crystallizing mixtures of various substances. Applications of zone melting are found in other fields than metallurgy. As a micro-method it has repeatedly contributed to the elucidation of the structure of natural products. It has been invaluable in the isolation of pure compounds from mixtures of isomers and homologues previously found difficult to separate.

Ice zone melting, a variant of this process, is of particular importance in biochemistry. It permits one to increase, without degradation and losses, the concentration of biologically active substances in biologically active solutions to such a degree that they may be chemically identified.

The author has drawn heavily on results from various laboratories in addition to his own, thus making the book valuable to a large group of laboratory workers.

Contents

General: The Solidification of a Melt; The Solid-liquid Phase Equilibrium · Eutectic Systems · Zone Melting Behavior of Crystallizing Mixed Phases with Mixed Crystal Formation · Modified Zone Melting Methods · Anomalies in Zone Melting – *Equipment*: General Considerations · Heating · Cooling · The Container · Transport of the Charge · Zone Melting Apparatus – *Special Section*: Zone Melting of Elements and Inorganic Substances · Zone Melting of Organic Compounds.

Translated from the German by Express Translation Service, London.
1966. XII, 224 pages, 220 figures and 29 tables. Plastic DM 36.00 = $ 9.00.
Detailed leaflet available on request.
The German edition of the book is available under the title »Zonenschmelzen«

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NEW YORK AND LONDON

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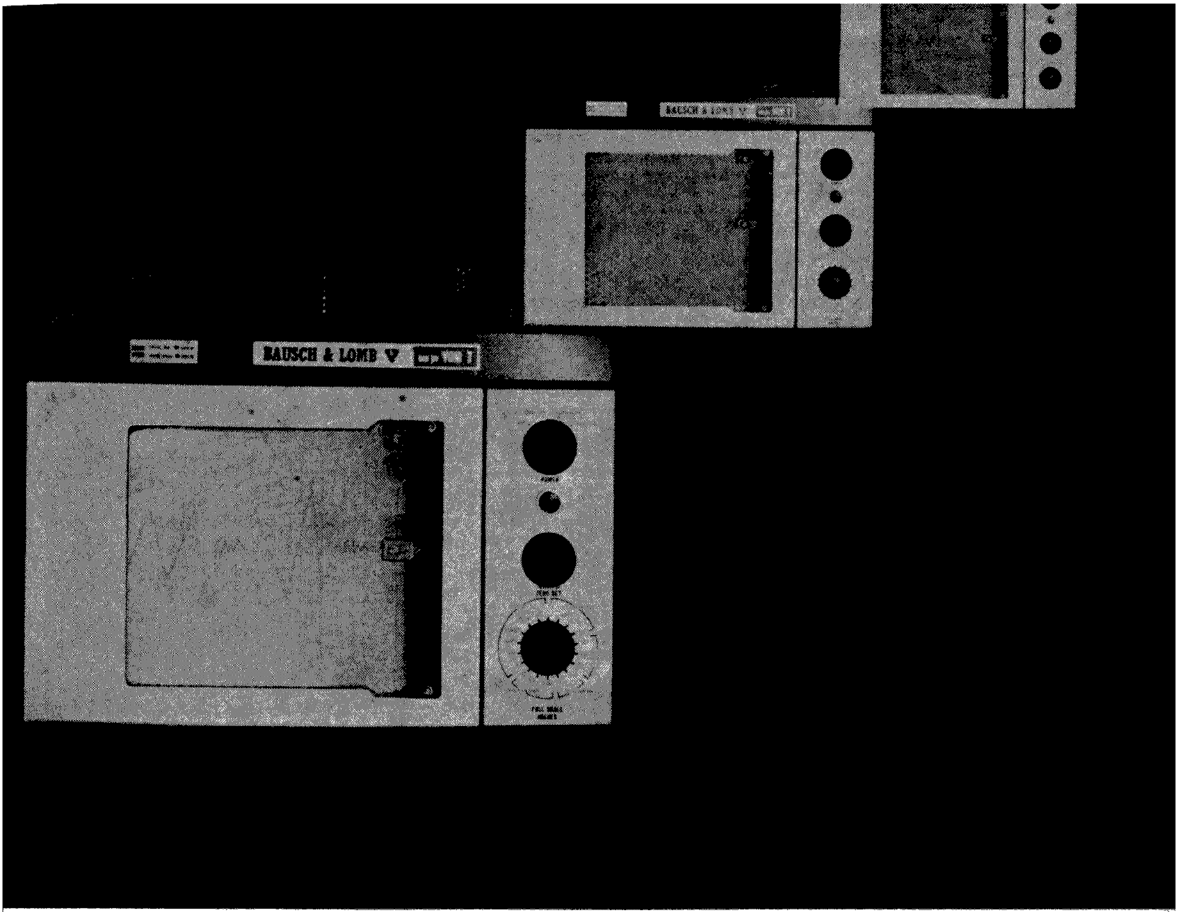
BAUSCH & LOMB

