ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 40, No. 3, 365–548, March 1968
Published monthly. Completing Vol. 40

ANALYTICA CHIMICA ACTA

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2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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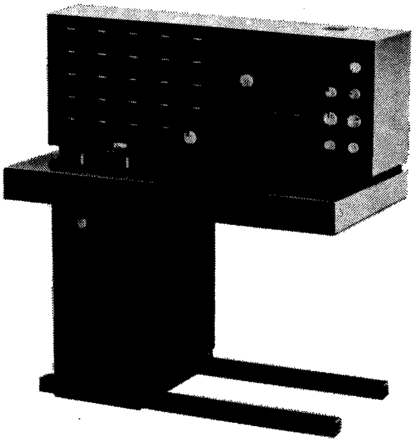

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Zn	Cd	Ag	Hg	Pb	Sn	As	Sb	Fe	Mn	Cr	W	V	Mo
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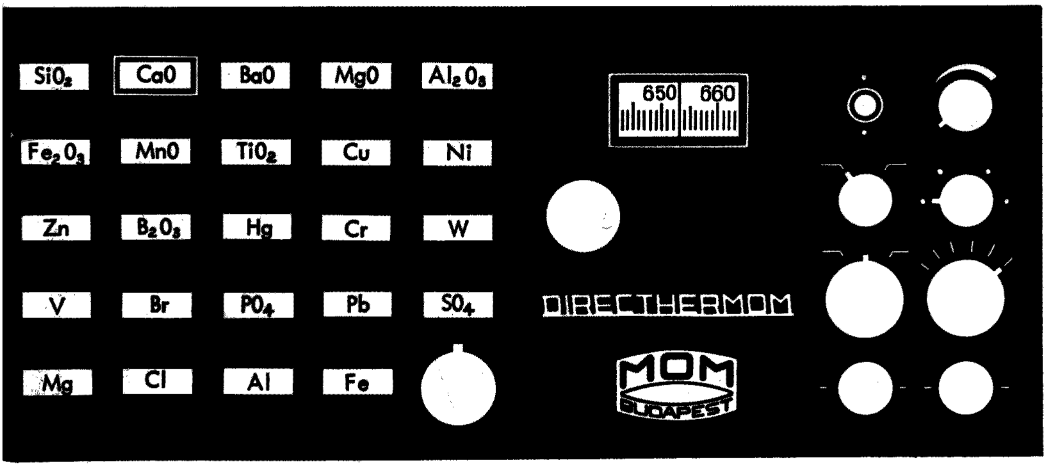

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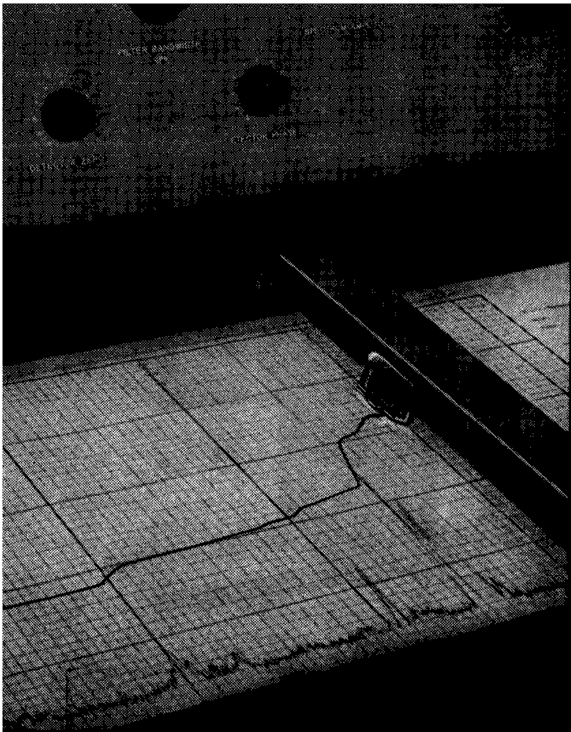

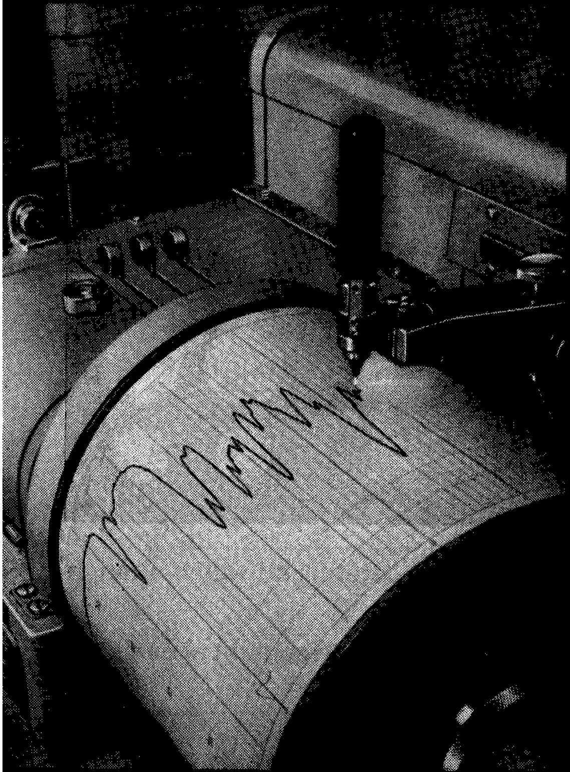

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 40, No. 3, March 1968

PRECISE, NON-DESTRUCTIVE DETERMINATION OF FLUORINE BY 14-MeV NEUTRON ACTIVATION ANALYSIS

A procedure is described for the precise determination of fluorine in organic and metal-organic compounds by 14-MeV neutron activation analysis using the reaction: ^{19}F (n, 2n)^{18}F ($\beta^+, t_{\frac{1}{2}} = 110$ min). A relative standard deviation of better than ±0.5% is achieved by irradiating samples and standard simultaneously. Uniform neutron exposures were ensured by rotating the samples during irradiation. Positron emitters of short half-life are allowed to decay before counting. In metal-organic compounds, Sc, Zn, Ga and Ag cause the most serious interference; for organic compounds the method is rapid, and specific for fluorine.

E. A. M. England, J. B. Hornsby, W. T. Jones and D. R. Terrey,
Anal. Chim. Acta, 40 (1968) 365–371

DETERMINATION OF RHENIUM IN MOLYBDENITES BY NEUTRON ACTIVATION ANALYSIS

A thermal neutron activation method for the determination of rhenium in molybdenites is described. The rhenium is separated from the matrix after irradiation by pyridine extraction from 4 *N* sodium hydroxide solution; γ- and β-spectrometry are applicable. For a neutron flux of $4 \cdot 10^{11}$ n/cm^2. sec, an irradiation of 2 h and a sample of *ca.* 50 mg, β-counting allows determinations in the p.p.b. range.

Iv. Boyadjov, R. De Neve and J. Hoste,
Anal. Chim. Acta, 40 (1968) 373–378

NON-DESTRUCTIVE ACTIVATION ANALYSIS OF TRACE IMPURITIES IN GERMANIUM

A non-destructive activation analysis of trace impurities in germanium giving rise to long-lived γ-emitting isotopes is described. Hg, Sn, Cr, Sb, Sc, Zn and Co were determined by γ-spectrometry after irradiation with thermal neutrons ($\phi_{th} = 10^{14}$ n.cm^{-2}.sec^{-1}, irrad. time: 15 h, cooling period: *ca.* 30 days). The complex γ-spectrum was analysed by a combination of Covell's method and matrix calculus. The detection limits are approximately 2 p.p.b. of Hg, 7 p.p.b. of Cr, 200 p.p.b. of Sn, 1 p.p.b. of Sb, 10 p.p.b. of Zn, 0.2 p.p.b. of Co and 0.1 p.p.b. of Sc.

R. De Neve, D. De Soete and J. Hoste,
Anal. Chim. Acta, 40 (1968) 379–386

NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PHOSPHORUS(V) PESTICIDES

PART II. A RAPID DETERMINATION OF THE ISOMER RATIO OF SYSTOX

The integration circuit of the Varian A-60 nuclear magnetic resonance spectrometer is used in conjunction with vapor phase chromatography, to develop a rapid analysis technique for the determination of isomer ratios in technical Systox–Sulfotepp mixtures. The complete analysis requires less than 0.1 g of sample and only 15 min. The isomer ratio in the sample may be determined to an accuracy of ± 1.5% and the undamaged sample may be recovered.

H. Babad, T. N. Taylor and M. C. Goldberg,
Anal. Chim. Acta, 40 (1968) 387–392

EMISSION SPECTROCHEMICAL DETERMINATION OF CHROMIUM IN ORGANIC ACIDS

An emission spectrochemical procedure is described which directly determines the chromium concentration in organic materials in the p.p.m. range. The only preparation of the sample which is necessary is dilution with a graphite matrix which contains the internal standard element and the spectral buffer, lithium carbonate. The effect of sodium on spectral line intensities of cobalt and chromium is shown. The effectiveness of lithium carbonate as a spectral buffer is illustrated. The precision of the technique is estimated to be ± 11.8% and the accuracy estimated to be 10.9%.

A. L. Schalge, B. D. McCarty and R. E. Lewis,
Anal. Chim. Acta, 40 (1968) 393–399

THE SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC HYDROXYL IN ESTERS WITH VANADIUM OXINATE

A method is described for the precise determination of small amounts of aliphatic alcohols in esters. The procedure is based on the formation of a red-coloured complex between the alcohol and a solution of vanadium oxinate in nitrobenzene. Studies have been made on the effect of solvent, reaction time and the stability of the complex on the accuracy of the determination.

R. Amos,
Anal. Chim. Acta, 40 (1968) 401–406

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH DITHIZONE USING THE SYNERGISTIC EFFECT OF PYRIDINE

The extraction of manganese with dithizone using the synergistic effect of pyridine has been studied. A method is described for determining manganese spectrophotometrically. Trace amounts of manganese can be determined, the sensitivity being 0.0014 μg Mn/cm^2 at 530 nm.

H. Akaiwa and H. Kawamoto,
Anal. Chim. Acta, 40 (1968) 407–412

COLORIMETRIC DETERMINATION OF PALLADIUM WITH PYRIDINE-2-ALDEHYDE-2′-PYRIDYLHYDRAZONE

The colorimetric determination of palladium described involves the extraction of chloro(PAP)palladium(II) from an acidic aqueous solution into *o*-dichlorobenzene and measurement of the absorbance of the extract solution. The method is suitable for the determination of 10–100 μg of palladium. Tolerance amounts for many metals have been determined and compare very favourably with those of other methods.

A. J. CAMERON AND N. A. GIBSON,
Anal. Chim. Acta, 40 (1968) 413–419

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART II. A THEORETICAL TREATMENT OF THE EFFECT OF MEMBRANE SELECTIVITY

The possible influence of the selectivity of the membrane used in an indicating electrode with potentiometric titrations was investigated by introducing some simple modifications in the calculations performed earlier. The influence of the selectivity is visible only before the equivalence point when the counter-ion is precipitated initially from the titrated solution. When the co-ion is precipitated initially, the shape of the titration curve is altered only after the equivalence point. The reliability of the determination of the equivalence point can be either advantageously or disadvantageously influenced by the selectivity, depending on the value of the selectivity coefficient and the ratio of the diffusion coefficients.

F. P. IJSSELING AND E. VAN DALEN,
Anal. Chim. Acta, 40 (1968) 421–430

THE COULOMETRIC PRODUCTION OF IODIDE ION FOR TITRATIONS OF MERCURY(I,II)

The dynamic behaviour of the silver/silver iodide electrode was studied. Iodide ions can be produced by cathodic polarization of the silver/silver iodide electrode in acidic and neutral media. This technique can be used for coulometric titrations of mercury(I) or mercury(II) both alone and in mixture. At the microequivalent level of mercury the error is less than 2%.

F. MAGNO,
Anal. Chim. Acta, 40 (1968) 431–435

COLOR REACTIONS OF PYRIDINES WITH PENTACYANOAMMINOFERRATE

Trisodium pentacyanoamminoferrate is proposed as a spot test, chromatographic spray or spectrophotometric reagent for pyridines. A 1:1 colored complex of the reagent and pyridine derivative is formed in aqueous solution. The intensity and stability of the color varies with the pH.

T. A. LARUE,
Anal. Chim. Acta, 40 (1968) 437–442

A DIFFERENTIAL SPECTROFLUORIMETRIC DETERMINATION OF ADRENALINE AND NORADRENALINE

A simple, sensitive method for the differential fluorimetric determination of 0.01–1 μg/ml amounts of adrenaline and noradrenaline is proposed. Oxidation is best done with potassium hexacyanoferrate(III) at pH 6.8. The fluorescent derivatives of adrenaline and noradrenaline, and of noradrenaline alone, are stabilized respectively with alkaline ascorbate or with cysteine–thioglycollic acid mixture, and the fluorescence is measured at 409 and 520 nm respectively.

R. F. C. Vochten, J. Hoste, A. L. Delaunois and A. F. de Schaepdryver,
Anal. Chim. Acta, 40 (1968) 443–449

CATION ANALYSIS BY THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY

PART II. THE DETERMINATION OF COPPER, NICKEL AND ZINC

A method has been developed whereby micro quantities of copper, nickel and zinc resolved on cellulose chromatoplates can be analyzed *in situ* by means of reflectance spectroscopy. Copper and nickel were determined in the presence of 11 other cations without any interference by employing neocuproine and dimethylglyoxime, respectively, as chromogenic reagents. In the case of zinc, the use of 3,3′-dimethylnaphthidine was equally successful except in the presence of tin, cadmium and iron. Deviations to be expected when the procedure is employed routinely to determine nickel, copper and zinc, were estimated to be 2.1, 2.8 and 5.6%, respectively.

M. M. Frodyma, D. F. Zaye and V. T. Lieu,
Anal. Chim. Acta, 40 (1968) 451–457

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XII. ANODIC WAVES OF MONOALKYLDITHIOCARBAMATES AND THEIR REACTIONS WITH HEAVY METALS

Monoalkyldithiocarbamates give two anodic polarographic waves, corresponding to a one-electron and a two-electron process. A reaction scheme is proposed. The unusual behaviour observed during controlled-potential electrolysis in sodium hydroxide media is interpreted as a chemical reaction of the primary electrolysis product; the species formed gives a wave similar to the original compound. Different adsorption phenomena are probably caused by varying orientation of the mercury compound on the electrode surface. The adsorbed layer formed in sodium hydroxide solution is so closepacked that it prevents hydroxyl ions from penetrating and thus giving an anodic wave. For analytical purposes, 0.1 M sodium hydroxide is the most suitable supporting electrolyte; linear calibration graphs can be obtained over the range $5\cdot10^{-5}$–$1\cdot10^{-3}$ M.

D. J. Halls, A. Townshend and P. Zuman,
Anal. Chim. Acta, 40 (1968) 459–472

THE CALCULATION OF INDICATOR ERROR IN OXIDATION–REDUCTION TITRATIONS

Both precise and approximate expressions are derived for the indicator error in oxidation–reduction titrations. Examples are given of the use of these expressions for the choice of the best indicator in titrations with ascorbic acid.

L. Erdey and G. Svehla,
Anal. Chim. Acta, 40 (1968) 473–478

CHELATING RESINS FOR THE CONCENTRATION OF TRACE ELEMENTS FROM SEA WATER AND THEIR ANALYTICAL USE IN CONJUNCTION WITH ATOMIC ABSORPTION SPECTROPHOTOMETRY

An investigation has been made of the uptake of trace elements from both distilled water and sea water by the chelating ion-exchange resins Chelex-100 and Permutit S1005. The resins retained the following elements with an efficiency of *ca.* 100%: Ag, Bi, Cd, Cu, In, Pb, Mo, Ni, rare earths, Re (90% only), Sc, Th, W, V, Y and Zn. Manganese was retained quantitatively only by the Chelex resin. The following elements are removed with 100% efficiency by means of 2 *N* mineral acids: Bi, Cd, Co, Cu, In, Ni, Pb, rare earths, Sc, Th, Y and Zn. Ammonia (4 *N*) completely removes molybdenum, tungsten, vanadium and rhenium. The resins have been used in conjunction with atomic absorption spectrophotometry for the simultaneous determination of zinc, cadmium, copper, nickel and cobalt in sea waters.

J. P. Riley and D. Taylor,
Anal. Chim. Acta, 40 (1968) 479-485

ISOTOPIC ANALYSIS OF NITROGEN WITH LOW ^{15}N CONTENT BY OPTICAL SPECTROMETRY

(in French)

For mixtures of $^{14}N_2$ and $^{14}N^{15}N$ low in ^{15}N (isotopic abundances less than 2%), previous optical spectrometric methods do not produce rapid results of sufficient precision. In this paper, operating conditions are described for the determination of the isotopic content to ±3% near the natural abundance and to ±1% when the sample contains an atom ratio of $^{15}N:^{14}N$ of 1.5:100. The time required for a determination is *ca.* 10 min. A spectrometer is modified by the substitution of an exit slit and a photomultiplier in place of a photographic plate. The excitation of the electrodeless discharge tube is made by a high-frequency field. The method has been applied to samples of ammonium salts, fertilisers and plant material. In all cases, the precision of the isotopic measurements was greater than that required for most agricultural studies (5–6%).

J. P. Leicknam, V. Middelboe and G. Proksch,
Anal. Chim. Acta, 40 (1968) 487–502

THE ANALYSIS OF ALUMINIUM ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY WITH SPECIAL REFERENCE TO THE DETERMINATION OF CHROMIUM AND ZIRCONIUM

The analysis of aluminium-base alloys for silver, copper, magnesium, zinc, chromium, and zirconium by atomic absorption spectroscopy is described. The use of hot flames (nitrous oxide–acetylene) allows improvements to earlier procedures for such analyses. Sensitivities are increased, interferences reduced, and the determination of more refractory elements, *e.g.* Cr and Zr, becomes possible. Hollow-cathode lamps with greatly increased resonance-line intensities are used for the determination of chromium and zirconium.

L. Wilson,
Anal. Chim. Acta, 40 (1968) 503–512

AN ELECTRON-MICROPROBE STUDY OF THE HOMOGENEITY OF GLASS DISCS FOR X-RAY FLUORESCENCE ANALYSIS

(Short Communication)

A. Parker,
Anal. Chim. Acta, 40 (1968) 513–514

BEAM CENTERING IN A NEUTRON GENERATOR

(Short Communication)

W. H. Spell and F. A. Iddings,
Anal. Chim. Acta, 40 (1968) 515–516

DETERMINATION OF MIXTURES OF MERCURY(II) AND ORGANOMERCURY(II) IONS BY DITHIZONE

(Short Communication)

A. M. Kiwan and M. F. Fouda,
Anal. Chim. Acta, 40 (1968) 517–520

ANION-EXCHANGE SEPARATION OF THORIUM FROM THE RARE EARTHS IN AN ACETONE–HYDROCHLORIC ACID MEDIUM

T. F. Cummings and J. Korkisch,

Anal Chim. Acta, 40 (1968) 520–523

VOLTAMMETRIC DETERMINATION OF CERIUM IN CONCENTRATED PHOSPHORIC ACID

(Short Communication)

Y. Lapid, E. Bazini and S. Gottesfeld,
Anal. Chim. Acta, 41 (1968) 524–526

THE AUTOMATIC DETERMINATION OF MANGANESE IN SILICATE ROCKS AND SEDIMENTS

(Short Communication)

M. I. Abdullah,
Anal. Chim. Acta, 40 (1968) 526–530

THE ABSORPTION SPECTRUM OF PHOSPHORUS(III) IODIDE

(Short Communication)

V. C. Anselmo, F. M. Wolters and C.-T. Sun,
Anal. Chim. Acta, 40 (1968) 531–534

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN ORGANIC SOLUTIONS OF TRIBUTYL PHOSPHATE

(Short Communication)

I. Obrenović-Paligorić, I. J. Gal and V. Vajgand,
Anal. Chim. Acta, 40 (1968) 534–537

THE EXTRACTION–SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH CRYSTAL VIOLET

(Short Communication; in German)

W. Likussar, O. Wawschinek and W. Beyer,
Anal. Chim. Acta, 40 (1968) 538–539

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PRECISE, NON-DESTRUCTIVE DETERMINATION OF FLUORINE BY 14-MeV NEUTRON ACTIVATION ANALYSIS

E. A. M. ENGLAND, J. B. HORNSBY, W. T. JONES AND D. R. TERREY
Atomic Weapons Research Establishment, Aldermaston, Berkshire (Great Britain)

(Received July 20th, 1967)

A rapid and precise method was required for the determination of the fluorine content of fluoro-organic chelating agents, and of the metal chelates formed from them. The time-consuming nature of conventional analytical techniques led to the investigation of 14-MeV neutron activation analysis for the determination.

Three reactions are induced in fluorine by 14-MeV neutron irradiation:

$$^{19}\text{F}\,(\text{n,p})^{19}\text{O} \quad (E_\gamma = 0.2\ \text{MeV},\ t_{\frac{1}{2}} = 29\ \text{sec}) \tag{1}$$

$$^{19}\text{F}\,(\text{n},\alpha)^{16}\text{N} \quad (E_\gamma = 6.13,\ 7.14\ \text{MeV},\ t_{\frac{1}{2}} = 7.4\ \text{sec}) \tag{2}$$

$$^{19}\text{F}\,(\text{n,2n})^{18}\text{F} \quad (\beta^+\text{-annihilation radiation } 0.51\ \text{MeV},\ t_{\frac{1}{2}} = 110\ \text{min}) \tag{3}$$

There is also the reaction

$$^{19}\text{F}\,(\text{n},\gamma)\,^{20}\text{F} \quad (E = 1.63\ \text{MeV},\ t_{\frac{1}{2}} = 11\ \text{sec}) \tag{4}$$

but this is a thermal neutron capture process.

Reaction (1) should have high sensitivity, owing to the short half-life of the product, ^{19}O, but the low energy of the main γ-activity makes it unsuitable for precise analytical use. It would be subject to interference from a great many sources, notably the Compton continua from higher energy radiations. There is a γ-ray of higher energy (1.37 MeV) but this is of low abundance.

Reaction (2)[1,2] gives rise to ^{16}N, which is also the product of the (n,p) reaction on the ^{16}O isotope of oxygen. This interference can be avoided[3] by using neutrons of energy below the threshold for the (n, p) reaction on ^{16}O. For instance, an isotopic neutron source or a generator using the reaction

$$^{2}_{1}\text{H} + ^{2}_{1}\text{H} = ^{1}_{0}\text{n} + ^{3}_{2}\text{He}$$

could be used, but the neutron intensities available from these are much lower than those from 14-MeV neutron generators.

Reaction (3), the one chosen for this work, has been used for trace fluorine determination, with reactor fission spectrum neutrons for activation[4]. It has the disadvantage that the product, ^{18}F, has a relatively long half-life. A relatively long irradiation time is needed to produce sufficient activity for the attainment of adequate precision. The same factor, however, enables sufficient time to be allowed for the decay of any short-lived positron emitters formed, which might otherwise cause serious interference.

Reaction (4) has been investigated[2,5] but the product, ^{20}F, has an inconveniently short half-life for reactor irradiation, and the thermalised neutron fluxes available from neutron generators are too low to give sufficient of the radioactive species for precise determination.

EXPERIMENTAL

The 14-MeV neutrons used for irradiation were produced by bombardment of a water-cooled titanium tritide target with a beam of deuterons accelerated to a potential of 200 kV by a conventional Cockcroft–Walton machine:

$$^{3}_{1}\mathrm{H}+{}^{2}_{1}\mathrm{H} = {}^{1}_{0}\mathrm{n}+{}^{4}_{2}\mathrm{He}$$

In most fast neutron activation procedures samples and standards are irradiated separately, and the integrated neutron dose during the irradiation is measured by an external monitor (for instance, by a fast fission chamber or recoil proton counter). The activities obtained from sample and standard are then normalised to an arbitrary neutron dose before comparison. This approach was used at first in the present work, but the results obtained were not sufficiently precise. The errors were attributed to two main sources.

(*a*) Instability of the deuteron beam of the neutron generator, causing randomly varying changes of neutron flux distribution near the target. Since the samples and standards were placed very much closer to the target than the neutron monitor, the former would be very much more affected by this.

(*b*) The difficulty of attaining exactly reproducible positioning of the samples and standards with respect to the target. As the irradiation position was very close to the target, very small differences in this could result in significant differences in the neutron dose which samples and standards received.

This problem has been overcome[6] by the use of an internal standard, but this has the disadvantage that thorough separation of the sample and standard is necessary after irradiation.

In the present work both samples and standards are mounted together in a special sample holder, which can be rotated in a position near the neutron generator target. The samples and standards are thus irradiated simultaneously, any differences in neutron flux distribution affecting both to the same extent. The sample holder is illustrated in Fig. 1.

Solid samples could frequently be pressed into pellets; these were 1 cm in diameter and 0.5 cm thick. In some cases, addition of up to 10% of stearic acid was necessary as a binding agent. For liquids, and solids which did not give satisfactory pressed pellets, the samples were contained in small polythene capsules, about 1.6 cm in diameter and 1 cm deep. Irradiation trials with empty capsules showed that they produced very little positron activity—about 0.1% of the count from fluorine-containing samples, when irradiated and counted under the same conditions.

Two sample holders were constructed, one accommodating the polythene capsules (illustrated in Fig. 1), the other for pressed pellets. Three samples and a standard are located in the stainless steel holder (A, Fig. 1) and held in place by the retaining disc, B. The holder is secured in a chuck mounted on the shaft of an electric motor. The motor is mounted on a swing bracket attached to the target plate of the neutron generator, and when the assembly is moved into the irradiation position, the sample holder is held at a distance of 1 inch from the generator target (Fig. 2). During irradiation, the device is rotated at about 3000 rev./min. The neutron flux through the samples in this position is of the order of 10^8 n/cm^2/sec when the generator is giving a total output of 10^{10} n/sec.

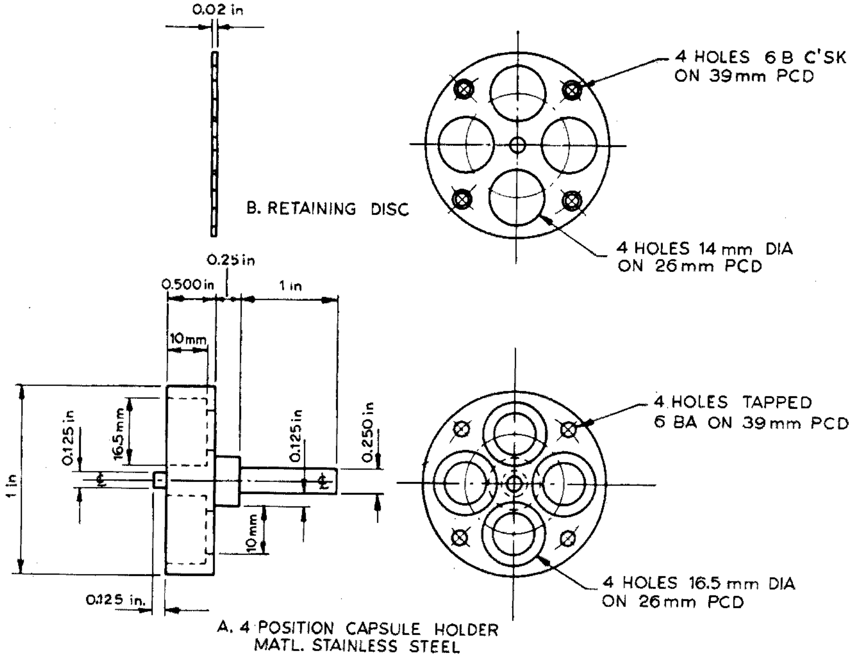

Fig. 1. Rotating irradiation device.

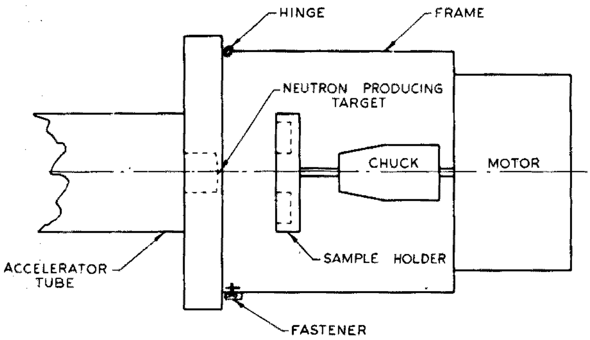

Fig. 2. Irradiation arrangement.

The positron counting equipment consisted chiefly of AERE Harwell "2000" series transistorised units, and is shown diagrammatically in Fig. 3. The counter is similar to that described by WEALE[7] in which positron annihilation photons are detected by two oppositely placed sodium iodide crystal–photomultiplier assemblies. A positron count is registered when coincident 0.51-MeV annihilation γ-pulses occur in each detector. The output pulse amplitude of each photomultiplier is equalised as far as possible by adjustment of the high voltage applied to each tube.

The 0.51-MeV γ-photopeak from each detector is selected by a single channel analyser, using a standard sodium-22 positron source.

Analytical procedure

Weighed samples, either in the form of pellets, or in polythene capsules, are loaded into the appropriate sample holder, and irradiated under the conditions described, for 20 min. A period of 2 h is allowed for the decay of short-lived positron emitters and other active species, which might interfere either by their positron emission or by overloading the counting equipment. After the decay period, first the standard, and then the samples, were each counted for 20 min, using the positron counter described. The accumulated count in each case was of the order of 10^6, giving a relative standard deviation from statistical fluctuations of count rate of $\pm 0.1\%$. Decay corrections were applied to the sample counts, to allow for the time elapsed between these and the standard count. This was derived from the radioactive decay law:

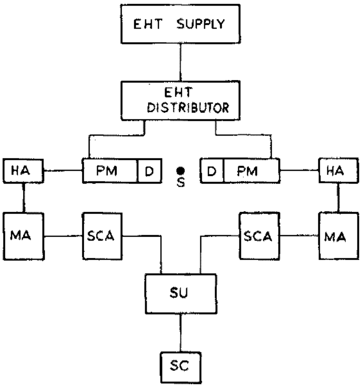

Fig. 3. Positron counter. HA, head amplifier; PM, photomultiplier; D, sodium iodide detector; S, sample; MA, main amplifier; SCA, single channel analyser; SU, coincidence unit; SC, scaler.

$$N = N_0 e^{-\lambda t}$$

where N_0 = original number of atoms, N = number of atoms after time t, and λ = decay constant.

For three consecutive sample counts of 20 min each, allowing one minute between each count, the correction factors are 1.139, 1.302 and 1.486. The fluorine content of the samples could then be calculated from the expression:

$$\text{Wt. F (sample)} = \text{Wt. F (std.)} \frac{\text{Corrected sample count}}{\text{standard count}}$$

Interferences

Forty elements which were known to be capable of giving positron-emitting products by the (n, 2n) reaction, with half-lives greater than 1 min, were irradiated under the conditions used for the fluorine determination, and the extent of any interference was measured. The results are presented in Table I, expressed as a percentage of the activity which would be obtained from the same weight of fluorine. Thus, interference would be expected from Sc, Zn, Ga and Ag and, to a lesser extent, from

TABLE I

INTERFERENCE FROM PRODUCTS OF (n,2n) REACTIONS

(ND = $<0.1\%$)

Product	*Half-life*	*% Interference*	*Product*	*Half-life*	*% Interference*
^{11}C	20.5 min	ND	^{88}Y	108 d	1
^{13}N	9.96 min	ND	^{89}Zr	4.2 min	ND
^{15}O	124 sec	ND	^{91}Mo	15.5 min	0.2
^{22}Na	2.58 yr	ND	^{95}Ru	99 min	0.8
^{30}P	2.5 min	ND	^{102}Rb	2.9 yr	ND
^{34}Cl	32 min	1	^{101}Pd	8.5 h	0.1
^{44}Sc	4.0 h	25	^{106}Ag	24 min	18
^{45}Ti	3.08 h	2	^{112}In	14 min	2.5
^{49}Cr	4.9 min	ND	^{111}Sn	35 min	ND
^{53}Fe	8.5 min	ND	^{120}Sb, ^{122}Sb	15.9 min, 2.8 d	1.5
^{58}Co	71 d	ND	^{119}Te	16 h	ND
^{57}Ni	36 h	0.2	^{129}Ba	2.2 h	0.3
^{62}Cu, ^{64}Cu	9.9 min, 12.9 h	1	^{135}Ce	18 h	0.1
^{63}Zn, ^{65}Zn	38 min, 245 d	50	^{140}Pr	3.4 min	ND
^{68}Ga	68 min	200	^{141}Nd	2.5 h	ND
^{69}Ge	40 h	0.4	^{143}Sm	9 min	ND
^{74}As	18 d	0.5	^{150}Eu, ^{152}Eu	12.8 h, 9.3 h	ND
^{73m}Sc, ^{73}Sc	4.4 h, 7.1 d	0.2	^{155}Dy	10 h	ND
^{78}Br	6.5 min	5	^{161}Er, ^{163}Er	3.1 h, 75 min	ND
^{83}Sr	33 h	ND	^{190}Ir	3.2 h	0.2

TABLE II

DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

Mode of irradiation	*Compound*	*% F (theory)*	*% F (found)*	*S.D.*[a]
Rotated, simultaneously with standards	*p*-Fluoro-benzoic acid (M.A.S.)	13.56	13.6, 13.6, 13.5 13.6, 13.7, 13.5 13.5 Mean = 13.57	±0.07
	Trifluoro-acetanilide (M.A.S.)	30.14	30.2, 30.0, 30.2 29.9, 30.1 Mean = 30.08	±0.13
	2-Fluoro-naphthalene	13.01	13.0, 13.0, 12.9 12.9, 12.9 Mean = 12.94	±0.04
	Trifluoro-acetophenone	32.76	32.7, 32.6, 32.6 32.7, 32.8 Mean = 32.68	±0.09
	Iodopentafluoro-benzene	32.32	32.3, 32.3, 32.4 32.2 Mean = 32.30	±0.10
Stationary, sample and standard consecutively	*p*-Fluorobenzoic acid (M.A.S.)	13.56	13.8, 13.6, 13.4 13.9, 13.2 Mean = 13.58	±0.30
	Trifluoro-acetanilide	30.14	31.0, 30.2, 29.6 29.8, 29.8, 30.7 Mean = 30.18	±0.56

[a] Calculated from the range by the method of DEAN AND DIXON[8].

Cl, Ti, Cu, Br, Y, Ru, In and Sb, if these elements were present as major constituents. The samples analysed have contained rare earths, N, P, As, O and C, as well as fluorine. Trace amounts of most elements would produce negligible interference in the analysis of materials with fluorine as a major constituent.

RESULTS AND DISCUSSION

Results obtained for the determination of fluorine in organic compounds (including some analytical standards) are shown in Table II. Results of the analysis of samples of metal-fluoro organic chelates are shown in Table III. The fluorodiketones used were synthesized by the Claisen condensation and the metal complexes were formed by adding the appropriate diketone and base (or a salt of the base) to an alcoholic solution of the metal salt. The results show that fluorine can be determined rapidly and non-destructively in fluoro-organic derivatives, with a relative standard deviation of better than ±0.5%. There appears to be no significant bias. Deviations of the analytical figures from the theoretical fluorine content for some of the compounds listed in Table III are attributed to variations in the purity of the starting materials. Comparison of the results obtained by simultaneous irradiation of samples and standards in the rotating holder with those obtained from separate irradiations indicate the superiority of the former.

TABLE III

DETERMINATION OF FLUORINE IN METAL CHELATES

Compound prepared	*Theoretical fluorine content (%)*	*Fluorine found (%)*
$\mathrm{Eu[C_6H_4F.CO.CH.CO.CF_3]_4C_5H_5NH}$[a]	26.1	25.2, 25.3
$\mathrm{Eu[CF_3.C_6H_4.CO.CH.CO.CF_3]_4C_5H_5NH}$[a]	33.4	32.3, 32.4
$\mathrm{Eu[CF_3.C_6H_4.CO.CH.CO.CF_3]_4C_5H_5NH}$[b]	33.4	32.4, 32.5
$\mathrm{Eu[C_6H_5.CO.CH.CO.CF_3]_4C_9H_7NH}$	20.0	19.9, 19.9
$\mathrm{Eu[C_6H_5.CO.CH.CO.CF_3]_4NH_4}$	22.1	23.5, 23.6
$\mathrm{Eu[C_6H_5.CO.CH.CO.CF_3]_4As.Ph_4}$	16.3	16.4, 16.2
$\mathrm{Eu[C_6H_5.CO.CH.CO.CF_3]_4P.Ph_4}$	16.9	16.8, 16.7
$\mathrm{Sm[C_6H_5.CO.CH.CO.CF_3]_4C_5H_5NH}$	20.9	20.2, 20.3
$\mathrm{Eu[C_6H_4F.CO.CH.CO.CF_3]_4C_5H_5NH}$[b]	26.1	25.8, 25.8

[a] Substitution of F^- or CF_3^- in *o*-position.

[b] Substitution of F^- or CF_3^- in *p*-position.

The authors are grateful to Mr. J. M. DONALDSON of A.W.R.E. for suggesting this work.

SUMMARY

A procedure is described for the precise determination of fluorine in organic and metal-organic compounds by 14-MeV neutron activation analysis using the reaction: $^{19}F\ (n,2n)^{18}F\ (\beta^+, t_{\frac{1}{2}} = 110\ \text{min})$.

A relative standard deviation of better than ±0.5% is achieved by irradiating samples and standard simultaneously. Uniform neutron exposures were ensured by rotating the samples during irradiation. Positron emitters of short half-life are allowed to decay before counting. In metal-organic compounds, Sc, Zn, Ga and Ag cause the most serious interference; for organic compounds the method is rapid, and specific for fluorine.

RÉSUMÉ

Un procédé est décrit pour le dosage précis du fluor dans des composés organiques et organométalliques, par activation au moyen de neutrons 14-MeV d'après la réaction: $^{19}F(n,2n)^{18}F(\beta^+, t_{\frac{1}{2}}=110\ \text{min})$.

Une déviation standard relative de ±0.5% est obtenue par irradiation simultanée des échantillons et de l'étalon. Des expositions aux neutrons uniformes sont réalisées par rotation des échantillons au cours de l'irradiation. Avec les composés organométalliques, Sc, Zn, Ga, et Ag causent les interférences les plus sérieuses. Avec les composés organiques la méthode est rapide et spécifique.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur genauen Bestimmung von Fluor in organischen und metallorganischen Verbindungen mit der Neutronenaktivierungsanalyse beschrieben. Es verwendet Neutronen mit einer Energie von 14 MeV und beruht auf der Reaktion $^{19}F(n,2n)^{18}F(\beta^+, t_{\frac{1}{2}}=110\ \text{min})$. Die relative Standardabweichung ist besser als 0.5% und wird durch gleichzeitige Bestrahlung von Probe und Standard erreicht. Da die Proben während der Bestrahlung rotieren, wird eine gleichmässige Aktivierung erzielt. Positronenstrahler mit kurzer Halbwertszeit müssen, bevor man mit dem Zählen beginnt, abklingen. In metallorganischen Verbindungen verursachen Sc, Zn, Ga und Ag die stärksten Störungen. Für organische Verbindungen ist die Methode schnell und spezifisch für Fluor.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF RHENIUM IN MOLYBDENITES BY NEUTRON ACTIVATION ANALYSIS

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(Received September 15th, 1967)

Interest in rhenium has increased in recent years because of its use in different branches of various new technologies. As the abundance of rhenium is generally low in rocks and minerals, sensitive methods for its determination are required. Neutron activation analysis appears to be one of the most appropriate. This technique has been used to determine rhenium in materials such as enzymes[1], marine organisms[2], rocks[3-5], ores[6], meteorites[7-9], tectites[10], granites[11], electrolytic zinc sulphate solutions[12] and molybdenites[13-15]. In all these determinations, separation techniques such as precipitation, distillation, ion exchange and liquid–liquid extraction have been applied; most of the procedures involve rather complicated chemical separations, with low chemical yields and are time-consuming.

The proposed method for the determination of rhenium in molybdenites by thermal neutron activation analysis, is based on a simple extraction with pyridine and γ- or β-counting. It applies simple operations in a very short time, thus ensuring quantitative recovery.

TABLE I

NUCLEAR DATA OF RHENIUM, MOLYBDENUM AND TECHNETIUM

Natural isotope	*Abundance (%)*	*Thermal cross-section (barn)*	*Isotope formed*	*Half-life*	*γ-Energy (MeV)*	*β-Energy E_{max} (keV)*
^{185}Re	37.07	104	^{186}Re	89 h	0.063, 0.128, 0.137, 0.631, 0.769	1072(70 %) 934(22%) 307(0.11%)
^{187}Re	62.93	69	^{188m}Re	19 m	0.064, 0.092, 0.106	
			^{188}Re	17 h	0.063, 0.155, 0.477, 0.632	2116(80%) 1500
^{92}Mo	15.84	0.006	^{93m}Mo	6.9 h	0.684, 0.148	
^{98}Mo	23.78	0.51	^{99}Mo	67 h	0.181, 0.740	1420(2%) 1278(75%)
			^{99m}Tc	6 h	0.140	—
			^{99}Tc	$2.12 \cdot 10^5$y	—	310 (100%)
^{100}Mo	9.63	0.20	^{101}Mo	14.6 m	0.191, 0.510, 0.590, 1.02	
			^{101}Tc	14.0 m	0.130, 0.186, 0.307	

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** Aspirant of the N.F.W.O.

Nuclear data

In Table I, the nuclear data for activation of rhenium and molybdenum are given. It appears that the isotopes ^{186}Re and ^{188}Re can be used for activation analysis of rhenium because of their high thermal neutron cross-section and appropriate half-life. As both isotopes emit β- and γ-rays, γ- and β-spectrometry can be applied. Molybdenum is the major constituent of the molybdenites. After irradiation it gives rise to the 6-h ^{99m}Tc (γ, 0.141 MeV). It is obvious that rhenium cannot be determined by γ- and β-spectrometry in the presence of the matrix, but can be determined after separation from molybdenum in the presence of ^{99m}Tc and ^{99}Tc by β-spectrometry or by γ-spectrometry after the decay of ^{99m}Tc.

Ishida *et al.*[14] state that selfshielding in the molybdenites can be neglected if quantities of *ca.* 50 mg are irradiated. Experimentally no sign of neutron shielding was found in the standards if less than 0.1 μg was used. The following interfering reactions:

$$^{184}\text{W}(\text{n},\gamma)^{185}\text{W} \xrightarrow{\beta} {}^{185}\text{Re}(\text{n},\gamma)^{186}\text{Re}$$

$$^{186}\text{W}(\text{n},\gamma)^{187}\text{W} \xrightarrow{\beta} {}^{187}\text{Re}(\text{n},\gamma)^{188}\text{Re}$$

$$^{186}\text{Os}(\text{n, p})^{186}\text{Re}$$

can also be neglected, as the tungsten and osmium content in the molybdenites is insignificant.

Separation of rhenium

Goishi and Libby[16] report a pyridine extraction method for the separation of rhenium (3.8 mg Re/ml) with a K_D (distribution coefficient) value of 255 in 4 N sodium hydroxide solution. Manganese(VII) and technetium(VII) are also extracted from 4 N sodium hydroxide solution. For the technetium ($3.8 \cdot 10^{-5}$ mg/ml) a K_D value of 778 was found. Later work[17] has shown that the K_D value for technetium increases with increasing concentrations of hydroxide.

By means of $^{186+188}$Re (5 μg/ml) and ^{99}Mo (10 μg MoO$_3$/ml) tracers, values of K_D and percent extraction in pyridine for both elements were determined for normalities ranging from *ca.* 1 N to 10 N sodium hydroxide. The changes of the volumes of both phases were also taken into account. The results are given in Table II. In order to check the extraction behaviour of tungsten the K_D value for a concentration of 4 N sodium hydroxide was determined by means of ^{187}W tracer. The results are also given in Table II.

The extractions were repeated in the presence of inactive molybdenite samples, after smelting with appropriate amounts of sodium hydroxide and dissolution in water, in order to check the influences of the other constituents on the extraction behaviour of rhenium and molybdenum. No interferences were detected.

The results shown in Table II indicate that the percentage extraction of rhenium slowly increases with the normality. The molybdenum extraction appears to be insignificant. For the adopted analytical method a 4 N hydroxide concentration was chosen. Back-extraction of the pyridine phase with an equal quantity of 4 N sodium hydroxide for the entire removal of molybdenum is preferable.

There appears to be no interference of manganese activity in the pyridine

TABLE II

EXTRACTION OF RHENIUM, MOLYBDENUM AND TUNGSTEN WITH PYRIDINE; K_D VALUES AND PERCENT OF EXTRACTION[a]

N NaOH before extn.	*N NaOH after extn.*	*Vol. after extn.*[a]		*Total vol.*	K_D	*% Extn.*[b]
		Py (ml)	*H_2O (ml)*			
Rhenium						
1.18	2.02	5.85	13.5	19.3	24.2	98.24
1.96	2.45	8.0	11.6	19.6	81.9	99.16
2.35	2.61	9.0	10.8	19.8	168.4	99.51
2.67	2.97	9.0	10.55	19.55	211.0	99.60
3.92	4.17	9.4	10.5	19.9	260.5	99.66
5.52	5.55	10.0	9.7	19.7	391.1	99.74
5.52	5.41	10.2	9.4	19.6	539.0	99.80
7.47	7.05	10.6	9.05	19.65	628.0	99.81
9.03	8.28	10.9	9.0	19.9	2264.0	99.95
Molybdenum						
1.18	2.03	5.8	13.7	19.5	$2.1 \cdot 10^{-3}$	0.49
2.70	4.21	6.4	13.2	19.6	$8.9 \cdot 10^{-4}$	0.17
3.59	5.12	7.0	12.5	19.5	$\geqslant 7.2 \cdot 10^{-4}$	$\leqslant 0.13$
3.87	5.38	7.2	12.4	19.6	$\geqslant 7.0 \cdot 10^{-4}$	$\leqslant 0.12$
8.41	9.55	8.8	10.7	19.5	$\geqslant 9.0 \cdot 10^{-4}$	$\leqslant 0.11$
Tungsten						
2.68	4.18	9.4	9.8	19.2	$1.1 \cdot 10^{-3}$	0.10

[a] In all cases, the volumes of aqueous phase and pyridine before extraction were 10 ml each.
[b] $K_D \cdot 100/\{K_D + V_{aq}/V_{py}\}$

fraction because of the insignificant amount of this element in the molybdenites and also because of the fact that it is in the manganese(VI) state and cannot be extracted into the pyridine phase[16].

Dissolution of the samples

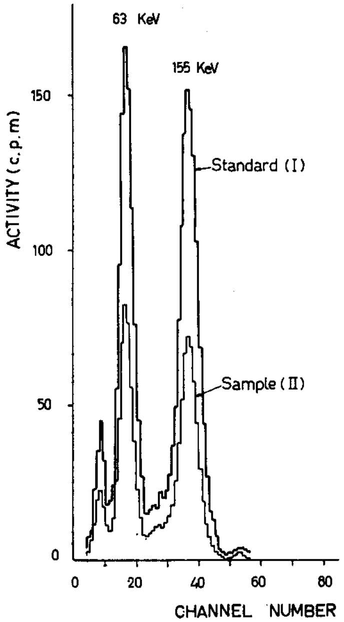
The most appropriate method for dissolving the molybdenite samples is fusion with sodium hydroxide. In order to determine possible losses of rhenium by the fusion and the dissolution processes, 50 mg of molybdenite and Re-tracer (5 μg/ml) were fused with 1.6 g of sodium hydroxide in a nickel crucible, cooled, dissolved in 10 ml of water and measured. A recovery of 99.6% was obtained.

Irradiation and measurement

Molybdenite samples (*ca.* 50 mg) were weighed and sealed in silica tubes. Standards were prepared by dissolution of pure rhenium metal in nitric acid and, after appropriate dilution, amounts of 5.0 μg in 50 μl were sealed in silica tubes. Samples and standards were packed in standard aluminium containers and irradiated.

γ-Measurements were made in 10-ml glass vials for the pyridine fraction or on sintered glass for the Re_2S_7 samples. A 400-multichannel analyser coupled to a NaI(Tl) detector (3″×3″) was used. The 63-keV peak was chosen for the γ-spectrometric determination. The measurements were made after the complete decay of ^{99m}Tc *i.e.* after 3 days. In Fig. 1, γ-spectra of $^{186+188}$Re are given for sample and standard.

β-Activities were measured by means of a 400-multichannel analyser coupled to a plastic detector (44 mm diam., 6 mm thickness) making use of Re_2S_7 samples precipitated on sintered glass. In Fig. 2, β-spectra are given for $^{186+188}$Re and ^{99m}Tc activities. From Fig. 2 it appears that ^{99m}Tc activity is in the low energy range due to the conversion electrons and permits the elimination of this part of the spectrum, without affecting the sensitivity of the measurement.



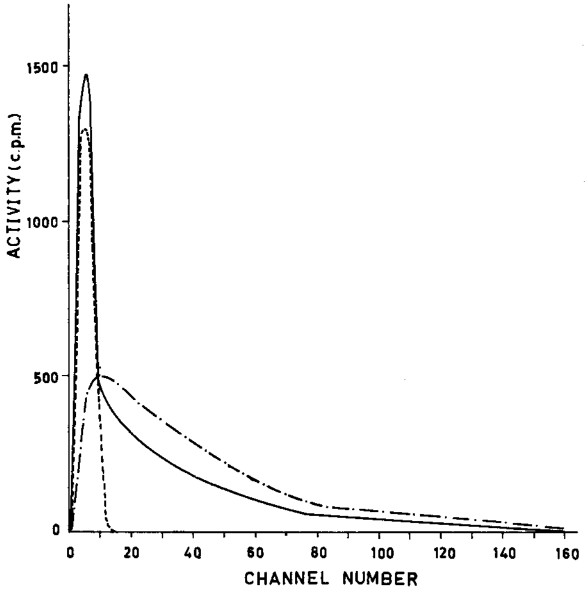


Fig. 1. γ-Spectra. Standard (I) $^{186+188}$Re; sample (II) $^{186+188}$Re.

Fig. 2. β-Spectra. (—.—.) Standard (I)$^{186+188}$Re; (——) sample (II) $^{186+188}$Re $+^{99m}$Tc; (----) sample (III) ^{99m}Tc.

G.M. counting can also be applied, making use of a 80 mg/cm^2 aluminium absorber to eliminate the conversion electrons due to ^{99m}Tc.

A comparison between β- and γ-measurements shows that the former is 20 times more effective. As β-counting is performed directly after the extraction and precipitation without waiting for the ^{99m}Tc decay, the total sensitivity is increased by a factor of 40.

For a neutron flux of $4 \cdot 10^{11}$ n/cm^2. sec, an irradiation time of 2 h and a sample of *ca.* 50 mg, β-counting allows determinations in the p.p.b. range.

EXPERIMENTAL

After irradiation in the BR-1 reactor at a neutron flux of $4 \cdot 10^{11}$ n/cm^2. sec for 2 h, and cooling for 12 h, the samples are fused in a nickel crucible with 1.6 g of sodium hydroxide, cooled, dissolved in 10 ml of water and transferred to a separation funnel. Pyridine (10 ml) equilibrated with 4 *N* sodium hydroxide is added, and after extraction and centrifugation, the aqueous phase is discarded.

Back-extraction is made with 4 *N* sodium hydroxide solution and again the aqueous phase is discarded. The pyridine fraction is transferred to a 10-ml glass vial and measured γ-spectrometrically as described above. Standards are also measured in 10-ml glass vials.

If β-spectrometry is applied to the pyridine fraction (10 ml), 15 mg of copper oxide (dissolved in hydrochloric acid), 15 ml of 6 *N* hydrochloric acid, 5 ml of water and excess of thioacetamide are added. The solution is boiled until formation of the sulphide precipitate occurs. The precipitate is filtered through a glass sintered filter. The yield is quantitative. Standards of Re_2S_7 are prepared in the same way.

RESULTS

In Table III some results of neutron activation analysis for rhenium in molybdenites are given.

TABLE III

ANALYSIS OF MOLYBDENITES

	γ-Spectrometry (p.p.m.)	*β-Spectrometry*	
		G.M.[a] *(p.p.m.)*	*Plastic detector (p.p.m.)*
Molybdenite roasted	11.15	10.61	10.45
Natural molybdenite	1.38	1.10	1.23

[a] Al absorber applied to eliminate conversion electrons.