Burette électrique

■ Ces burettes sont destinées à délivrer progressivement un réactif ou une liqueur titrée. Le volume de liquide écoulé est engendré par le déplacement d'un piston calibré, commandé par rotation à l'aide d'une vis micrométrique. La quantité de liquide écoulée est lue directement sur un cadran numérique.

Le piston des burettes PROLABO, pièce dont la qualité détermine la précision de l'instrument, est en invar, métal dont le coefficient de dilatation est pratiquement nul. Il est usiné, rectifié avec une précision impossible à obtenir avec un piston en verre.

Le piston se déplace dans un réservoir à huile, séparé de la chambre à réactif par une membrane souple en « SOREFLON ».
Les réactifs ne sont au contact que de la membrane en « SOREFLON » et d'une pièce en verre « PYREX ».

■ La capacité des burettes à piston PROLABO est de 12,5 cm^3. Les lectures sont faites en centièmes de cm^3 sur un cadran numérique à quatre chiffres. La burette à *commande manuelle* n° 1030.00 est manœuvrée en tournant un seul bouton qui détermine le remplissage ou le vidage. La burette *électrique* n° 1031.02 est mise en œuvre par le jeu de plusieurs interrupteurs électriques qui commandent les opérations suivantes : remplissage, suivi d'une remise au zéro automatique ; vidage rapide ; vidage lent ; vidage « coup par coup », par dixièmes de cm^3. Les moteurs électriques sont tous synchrones, et le réactif toujours délivré à vitesse constante. La burette électrique peut évidemment être commandée à distance, soit à l'aide d'un interrupteur manuel, soit par le signal de sortie d'un titrimètre automatique.

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Vol. 35 No. 1 ANALYTICA CHIMICA ACTA MAY 1966

CONTENTS

Short communications

PRINTED IN THE NETHERLANDS

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

6 x 9″, xxiii + 772 pages, 18 tables, over 2000 lit.refs., 1966, Dfl. 85.00, £8.10.0, $30.00

This 7th edition has involved complete revision and reorganisation of the subject in order to present a still clearer picture of the multitudinous applications open to organic spot test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot test techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis*) and by limiting the number of tables and structural formulae.
Comparison with the 6th edition reveals the following differences:

	Number in 6th Edn.	7th Edn.
Preliminary tests	32	45
Functional group tests	70	109
Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
Differentiation of isomers etc.	0	54
Applications in the testing of materials etc.	111	131

In total the book now gives in 561 sections information on more than 900 tests compared with 600 tests in 346 sections in the preceding edition.

An important feature is the inclusion of a large number of recently developed tests and comments which have not hitherto been published in any form.

It is the author's hope that this work will help to correct the widespread impression that physical instrumentation is always superior to chemical methods for solving analytical problems. Each of the chapters presents instances of problems for which no solutions by physical means have yet been developed, or for which the rapid spot tests are equal or superior to the expensive instrumental procedure.

CONTENTS: 1. Development, present state and prospects of organic spot test analysis. 2. Preliminary (exploratory) tests. 3. Detection of characteristic functional groups in organic compounds. 4. Detection of structures and certain types of organic compounds. 5. Identification of individual organic compounds. 6. Application of spot tests in the differentiation of isomers and homologous compounds. Determination of constitutions. 7. Application of spot reactions in the testing of materials, examinations of purity, characterization of pharmaceutical products, etc... Appendix: Individual compounds and products examined. Author index. Subject index.

FROM REVIEWS OF THE SIXTH EDITION

... This new book, like its author, is unquestionably a giant on the analytical scene...
Journal of the Royal Institute of Chemistry

... Die Tatsache, dass Feigls klassisch gewordenes Werk, welches überall mit Begeisterung aufgenommen wurde, bereits in 6. Auflage erscheint, ist an sich Empfehlung genug... Es ist also eine wahre Fundgrube für neue Experimentaluntersuchungen... *Chimia*

... Even in these days of physical instrumentation there is ample room for the techniques described in this book which were originated and largely developed by Prof. Feigl. They are mostly very quick and very economical on materials. They sometimes present solutions to problems so far insoluble by expensive physical methods...
Laboratory Practice

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