Acknowledgements are due to the I.A.E.A. who provided a fellowship to I.B. and to Mr. TOMBU of the Metallurgie Hoboken who provided the molybdenite samples.

SUMMARY

A thermal neutron activation method for the determination of rhenium in molybdenites is described. The rhenium is separated from the matrix after irradiation by pyridine extraction from 4 *N* sodium hydroxide solution; γ- and β-spectrometry are applicable. For a neutron flux of $4 \cdot 10^{11}$ n/cm^2.sec, an irradiation of 2 h and a sample of *ca.* 50 mg, β-counting allows determinations in the p.p.b. range.

RÉSUMÉ

Une méthode d'analyse par activation à l'aide de neutrons thermiques a été élaboré pour la détermination du rhenium dans les molybdenites. Le rhenium est séparé par une simple extraction à la pyridine dans 4 *N* NaOH. On peut appliquer un comptage γ ou β. Pour un flux de neutrons $4 \cdot 10^{11}$ n/cm^2.sec, temps d'irradiation de 2 h et échantillon de *ca.* 50 mg le comptage-β permet la détermination dans la région de p.p.b.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Rhenium in Molybdänglanz mit Hilfe der Neutronenaktivierungsanalyse beschrieben. Rhenium wird durch Extraktion mit Pyridin aus 4 N NaOH abgetrennt und mit der γ- und β-Spektrometrie bestimmt. Bei einem Neutronenfluss von $4 \cdot 10^{11}$ n/cm^2.sec, einer Bestrahlungszeit von 2 Stunden und mit 50 mg Probe ermöglicht die β-Spektrometrie Bestimmungen im p.p.b.-Bereich.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NON-DESTRUCTIVE ACTIVATION ANALYSIS OF TRACE IMPURITIES IN GERMANIUM

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(Received August 1st, 1967)

Germanium dioxide and elementary germanium are widely used in the production of transistors and diodes. As the impurity concentrations are often in the p.p.b. range, activation analysis is one of the most suitable methods. Neutron activation determinations of As, Cu, Mo, Zn, Na, Ag, Ga, In and Sb have already been described[1-7]. All these methods make use of chemical separations.

This paper deals with non-destructive activation analysis of trace impurities of Hg, Sn, Cr, Sb, Sc, Zn and Co which give rise to long-lived γ-emitting isotopes.

Nuclear data

Irradiation of germanium with thermal neutrons gives rise to several radio isotopes, the characteristics of which are shown in Table I. Irradiation of 1 g of germanium during 15 h at a thermal neutron flux of 10^{14} n cm^{-2} sec^{-1} gives rise to

TABLE I

NUCLEAR DATA

Isotope	% *Abundance*	*Act. cross section*[9]	*(n,γ) Isotope*	*Half-life*[8]	*γ-Energy*[8] *(keV)*
^{70}Ge	20.55	3.42	^{71}Ge	12 d	E.C. (E_{max} 237 keV)
^{74}Ge	36.74	0.48	^{75m}Ge, ^{75}Ge	49 s, 79 m	139, 199, 265 ...
^{76}Ge	7.67	0.08, 0.08	^{77m}Ge, ^{77}Ge	54 s, 11.3 h	159, 215, 210, 215 ...
			^{77}As	38.7 h	162, 245, 525
^{45}Sc	100	22	^{46}Sc	83.9 d	885, 1119
^{50}Cr	4.31	15.9	^{51}Cr	27.8 d	323
^{59}Co	100	36	^{60}Co	5.24 y	1173, 1333
^{64}Zn	48.89	0.47	^{65}Zn	245 d	1119
^{112}Sn	0.95	1.3	^{113}Sn	115 d	256
			^{113m}In	104 m	392
^{116}Sn	14.24	0.006	^{117m}Sn	14 d	156, 159, 320
^{118}Sn	24.01	0.010	^{119}Sn	275 d	24, 65
^{122}Sn	4.71	0.001	^{123m}Sn	131 d	1080
^{124}Sn	5.94	0.004	^{125}Sn	9.4 d	331, 468 ...
			^{125}Sb	2.0 y	171, 668
^{123}Sb	42.75	2.5	^{124}Sb	60.9 d	603, 1690
^{202}Hg	29.80	3.8	^{203}Hg	46.9 d	279

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[*] Aspirant of the N.F.W.O.

ca. 160 mC of ^{77}Ge. This large activity does not allow manipulation of the irradiated samples without special precautions. However, after a cooling period of *ca.* 30 days, the only matrix activity left is ^{71}Ge. This isotope decays by electron capture to stable ^{71}Ga and only emits internal Bremsstrahlung ($E_{max}=237$ keV).

The γ-spectrum of a 0.14-g GeO_2 sample, irradiated in BR-2 during 15 h at 10^{14} n.cm^{-2}.sec^{-1} and measured after a decay time of 30 days is given in Fig. 1. The γ-peak at 279 keV is due to ^{203}Hg.

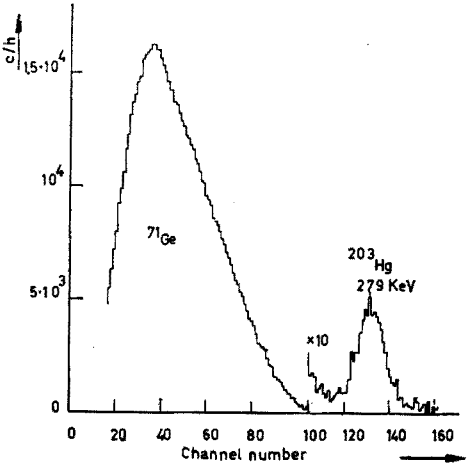


Fig. 1. γ-Spectrum of irradiated GeO_2.

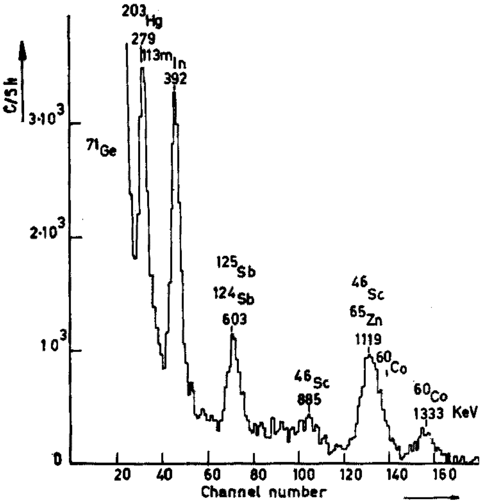


Fig. 2. γ-Spectrum of GeO_2 (T1-b).

In Table I, the nuclear data for the formation of long-lived γ-emitting nuclides of Hg, Sn, Cr, Sb, Sc, Zn and Co are also summarized. From Table I it appears that these elements can be determined by γ-spectrometry in an irradiated germanium matrix, using the isotopes ^{203}Hg, ^{113}Sn via the ^{113m}In, ^{51}Cr, ^{124}Sb, ^{46}Sc, ^{65}Zn and ^{60}Co.

Irradiation and counting

The samples and the standards were prepared for irradiation as follows: 0.14 g of GeO_2 or 0.1 g of Ge, were packed respectively in a quartz tube or in an aluminium foil; 0.5 mg of Sb_2O_3, 2 mg of ZnO and 0.5 mg of Sc_2O_3 were packed in quartz tubes; 2 mg of Sn and 5 mg of a Co–Al alloy (1.00% Co) were packed in an aluminium foil; and 10 μg of Cr and 1 μg of Hg were packed in a quartz tube.

Samples and standards were packed in a standard aluminium container, irradiated in BR-2 for 15 h at a thermal neutron flux of 10^{14} n.cm^{-2}.sec^{-1} and allowed to cool for *ca.* 30 days.

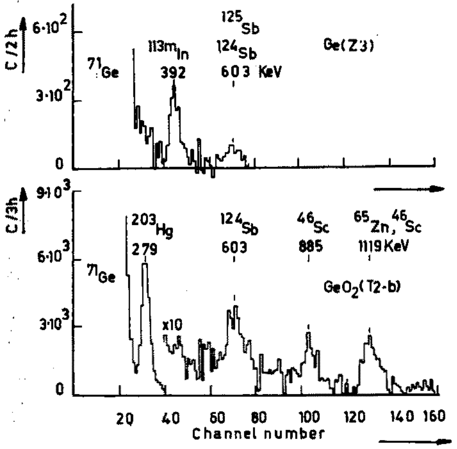
The GeO_2 or Ge was transferred to a 4-ml counting vial. Elementary germanium was etched 3 times with hot nitric acid and with hydrofluoric–nitric acid (1:1) in a platinum crucible, washed, dried and weighed. The standards were dissolved as follows: Sb_2O_3 in 6 *N* sodium hydroxide, ZnO in 6 *N* nitric acid, Sc_2O_3 in 12 *N* hydrochloric acid, Co(Al) in 6 *N* nitric acid, Cr in 8 *N* hydrochloric acid, Sn in 8 *N* hydrochloric acid–0.5 N oxalic acid and Hg in 6 N nitric acid. The solutions were diluted in volumetric flasks of appropriate sizes and 1-ml aliquots were transferred to 4-ml counting vials.

The solutions were partially evaporated in order to obtain similar geometric counting conditions for samples and standards. The germanium samples were measured with a flat 3 × 3″ cylindrical NaI(Tl) detector coupled to a 400-channel analyser, during 3–5 h and the standards during 5–10 min.

Qualitative and quantitative analysis

The photopeaks in the recorded spectra were identified by energy and if necessary by half-life determination. In some cases, chemical identification of the presumed isotope was performed. In the different analysed Ge and GeO_2 samples, the isotopes ^{203}Hg, ^{51}Cr, ^{124}Sb, ^{46}Sc, ^{65}Zn and ^{113m}In could be identified.

The γ-spectra obtained from a number of irradiated GeO_2 and Ge samples are shown in Figs. 2 to 4.



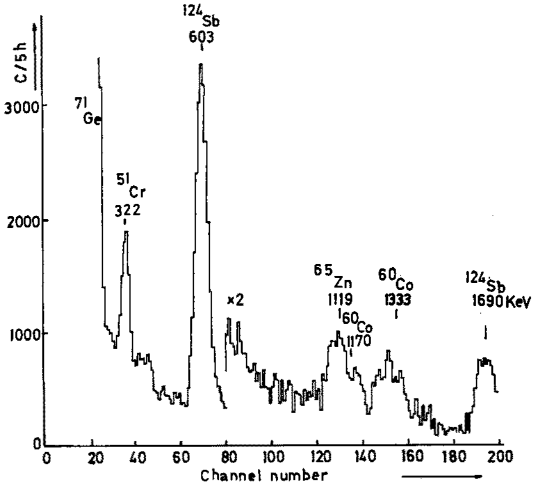


Fig. 3. γ-Spectra of Ge (Z 3) and GeO_2 (T 2-b).

Fig. 4. γ-Spectrum of Ge (Z 4).

Compositional analysis of multicomponent spectra with the aid of mathematical techniques has been extensively described in the literature. In most cases, computer programming is used[10–13].

If only four or less isotopes contribute to the spectrum, the different activities can be computed by simple matrix calculus. This technique has already been described by YUDILEVITCH AND MARTIN[14] for the determination of ^{113}I, ^{86}Rb, ^{59}Fe and ^{22}Na, and by OP DE BEECK AND HOSTE[15] for the activation analysis of Ag, Au and Hg in lead.

The complex γ-spectrum is considered as a superposition of the simple spectra of the pure isotopes. For a mixture of n isotopes, n energy regions are selected and the activity A_j of the isotope j in the region $i=j$ can be calculated, if the relative activities of the isotope j in the different regions are known. Thus:

$k_{i,j}$ = activity of the isotope j in a region i, normalised to the activity of the isotope j in region $i=j$

$$(k_{i=j,j}=1).$$

The coefficients $k_{i,j}$ can be determined by means of the pure isotopes (standards).

If T_i = the total activity in region i, and A_j = the activity of the isotope j in the region $i=j$, then:

$$T_1=k_{11}A_1+k_{12}A_2+k_{13}A_3+\ldots \tag{1}$$

$$T_i=\sum_{j=1}^{n} k_{i,j}\,A_j \tag{2}$$

This set of equations can be written as a matrix equation:

$$T_i=k_{i,j}\,A_j \tag{3}$$

Or, inverting the matrix of coefficients:

$$A_j=l_{j,i}\,T_i \tag{4}$$

where

$$l_{j,i}=(-1)^{i+j}\,M_{i,j}/D, \tag{5}$$

$M_{i,j}$ = minor of the element $k_{i,j}$ in the matrix $(k_{i,j})$

and

D = determinant of the matrix $(k_{i,j})$.

The activity A_j can be calculated from

$$A_j=\sum_{i=1}^{n} l_{j,i}\,T_i \tag{6}$$

Op de Beeck and Hoste[15] give a more detailed discussion of this method and they state that the best results are obtained if narrow regions, including the main photopeak areas of the individual isotopes, are chosen for the calculations. Usually the standard deviation $l_{j,i}$ can be neglected in comparison with the standard deviation on T_i. Thus a simple expression for the standard deviation on A_j can be derived:

$$s^2(A_j)=\sum_{i=1}^{n} l_{j,i}^2\,s^2(T_i) \tag{7}$$

where

$$s^2(T_i)=T_i+2b_i,\ \text{and} \tag{8}$$

b_i = activity of the background in region i.

Matrix calculation of a complex γ-spectrum of ^{124}Sb, ^{46}Sc, ^{65}Zn and ^{60}Co can be applied since ^{71}Ge, ^{51}Cr, ^{203}Hg and ^{113m}In do not affect the γ-activity in the energy regions selected for the determination of Sb (603 keV), Sc (885 keV), Zn (1119 keV) and Co (1333 keV). If, however, tin is present, the activity in the 603-keV region must be corrected for the ^{125}Sb activity. This correction is performed by means of a tin standard. The activities of ^{203}Hg, ^{113}Sn (^{113m}In) or ^{51}Cr were determined by Covell's method[16], where the activity under a photopeak is given by:

$$A=\sum_{-n}^{n} a_n-\tfrac{1}{2}(2n+1)\,(a_{(+n)}+a_{(-n)}) \tag{9}$$

where

n = number of channels at both sides of the maximum of the γ-peak ($n=0$), chosen for a calculation of A (total number of channels: $2n+1$).

a_n = activity in channel n.

The standard deviation is given by:

$$s^2(A)=\sum_{-n}^{+n} a_n+2\sum_{-n}^{n} b_n+\tfrac{1}{2}(2n+1)\left(a_{(+n)}+a_{(-n)}+2b_{(+n)}+2b_{(-n)}\right) \qquad (10)$$

where

b_n = measured activity of the background in channel n.

RESULTS

COVELL's method and the matrix calculus were checked successfully for artificial activity mixtures and were applied to the irradiated germanium samples.

As an example, the calculations for the analysis of the spectrum of sample $T1(b)$ are given. In this case, the isotopes ^{203}Hg, ^{113}Sn (^{113m}In); ^{124}Sb, ^{65}Zn, ^{46}Sc and ^{60}Co were identified (Fig. 2). The calculated activities were:

^{203}Hg: Channel 27–35 (COVELL's method) 9.755 c/h/g GeO_2

^{113}Sn (^{113m}In): Channel 40–50 (COVELL's method) 16910 c/h/g GeO_2.

The ^{125}Sb activity in the 603-keV energy region is determined by

$$k=\frac{^{113m}\text{In activity (COVELL's method)}}{^{125}\text{Sb activity in 603-keV region}}$$

The value of k can be calculated by means of a tin standard (^{124}Sb activity in this standard can be detected by means of the 1.69-MeV γ-ray of ^{124}Sb).

Under the experimental conditions used, $k=10.2$.

The activities of ^{124}Sb, ^{46}Sc, ^{65}Zn and ^{60}Co in the channels 64–79, 97–109, 122–142 and 147–165 were calculated by means of a matrix which was determined by means of Sb, Sc, Zn and Co standards:

$$\underset{\text{(a)}}{\begin{vmatrix}\text{act.}^{124}\text{Sb}\\ \text{act.}^{46}\text{Sc}\\ \text{act.}^{65}\text{Zn}\\ \text{act.}^{60}\text{Co}\end{vmatrix}}=\begin{vmatrix}1.060 & -0.278 & 0.207 & -0.132\\ -0.0202 & 1.190 & -0.204 & -0.305\\ 0.075 & 0.846 & 1.130 & 1.125\\ 0.130 & 0.049 & 0.040 & 1\end{vmatrix}\;\underset{\text{(b)}}{\begin{vmatrix}\text{act.chan. (64–79)} - \text{act.}^{113m}\text{In}/k\\ \text{act.chan. 97–109}\\ \text{act.chan.122–142}\\ \text{atc.chan.147–165}\end{vmatrix}}$$

$$\text{From (b)}=\begin{vmatrix}13081\ \text{c/h/g GeO}_2\\ 6387\ \text{c/h/g GeO}_2\\ 16353\ \text{c/h/g GeO}_2\\ 4488\ \text{c/h/g GeO}_2\end{vmatrix}\ \text{follows (a)}=\begin{vmatrix}8114\ \text{c/h/g GeO}_2\\ 2632\ \text{c/h/g GeO}_2\\ 9012\ \text{c/h/g GeO}_2\\ 3128\ \text{c/h/g GeO}_2\end{vmatrix}$$

From these activities, the impurity concentrations (p.p.b.) were calculated and are given in Table II.

In Tables II and III the results of the analyses of GeO_2 and Ge samples are given. The standard deviations on the Sb, Sc, Zn and Co concentrations were calculated from eqn. (7). Sb, Zn, Co and Sc were considered to be absent if the computed activity values were below 2 standard deviations. The computed 2 *s* values, moreover, allowed an estimation of the lower detection limit of the considered elements.

For the elements Cr, Sn and Hg, where COVELL's method was used to estimate the respective photopeak areas, the same criterion was applied. The computed detection limits are also reported in Tables II and III. T_1–T_4 are transistor-quality GeO_2 samples whereas Z_4–Z_2 and M_1–M_6 are germanium samples. M_4, M_5 and M_6 are antimony-doped (N type) germanium crystals with a resistivity of respectively 1.3 ohm.cm (60 p.p.b. Sb), 8.85 ohm.cm (7.8 p.p.b. Sb) and 35 ohm.cm (1.76 p.p.b. Sb). As these samples showed only ^{71}Ge and ^{124}Sb activities, their antimony concentration was determined in different ways (Table IV), namely from the activity measured with a flat NaI(Tl) crystal in the 603-keV region (a), the 1.69-MeV region

TABLE II

DETERMINATION OF Hg, Sn, Cr, Sb, Zn, Co AND Sc IN GeO_2

Sample	*mg GeO_2*	*Concentration in p.p.b.*						
		Hg	*Cr*	*Sn*	*Sb*	*Sc*	*Zn*	*Co*
T_1(a)	144	9.0±0.6	<7	3600±180	19.2±0.3	0.057±0.011	82±7	1.1±0.2
T_1(b)	139	7.9±0.6	<7	3300±170	4.1±0.2	0.071±0.008	101±5	1.1±0.1
T_1(c)	163	—	—	3200±170	—	—	—	—
T_2(a)	156	42±3	<7	<190	2.8±0.2	0.033±0.010	32±5	<0.2
T_2(b)	126	43±3	<8	<230	4.2±0.3	0.11±0.01	29±7	<0.2
T_3(a)	124	23±2	<8	<250	7.4±0.3	0.12±0.01	139±8	0.28±0.11
T_3	137	22±2	<7	<210	18.9±0.4	0.11±0.02	149±11	0.59±0.17
T_4(a)	133	11±1	<8	<230	5.5±0.3	—	74±9	8.0±0.2
T_4(b)	140	13±1	<7	<210	6.8±0.3	—	66±9	7.9±0.2

TABLE III

DETERMINATION OF Hg, Sn, Cr, Sb, Zn AND Co IN Ge

Sample	*mg Ge*	*Concentration in p.p.b.*					
		Hg	*Cr*	*Sn*	*Sb*	*Zn*	*Co*
Z_4	74	<2	37±4	300	28.3±0.4	72±9	2.9±0.2
Z_3	96	<1.5	<7	1200±200	2.5±0.4	<15	<0.3
Z_2	103	<1.4	<7	<210	0.4±0.3	<16	<0.3
M_1	132	<1.2	<5	<160	2.0±0.2	<12	<0.2
M_1	177	<0.9	<4	<120	2.4±0.4	<9	<0.3
M_2	65	<2.5	<11	<320	<0.8	<23	<0.4
M_3	142	<1.1	<5	<150	<0.4	<11	<0.2
M_4	55	<2.8	<13	<380	60.0±1.4	<74	<1.2
M_4	70.9	<2.5	<10	<300	45±1	<57	<1.2
M_5	120.3	<1.3	<6	<170	8.5±0.4	<16	<0.4
M_5	161.4	<2	<9	<260	6.9±0.4	<24	<0.5
M_6	143	<1.1	<5	150	2.1±0.3	<12	<0.3
M_6	120.4	<1.3	<6	170	1.6±0.3	<14	<0.4

TABLE IV

ANALYSIS OF Sb-DOPED Ge

Sample	*Dope (p.p.b. Sb)*	*mg Ge*	*Concentration Sb (p.p.b.)*			
			(a)[a]	*(b)*	*(c)*	*(d)*
M_4	60	70.9	60.0±1.4	60.1±2.8	60.2±1.4	58±1.2
M_4	60	55.0	45±1	46±2	44.7±1.1	44.8±0.8
M_5	7.8	120.3	8.5±0.4	7.3±0.7	8.5±0.4	7.8±0.6
M_5	7.8	161.4	6.9±0.4	6.1±0.7	6.9±0.4	6.3±0.6
M_6	1.76	143.0	2.1±0.3	1.8±0.5	2.1±0.3	—
M_6	1.76	120.4	1.6±0.3	2.0±0.6	1.6±0.3	—

[a] See text.

(b) or by matrix calculus (c). The Sb activities were also measured under different geometric conditions (well-type NaI (Tl) crystal) (d).

From Table IV it appears that the results are in good agreement.

SUMMARY

A non-destructive activation analysis of trace impurities in germanium giving rise to long-lived γ-emitting isotopes is described. Hg, Sn, Cr, Sb, Sc, Zn and Co were determined by γ-spectrometry after irradiation with thermal neutrons ($\phi_{th} = 10^{14}$ n. cm^{-2}.sec^{-1}, irrad. time: 15 h, cooling period: *ca.* 30 days). The complex γ-spectrum was analysed by a combination of COVELL's method and matrix calculus. The detection limits are approximately 2 p.p.b. of Hg, 7 p.p.b. of Cr, 200 p.p.b. of Sn, 1 p.p.b. of Sb, 10 p.p.b. of Zn, 0.2 p.p.b. of Co and 0.1 p.p.b. of Sc.

RÉSUMÉ

On a élaboré une méthode d'analyse par activation non destructive pour la détermination de traces d'impuretés dans le germanium par la mesure gamma spectrométrique d'isotopes de longues périodes, notamment le Hg, Sn, Cr, Sb, Sc, Zn et Co. Le spectre gamma complexe fut analysé en combinant la méthode de COVELL avec le calcul de matrice. La limite de dosage inférieure est d'environ 2 p.p.b., 7 p.p.b., 200 p.p.b., 1 p.p.b., 10 p.p.b., 0.2 p.p.b. and 0.1 p.p.b. pour resp. Hg, Cr, Sn, Sb, Zn, Co et Sc après une irradiation durant 15 h à un flux de neutrons thermiques d'environ 10^{14} n.cm^{-2}.sec^{-1} et une période de refroidissement de 30 jours.

ZUSAMMENFASSUNG

Es wird die zerstörungsfreie aktivierungsanalytische Bestimmung von Spuren Verunreinigungen in Germanium beschrieben. Hg, Sn, Cr, Sb, Sc, Zn und Co wurden nach einer Bestrahlung mit thermischen Neutronen mittels des γ-Spektrums bestimmt. Das komplexe γ-Spektrum wurde durch Kombination der Covell'schen Methode mit Matrixberechnungen analysiert. Die Nachweisgrenzen liegen näherungsweise bei 2 p.p.b. Hg, 7 p.p.b. Cr, 200 p.p.b. Sn, 1 p.p.b. Sb, 10 p.p.b. Zn, 0.2 p.p.b. Co und 0.1 p.p.b. Sc.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PHOSPHORUS(V) PESTICIDES

PART II. A RAPID DETERMINATION OF THE ISOMER RATIO OF SYSTOX[†]

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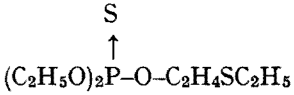
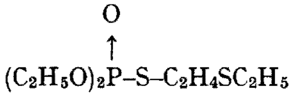
(Received July 19th, 1967)

Systox (demeton) is a systemic insecticide composed of two isomers, O,O-diethyl-O-(2-(ethylthio)ethyl)phosphorothionate (compound A, the thiono isomer), and O,O-diethyl-S-(2-(ethylthio)ethyl)phosphorothionate (compound B, the thiol isomer). The ratio of thiono to thiol isomer in technical Systox normally varies from 2:1 to 1:1.



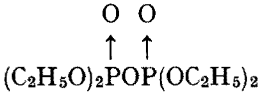
$(C_2H_5O)_2\overset{\overset{S}{\uparrow}}{P}-O-C_2H_4SC_2H_5$

Compound A (thiono)



$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}-S-C_2H_4SC_2H_5$

Compound B (thiol)



$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}O\overset{\overset{O}{\uparrow}}{P}(OC_2H_5)_2$

Compound C (Sulfotepp)

Technical Systox samples also contain an additional 1–5% concentration of tetraethyl dithionopyrophosphate (compound C, Sulfotepp) resulting from side reactions in the synthesis. Since the chemical properties and toxicities of the two isomers differ, it would be of interest to find a rapid instrumental technique for determining the isomer ratio in Systox.

BETKER *et al.*[1] have recently reviewed the analytical procedures for the determination of the isomer ratio in Systox mixtures. A number of coulometric and instrumental techniques are described including differential hydrolysis methods, augmented by iodimetry, and infrared analysis augmented by vapor phase chromatography (VPC). The wet procedures suffer uniformly from two drawbacks: they are time-consuming, both in terms of reagent preparation and in analytical manipulation; and at least 4 g of sample is needed which is destroyed in analysis. In addition to the wet methods a number of authors have utilized the P=O and P=S stretching frequencies in the infrared to calculate the isomer ratio[2]. The proposed method is designed to supplement the I.R. methods, and makes analysis of Systox mixtures possible without a need for standard compounds and extensive instrument calibration. The combination of NMR with VPC analysis results in an analytical tool which is both rapid and utilizes only 0.1 g of sample in the total analysis of technical-grade samples of Systox.

MULLER AND GOLDENSON have reported the use of ^{31}P NMR for the analysis of Sulfotepp-free Systox mixtures[3]. The present study is limited to proton resonance.

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[†] Publication authorised by the Director U.S. Geological Survey.

DISCUSSION AND RESULTS

The NMR spectrum of the mixture of compounds in technical-grade Systox is shown in Fig. 1. The spectrum shows 3 distinct and separate sets of peaks corresponding to protons in the 3 magnetic environments in the sample. The alkyl protons appear at a chemical shift of 1.1–1.5 p.p.m. (with reference to TMS as internal standard, at 0.0 p.p.m.); the thioether protons appear as a multiplet at 2.3–3.1 p.p.m. while the oxyether protons appear as a multiplet at 3.8–4.3 p.p.m. The areas of these peaks, obtained by integration, can be used for the analysis of the mixture, if the Sulfotepp concentration in technical-grade Systox is known. BETKER *et al.*[1] have described an analytical VPC procedure for determining the amount of Sulfotepp in Systox mixtures, which proved adequate for the present purpose.

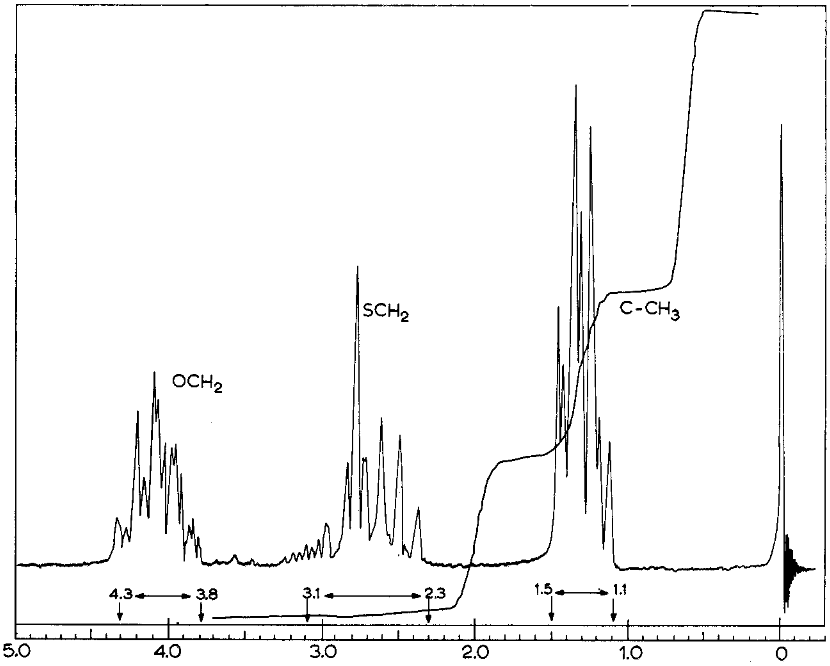

Fig. 1. Sample Systox spectrum.

Since the area under each set of peaks in the NMR spectrum of a mixture is proportional to the number of protons absorbing energy at that frequency[4], one can set up the simultaneous equations expressing the areas of the peaks as a function of the mole fraction of the components in the mixture.

$$A_{\mathrm{OH}} = n_{\mathrm{AO}}X_{\mathrm{A}} + n_{\mathrm{BO}}X_{\mathrm{B}} + n_{\mathrm{CO}}X_{\mathrm{C}} \qquad (1)$$

$$A_{\mathrm{SH}} = n_{\mathrm{AS}}X_{\mathrm{A}} + n_{\mathrm{BS}}X_{\mathrm{B}} + n_{\mathrm{CS}}X_{\mathrm{C}} \qquad (2)$$

$$A_{\mathrm{CH}} = n_{\mathrm{AC}}X_{\mathrm{A}} + n_{\mathrm{BC}}X_{\mathrm{B}} + n_{\mathrm{CC}}X_{\mathrm{C}} \qquad (3)$$

where A_{OH} = area of the peak due to protons near a normal ether linkage; A_{SH} = area of the peak due to protons near a thioether linkage; A_{CH} = area of the peak due to normal aliphatic protons; X_A, X_B and X_C are the mole fractions of compounds A, B and C respectively; n_{AO}, n_{BO} and n_{CO} are the numbers of normal ether linkage protons in compounds A, B and C respectively; n_{AS}, n_{BS} and n_{CS} are the numbers of thioether linkage protons in compounds A, B and C respectively; n_{AC}, n_{BC} and n_{CC} are the numbers of normal alkyl protons in compounds A, B and C respectively.

Substituting the numbers of protons for Systox and Sulfotepp into eqns. (1), (2) and (3), one obtains:

$$A_{OH}=6X_A+4X_B+8X_C \tag{4}$$

$$A_{SH}=4X_A+6X_B \tag{5}$$

$$A_{CH}=9X_A+9X_B+12X_C \tag{6}$$

Solving for X_A, X_B and X_C:

$$X_A=3/8A_{OH}+1/8A_{SH}-1/4A_{CH} \tag{7}$$

$$X_B=1/6A_{CH}-1/4A_{OH} \tag{8}$$

$$X_C=5/48A_{CH}-3/32A_{SH}-3/32A_{OH} \tag{9}$$

The NMR spectrum alone yields the mole fractions of components A, B and C.

If the sample weight (W_T) is known, and one assumes that the sample contains only compounds A, B and C, it becomes a simple matter to find the weight of the Systox isomers (W_A and W_B). The weight percent of Sulfotepp in the mixture ($\%W_C$) can be determined by VPC analysis and in conjunction with the sample weight gives the weight of Sulfotepp in the mixture (W_C).

From the mole fraction expression for component A (eqn. (10))

$$X_A=\frac{W_A/M_{AB}}{W_A/M_{AB}+W_B/M_{AB}+W_C/M_C} \tag{10}$$

one can obtain an equation for W_B:

$$W_B=W_A(1-X_A)/X_A-W_CM_{AB}/M_C \tag{11}$$

where M_{AB} and M_C are the molecular weights of Systox and Sulfotepp respectively.

Combining eqn. (11) with the expression for the total weight of the sample (eqn. (12)):

$$W_T=W_A+W_B+W_C \tag{12}$$

one obtains an expression for the weight of component A in terms of known quantities (eqn. (13)):

$$W_A=W_TX_A-W_CX_A(1-M_{AB}/M_C) \tag{13}$$

Alternatively, by substituting predetermined values for X_A, X_B and X_C into eqns. (4)–(7), one can obtain sets of data that correlate the mole fraction X_A (and therefore the wt % of A) with the (OH/SH) peak area obtained from the spectrum, for any given value of C, as determined by VPC. The results of such calculations are given in Fig. 2. From the percentage of A and C in the mixture, the concentration of B is obtained by subtraction.

Several samples were prepared from samples of known purity A, B and C and

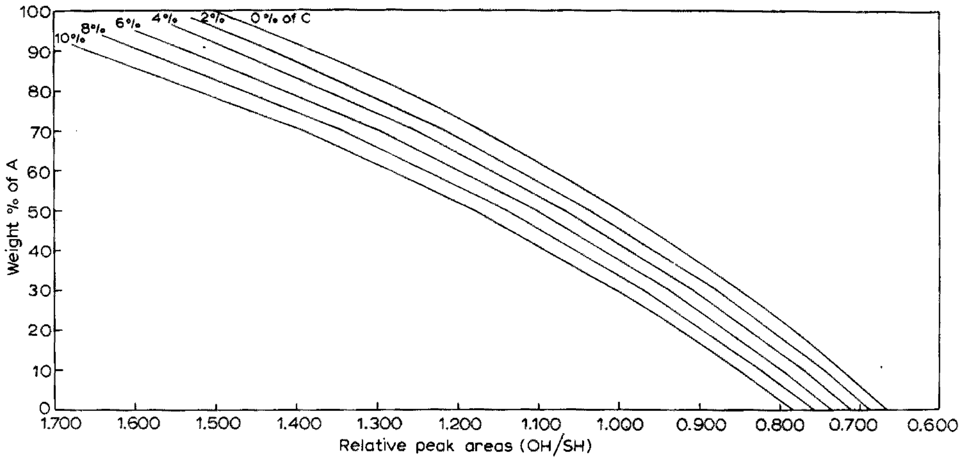

Fig. 2. Systox analysis.

TABLE I

ANALYSIS OF LABORATORY-PREPARED TECHNICAL SYSTOX

Thiono isomer (% added)	*Thiol isomer (% added)*	*Sulfotepp (% added)*	*% Thiono isomer found*	
			Calculated	*Graph*
84.7	15.3	0.0	83.9	84.3
63.8	36.2	0.0	64.2	61.9
49.3	50.7	0.0	49.0	50.8
22.6	77.4	0.0	23.1	22.9
16.4	83.6	0.0	15.8	16.9
53.5	44.6	1.9	53.8	52.9
75.5	20.6	3.9	73.9	74.8
20.9	75.0	4.1	19.5	20.7

analyzed both graphically (Fig. 2) and by direct calculation. The results of representative analyses are given in Table I.

The data in Table I illustrate the limitations of the NMR method for analyzing Systox ratios. There is an error of ±1% both in the application of the graphical method and in use of the mathematical treatment. This error in analysis results in large part from the limitations of the integration circuit of the A-60, and is comparable to the errors obtained by alternative analytical techniques.

CONCLUSIONS

This analytical technique is useful for rapidly determining the Systox ratio in 0.1-g samples, if a ±1% error in the thiol to thiono ratio is permitted. The use of micro NMR sample tubes can further reduce the sample size, but may increase the error, so that a complete analysis may be carried out on $1 \cdot 10^{-5}$ moles of technical-grade Systox in less than 15 min. Another advantage to this method is that the sample remains available for biological testing if desired, since it is not destroyed in the analysis.

EXPERIMENTAL

Spectra were measured with a Varian A-60 NMR Spectrometer calibrated with TMS as zero in carbon tetrachloride as solvent. The solutions were approximately 20% by volume in concentration. The instrument was adjusted to maximum sensitivity with an acetaldehyde standard, and the integration circuit was balanced against spectral-grade toluene. Under these conditions the integration error was less than 0.7%. When a less elaborate means of adjusting the instrument was used, by simply maximizing the TMS signal with the homogeneity controls, the integration error was increased to a maximum of ±1.5%. This latter procedure was followed for the analyses reported. Known mixtures were prepared from analyzed samples of the Systox isomers and Sulfotepp, and were analyzed by the NMR method. As an additional check, the procedure of BETKER *et al.*[1] was used to determine the Sulfotepp concentration in the mixtures by VPC and the validity of this technique was reaffirmed. The starting materials consisted of Sulfotepp (99%), Systox (thiono isomer) (84.7%) and Systox (thiol isomer) (83.6%), the latter containing no Sulfotepp, and the mixtures were analyzed as follows.

A second sample of technical Systox (or the synthetic mixture) was analyzed by the technique of BETKER *et al.*[1] and the % Sulfotepp in the mixture determined. An accurately weighed 0.05–0.1 g sample was then dissolved in 0.5 ml of carbon tetrachloride containing TMS as an internal standard and the spectrum was taken. The peaks in the spectrum were integrated 4 times and the heights of the OH, SH and CH peaks were measured with a millimeter rule. The average of the areas defined by these readings were used for analysis. From the percent Sulfotepp in the mixture and the (OH/SH) ratio the percent of the thiono isomer could be obtained directly from Fig. 2.

The authors express their thanks to Dr. ALVIN L. SCHALGE, Marathon Oil Company, Denver Research Center, for access to the A-60 spectrometer, to WASHINGTON HERBERT for assistance in sample preparation, and to Dr. F. D. ALDRICH, Colorado State Public Health Service and the Chemargo Corporation, Kansas City for samples of Systox and Sulfotepp.

SUMMARY

The integration circuit of the Varian A-60 nuclear magnetic resonance spectrometer is used in conjunction with vapor phase chromatography, to develop a rapid analysis technique for the determination of isomer ratios in technical Systox–Sulfotepp mixtures. The complete analysis requires less than 0.1 g of sample and only 15 min. The isomer ratio in the sample may be determined to an accuracy of ±1.5% and the undamaged sample may be recovered.

RÉSUMÉ

Le circuit d'intégration du spectromètre de résonance nucléaire magnétique Varian A-60 est utilisé en conjonction avec la chromatographie en phase gazeuse pour développer une technique d'analyse rapide pour la détermination de teneurs en isomères dans des mélanges Systox–Sulfotepp. Une analyse complète n'utilise que 0.1 g d'échantillon et ne demande que 15 min. La teneur en isomère de l'échantillon peut être déterminée avec une exactitude de ±1.5%; l'échantillon, non endommagé, peut être récupéré.

ZUSAMMENFASSUNG

Ein KMR-Spektrometer wird in Verbindung mit der Gasphasenchromatographie verwendet, um eine schnelle Analysentechnik zur Bestimmung von Isomerenverhältnissen in technischen Phosphor(V)-Pesticiden zu entwickeln. Zur vollständigen Analyse werden weniger als 0.1 g Probe und nur 15 min benötigt. Das Isomerenverhältnis der Probe kann mit einer Genauigkeit von ±1.5 % bestimmt werden. Die unzerstörte Probe kann zurückgewonnen werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

EMISSION SPECTROCHEMICAL DETERMINATION OF CHROMIUM IN ORGANIC ACIDS*

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Few publications have dealt with the direct emission spectrographic determination of metallic impurities in organic compounds. GIORGINI AND LUCCHESI[1] have reported on the direct determination of boron in terphenyls and NEGISHI[2] has described a technique which directly determines aluminum, iron and titanium in polypropene using an a.c. arc. NASH[3] ashed polypropylene samples and other organic materials directly in the electrode with a hand torch using an oxygen–gas flame. The ashed sample was analyzed with a d.c. arc in an argon–oxygen atmosphere. The indirect approach is the more popular. Even here, the number of techniques is limited. PERIZULAEV *et al.*[4] describe a method where the sample is mixed with strontium sulfate, treated with concentrated sulfuric acid, ignited and powdered. There are numerous techniques described which use either dry ashing or wet ashing and subsequent emission spectrographic analysis. The many chemical techniques described are usually long and tedious. Some workers[5-7] have used the X-ray fluorescence spectrometer to determine directly trace elemental impurities in organic compounds.

In this paper, the development of a technique which allows direct determination of the chromium concentration in organic acids by d.c. arc emission spectrochemical analysis is described. The analysis of traces of chromium in mono- and dicarboxylic aromatic acids is made difficult by the fact that these acids are not always soluble in common organic solvents or mineral acids. The analysis, however, is quite easily accomplished by mixing the sample as received with graphite which contains a spectrochemical buffer and an internal standard. Chromium concentrations from 10 to 10,000 p.p.m. are determined using a single set of standards, two analysis lines, and the technique of dilution.

EXPERIMENTAL

Preparation of standards

The organometallic compound, tris(2′-hydroxyacetophenono)chromium(III) (10.6% Cr; National Bureau of Standards Standard Sample 1072) was used as the source of chromium. Cobalt, which serves as the internal standard element, was added as the cobalt cyclohexanebutyrate (17.1% Co, National Bureau of Standards Standard Sample 1055).

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* Presented at the Eighth Annual Rocky Mountain Spectroscopy Conference, Denver, Colo., August, 1966.

It was found convenient to prepare 1% dilutions of the organometallic compounds of chromium and cobalt in spectrographically pure graphite (National Carbon Company's SP-2 graphite). These 1% preparations were blended with a Wig-L-Bug by weighing the constituents into a ½″-diameter by 1″-long polystyrene vial (Spex Industries Catalog No. 3111) and adding three 1/8″-diameter plexiglas balls. The material was blended for a period of 30 sec.

A set of standards covering a concentration range of 10 to 100 p.p.m. chromium was prepared by weighing the proper amounts of 1% chromium, 1% cobalt, graphite, and lithium carbonate, which is used as a spectral buffer. Enough lithium carbonate was used so that the concentration of lithium in the standards was 1%. The final concentration of cobalt was 0.086%.

It was found convenient to prepare 200-mg quantities using the previously mentioned polystyrene vial. The mixing procedure was the same as that used to prepare the 1% chromium and cobalt dilutions.

Preparation of samples

One part of sample was weighed into a ½″-diameter polystyrene vial with 9 parts of diluent. This provided a dilution factor of 10. The diluent consisted of one part lithium carbonate, two parts 1% cobalt (NBS Standard Sample 1055 diluted with graphite as described under preparation of standards) and 15 parts National Carbon Company's SP-2 graphite. The sample and diluent were mixed with a Wig-L-Bug as the standards were prepared.

Occasionally, it was necessary to use dilution factors other than 10 on the

TABLE I

INSTRUMENTAL AND SPECTROCHEMICAL OPERATING CONDITIONS

Electrodes:	7 mg of diluted sample is loaded into a National Carbon Co. L-4206 electrode which is made the anode. A National Carbon Co. L-4236 (ASTM C-1) is used as the counter electrode.
Analytical gap:	4 mm.
Excitation conditions:	d.c. arc, 10 A, closed circuit.
Spectrograph:	Jarrell-Ash 3.4-m Ebert, 15,000 line per inch grating, first order.
Wavelength range (Å):	To include 2500 to 2900 and 3900 to 4300.
Slit width *(μ)*:	10
Filter:	Three-step (100/20/4) with Jarrell-Ash Company's three-lens system (catalog No. 18-060). The three-lens system mask is set so that the analytical gap region from 1 mm off the cathode tip out to 2-1/2 mm is used.
Exposure (sec):	20
Photographic emulsion:	Kodak Type III-o.
Developer:	Kodak D-19, 65°F, 4 min.
Plate calibration:	Two-step, iron arc[8].

sample. In these cases, two dilutions were made. The first dilution involved mixing the sample with SP-2 graphite. For the second dilution one part of the diluted sample was mixed with 9 parts of diluent. By doing this, the cobalt and lithium concentration remained constant in the samples. At no time was it necessary to use a dilution factor of less than 10.

Working curve and analysis procedure

The standard or diluted sample (7 mg) was weighed into a National Carbon Company No. L-4206 electrode. Both the standards and analytical samples were run in triplicate using the spectrochemical conditions mentioned in Table I.

Transmittance values were obtained for the cobalt internal standard at 2521.4 Å (20% T filter step), at 3952.9 Å (20% T filter step), and 3935.97 Å (20% T filter step). The transmittance values for chromium were obtained at 2843.25 Å (100% T filter step) and 4254.35 Å (both read in the 20% T filter step). Typical working curves are shown in Fig. 1. The slopes of the curves were nearly 45°. Cr(2843.25) with Co(2521.4) as the internal standard line, had a slope of 57° and was linear between 10 and 100 p.p.m.

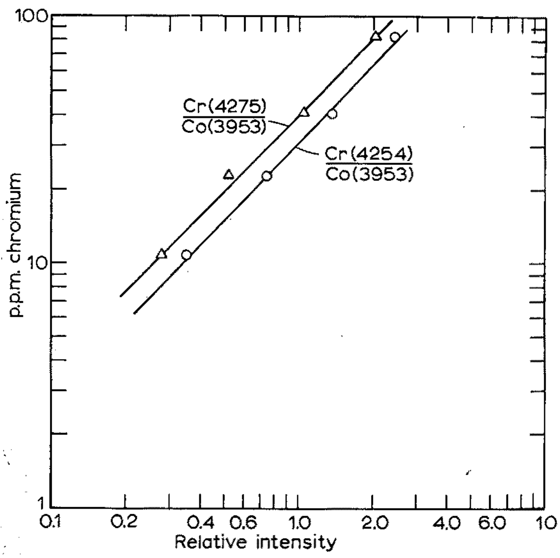

Fig. 1. Analytical curve for chromium in mixed dicarboxylic aromatic acids.

The concentration of chromium in the analytical samples was read directly from the analytical curve. The concentration of chromium in the sample is the product of the analytical sample concentration multiplied by the dilution factor.

RESULTS

Effects of sodium

Because some samples were contaminated with sodium salts, it was necessary to investigate the effect of varying concentrations of sodium on the spectral intensities of chromium and cobalt. A sample was prepared from National Bureau of Standard's organometallic compounds so that the chromium and cobalt concentrations were 0.10%. Sodium as sodium chloride, was varied from 0 to 31.5%. The results of the experiment are shown in Fig. 2 for a chromium and cobalt line. Other chromium and cobalt lines showed similar behaviors. Because there appeared to be a significant dependence of the spectral intensities at sodium concentrations less than 5%, the effect of sodium between 0 and 0.5% was studied. The results of this study are shown in Fig. 3. As can be seen, sodium has little effect on the spectral intensities at sodium concentrations less than 0.01%. However, at sodium concentrations greater than 0.01%, both chromium and cobalt spectral lines sharply decrease in percent transmittance (increase in spectral intensity) and reach a minimum between 1 and 2% sodium, as shown in Fig. 2. Because of this effect, it is necessary to maintain a constant sodium concentration or find some means of minimizing the effect. In a first attempt, everything was reduced to a sodium carbonate matrix. This was unsatisfactory from the reproducibility standpoint and the desired sensitivity for chromium could not be obtained. To overcome the problem caused by sodium, lithium carbonate was used as a spectral buffer. Lithium concentrations from 1 to 12% were investigated for their efficiency in minimizing the effect of sodium on the chromium and cobalt spectral line intensities. It was found that 1% lithium was the most effective concentration level in minimizing the sodium effect. Figure 4 illustrates the effectiveness of 1% lithium in minimizing the effect of sodium on the spectral

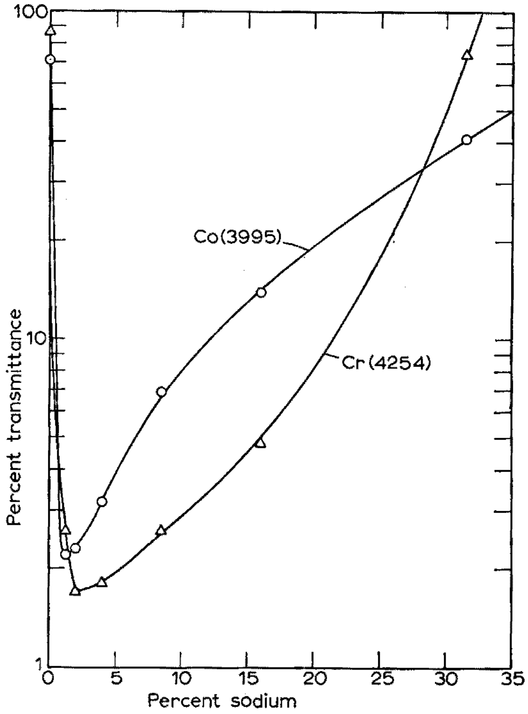

Fig. 2. Effect of sodium on the spectral lines of chromium and cobalt.

intensities of chromium and cobalt. The samples used to obtain these curves contained 20 p.p.m. chromium, 1000 p.p.m. cobalt, and 1% lithium as lithium carbonate. As is shown in Fig. 4, lithium was quite effective in minimizing the effect of sodium out to 2%. Beyond the 2% level, the relative intensities of the various spectral lines as well as the intensity ratio of chromium to cobalt varied significantly. Between 0 and 2%

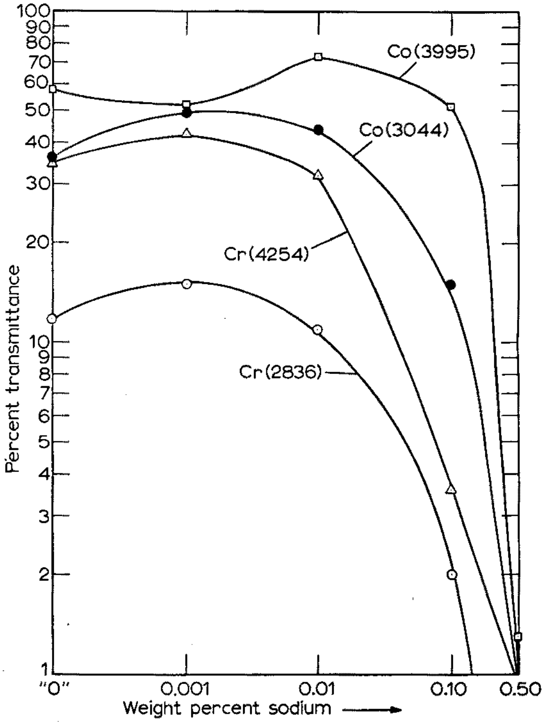

Fig. 3. Effect of low sodium concentration on chromium and cobalt spectral intensities. The zero sodium level values are shown as "O" and are plotted where 0.0001% sodium would normally be.

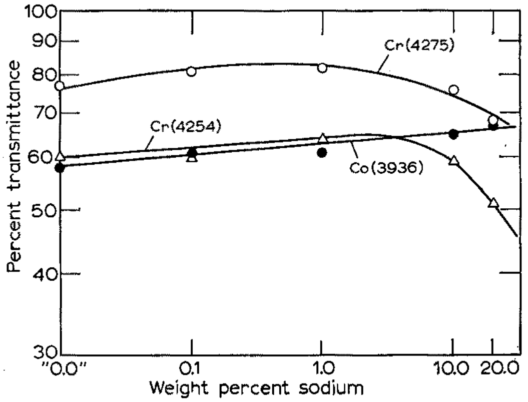

Fig. 4. Effectiveness of lithium carbonate as a spectral buffer. The zero level sodium values are plotted where 0.01% sodium would be and are labelled "O.O". Cr, 20 p.p.m.; Co, 1000 p.p.m.

sodium, the intensity ratio of Cr (4254) to Co (3936) did not vary more than ±5% from the 0 sodium concentration level value.

Precision and accuracy

The precision of the method was tested on a sample of trimesic acid which had an average chromium concentration of 14.7 p.p.m. Eleven replicate determinations were made with an estimated standard deviation of ±1.7 p.p.m. The relative standard deviation was ±11.8% at the 1 S level.

In order to check the accuracy of the method, a sample of technical-grade chromium acetylacetonate [$Cr(C_5H_7O_2)_3$] (MacKenzie Chemicals Works Inc., Central Islip, Long Island, New York) was diluted to a desirable concentration range with trimesic acid. Six separate determinations were made which resulted in a relative standard deviation of ± 3.3% and an average value of 66.3 p.p.m. Assuming the chemical is 100% pure, the relative error of the technique is 10.9%.

TABLE II

DETERMINATION OF CHROMIUM IN DICARBOXYLIC AROMATIC ACIDS

Sample	*Dilution factor*	*p.p.m. Cr*
S-148	36	4140, 3560, 3600
S-149	39	10210, 11400, 11400
S-48	19	100
S-49	51	9500
S-153	20	1800
S-154	10	320, 285
9910-A	36	317
9912-R	30	858
9915-A	40	265
9915-R	25	496

In Table II data are presented which show some typical chromium concentrations and the dilution factors which were used. The materials were research samples which were being made by a new synthetic procedure. There was no comparison method available to check the results of the technique.

CONCLUSIONS

This d.c. arc emission spectrochemical procedure allows one to determine the chromium concentration in organic material over a wide concentration range. The sample need only be mixed with a graphite diluent before analysis. The technique was successfully applied to a variety of solid organic acids ranging from dicarboxylic polynuclear aromatic acids to trimesic acid and an acetylacetonate.

Sodium has a considerable effect upon the spectral intensities of chromium and cobalt lines. This effect is very pronounced between 0.01 and 15% sodium. Lithium carbonate is very effective in minimizing the effect varying sodium concentrations have on the relative intensity of chromium and cobalt if the sodium concentration remains below 5%.

SUMMARY

An emission spectrochemical procedure is described which directly determines the chromium concentration in organic materials in the p.p.m. range. The only preparation of the sample which is necessary is dilution with a graphite matrix which contains the internal standard element and the spectral buffer, lithium carbonate. The effect of sodium on spectral line intensities of cobalt and chromium is shown. The effectiveness of lithium carbonate as a spectral buffer is illustrated. The precision of the technique is estimated to be ±11.8% and the accuracy estimated to be 10.9%.

RÉSUMÉ

Une méthode spectrochimique par émission est décrite pour déterminer directement les concentrations en chrome (de l'ordre du p.p.m.) dans des substances organiques. La seule préparation de l'échantillon nécessaire est la dilution avec une matrice de graphite contenant l'étalon interne et le tampon spectral (carbonate de lithium). On examine l'influence du sodium sur les intensités de la raie spectrale du cobalt et du chrome, de même que l'efficacité du carbonate de lithium comme tampon. La précision de la technique est estimée à ±11.8% et l'exactitude à 10.9%.

ZUSAMMENFASSUNG

Es wird ein emissionsspektralanalytisches Verfahren zur Bestimmung von Chrom in organischen Materialien im p.p.m.-Bereich beschrieben. Die einzige notwendige Präparation der Probe ist die Verdünnung mit einer Graphitmatrix, welche das innere Standardelement und den Spektralpuffer Lithiumcarbonat enthält. Der Einfluss von Natrium auf die Linienintensität von Cobalt und Chrom wird gezeigt, ebenso die Wirksamkeit des Lithiumcarbonats. Die Reproduzierbarkeit des Verfahrens beträgt 11.8, die Richtigkeit 10.9%.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC HYDROXYL IN ESTERS WITH VANADIUM OXINATE

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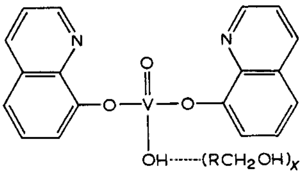
(Received July 20th, 1967)

During esterification studies of fumaric acid by even-carbon-numbered straight-chain aliphatic alcohols covering the range octanol to octadecanol, the concentration of unreacted alcohols had to be measured. These were usually present in the concentration range 0.05–2.0 wt.% in the finished ester. Although the normal acylation[1] procedures were perfectly satisfactory at the higher levels of alcohol concentration, the precision deteriorated as the alcohol concentrations fell below 1.0 wt.%, and a more sensitive spectrophotometric method was therefore sought.

The first spectrophotometric method to be considered was that of JOHNSON AND CRITCHFIELD[2] who described a rapid and simple procedure for the determination of hydroxyl groups in primary and secondary alcohols. The method is based on the reaction of hydroxyl with 3,5-dinitrobenzoyl chloride in the presence of pyridine. After the reaction has been completed the pyridine is neutralised with hydrochloric acid and the dinitrobenzoate ester is extracted into hexane. Treatment of the hexane extract with a solution of sodium hydroxide in acetone causes a blue colour to develop, probably due to the formation of a mesomeric quinoidal structure. The absorbance of this solution, the colour of which is only stable for 5 min, is measured at a wavelength of 575 nm against a blank prepared in an identical manner. The method was found to be unsatisfactory because very high blanks were obtained, probably because of impurities in the pyridine.

A literature search suggested that a method based on the colour reaction between alcohols and vanadium oxinate might be utilised to advantage, especially since the vanadium oxinate reagent has recently become commercially available. This obviates the lengthy and tedious preparation of the reagent reported by previous workers.

BUSCARONS, MARIN AND CLAVER[3] first demonstrated in 1949 the usefulnes- of vanadium oxinate as a reagent for detecting small amounts of alcohols in hydrocarbon solutions; FEIGL AND STARK[4] later developed the reagent as a spot test for primary, secondary and tertiary alcohols. On addition of an alcohol to the greens black solution of vanadium oxinate in benzene, a reddish colour is developed when the mixture is heated for a few minutes on a water bath at 60°. The red colour is probably due to the formation of a complex of the type:



TANAKA[5] attempted to use the reagent quantitatively in chloroform or nitrobenzene solution but found that excess of reagent interfered in the determination. Similar work was reported by KUDO AND AOKI[6] and MARUTA AND IWAMA[7], all of whom used the reagent in xylene–acetic acid media. STILLER[8] showed that excess of vanadium oxinate could be removed from the organic layer by washing with sodium hydroxide solution, while PESEZ AND BARTOS[9] demonstrated that the red-coloured vanadium oxinate–alcohol complex could be stabilised by the addition of dichloracetic acid in glacial acetic acid. Finally, VAN GENT AND KERRICH[10] applied the procedure to the colorimetric determination of ethanol in blood.

The purpose of this paper is to report the development of a spectrophotometric procedure for the determination of small amounts of higher alcohols, and its application to the estimation of free aliphatic alcohols in esters.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 137 UV spectrophotometer was used in the development of the method.

Reagents

"Vanadium oxinate" (oxohydroxybis(8-hydroxyquinolino)-vanadium(V)) was obtained from the Eastman Kodak Company. The reagent was prepared by dissolving 0.1 g of vanadium oxinate and 0.25 g of 8-hydroxyquinoline in 250 ml of nitrobenzene. This solution was stable for at least two weeks.

Pure grade *n*-alcohols were obtained from B.D.H., Poole, Dorset, England.

Procedure

Weigh out sufficient sample and dissolve in nitrobenzene so that the solution contains approximately 10^{-4} g hydroxyl per ml. (In the present work it was found convenient to weigh out accurately 1.0 g of ester, make up to 25.0 ml with nitrobenzene and take a 5.0-ml aliquot). To a 5.0-ml aliquot of sample solution, add 5.0 ml of vanadium oxinate solution and heat on a boiling water bath for 30 ± 1 min. Cool and adjust the final volume to 10.0 ml with nitrobenzene (A.R., redistilled). Transfer to a separatory funnel and shake with 5 ml of 1 *M* sodium hydroxide solution until the green-black colour of the excess of vanadium oxinate has been discharged. Draw off the nitrobenzene layer and immediately dry by shaking with anhydrous sodium sulphate (A.R.) for 15 sec. Measure the absorbance of the dried solution in a 1-cm cell at 480 nm using nitrobenzene as a blank. This absorbance should be measured within 10 min of removing the reaction mixture from the water bath. Deduce the weight of hydroxyl in the aliquot by reference to a previously prepared calibration graph and calculate the percentage hydroxyl in the sample.

Alternatively treat the reddish coloured vanadium oxinate–alcohol solution with 0.5 ml of 5% dichloracetic acid in glacial acetic acid. This produces a more stable blue solution, whose absorbance is measured at 620 nm in a similar manner.

Calibration

Prepare a fresh calibration graph daily and on each batch of vanadium oxinate reagent. Prepare a standard solution of a suitable alcohol in nitrobenzene to contain about 10^{-4} g hydroxyl per ml, *e.g.* dissolve 0.1 g of *n*-decanol in 100 ml of nitrobenzene. Pipette 1.0, 2.0, 3.0, 4.0, 5.0 ml of the standard alcohol solution into a series of beakers, add 5.0 ml of vanadium oxinate solution and carry out the hydroxyl determination as given under *Procedure*. Obtain a calibration graph giving the absorbance at 480 nm *versus* the weight of hydroxyl taken. It was found that the plots derived from all pure *n*-alcohols in the C_8–C_{18} range fell on the same straight line.

RESULTS AND DISCUSSION

Availability of reagent

Previous workers[2–9] have been forced to prepare their reagent *in situ*. This is tedious and has undoubtedly retarded the development of the method as a rapid analytical procedure. The recent introduction of a commercial preparation of vanadium oxinate has removed this barrier. The addition of 8-hydroxyquinoline to the reagent solution increases its stability in nitrobenzene solution. It was found that the solution was still usable two weeks after preparation, though it was found necessary to prepare a fresh calibration curve daily on account of the gradual deterioration of the reagent.

Choice of solvent

Chloroform, benzene, xylene and nitrobenzene have all been used by previous workers. Commercially available chloroform contains 1% ethanol as stabiliser. Consequently, this has to be removed before use. It was found, however, that "purified" chloroform rapidly deteriorated after removal of the ethanol with potassium dichromate–sulphuric acid mixtures. The use of benzene was not favoured on the ground of volatility and high toxicity. Xylene is preferable but vanadium oxinate is not very soluble. Addition of acetic acid increases its solubility but decreases its stability. Nitrobenzene was thus chosen because it gave a stable involatile solution. However, objections to its harmful and unpleasant vapour still remain.

Figure 1 shows the absorption curves of both red and blue complexes of ethanol and decanol with vanadium oxinate in chloroform and nitrobenzene solutions. It can be seen that the effect of substituting nitrobenzene for chloroform as used by STILLER[8], was to shift the position of the absorption maxima from 350–400 nm to 430–510 nm in the case of the red complex although no shift was observed in the absorption maximum (620 nm) of the blue complex. The positions of the maxima were independent of alcohol carbon number. Since the red complex gave a plateau in the absorption curve between 460–500 nm, 480 nm was chosen as the wavelength at which absorbance measurements were made.

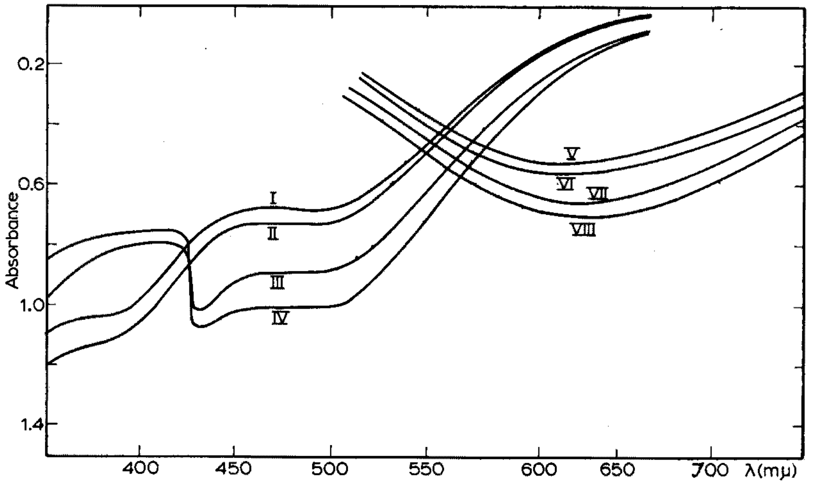


Fig. 1. Absorption of 0.1% alcoholic vanadium oxinate complexes as function of wavelength (Perkin-Elmer Model 137 U.V.). (I) red decanol complex in chloroform, (II) red ethanol complex in chloroform, (III) red decanol complex in nitrobenzene, (IV) red ethanol complex in nitrobenzene, (V) blue decanol complex in chloroform, (VI) blue decanol complex in nitrobenzene, (VII) blue ethanol complex in chloroform, (VIII) blue ethanol complex in nitrobenzene.

Effect of reaction time

A portion (5.0 ml) of a standard *n*-decanol solution in nitrobenzene was mixed with 5.0 ml of vanadium oxinate solution and allowed to react on the steam bath for differing lengths of time covering the range 10–60 min. Excess of vanadium oxinate was destroyed with 1 *M* sodium hydroxide solution and the nitrobenzene layer was dried by shaking with anhydrous sodium sulphate. The absorbance of the solution was measured immediately, the results being shown in columns 2 and 5 of Table I. The experiment was repeated using a standard dodecanol solution. The absorbance of the blue coloured solution resulting from treatment of the vanadium oxinate–alcohol complex with the dichloracetic acid reagent is given in columns 3 and 6 of Table I. It can be seen that good repeatability by both methods was obtained after a reaction time of 30 min, although a reaction was still taking place after 60 min. In order to keep the reaction time as small as possible it was decided to standardise on a reaction time of 30 min.

TABLE I

EFFECT OF REACTION TIME ON ABSORBANCE

Reaction time (min)	*Absorbance at 480 nm (red decanol complex)*	*Absorbance at 620 nm (blue dodecanol complex)*	*Reaction time (min)*	*Absorbance at 480 nm (red decanol complex)*	*Absorbance at 620 nm (blue dodecanol complex)*
10	0.461	0.270	30	0.569	0.415
	0.572	0.336		0.571	0.417
20	0.526	0.372	60	0.610	0.445
	0.552	0.399		0.620	0.446

Colour stability of alcohol complexes

Two 5.0-ml portions of a standard dodecanol solution in nitrobenzene were each mixed with 5.0 ml of vanadium oxinate solution and allowed to react on the steam bath for 30 min. Removal of the excess vanadium oxinate was followed by simultaneous addition of anhydrous sodium sulphate to one portion and dichloracetic acid reagent to the other portion. The absorbances were measured after given intervals of time as shown in Table II.

TABLE II

COLOUR STABILITY OF ALCOHOL COMPLEXES

Time (min)	*Absorbance at 480 nm*	*Absorbance at 620 nm*	*Time (min)*	*Absorbance at 480 nm*	*Absorbance at 620 nm*
15	0.636	0.371	120	0.410	0.354
30	0.525	0.369	240	0.422	0.350
60	0.450	0.369	360	0.467	0.340

The results show that the time elapsed after the development of the colour was critical in the case of the addition of anhydrous sodium sulphate. The colour rapidly faded after 15 min but after 3–4 h gradually darkened again. The colour could be stabilised by the addition of the dichloracetic acid reagent. No noticeable fading then occurred for a period of 1 h.

Choice of procedure

Figure 1 shows the absorption curves for the *n*-decanol–vanadium oxinate complex after (a) anhydrous sodium sulphate treatment (curves I and III) and (b) addition of the dichloracetic acid reagent (curves V and VI). It can be seen that the sodium sulphate method is approximately twice as sensitive as the dichloracetic acid method. On the other hand, it was shown that the blue complex is more stable than the red complex and therefore greater accuracy might be expected using the dichloracetic acid procedure. Nevertheless, in practice, it was found that the sodium sulphate procedure gave the more repeatable results provided that rigorous attention was given to timing. This is probably due to the lack of control in adjusting the final pH of the solution when the dichloracetic acid reagent is used. Therefore, in applying the method to the measurement of hydroxyl content of esters, the use of anhydrous sodium sulphate followed by measurement of the absorbance of the red complex is to be preferred.

Calibration

Calibration curves showing the absorbance plotted against the weight of hydroxyl were obtained on a series of standard solutions of *n*-octanol, *n*-decanol, *n*-dodecanol, *n*-tetradecanol, *n*-hexadecanol and *n*-octadecanol in nitrobenzene. All points fell on the same straight line showing that (a) Beer's law is obeyed over the range $5 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$ g hydroxyl and (b) a single standard alcohol solution can be used for calibration purposes over the C_8–C_{18} alcohol range.

Application of method

The procedure described was applied to the determination of the alcohol content of fumarate esters formed by esterifying alcohols covering the range *n*-octanol to *n*-octadecanol, either singly or in mixtures, with fumaric acid. The alcohol content of the finished ester ranged from 0.05–10.0 wt.%. The determinations were carried out on 0.2 g of ester and the repeatability at the 0.5 wt.% level was ±0.02%. It can be seen that the lower limit of measurement of alcohol in ester can be reduced well below 0.05 wt.% simply by increasing the sample size, the only limit being the solubility of the ester in nitrobenzene.

SUMMARY

A method is described for the precise determination of small amounts of aliphatic alcohols in esters. The procedure is based on the formation of a red-coloured complex between the alcohol and a solution of vanadium oxinate in nitrobenzene. Studies have been made on the effect of solvent, reaction time and the stability of the complex on the accuracy of the determination.

RÉSUMÉ

Une méthode est décrite pour le dosage précis de faibles quantités d'alcools aliphatiques dans des esters. Ce procédé est basé sur la formation d'un complexe rouge entre l'alcool et une solution d'oxinate de vanadium dans le nitrobenzène. On examine l'influence du solvant, du temps de réaction et de la stabilité du complexe sur l'exactitude du dosage.

ZUSAMMENFASSUNG

Es wird eine spektralphotometrische Methode zur genauen Bestimmung kleiner Gehalte aliphatischer Alkohole in Estern beschrieben. Das Verfahren beruht auf der Bildung eines rotgefärbten Komplexes zwischen dem Alkohol und einer Lösung von Vanadinoxinat in Nitrobenzol. Näher untersucht wurde der Einfluss des Lösungsmittels, die Reaktionszeit und die Stabilität des Komplexes.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH DITHIZONE USING THE SYNERGISTIC EFFECT OF PYRIDINE

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(Received July 16th, 1967)

Dithizone (diphenylthiocarbazone) is widely employed for the separation and sensitive colorimetric determination of trace amount of heavy metals. The sensitivity of the dithizone method approaches, or even exceeds that of the spectrographic method[1]. Although manganese(II) forms a colored complex with dithizone at pH of about 11[2], it has been reported that the resulting chelate has no analytical use because it is readily destroyed by atmospheric oxidation during extraction[3].

In the work described below, it was found that the extractability of the manganese–dithizone complex into carbon tetrachloride can be increased by the addition of pyridine and that the extracted complex is stable enough for analytical purposes. Such synergistic effects are due to an increase in the distribution ratio of a metal chelate on addition of a neutral base such as pyridine. The detailed mechanism of synergistic effects for various metal chelates in the presence of neutral bases has been investigated extensively in recent years[4] and some applications to analytical chemistry have also been reported[5,6]. In general, the mechanism seems to involve the formation of a base adduct of a metal chelate.

The synergistic effect in the present extraction is considered to result from the formation and the preferential extraction of a pyridine adduct of manganese(II) dithizonate.

EXPERIMENTAL

Apparatus

Visible absorption spectra were measured with a Hitachi EPS-2U type recording spectrophotometer. Various conditions for determining manganese were established by using absorbances at 530 nm and 610 nm obtained with a Hitachi EPO-B type photoelectric photometer. The pH value of the aqueous phase after extraction was measured with a Hitachi-Horiba F-5 type pH-meter using glass electrodes.

Reagents

All reagents used were of analytical-reagent grade. Twice-distilled water was used throughout.

Dithizone solution. A carbon tetrachloride solution of dithizone was purified as described by SANDELL[1]; the concentration was estimated by calculation using the molar absorptivity and the measurement of the absorbance of dithizone at 620 nm.

10% Hydroxylamine hydrochloride solution. Dissolve 10 g of hydroxylamine hydrochloride and dilute to 100 ml with water after neutralizing the reagent with ammonia. Remove impurities by extracting with 0.02% dithizone solution.

Standard solution of manganese. Prepare a manganese solution (*ca.* 100 mg/l) by dissolving manganese(II) sulfate in 0.1 *N* sulfuric acid. Standardize the solution spectrophotometrically by the permanganate method.

Ammoniacal buffer solution. Dissolve 13 g of ammonium chloride in water, add concentrated aqueous ammonia and dilute to 100 ml.

General procedure

Transfer a suitable aliquot of manganese(II) solution to a separatory funnel. Add 1 ml of 10% hydroxylamine hydrochloride solution, 0.5 ml of pyridine and 1 ml of ammonia buffer, and adjust the volume to 20 ml with water. Then extract the manganese ion with 5 ml of dithizone solution by shaking for 15 sec. Allow the phases to separate and measure the absorbance of the organic phase against carbon tetrachloride as a reference, in 1-cm glass cells.

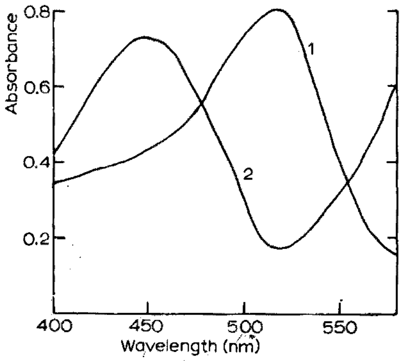
RESULTS AND DISCUSSION

Erratic results were obtained from extraction in the absence of either pyridine or hydroxylamine hydrochloride. In order to obtain sufficient reproducibility in absorbance measurements, both pyridine and hydroxylamine hydrochloride should be added before the extraction. The addition of hydroxylamine hydrochloride may prevent both atmospheric oxidation of manganese(II) in alkaline medium and oxidation of dithizone.

The extraction of manganese(II) with dithizone in the presence of pyridine was very rapid and extraction equilibrium could be obtained by shaking for only 15 sec. In order to obtain good reproducibility, the resulting complex should not be exposed to strong light.

Absorption spectrum of the extracted complex

The visible absorption spectra of dithizone and its complex with manganese in carbon tetrachloride are shown in Fig. 1. The spectrum of the extracted complex



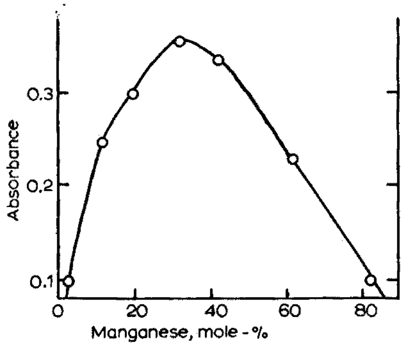


Fig. 1. Absorption spectra of (1) the extracted species (Mn(II) complex); (2) dithizone.

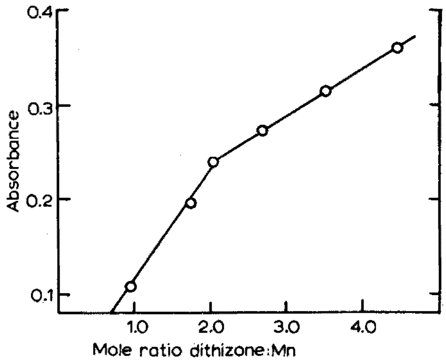
Fig. 2. Continuous variation method. Total (dithizone + Mn) concn.: $1.9 \cdot 10^{-5}$ *M* in the final soln.

has a maximum absorbance at *ca.* 515 nm. The intensity is stable for at least 90 min in a separatory funnel in which the organic phase is covered with the aqueous solution.

The extracted complex decomposed gradually with time in the measuring cell, and the production of dithizone molecules increased the absorbance at 620 nm. However, the detailed behavior of the extracted complex in carbon tetrachloride could not be confirmed with the limited evidence.

Composition of the extracted complex

The mole ratio of dithizone to manganese in the extracted complex was determined by Job's method of continuous variation and the mole ratio method. For the continuous variation method, the mole ratio of dithizone in carbon tetrachloride to manganese in the aqueous phase was varied keeping the total concentration of two variables constant ($1.9 \cdot 10^{-5}$ *M*), and the coloured complex was extracted in the presence of 0.5 ml of pyridine. From Fig. 2, it is apparent that the combined mole ratio of manganese to dithizone in the extracted complex was 1:2. For the mole ratio method, a definite amount of manganese ($4.3 \cdot 10^{-6}$ *M*) was extracted into various concentrations of dithizone in carbon tetrachloride. The formation of a 1:2 complex, manganese(II) dithizonate, was confirmed (Fig. 3).



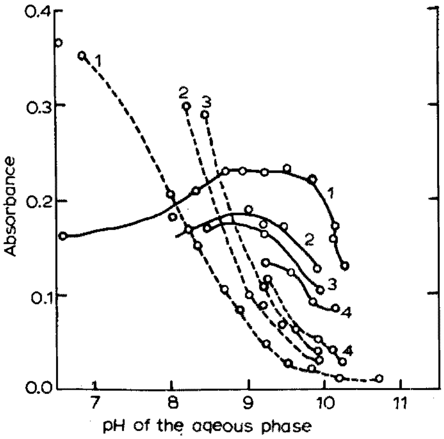


Fig. 3. Mole ratio method. Concn. of Mn in the final soln. $4.3 \cdot 10^{-8}$ *M*.

Fig. 4. Effect of pH on absorbance. Total concn. of dithizone $1.7 \cdot 10^{-5}$ *M*. (---) absorbance at 610 nm; (—) absorbance at 530 nm. Concn. of pyridine (1) 0.63 *M* and 0.32 *M*; (2) 0.063 *M*; (3) 0.032 *M*; (4) 0.0063 *M*.

Similar experiments for determining the mole ratio of pyridine to manganese(II) dithizonate failed, mainly because of the poor extractability of manganese(II) dithizonate and poor reproducibility in absorbance measurements for low pyridine concentration. However, the increase in the extractability of manganese(II) dithizonate on addition of pyridine indicates that pyridine is involved in the extraction reaction and that the extracted species may be a pyridine adduct, *e.g.* $Mn(HDz)_2Py_n$.

Effect of pH and pyridine on the extraction of manganese

Although previous workers state that manganese dithizonate can be extracted into carbon tetrachloride at pH 11[2], the optimum pH range for quantitative extraction of manganese has not yet been reported. In order to obtain the optimum pH for the extraction, particularly in the presence of pyridine, manganese (7.2 µg) was extracted from aqueous solutions of various pH values (Fig. 4). The absorbance at 610 nm, which is mainly due to the absorbance of dithizone, decreases as either the pH or the volume of added pyridine increases, because the formation of the manganese dithizonate and the increase in pH lead to a decrease in the concentration of residual dithizone. In contrast, the absorbance at 530 nm tends to increase at lower pH values and decrease above pH 9.8. Such variations in absorbance show that the optimum pH range for the extraction exists at around pH 9.5. The decrease of the absorbance above pH 10 is probably due to the hydration of manganese(II). When 1 ml or 0.5 ml of pyridine was added, the extractabilities obtained were equal, therefore the addition of 0.5 ml of pyridine was sufficient to extract manganese quantitatively.

When manganese is extracted with dithizone of higher concentration, the effect of pH on absorbance is slightly different from the previous case (Fig. 5). The dotted line shows the absorbance corrected for the reagent blank, and can be considered as proportional to the concentration of manganese extracted into carbon tetrachloride. In order to obtain high sensitivity and good reproducibility in absorbance measurements, the pH of the aqueous solution should be chosen so as to give high extractability of manganese and low reagent absorbance. Accordingly, a pH value of 9.7 was adopted as the optimum.

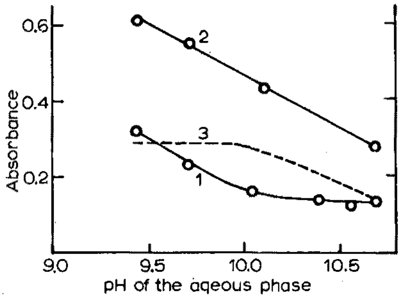


Fig. 5. Effect of pH on absorbance. Total concn. of dithizone $8\cdot10^{-5}$ M. (1) reagent blank; (2) 1.6 µg Mn(II) added; (3) (2) – (1).

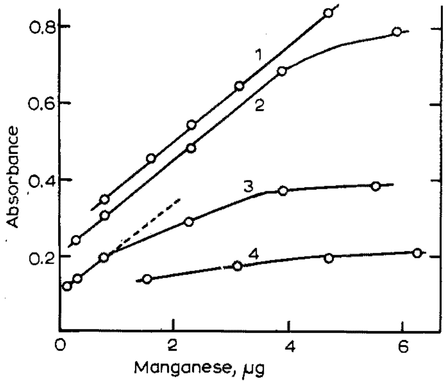


Fig. 6. Effect of dithizone concn. on the absorbance at 530 nm. Dithizone concn.: (1) $10\cdot10^{-5}$ M; (2) $6.6\cdot10^{-5}$ M; (3) $3.3\cdot10^{-5}$ M; (4) $1.7\cdot10^{-5}$ M.

Effect of dithizone concentration

As shown in Fig. 6, a plot of absorbance against manganese concentration gave a straight line and its slope was not affected by dithizone concentration. The increase in absorbance with relatively concentrated dithizone solution is caused by an increase in the absorbance of reagent blank. These straight lines may be used as calibration curves. For example, when a $8\cdot10^{-5}$ M dithizone solution was used, the amount of manganese which could be determined was in the range 0.4–4 μg. The reproducibility of the absorbance measurements was better than 1% and the sensitivity was 0.0014 μg Mn/cm^2. These results show that the present method has an advantage over the permanganate method in the determination of small amounts of manganese.

Diverse ions

The dithizone extraction of many metal ions has been extensively investigated and their extraction behaviors have been reported by several workers[1-3]. Metals reacting with dithizone at pH *ca.* 9.7 interfere with the determination of manganese; among these metals, copper, zinc, lead, cobalt and nickel can be separated by preliminary extraction from slightly acidic solution. Iron(II) is reported[3] to be extracted with dithizone above pH 7. In order to remove iron(II) by preliminary extraction, its extraction behavior in the presence of pyridine was investigated (Fig. 7). The decrease of absorbance at 610 nm implies an increase of the extractability of iron. The plots in Fig. 7 show that iron(II) can be removed from slightly acidic solution by the addition of pyridine.

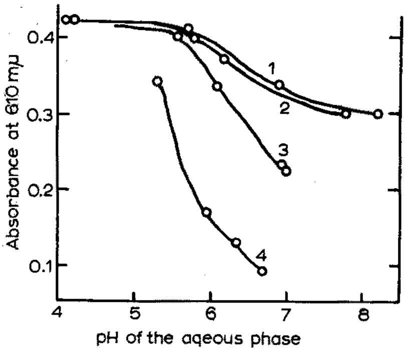


Fig. 7. Extraction of Fe(II) with dithizone. (1) 1.0 μg Fe; (2) 5.0 μg Fe; (3) 10 μg Fe; (4) 5 μg Fe (extracted in the presence of 0.5 ml of pyridine).

TABLE I

ANALYTICAL RESULTS AND RECOVERY TEST BY ADDITION METHOD

Sample no.[a]	*Mn present*[b] *(μg/ml)*	*Relative standard deviation (%)*	*Mn added (μg/ml)*	*Mn found (μg/ml)*
1	0.77	3.3	1.5	2.3
2	0.90	3.5	1.5	2.4
3	0.78	4.5	0.75	1.6
4	0.94	2.7	0.75	1.7
5	1.1_5	3.0	0.75	1.9

[a] Samples taken from the Yazawa river.
[b] Average of 4 determinations.

When the preliminary extraction in the presence of pyridine was carried out at pH *ca.* 6.5, iron (20 μg), copper (5 μg), lead (10 μg), nickel (0.5 μg), zinc (10 μg), and cobalt (2 μg) did not interfere with the determination.

Analysis of manganese in natural water

The results obtained by the present procedure after preliminary extraction are shown in Table I. The reproducibility of the method was in the range 4.5–2.7% (relative standard deviation). Recovery tests (Table I) also gave satisfactory results.

Conclusion

The dithizone complex of manganese can be utilized for the determination of this element by using the synergistic effect of pyridine; an adduct, probably $Mn(HDz)_2Py_n$, seems to be formed. Although the selectivity of the method is poor, so that a preliminary extraction of diverse ions is needed, the proposed dithizone method is rapid and has a very high sensitivity.

SUMMARY

The extraction of manganese with dithizone using the synergistic effect of pyridine has been studied. A method is described for determining manganese spectrophotometrically. Trace amounts of manganese can be determined, the sensitivity being 0.0014 μg Mn/cm^2 at 530 nm.

RÉSUMÉ

Les auteurs ont étudié l'extraction du manganèse au moyen de dithizone, en utilisant l'effet synergétique de la pyridine. On décrit une méthode pour le dosage spectrophotométrique du manganèse. On peut ainsi doser des traces de manganèse; la sensibilité est de 0.0014 μg Mn/cm^2 à 530 nm.

ZUSAMMENFASSUNG

Es wurde die Extraktion von Mangan mit Dithizon unter Verwendung des synergistischen Effekts von Pyridin untersucht. Spuren von Mangan können mit einer Empfindlichkeit von 0.0014 μg Mn/cm^2 bei 530 nm bestimmt werden.

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6 x 9", vii + 301 pages, 19 tables, 64 illus., 311 lit. refs., 1968
Dfl. 60.00, US$21.00

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Printed in The Netherlands

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COLORIMETRIC DETERMINATION OF PALLADIUM WITH PYRIDINE-2-ALDEHYDE-2'-PYRIDYLHYDRAZONE

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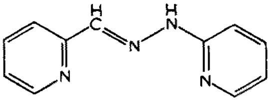
(Received July 6th, 1967)

The tridentate chelating agent 1,3-bis(2'-pyridyl)-1,2-diazaprop-2-ene (pyridine-2-aldehyde-2'-pyridylhydrazone; PAPH; I) was first described by LIONS AND MARTIN[1] in 1958. Later, GELDARD AND LIONS[2] prepared many metal–PAPH complexes and demonstrated the removal of the imino proton by the addition of alkali. For example, treatment of the complex cation $[Ni(PAPH)_2]^{2+}$ with sodium hydroxide resulted in the formation of $[Ni(PAP)_2]^0$.



I

In 1963 CAMERON, GIBSON AND ROPER[3] published the results of a survey of the visible spectra of aqueous solutions containing a number of metal ions, including palladium, in the presence of PAPH; it was stated that PAPH should be a useful colorimetric reagent. A method for the spectrophotometric determination of palladium with PAPH in aqueous solution at pH 11.6 has recently been published[4] by BELL AND ROSE; this method had rather low tolerance for some metals. The extractive method presented in the present paper involves the extraction of chloro(PAP) palladium(II) from an aqueous solution of pH 3.1 into *o*-dichlorobenzene.

An extractive method for the colorimetric determination of palladium with PAPH has several advantages. As the palladium(II) complex is deprotonated in weakly acidic solutions, extraction can be performed from aqueous solutions of relatively low pH. This minimises interferences from other metal–PAPH complexes, the majority of which are not extracted under these conditions. Moreover, at low pH, excess free ligand is protonated and therefore remains in the aqueous phase. Moreover, the neutral palladium complex precipitates from aqueous acidic solutions even at microgram concentrations of palladium; higher solubility is achieved in organic solvents. Additional advantages common to all extractive methods are well-known.

NATURE OF THE COMPLEX OF PAPH WITH PALLADIUM(II)

Preparation

An aqueous solution of potassium tetrachloropalladate(II) was treated with an ethanolic solution of PAPH in a molar ratio of 1:2.5. The mixture was heated on a steam bath for 5 min, cooled, and the product collected. Recrystallisation was effected by dissolving the brown-red crystals in chloroform, cooling, and adding petroleum ether. ($PdC_{11}H_9N_4Cl$ requires: C 39.0%, H 2.7%, Cl 10.5%, Pd 31.4%; found: C 38.7%, H 3.0%, Cl 10.0% Pd, 31.1%.)

Conductivity

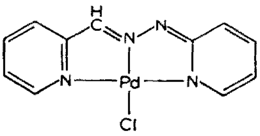
The compound was a non-electrolyte in nitrobenzene solution, having a molar conductance of less than 0.1 ohm^{-1} cm^2 at 24°.

Infrared spectrum

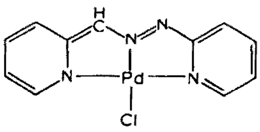
The infrared spectrum of the compound showed no absorption band which could be attributed to the N–H stretching frequency, indicating that the imino proton had been lost. The spectrum of the free ligand, PAPH, had an N–H stretching peak at 3260 cm^{-1}.

Structure

The above evidence is consistent with the square-planar structure (II) for the palladium complex. Two possible resonance forms of the complex are represented by IIa and IIb.



II^{a}



II^{b}

The mass spectrum of the compound was examined and found to support the above structure.

EXPERIMENTAL

Apparatus

Extractions were carried out in a glass-stoppered 100-ml separating funnel with a short stem.

The organic extracts were run into a 40-ml conical side-arm flask. Water droplets present adhered to the surface of this flask when the extract solutions were transferred, via the side-arm, to the volumetric flasks.

Absorbance measurements were obtained using a Hilger and Watts type H760 Spekker absorptiometer. Kodak No. 5 filters were employed. These filters show a maximum transmission of 12% at 545 nm, a wavelength at which an *o*-dichlorobenzene solution of the complex absorbs strongly.

Reagents

PAPH solution. Dissolve PAPH (0.050 g) in ethanol (15 ml) and dilute to 250 ml with water.

Buffer solution. Dissolve $Na_2HPO_4 \cdot 12H_2O$ (14.3 g) and citric acid monohydrate (16.8 g) in water and dilute to 250 ml. Use of 5.0 ml of this buffer solution in the procedure detailed below resulted in an aqueous phase of pH 3.1.

Procedure

To the separating funnel, add (*a*) a volume (preferably not more than 25 ml) of an acidic solution containing 10–100 μg of palladium, (*b*) 10 ml of PAPH solution, (*c*) sufficient sodium hydroxide solution for approximate neutrality, (*d*) 5 ml of the buffer solution and (*e*) 5 ml of *o*-dichlorobenzene. The aqueous solution should be 0.01–0.1 *M* with respect to chloride ions. Extract with four 5-ml portions of organic solvent, running the extracts into the side-arm conical flask. Quantitatively transfer the combined organic extracts to a 25-ml volumetric flask and make up to the mark with *o*-dichlorobenzene. Compare the absorbance of the solution with a blank solution in a Spekker absorptiometer using 2-cm cells and Kodak No. 5 filters. Obtain the palladium content of the solution by reference to a calibration curve prepared by treating a series of palladium solutions of known concentration as described above.

RESULTS AND DISCUSSION

Precision and accuracy

Results of estimations obtained over the range 10–100 μg of palladium are shown in Table I. The largest error obtained for a single determination was 1.4%. With the exception of this determination, errors did not exceed 1%.

TABLE I

PRECISION AND ACCURACY OF DETERMINATION

(Five samples taken at each concentration)

Pd present (μg)	*Pd found (μg)*		*Largest % error*	*Mean Pd found (μg)*	*Maximum deviation from the mean*		*Average deviation from the mean*	
	min.	*max.*			*(μg)*	*(%)*	*(μg)*	*(%)*
10.0	10.0	10.1	+1	10.1	0.1	1	0.04	0.4
30.0	30.0	30.2	+0.7	30.2	0.2	0.7	0.04	0.1
50.0	49.7	50.7	+1.4	50.2	0.5	1.0	0.3	0.6
100.0	99.2	99.8	−0.8	99.5	0.3	0.3	0.2	0.2

Blank determination

A blank determination afforded a Spekker reading relative to pure solvent of 0.004. This low reading would be due to the very slight extraction of PAPH associated with the low extinction coefficient of the ligand in the vicinity of 550 nm. As a relatively large excess of PAPH is used in the colorimetric method, this blank value should be constant over the range of palladium concentrations determinable by the method.

Calibration curve

The system obeys Beer's law within the suggested range of concentrations as demonstrated by the straight line calibration curve obtained.

Stability of the extract solution

The extracting solvent chosen, *o*-dichlorobenzene, afforded highly stable solutions of the complex, the absorbance of a solution showing only a 0.6% drop after storage away from light for 3 days in a stoppered flask.

Visible absorption spectrum

The visible absorption spectrum of the extracted species in *o*-dichlorobenzene has an absorption maximum at 562 nm and a shoulder from 535 to 545 nm. This spectrum is identical with that obtained for a solution prepared by dissolving solid Pd(PAP)Cl in *o*-dichlorobenzene, which indicates that the compound Pd(PAP)Cl is in fact the species extracted in the colorimetric method. The compound in *o*-dichlorobenzene has a molar extinction coefficient of $1.65 \cdot 10^4$ at 562 nm. The sensitivity of the reaction, as defined by SANDELL[5] and calculated from the absorption spectrum, is 0.0065 μg of Pd/cm^2 at 562 nm for $\log I_0/I = 0.001$.

The effect of pH

Reproducible results were obtained after extraction from aqueous solutions of pH 7 down to at least 2.5, the lowest pH tested. At pH 2.5 the aqueous phase before extraction was pale yellow-orange, instead of pink, indicating that the complex was only partly deprotonated. Extraction of Pd(PAP)Cl, associated with negligible extraction of free ligand (largely protonated at the two heterocyclic nitrogen atoms, $pK_1 = 2.87$ and $pK_2 = 5.71$[6]), presumably displaces the aqueous solution equilibria sufficiently to the right to enable quantitative extraction of palladium to be obtained.

$$\begin{tikzcd}
{[\mathrm{H_2PAPH}]^{2+}} \arrow[d, shift left, "-\mathrm{H}^+"] & & \\
{[\mathrm{H\ PAPH}]^{+}} \arrow[u, shift left] \arrow[d, shift left, "-\mathrm{H}^+"] & & \\
\mathrm{PAPH} + \mathrm{Pd}^{2+} + \mathrm{Cl}^- \arrow[u, shift left] \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Pd(PAPH)Cl}]^{+}} \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Pd(PAP)Cl}]^{0} + \mathrm{H}^{+}}
\end{tikzcd}$$

Extraction from slightly alkaline aqueous solutions resulted in low absorbance readings. Such readings would appear to be due to the formation of a different species, such as Pd(PAP)OH.

Variation of the amounts of buffer, chloride ion and reagent

Use of 0.5, 5 and 30 ml of the buffer solution resulted in similar absorbance readings. Consequently, the amount of buffer used is not critical.

Varying the chloride ion concentration from 0.005 to 0.5 *M* resulted in errors much less than 2% in the estimation of 50 μg of Pd. For the palladium range used (10–100 μg), a chloride ion concentration within the limits 0.01–0.1 *M* would not be expected to cause significant error. With very low (but stoichiometrically sufficient) chloride ion concentrations, poor extraction of Pd(PAP)Cl resulted.

Use of one-third to twenty times the recommended quantity of PAPH resulted in errors less than 1%. Smaller amounts of PAPH gave low absorbance readings.

PAPH solution stability

The ultraviolet absorption spectrum of a freshly prepared PAPH solution showed a strong absorption band at 335 nm. The solution was stored for 30 days in a stoppered glass container away from direct sunlight but exposed to diffuse daylight and artificial light. Remeasurement of the spectrum after this period revealed a shift in λ_{max} to 342 nm and a 12% drop in the extinction at λ_{max}. As a large excess of PAPH is recommended in the colorimetric method, the use of a 1-month old solution would not be expected to cause error. This was found to be the case. Use of a solution 7 months old resulted in poor extraction of palladium.

Interferences

The effect of the presence of various ions was studied by introducing them into a solution containing 50 μg of palladium. The tolerance limit of an ion was fixed as the maximum amount causing an error no greater than 2% in the absorbance of the extract solution.

The common anions of strong acids, chloride, nitrate, sulphate and perchlorate were tested for possible interference together with the ions bromide, iodide, sulphide, cyanide, thiocyanate and ethylenediaminetetraacetate. These last 6 ions all react with palladium. The components of the disodium hydrogen phosphate/citric acid buffer were also tested. Although addition of each of the last 2 substances caused the pH of the aqueous palladium solution to change, no effort was made to readjust this pH. The tolerance limits are listed in Table II; in all cases interferences were negative.

No evidence was found in work previously described[3] to support complex formation in aqueous solutions containing PAPH and the metals Mg(II), Ca(II), Sr(II), Ba(II), Al(III), La(III), Mo(VI), W(VI), Tl(I), Sn(IV) and As(III). These metals should not interfere with the colorimetric method and therefore were not tested. The

TABLE II

ANION INTERFERENCES

(Solutions contained 50 μg of Pd)

Anion	*Added as*	*Tolerance amount*	
		Volume (ml)	*Concentration in test solution (M)*
Cl^-	KCl (1 M)	>25[a]	>0.33
NO_3^-	KNO_3 (1 *M*)	>25[a]	>0.33
SO_4^{2-}	Na_2SO_4 (1 *M*)	>10 but <25	>0.17 but <0.33
ClO_4^-	$NaClO_4$ (1 *M*)	>5 but <10	>0.1 but <0.17
Br^-	KBr (0.1 *M*)	>0.05 but <0.2	$>10^{-4}$ but $<4 \cdot 10^{-4}$
I^-	KI (0.1 *M*)	<0.05[b]	$<10^{-4}$
S^{2-}	Na_2S (0.1 *M*)	<0.05[b]	$<10^{-4}$
CN^-	KCN (0.1 *M*)	<0.05[b]	$<10^{-4}$
SCN^-	KSCN (0.1 *M*)	<0.05[b]	$<10^{-4}$
EDTA	Disodium salt (0.1 *M*)	>25[a]	>0.033
HPO_4^{2-}	Na_2HPO_4 (1 *M*)	>5 but <25	>0.1 but <0.33
$C_6H_8O_7$ (citric acid)	$C_6H_8O_7$ (1 *M*)	>5 but <25	>0.1 but <0.33

[a] The maximum quantity of these solutions tested was 25 ml. The addition of this volume of 1 M salt solution resulted in a molar salt concentration in excess of 50,000 times that of the total palladium.

[b] Quantities of solution less than 0.05 ml were not tested.

tolerance amounts of most metals which caused negative interference could be increased by using a larger excess of PAPH. With these metals the tolerance amounts were found using 10 times the quantity of reagent recommended in the determination procedure. To add this amount of reagent it was necessary to prepare a more concentrated PAPH solution. The tolerance limits for various cations are listed in Table III.

TABLE III

CATION INTERFERENCES

(Solutions contained 50 μg of Pd)

Cation	*Recommended quantity of PAPH*		*Recommended quantity of PAPH × 10*	
	Tolerance amount (μg)	*Tolerance ratio (Me:Pd)*	*Tolerance amount (μg)*	*Tolerance ratio (Me:Pd)*
Pt(II)	15,000	300		
Pt(IV)	1,000	20	< 1,500	< 30[a]
Mn(II)	<500	<10	500	10
Co(II)	<500	<10	500	10
Zn(II)	<500	<10	5,000	100
Fe(II)	<250	<5	1,500	30
Fe(III)	<1,500	<30	>10,000	>200[b]
Ni(II)	<500	<10	2,500	50
Cu(II)	<500	<10	5,000	100
Cd(II)	<50,000	<1,000	>50,000	>1,000[c]
Cr(III)	>50,000	>1,000[c,d]		
Ru(III)	<1,000	<20	1,500	30[d]
Os(IV)	<1,000	<20	2,500	50[d]
Rh(III)	<500	<10	500	10
V(IV)	250	5	2,500	50
Sb(III)	<2,500	<50	5,000	100
Ir(IV)	<250	<5[e]	<250	<5[e]
Au(III)	<250	<5[e]	<250	<5[e]
Sn(II)	<250	<5[e]	<250	<5[e]
Hg(I)	<250	<5[e]	<250	<5[e]
In(III)	10,000	200		
Zr(IV)	5,000	100[f]		
Ti(IV)	<5,000	<100[f]		
Ce(IV)	<5,000	<100[f]		
U(VI)	<5,000	<100[f]		
Hg(II)	<5,000	<100[f]		
Bi(III)	<5,000	<100[f]		
Ag(I)	<5,000	<100[f]		
Pb(II)	5,000	100		

[a] A 10-fold increase in the quantity of PAPH caused the interference by Pt(IV) to change from negative to positive with no increase in tolerance. Pt(II) also gave a positive interference. Interferences by all other metals were negative.

[b] The maximum amount of Fe(III) tested was 10,000 μg. With this amount, filtration of the organic extracts was necessary because of $Fe(OH)_3$.

[c] The presence of 50,000 μg of Cd(II) or Cr(III) did not interfere; larger amounts were not tested. These metals could be classed as non-interfering.

[d] The intensely coloured Cr(III), Ru(III) and Os(IV) solutions would have caused severe interference had an extractive method of analysis not been employed.

[e] The minimum amount of metal tested was 250 μg. The metals Ir(IV), Au(III), Sn(II) and Hg(I) caused negative interference when present to this extent, even when a large excess of PAPH was used. Interference by these metals could be classed as serious.

[f] Zr(IV), Ti(IV), Ce(IV), U(VI), Hg(II), Bi(III) and Ag(I) caused interference by precipitation of hydroxides, basic salts and/or chlorides. This necessitated filtration of the organic extract solutions. The only quantity of these metals tested was 5,000 μg.

Conclusion

Examination of the above interferences indicates that the extractive method can, in general, tolerate greater amounts of metals than other methods, unless such methods involve laborious separation procedures.

SUMMARY

The colorimetric determination of palladium described involves the extraction of chloro(PAP)palladium(II) from an acidic aqueous solution into *o*-dichlorobenzene and measurement of the absorbance of the extract solution. The method is suitable for the determination of 10–100 μg of palladium. Tolerance amounts for many metals have been determined and compare very favourably with those of other methods.

RÉSUMÉ

On décrit un dosage colorimétrique du palladium par extraction du chloro(PAP)palladium(II) en solution aqueuse acide, dans l'*o*-dichlorobenzène. Cette méthode permet le dosage de 10–100 μg de palladium. On a examiné l'influence de plusieurs métaux. Procédé avantageux comparé à d'autres méthodes.

ZUSAMMENFASSUNG

Es wird eine kolorimetrische Bestimmung von Palladium beschrieben, bei der Chloro(PAP)-Palladium(II) aus saurer wässriger Lösung mit *o*-Dichlorbenzol extrahiert und die Absorption des Extraktes gemessen wird. Die Methode ist zur Bestimmung von 10–100 μg Palladium geeignet. Die zulässigen Gehalte für viele Metalle erwiesen sich als sehr günstig gegenüber anderen Methoden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART II. A THEORETICAL TREATMENT OF THE EFFECT OF MEMBRANE SELECTIVITY

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(Received July 9th, 1967)

In a recent publication[1], theoretical titration curves were calculated for potentiometric titrations which involve a membrane electrode consisting of ion-exchanging material as the indicating electrode. The titration curves were derived for simple precipitation titrations with only monovalent ions present in the solution. Moreover, the following assumptions were made:

(*1*) no convection of solution through the membrane,

(*2*) constant values for the diffusion coefficients and the capacity throughout the membrane,

(*3*) the diffusion through the membrane is the rate-determining step,

(*4*) the membrane has no preference for one of the diffusing species,

(*5*) the activity coefficients are unity in all cases.

In the present paper, the problem of how the titration curves obtained are modified when the membrane has selective properties for one of the diffusing ionic species, is discussed.

Selectivity and its causes

For a complete discussion of this subject, the monograph of HELFFERICH[2] should be consulted; only a short survey is given here. When an ion-exchanger that has previously been completely converted to the A-form is placed in a solution containing an electrolyte with counter-ions B, the following exchange reaction takes place:

$$\bar{A}+B \rightleftarrows A+\bar{B}$$

In the ultimate state of equilibrium the ion-exchanger will contain both counter-ions A and B. As a rule, the exchange reaction is reversible and therefore it makes no difference from which side the equilibrium state is approached, provided that the amounts of all the components in the system remain the same. In most cases, the concentration ratio of the two competing counter-ions inside the membrane differs from that in the external solution: the ion-exchanger displays a certain preference (selectivity) for one of the counter-ions.

For theoretical studies the selectivity can best be characterized by:

(*1*) the separation factor $\alpha_{B}^{A} = C_{A}c_{B}/c_{A}C_{B}$

or

(*2*) the molar selectivity coefficient $K'^{A}_{B} = C_{A}^{z_{B}} c_{B}^{z_{A}} / c_{A}^{z_{B}} C_{B}^{z_{A}}$

where C_A and C_B are the concentrations of the counter-ions A and B inside the ion-exchanger; c_A and c_B are the concentrations of these ions in the external solution; z_A and z_B are the valences.

For the present purpose, there are only monovalent ions present in the system and for this simple case the separation factor and the molar selectivity coefficient have the same value. As a rule, the selectivity coefficient is not constant but depends on the total concentration of the solution with which the ion-exchanger is equilibrated, as well as on the concentration ratio of both competing counter-ions (Fig. 1).

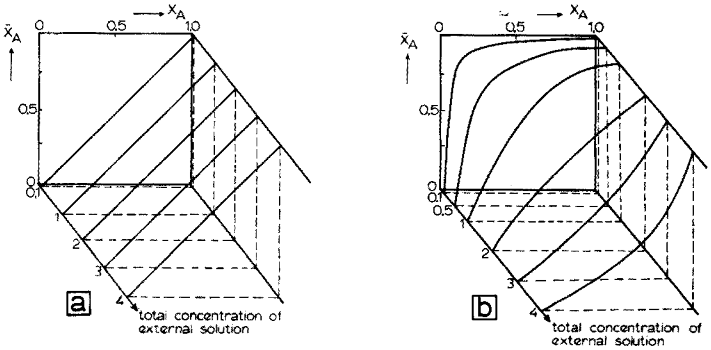


Fig. 1. The selectivity of an ion-exchanger as a function of the ionic composition and the total ionic concentration in the solution. The ionic composition of the solution, containing counter-ions A and B, is given as the equivalent ionic fraction of A (x_A), defined by: $x_A = z_A m_A/(z_A m_A + z_B m_B)$ (z = valence, m = molar concentration). For the ionic composition of the solution inside the ion-exchanger ($\bar{x}_A$), an identical definition is used, with of course the internal molar concentrations. Case a: ion-exchanger without selective properties; case b: ion-exchanger with preference for counter-ion A at low total concentration in the external solution, changing to a preference for counter-ion B at higher external concentrations.

An ion-exchanging material owes its selective properties to one or more of the following causes:

(*1*) *electroselectivity*: through the action of the Donnan potential the counter-ion with the greatest valence is preferred. With decreasing total external concentration this effect is augmented, because the Donnan potential is also increasing. The electroselectivity must be considered as a common effect that is always present and not as a special property;

(*2*) *ionic solvation and swelling pressure*: an ion-exchanger will prefer the counter-ion with the smaller solvated equivalent volume because of the elastic properties of the matrix;

(*3*) *sieve action*: very large counter-ions can be excluded mechanically from an ion-exchanger (for example, a zeolite with a very rigid lattice) when the meshes of the matrix are too narrow to accommodate the ion;

(*4*) *special interactions of the counter-ions with the fixed groups or the matrix within the ion-exchanger*: ion-pair formation, association, electrostatic attraction, London interaction;

(5) *association and complex formation of the counter-ions in the solution;*
(6) *formation of precipitates in the solution, involving the counter-ions;*
(7) *temperature and pressure.*

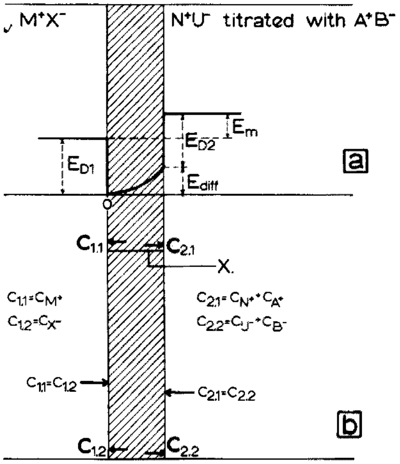
In many cases the selectivity of an ion-exchanger for a particular counter-ion is determined by several opposing effects. For example, the uptake of an ion that is subject to specific interaction within the ion-exchanging material can be counteracted by the swelling pressure when the ion has a large volume.

The ion-exchanger tends to prefer counter-ions which have the higher valence, the smallest (solvated) equivalent volume, and the greater polarizability; preference is also given to ions which interact more strongly with the fixed ionic groups or with the matrix, or which participate least in complex formation with co-ions in the solution.

Theoretical approach

A membrane, consisting of ion-exchanging material, that is used for potentiometric indication, is in contact with two solutions (Fig. 2).

On one side, there is the reference solution (M^+X^-), which is supposed to remain unchanged during the titration; in fact it is assumed that the reference



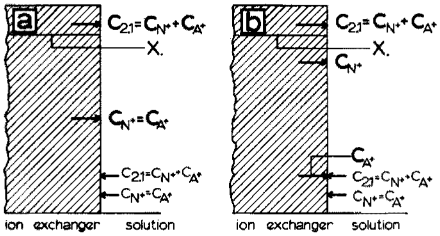


Fig. 2. Potential profile (a) and equilibrium concentrations at the membrane surfaces (b) during the titration. The case is shown of a cation-selective membrane with a positive diffusion potential; the titration has not proceeded to the equivalence point and therefore the concentration at the titration side is lower than at the reference side, provided that the initial concentrations were the same. The value of the capacity of the membrane is indicated by X (meq/cm^3).

Fig. 3. The method of calculation of the equilibrium surface concentrations of the counter-ions when an ion-exchanger has selective properties, compared to the original method where the selectivity was not taken into account. The case is shown where the concentrations of the counter-ions A^+ and N^+ in the external solution are the same:

(*a*) non-selective membrane; the Donnan equation holds for the group concentration as well as for the individual concentrations of the counter-ions:

$$C_{2.1}/c_{2.1} = C_{2.N^+}/c_{2.N^+} = C_{2.A^+}/c_{2.A^+} = E_{D2}^{-1}$$

(*b*) the membrane has preference for the counter-ions N^+; in this case, the Donnan equation still holds for the group concentration; the individual surface concentrations of the counter-ions are calculated as explained in the text.
The value of the capacity of the membrane is indicated by X (meq/cm^3).

solution is not contaminated by species diffusing from the solution to be titrated. On the other side, there is the solution to be titrated (N^+Y^-) with the reagent (A^+B^-); in this solution the total concentration and the ionic composition change continuously during the titration by the occurrence of one of the following precipitation reactions:

$$N^+Y^- + A^+B^- \rightarrow NB\swarrow + A^+Y^-$$

$$N^+Y^- + A^+B^- \rightarrow AY\swarrow + N^+B^-$$

Because of the assumption that there is no contamination, it is only necessary to introduce one molar selectivity coefficient at the side of the solution to be titrated:

$K'^{N^+}_{A^+}$ for cationic membranes or $K'^{Y^-}_{B^-}$ for anionic membranes.

According to the theory of TEORELL, MEYER AND SIEVERS[3] the membrane potential consists of three distinct potential differences: two equilibrium potentials (Donnan potentials) at the membrane/solution interfaces (E_{D1} and E_{D2}), and the intramembrane potential, of which the diffusion potential (E_{diff}) is a special case when no electric charge is transferred across the membrane.

With the aid of a digital computer the membrane potential was calculated as a function of the added volume of the reagent solution (the programme was written in ALGOL 60).

Generally, the scheme for the calculations was the same as that introduced by SCHLÖGL[4] and described in the first paper[1]. However, in order to account for the influence of the selectivity, the following modifications were introduced (see also Fig. 2).

(*a*) The calculation of the Donnan potential E_{D2} was accomplished with the group concentrations $c_{2.k}$:

$$c_{2.1} = c_{N^+} + c_{A^+};\quad c_{2.2} = c_{Y^-} + c_{B^-};\quad \sum_k z_k c_k E_{D2}^{-z_k} = -wX$$

where w has a value of $+1$ for anionic and -1 for cationic membranes; X is the capacity of the membrane; the first number of the subscript indicates the solution at either side of the membrane and the second number the valence group;

(*b*) By means of E_{D2} the internal group concentration of the counter-ions at the surface of the membrane ($C_{2.1}$) was calculated as follows:

$$C_{2.k} = c_{2.k}\, E_{D2}^{-z_k}$$

It must be kept in mind that E_D has the meaning of the normalized potential difference ($\Delta\varphi$) between the surface of the membrane and the surrounding solution:

$$\ln E_D = (RT/F)\Delta\varphi$$

(*c*) The individual concentrations of the counter-ions at the surface of the membrane were then calculated as follows (*e.g.* for a cationic membrane):

$$C_{2.1} = C_{N^+} + C_{A^+} = c_{2.1}/E_{D2}$$

$$C_{N^+} = c_{2.1}/E_{D2} - C_{A^+}$$

From the definition of the selectivity coefficient $K'^{N^+}_{A^+}$, it follows that:

$$C_{A^+} = C_{N^+}\, c_{N^+}/c_{A^+}\, K'^{N^+}_{A^+}$$

and when this value is substituted for C_{A^+}, then

$$C_{N^+} = c_{2.1}\, c_{N^+}\, K'^{N^+}_{A^+}\, E_{D2}^{-1} / (c_{N^+}\, K'^{N^+}_{A^+} + c_{A^+})$$

The equation for C_{A^+} can be derived in a similar manner:

$$C_{A^+} = c_{2.1}\, c_{A^+}\, E_{D2}^{-1} / (c_{N}\, {}^{+}K'^{N^+}_{A^+} + c_{A^+})$$

For anion-selective membranes, analogous expressions can be derived, in which however the exponent of E_{D2} is $+1$ and $K'^{Y^-}_{B^-}$ is substituted for $K'^{N^+}_{A^+}$.

The individual concentrations of the co-ions at the surface of the membrane were calculated as described in the first paper[1]:

$$\left.\begin{array}{l} C_{Y^-} = c_{Y^-}\, E_{D2}^{+1} \\ C_{B^-} = c_{B^-}\, E_{D2}^{+1} \end{array}\right\} \text{for cation-selective membranes}$$

$$\left.\begin{array}{l} C_{N^+} = c_{N^+}\, E_{D2}^{-1} \\ C_{A^+} = c_{A^+}\, E_{D2}^{-1} \end{array}\right\} \text{for anion-selective membranes}$$

With the surface concentrations of the individual ionic species obtained as described above, the ionic fluxes were calculated as a function of the intramembrane potential. The diffusion potential was found as the intramembrane potential at zero total flux. Lastly, the membrane potential was calculated by adding algebraically the diffusion and the Donnan potentials. The difference from the original method of calculation is illustrated in Fig. 3.

For the calculation of the titration curves, it is assumed that the selectivity coefficient has a constant value during the titration, independent of the ionic composition and the total concentration of the solution to be titrated. As a first approximation and in order to see clearly the influence of the selectivity on the shape of the theoretical titration curves this simplification seemed to be permissible.

Calculations

For a given capacity of the membrane, the theoretical titration curves were calculated for cationic as well as for anionic membranes and for both possible titration reactions. The reference solution contains the ions M^+ and X^-. The diffusion coefficients of the counter-ions were varied in a ratio of 0.25 to 4 and the molar selectivity coefficients for these ions as defined before were varied between 0.1 and 10. The results are illustrated in Fig. 4.

Discussion and conclusions

From Figs. 4-3 and 4-4 it can be seen that in the cases where the initial co-ion is precipitated from the solution to be titrated, the influence of the selectivity appears only after the equivalence point. This is understandable because in these cases initially only the counter-ion of the salt to be titrated is present in the solution. Only when the precipitation has been completed, the counter-ions belonging to the reagent also appear in the solution and a change of the titration curve is to be expected when the membrane prefers one of the two kinds of counter-ions.

On the other hand, when the initial counter-ion in the solution to be titrated is precipitated (Figs. 4-1 and 4-2), the influence of the selectivity is perceptible up to the equivalence point. In these cases only the counter-ions added with the reagent remain in the solution when the precipitation has been completed. Before the equivalence point there are two competing kinds of counter-ions and the selectivity of

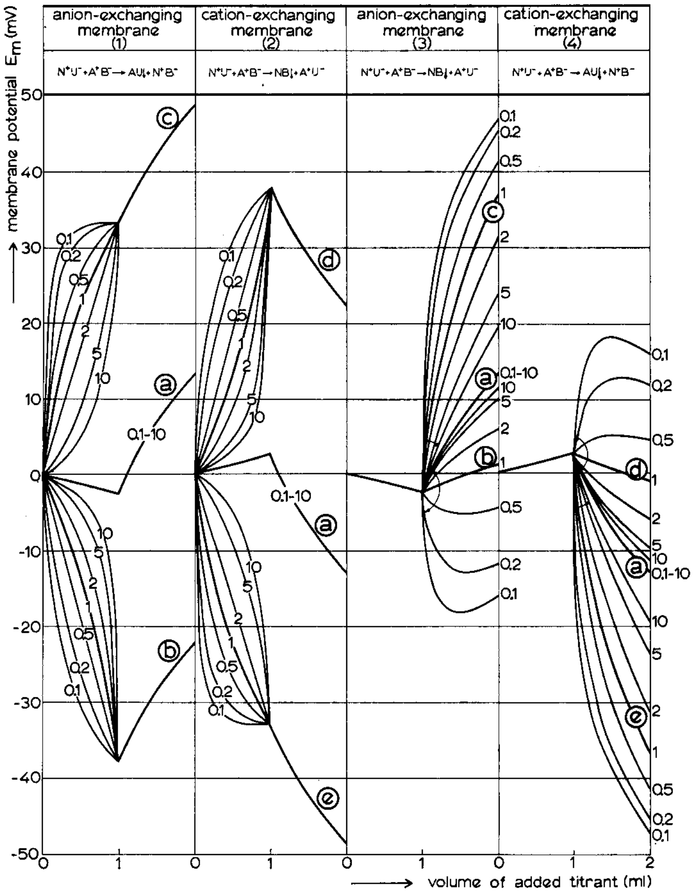


Fig. 4. Potentiometric titration curves for the titration of 10 ml of a 0.01 M solution of N^+Y^- with 0.1 M solution of A^+B^-; 0.01 M solution of M^+X^- as reference solution. The reagent is added in volumes of 0.2 ml. The capacity of the membrane is 1 meq/cm³. The number at each titration curve indicates the value of the selectivity coefficient introduced in the calculation ($K'^{N^+}_{A^+}$ for cationic and $K'^{Y^-}_{B^-}$ for anionic membranes). The letters at the titration curves indicate the values of the diffusion coefficients (in units of $1 \cdot 10^{-6}$ cm²/sec) as explained in the following table:

	D_{M^+}	D_{N^+}	D_{A^+}	D_{X^-}	D_{Y^-}	D_{B^-}	*ratio* D_{Y^-}/D_{B^-}	*ratio* D_{N^+}/D_{A^+}
curve a	4	4	4	6	6	6	1	1
curve b	4	4	4	6	6	1.5	4	1
curve c	4	4	4	1.5	1.5	6	0.25	1
curve d	4	4	1	6	6	6	1	4
curve e	1	1	4	6	6	6	1	0.25

the membrane can affect the shape of the titration curve. In practical titrations the presence of indifferent salts besides the compound to be determined is to be expected. As the membrane potential is primarily determined by all the counter-ions, in such cases the selectivity of the membrane for all the species of counter-ions must be taken into account.

When the diffusion coefficients of the counter-ions present in the solution to be titrated and the counter-ions added with the reagent are the same, the selectivity has no influence on the shape of the titration curves. In these cases both counter-ions can be regarded as belonging to the same ionic species (this statement is only valid when the valences of both competing kinds of counter-ions are the same).

In order to understand the influence of the selectivity on the shape of the titration curves it is desirable to keep the origin of the membrane potential for a bi-ionic case in mind. In this respect the diffusion potential is of primary interest. The direction of the inner electric field in the membrane can be deduced from the following considerations:

(*a*) the faster counter-ion tends to diffuse at a higher rate;

(*b*) there is an accumulation of charge at the side of the membrane opposing the solution containing the faster counter-ion;

(*c*) the sign of the accumulated charge (dependent on the sign of the charge of the counter-ions), determines the direction of the inner electric field;

(*d*) the diffusion potential accelerates the slower counter-ions and slows the faster ones down until the net charge transfer across the membrane is zero.

For the bi-ionic case the electric potential profiles are given for several calculated titration curves, taken in the equivalence point (Fig. 5).

The influence of the selectivity coefficient can be explained also as stated above for the bi-ionic case. As an example, a cationic membrane is chosen for the case that NB is precipitated (Fig. 4-2) and the titration is 60% complete. With a selectivity coefficient greater than unity, it follows that from the two competing counter-ions N^+ and A^+, the first is preferred. When the diffusion coefficient of this ionic species is greater, the flux of positive charge in the direction of the reference solution will initially be increased. As a result, the diffusion potential (and also the

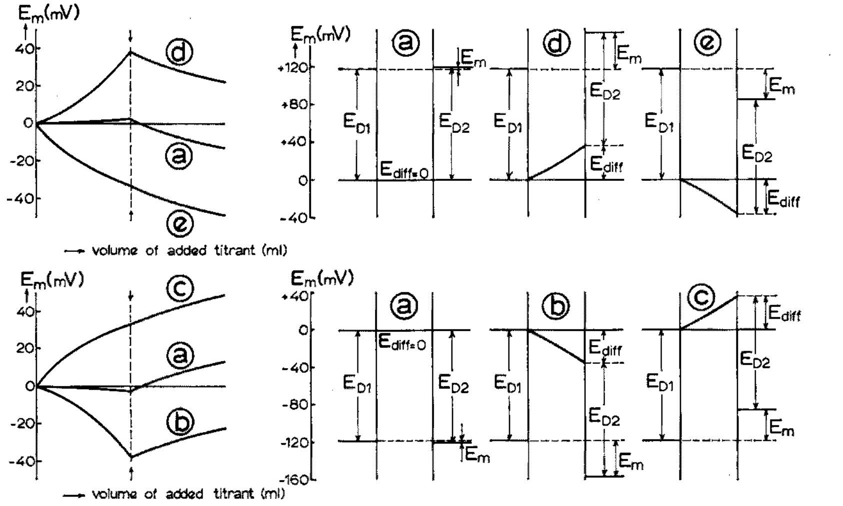


Fig. 5. The origin of the membrane potential for a bi-ionic case for six different titration curves (taken at the equivalence point):

upper figures—cation-exchanging membrane, corresponding to Fig. 4-2, curves a, d and e.

lower figures—anion-exchanging membrane, corresponding to Fig. 4-1, curves a, b and c.

The calculated values of the Donnan potentials, the diffusion potential and the membrane potential are given in mV. Data similar to Fig. 4.

membrane potential) will be less positive or more negative. In the upper part of Fig. 6 several possibilities are shown; in the lower part of Fig. 6 the influence of the selectivity is demonstrated also for a cationic membrane and for the case that AY is precipitated. For anionic membranes the results can also be analysed, taking the same considerations into account.

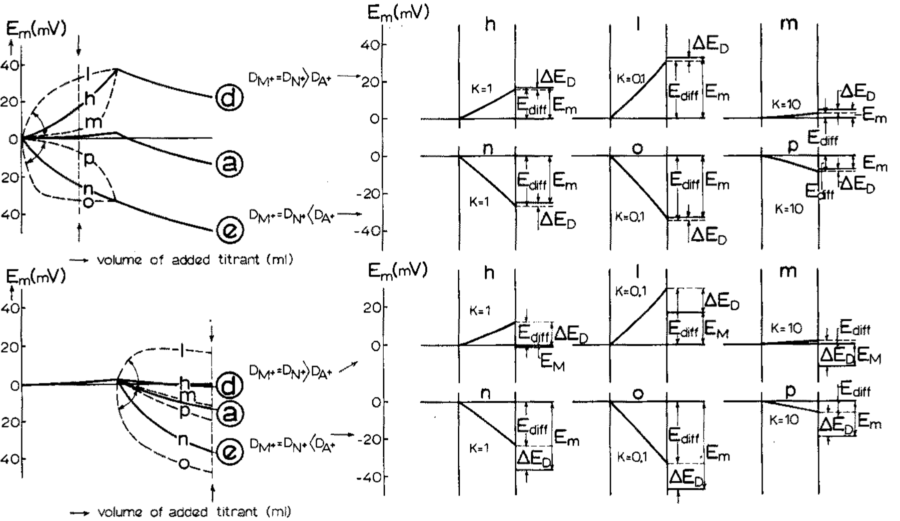


Fig. 6. The influence of the selectivity of the membrane on the value of the diffusion potential. upper figures—a cation-selective membrane when 60% of the counter-ion to be determined is precipitated. The examples given correspond to Fig. 4-2, curves a, d and e.

lower figures—a cation-selective membrane when 200% of the reagent needed for the precipitation of the co-ion, is added to the solution to be titrated. The examples given correspond to Fig. 4-4, curves a, d and e.

Data similar to Fig. 4. For the case of simplicity only the diffusion potentials and the algebraic sum of the Donnan potentials ($\Delta E_D = E_{D2} - E_{D1}$) are given.

In practical titrations it is to be expected that the selectivity coefficient is not constant but varies during the titration, because the total ionic concentration and the concentration ratio of the competing counter-ions change continuously during the titration. When, for example, the selectivity coefficient varies from 0.1 to 10 during the titration (a rather extreme case), the resulting titration curve can be expected to have a shape such as that shown in Fig. 7. It must be noted that for the case where the initial counter-ion is precipitated out of the solution to be titrated (Fig. 7a), a greater variation of the selectivity coefficient during the titration is to be expected than when the co-ion is initially precipitated (Fig. 7b). The reason is that in the first case the concentration ratio of the two competing counter-ions will change over a larger magnitude during the titration than in the second case, as can be seen in the figures.

The accuracy and precision of the determination of the end-point of the titration (by extrapolation) depend on the shape of the titration curve in the vicinity of the equivalence point. As can be seen from the titration curves in Fig. 4, the reliability of the extrapolation can be either advantageously or disadvantageously influenced, depending on the value of the selectivity coefficient and the ratio of the diffusion coefficients of the counter-ions.

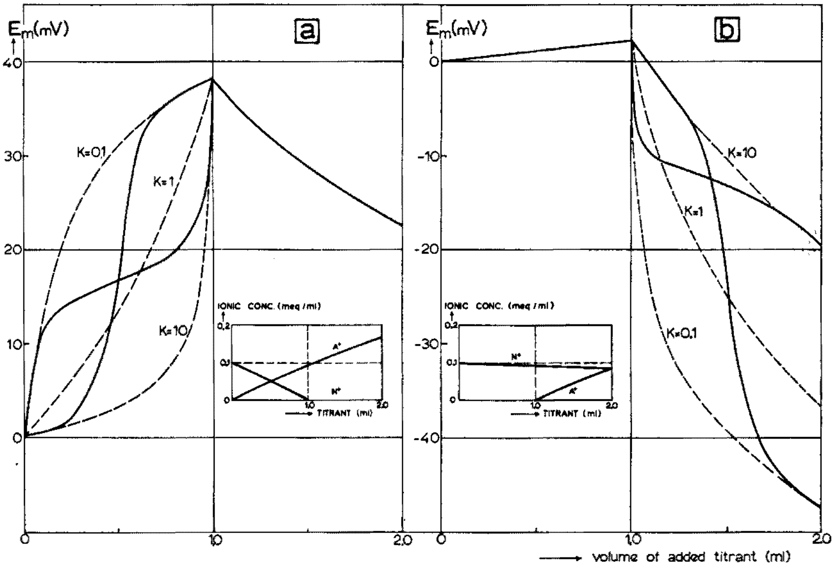


Fig. 7. The change in the shape of the titration curves that are to be expected when the selectivity coefficient of the membrane for the counter-ions varies during the titration from 0.1 to 10 or the reverse.

(*a*) the initial counter-ion is precipitated; this case corresponds to Fig. 4-2, curve d.

(*b*) the initial co-ion is precipitated; this case corresponds to Fig. 4-4, curve e.

Data similar to Fig. 4. For both cases two possible titration curves are illustrated; the changes of the concentrations of the counter-ions during the titration are also given.

The authors gratefully acknowledge the valuable assistance of Dr. W. T. DE VRIES of this Laboratory, who carried out the programming of the calculations; thanks are also due to the Mathematical Centre at Amsterdam for generous donation of computer time.

SUMMARY

The possible influence of the selectivity of the membrane used in an indicating electrode with potentiometric titrations was investigated by introducing some simple modifications in the calculations performed earlier. The influence of the selectivity is visible only before the equivalence point when the counter-ion is precipitated initially from the titrated solution. When the co-ion is precipitated initially, the shape of the titration curve is altered only after the equivalence point. The reliability of the determination of the equivalence point can be either advantageously or disadvantageously influenced by the selectivity, depending on the value of the selectivity coefficient and the ratio of the diffusion coefficients.

RÉSUMÉ

On examine l'influence possible de la sélectivité d'une membrane utilisée à l'électrode indicatrice, lors de titrages potentiométriques. L'influence de la sélectivité n'est visible qu'avant le point équivalent lorsque l'ion critique est précipité le premier de la solution titrée. Au contraire si l'ion non-critique est précipité le premier la pente de la courbe de titrage n'est affectée qu'après le point équivalent. La précision de la détermination du point équivalent peut être avantageusement, ou non, influencée par la sélectivité, dépendant du coefficient de sélectivité et du rapport des coefficients de diffusion.

ZUSAMMENFASSUNG

Der mögliche Einfluss der Selektivität der Membrane, die in einer Indikatorelektrode bei potentiometrischen Titrationen verwendet wird, wurde untersucht, indem einige einfache Modifikationen in die früher angegebenen Gleichungen eingeführt wurden. Der Einfluss der Selektivität ist nur vor dem Äquivalenzpunkt sichtbar, wenn das Gegenion anfangs aus der titrierten Lösung gefällt wird. Wird das Mition anfangs gefällt, so wird die Form der Titrationskurve nur nach dem Äquivalenzpunkt geändert. Die Zuverlässigkeit der Äquivalenzpunktsbestimmung kann durch die Selektivität entweder günstig oder ungünstig beeinflusst werden, das hängt von dem Wert des Selektivitätskoeffizienten und dem Verhältnis der Diffusionskoeffizienten ab.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE COULOMETRIC PRODUCTION OF IODIDE ION FOR TITRATIONS OF MERCURY(I,II)

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(Received July 26th, 1967)

The internal coulometric production of reagents has been widely applied for many years[1-3] but because of the remarkable results which can be obtained in microdeterminations and the possible application in automatic analytical apparatus, the development of methods involving this technique continues to be of interest[4].

The utilization of the iodide species in many analytically important reactions suggested that it would be useful to establish the conditions for its coulometric production. This was done by means of cathodic polarization of a silver/silver iodide electrode. The dynamic behaviour of this electrode, which has been already studied as an indicator electrode in potentiometric determinations[5], was studied in some detail.

EXPERIMENTAL

Materials

Materials and all chemicals were reagent grade (C. Erba, Milan).

Apparatus

For the plotting of current–voltage curves and the diagrams of i (in μA) *vs.* iodide concentration, the apparatus described previously[6] was employed. The rotating platinum disk electrode was silvered for 15 min at 3 mA with a silver cyanide solution. It was then iodized at 2 mA for 3 min with a neutral solution of 0.1 M potassium iodide.

For the production of iodide by means of the reaction $AgI + e^- \rightarrow Ag + I^-$, a silver spiral electrode with a surface area of about 6 cm^2 was employed.

The layer of silver iodide on the electrode was obtained by anodic deposition from a neutral potassium iodide solution with a current of 5 mA for about 1 h. The electrode was then washed and stored in twice-distilled water in the dark.

The electrical apparatus consisted of the following: a constant-current electronic generator, the stability of which was greater than 0.1%, a stabilized power supply (J. Fluka model 407 D), a Leeds and Northrup model K-3 potentiometer, a standard Siemens 1000 resistor, a Sefram Verispot galvanometer, a Solartron model LM 1420 electrometer and a 100 Metrohm potentiometer.

A platinum gauze electrode was employed as anode in the oxidation of mercury(I) to mercury(II).

PROCEDURES

For the plotting of current–voltage curves as shown in Fig. 1, the points were measured after 5 min. The potential was varied from positive to negative values with reference to a saturated calomel electrode.

To verify the efficiency of the production of iodide at the cathode, the silver/silver iodide electrode, prepared by the above procedure, was introduced into a cell containing about 55 ml of base electrolyte (potassium nitrate or perchloric acid). This acted as cathode for some minutes. Then a silver electrode was utilized for the production of silver(I) to titrate the previously generated iodide ions, and two silver/silver iodide wire electrodes were used for the biamperometric indication of the end-point of the titration of iodide with silver(I). A platinum electrode, immersed in the same electrolyte solution, separated by a sintered glass disc, was the counter-electrode, both as the anode in the production of iodide and then as the cathode in the production of silver. The production of iodide was carried out in a neutral solution (0.1 M potassium nitrate) and in an acidic solution (0.1 M and 2 M perchloric acid); the different currents used were produced by a constant-current generator.

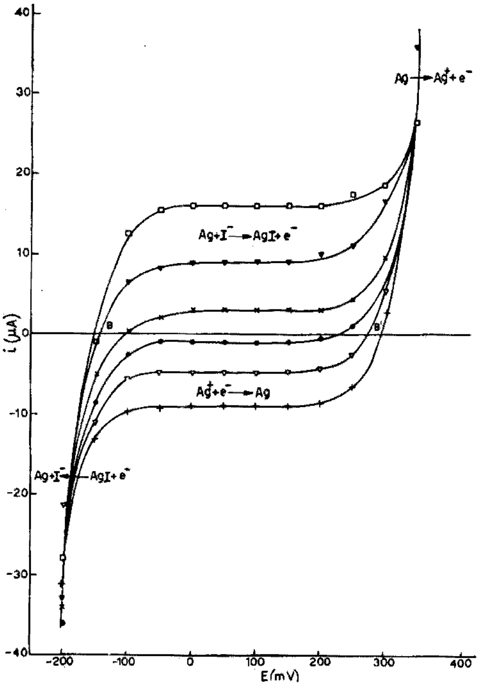

Fig. 1. Polarization curves for the Ag/AgI electrode in 0.1 M potassium nitrate. □ $9.80 \cdot 10^{-5}$ N iodide ion; ▼ $5.05 \cdot 10^{-5}$ N iodide ion; × $1.70 \cdot 10^{-5}$ N iodide ion; ● $8.99 \cdot 10^{-6}$ N silver ion; ▽ $4.34 \cdot 10^{-5}$ N silver ion; + $8.32 \cdot 10^{-5}$ N silver ion.

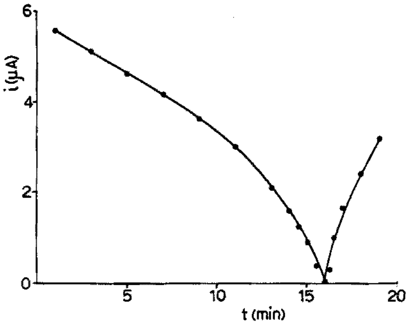

Fig. 2. Biamperometric titration of iodide with electrically generated silver(I). Base electrolyte 10^{-1} M $HClO_4$. I^- produced for 4 min at 4 mA and Ag^+ for 4 min at 1 mA.

The current was measured potentiometrically at the ends of a standard resistor. An electric contact chronometer was used as switch.

Titrations of mercury(I) and mercury(II) alone and in mixtures were carried out by coulometric generation of iodide. The end-point was detected potentiometrically by using a silver/silver iodide electrode as indicator. A known volume of mercury-(I) or mercury(II) solution was placed in the cell, and 0.1 *M* perchloric acid solution was added to give a total volume of *ca.* 60 ml. (Mercury(II) standard solution was obtained by simply dissolving mercuric oxide (primary standard) in 0.1 *M* perchloric acid. Mercury(I) solution, obtained from mercurous nitrate, was standardized by means of a potentiometric titration with sodium chloride solution[7].) In order to determine the separate amounts of mercury(I) and mercury(II) simultaneously present in the solution, mercury(I) was converted quantitatively to mercury(II) by constant potential coulometry. A platinum gauze electrode acted as anode and the anodization potential (1.2 V *vs.* S.C.E.) was such as to allow a quick and quantitative oxidation of mercury(I). Oxygen development was not observed. The approach of the completion of the oxidation reaction was indicated by the progressive exponential lowering of the electrolysis current. After this oxidation, the total amount of mercury, as mercury(II), was determined. A comparison of the number of equivalents required for this titration and that required for the titration of the mixture immediately gave the separate amounts of mercury(I) and mercury(II).

RESULTS AND DISCUSSION

Figure 1 shows a series of current–voltage curves, plotted at different values of iodide and silver(I). Since every curve was plotted after regeneration of the electrode, the currents read at *ca.* +100 mV (*vs.* S.C.E.) departed by 5–6% from linearity, in relation to the concentration, obviously because of the incomplete reproducibility of the active surface. The distance of about 420 mV between the intersection points of the curves B and B′ with the $i=0$ axis, at the concentrations of iodide and silver(I) used, gives a pK_s value of 15.6 for silver iodide which is in rather good agreement with the value quoted in the literature.

The limiting currents, measured by the silver/silver iodide electrode, used for the determination of iodide with this electrode were proportional to the iodide concentration in the same concentration range ($2\cdot10^{-6}$–$2\cdot10^{-4}$ *M*) as was found for

TABLE I

PERCENTAGE DIFFERENCES BETWEEN THE NUMBER OF COULOMBS REQUIRED FOR IODIDE PRODUCTION AND FOR SILVER(I) PRODUCTION

Current for I$^-$ production (mA)	*Time of I$^-$ production (min)*	*Difference in various base electrolytes*		
		in 0.1 M KNO_3	*in 0.1 M $HClO_4$*	*in 2 M $HClO_4$*
1	15	0.00	+0.20	0.00
4	4	+0.75	+0.05	+0.75
8	4	−0.40	−0.20	−0.80
12	2	−0.30	0.00	+0.46
16	2	+0.50	+0.02	+2.70
20	2	0.00	+0.05	—

the silver electrode[6]. The slope of this dependence ($4 \cdot 10^{-4}$ μA *vs.* iodide concentration) was also the same for both electrodes.

Table I lists the percentage differences between the number of coulombs required for iodide production and those required for silver(I) production. The silver ions were always generated by a current of 1 mA. The differences observed can generally be ascribed to the uncertainty of the end-point definition. However, the rather large difference observed when 2 M perchloric acid media was used with a current of 16 mA must be ascribed to the incipient development of hydrogen simultaneously with the production of iodide. The employment of the silver/silver iodide electrode for the biamperometric indication proved to be particulary advantageous for good definition of the end-point; this is due to reversibility with regard to silver(I) and iodide, as verified for the above-mentioned current–voltage curves. An example of a titration curve is shown in Fig. 2.

Table II lists the results obtained for determinations of mercury(I) and mercury(II). The point of maximum slope was considered, as usual, as the end-point of the titration. Naturally, the equivalence point and the point of maximum slope did not coincide, since these titrations were asymmetrical. The resulting error was calculated from the equation of the titration curve

$$[HgI^+] - [I^-] - [HgI_3^-] = (1 - \phi) \cdot K$$

where ϕ = fraction titrated and K = constant.

TABLE II

POTENTIOMETRIC TITRATIONS OF MERCURY(I) AND MERCURY(II) WITH COULOMETRICALLY GENERATED IODIDE

	Taken *(μeq)*	*Found (av.)*[a] *(μeq)*	*Error* *(%)*
Hg(II)	4.40_4	4.44_5	+0.93
Hg(II)	8.80_8	8.86_0	+0.59
Hg(I)	3.04_5	3.07_4	+0.95
Hg(I)	9.13_5	9.17_2	+0.41
Hg(I)–Hg(II)	3.04_5–3.52_3	3.06_1–3.55_9	+1.54
Hg(I)–Hg(II)	5.22_3–3.52_3	5.25_5–3.54_3	+1.20
Hg(I)–Hg(II)	7.83_4–3.52_3	7.83_9–3.59_1	+2.00
Hg(I)–Hg(II)	3.48_2–7.04_6	3.50_4–7.08_6	+1.20

[a] Average of 3 determinations.

The second derivative was made equal to zero and the resulting value of mercury(II), at the point of maximum slope, was introduced in the titration equation. It was thus possible to calculate $1 - \phi_{e.p.}$, the titration error[8]. The employment of the above equation near the equivalence point was correct since the predominant species were HgI^+, HgI_3^-, HgI_2, I^- as was shown by means of a logarithmic concentration diagram[9]. It was found that, for a $3.6 \cdot 10^{-5}$ M solution of mercury(II), $1 - \phi_{e.p.}$ was $-7 \cdot 10^{-5}$, *i.e.* a negligible error compared to the experimental ones. It should be noted that the error in the titrations of mercury(I) or mercury(II) alone decreased as the concentration increased, probably because of the retardation in the precipitate formation.

SUMMARY

The dynamic behaviour of the silver/silver iodide electrode was studied. Iodide ions can be produced by cathodic polarization of the silver/silver iodide electrode in acidic and neutral media. This technique can be used for coulometric titrations of mercury(I) or mercury(II) both alone and in mixture. At the microequivalent level of mercury the error is less than 2%.

RÉSUMÉ

On a étudié le comportement dynamique de l'électrode argent/iodure d'argent. Les ions iodures peuvent être produits par polarisation cathodique de l'électrode argent/iodure d'argent, en milieu acide et neutre. Cette technique peut être utilisée pour des titrages coulométriques du mercure(I) ou du mercure(II), soit individuellement, soit dans des mélanges. Pour des microquantités de mercure, l'erreur est inférieure à 2%.

ZUSAMMENFASSUNG

Das dynamische Verhalten der Silber/Silberjodid-Elektrode wurde untersucht. Jodidionen können durch kathodische Polarisation dieser Elektrode in saurem und neutralem Medium erzeugt werden. Diese Technik kann zur coulometrischen Titration von Quecksilber(I) oder Quecksilber(II) sowohl allein als auch in Mischungen verwendet werden. Der Fehler beträgt im Mikroequivalent-Bereich weniger als 2%.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COLOR REACTIONS OF PYRIDINES WITH PENTACYANOAMMINOFERRATE*

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(Received July 24th, 1967)

SCARDI AND BONAVITA[1,2] have described a colorimetric determination of isonicotinic acid hydrazide which involves its reaction at pH 6.5 with trisodium pentacyanoamminoferrate, ($Na_3Fe(CN)_5NH_3$; TPF) to produce a yellow complex. This procedure is based on a spot-test reaction of hydrazines and TPF at a slightly alkaline pH[3,4]. However, when SCARDI's procedure was applied to hydrazides, it was found that most either failed to react with TPF, or produced the red or violet color described by FEARON[3] and FEIGL[4]. This suggested that the yellow complex was due to the pyridine moiety of isonicotinic hydrazide, and not to the hydrazide group.

Pyridine in a chromatographic solvent must be completely removed from chromatograms before TPF can be used as a spray reagent for guanidines[5]. Similarly pyridine, but not α-picoline, interferes with the formation of colored complexes of TPF and nitrosobenzene compounds[6]. BIDDISCOMBE AND HERRINGTON[7] applied this effect to the determination of some pyridines, not substituted on the α-position, by measuring the decrease caused in the concentration of a colored TPF–*p*-nitrosodimethylaniline complex. In a glycerol–acetic acid solvent, isonicotinic, but not nicotinic or dipicolinic acid, reacts with TPF to produce a red color[8].

The results reported here show that TPF forms colored complexes with pyridine and many of its derivatives, including some with α-substituents. The formation of the complexes may serve to identify or measure pyridines colorimetrically.

EXPERIMENTAL

Apparatus and reagents

Absorbance curves were obtained with a Beckman DK recording spectrophotometer, using 1-cm corex glass cells; other optical density measurements were obtained with a Beckman DU spectrophotometer.

Trisodium pentacyanoamminoferrate (Fisher Scientific Co., Pittsburgh). Prepare a 0.2% (w/v) solution in 0.02 *N* ammonia immediately before use[1]. For use as a chromatographic spray or spot-test reagent, prepare a 0.2% solution in pH 6.5 citrate–phosphate buffer immediately before use.

Citrate phosphate buffer, pH 6.5. Prepare from 3 volumes of 0.1 *M* citric acid

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[*] Issued as N.R.C. No. 9821.

and 7 volumes of 0.2 *M* Na_2HPO_4[1]. Prepare phosphate buffers from 0.4 *M* NaH_2PO_4, and 0.4 *M* Na_2HPO_4.

Pyridines were dissolved at a concentration of 10 mg/ml in suitable solvents, and stored in the cold. Standard solutions containing 5–50 µg/ml were prepared daily by dilution in distilled water.

Absorbance curves

SCARDI's procedure[1] was used to obtain colored complexes of TPF with pyridine and its derivatives. To 2 ml of solution containing 100 µg of sample, were added 1.5 ml of citrate–phosphate buffer and 0.5 ml of TPF. After 20 min at room temperature, the absorbance spectra from 360 to 750 nm were measured against a reagent blank prepared in the same way. The absorbance curves (Fig. 1) vary for different pyridine derivatives. Table I lists the wavelength of maximum absorption, and the corresponding absorbance for all the pyridine derivatives forming colored complexes. Only very slight absorbances were observed with 2-hydroxypyridine, 4-hydroxypyridine, pyridyl-2 methyl ketone, 2-ethylpyridine, picolinic acid, 2,5-lutidine, 2-methyl-5-ethylpyridine, dipicolinic acid, lutidinic acid, isonepectonic acid and isocinchomeronic acid.

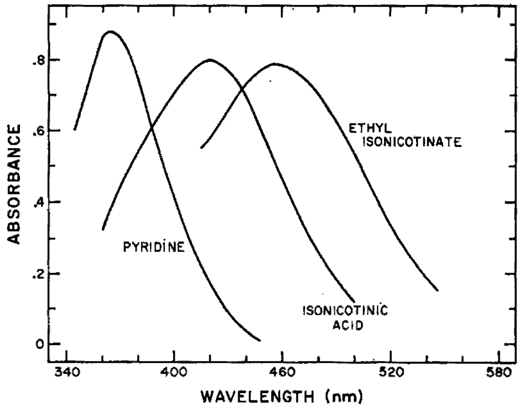


Fig. 1. Absorbance spectra of complexes of TPF and pyridine derivative (100 µg).

pH, time and reagent

Two ml of sample, 1.5 ml of 0.4 *M* phosphate buffer and 0.5 ml of TPF were mixed, and the absorbance at the wavelength of maximum absorption determined at intervals during 40 min. There was a remarkable variation in the stability of the color with different pyridines. With pyridine (Fig. 2a) and 3-hydroxypyridine, the optical density reached its maximum within 2 min in acidic medium, and decreased rapidly at first and then more slowly. In alkaline media, the optical density did not achieve a high initial value. 2-Cyanopyridine (Fig. 2b) formed a complex, the color of which decreased in intensity very rapidly at all pH values. 4-Cyanopyridine (Fig. 2d) in acid or neutral media produced a complex, the absorbance of which fell off rapidly from its high initial value; in alkaline medium the maximum absorbance was not reached for 5–10 min. Pyridyl-4 methyl ketone (Fig. 2c) produced a complex

TABLE I

REACTION OF PYRIDINES AND TRISODIUM PENTACYANOAMMINOFERRATE

Compound	*Wavelength of maximum absorption*	*Absorbance*	*Spot test color*	*Paper chromatography color*
Pyridine	365	0.81	—	—
2-Cyanopyridine	380	0.42	Yellow	—
2-Aminopyridine	705	0.23	—	—
3-Hydroxypyridine	365	0.86	Yellow	Yellow
3-Cyanopyridine	415	0.84	Orange-yellow	—
Nicotinic acid	375	0.48	Yellow	Yellow
3-Methylpyridine	360	0.83	—	—
3-Pyridyl methyl ketone	365	0.58	Yellow	Yellow
Nicotinic acid amide	390	0.78	Yellow	Yellow
Nicotine	390	0.48	Yellow	Yellow
L-Anabasine	380	0.51	Yellow	Yellow
Pyridine-3 sodium sulfonate	405	0.34	Yellow	Yellow
Ethyl nicotinate	380	0.40	Yellow	Yellow
Hexyl nicotinate	380	0.26	Yellow	Yellow
3-Aminopyridine	360	0.94	Yellow	Yellow
4-Cyanopyridine	470	0.72	—	—
Isonicotinic acid	420	0.80	Yellow	Yellow
4-Methylpyridine	355	0.96	Orange-pink	—
4-Ethylpyridine	365	0.89	Yellow	Yellow
Isonicotinic acid amide	435	1.10	Orange-yellow	Orange-yellow
Ethyl isonicotinate	460	0.79	Orange	Orange
Pyruvic isonicotinyl hydrazone	435	0.63	Orange-pink	Orange
Isonicotinic hydrazide	430	0.86	Orange	Orange
4-Pyridyl methyl ketone	475	0.98	Purple	Purple
4-Aminopyridine	550	0.15	Purple	Purple

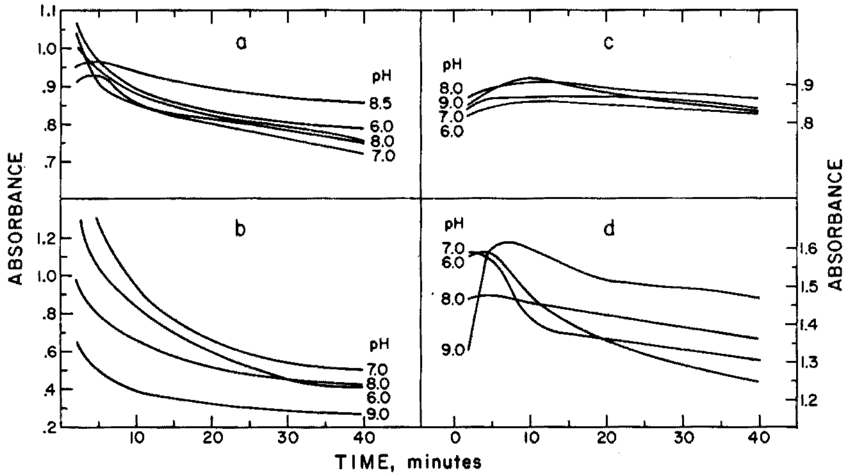


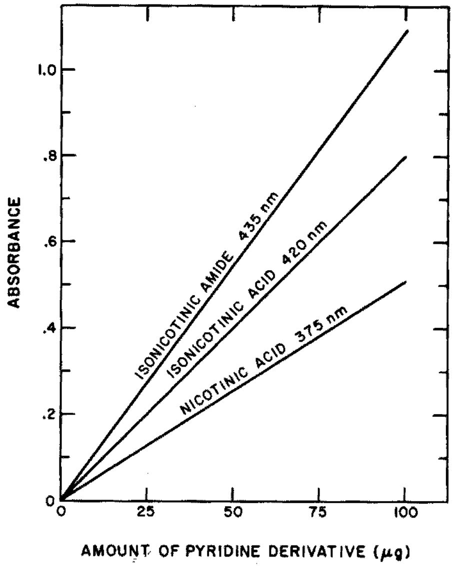
Fig. 2. Effect of pH on stability of colored complexes of TPF and pyridine derivatives. (a) Pyridine, 365 nm. (b) 2-Cyanopyridine, 380 nm; (c) Pyridyl-4 methyl ketone, 475 nm; (d) 4-Cyanopyridine, 470 nm.

with a fairly stable absorbance at all pH values. The wavelengths of maximum absorbance did not change significantly over the pH range studied.

The stability of the complexes was not improved when 0.1% or 0.5% TPF solution was used in the procedure. Different commercial lots of TPF showed some variation in the speed and stability of color development.

Beer's law

When care was taken to determine the absorbance exactly 20 min after mixing the reagents, the absorbance was proportional to the concentration over the range 10–100 µg (Fig. 3).



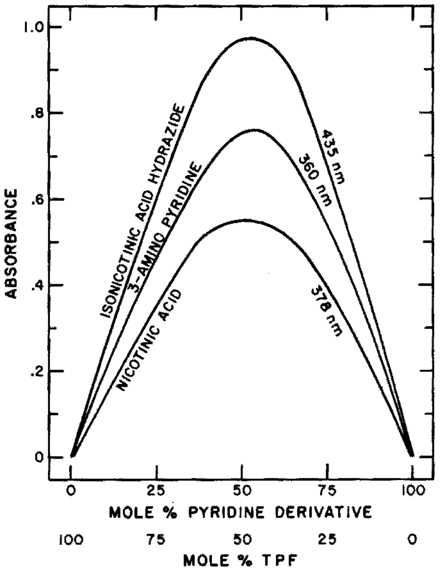


Fig. 3. Standard curves for reaction of TPF and pyridine derivatives.

Fig. 4. Job's method to determine the nature of the TPF–pyridine derivative complex.

Composition of the complex

The composition of the colored complexes was determined by Job's method of continuous variation[9]. Equimolar solutions (10^{-3} *M*) of TPF and isonicotinic acid hydrazide, nicotinic acid or 3-aminopyridine were mixed in different proportions (10 ml of total mixture) and 5 ml of citrate–phosphate buffer were added. After 20 min the absorbances of the solutions were recorded at the wavelength of maximum absorption. The results (Fig. 4) indicated that in each case the pyridine derivative and TPF form a dissociable complex in the ratio of 1:1.

Spot test

The pyridine derivative (10 µg) in 10 µl of solvent (usually 50% ethanol) was spotted on Whatman #1 paper and sprayed immediately with TPF in buffer. Colors (Table I) developed within 5 min. At a concentration of 50 µg, most spots appeared orange or red.

Paper chromatography

Ten μg of pyridine derivative was applied to Whatman #1 paper and chromatographed in 3:1 *n*-propanol–2% ammonia solution, 45:5:50 *n*-butanol–acetone–H_2O (top phase), or 3:1 *n*-propanol–6% acetic acid. The sheets were air-dried and sprayed with TPF in buffer. The colors developed within 10 min. Table I lists the colors observed. The solvents were chosen as representative of acidic, neutral and basic solvents, and the colors produced by the TPF spray on each pyridine derivative were identical on sheets run in three solvents. Pyridine and some of its derivatives, which reacted with TPF in solution, did not give a spot test or react with the spray after chromatography, probably because of evaporation from the paper.

DISCUSSION

According to FEIGL[4] the reactions of TPF depend on the replacement of ammonia by a molecule of the reacting compound to form a colored complex. The 1:1 ratio of the reactants, found in the present work, indicates that this is the mechanism by which TPF forms colored complexes with pyridines. A different mechanism may be operative in a strongly acidic medium, since HERRINGTON[8] found that in acetic acid, isonicotinic acid but not nicotinic acid reacted with TPF to form a red color.

Isonicotinic acid and pyruvic isonicotinyl hydrazone reacted with TPF to form complexes absorbing at almost the same wavelength as isonicotinyl hydrazide. This indicates that SCARDI's analysis[1,2] for this compound is based on a reaction of the pyridine rather than the hydrazine part of the molecule.

BIDDISCOMBE AND HERRINGTON[7] found that TPF formed a pale yellow complex with pyridine, 3-methylpyridine and 4-methylpyridine, but not with the 2-substituted pyridines tested. Since the pyridine could displace *p*-nitrosodimethylaniline from its complex with TPF, these workers measured the non α-substituted pyridines by the decrease caused by the pyridine derivatives in the green color of the TPF–*p*-nitrosodimethylaniline complex. Though most α-substituted pyridines failed to react with TPF in the present experiments, nevertheless colored complexes were formed with 2-cyanopyridine and 2-aminopyridine. Therefore, a positive reaction with TPF cannot be considered as a positive indication that the α-position is not substituted.

It is apparent that if TPF is to be used as a spectrophotometric assay, the optimum pH and time conditions must be determined for each pyridine derivative. Since the wavelength of maximum absorption differs for different pyridines, it may be possible to determine certain pairs of pyridines in the presence of each other.

SUMMARY

Trisodium pentacyanoamminoferrate is proposed as a spot test, chromatographic spray or spectrophotometric reagent for pyridines. A 1:1 colored complex of the reagent and pyridine derivative is formed in aqueous solution. The intensity and stability of the color varies with the pH.

RÉSUMÉ

On propose le pentacyanoaminoferrate trisodique comme réactif des pyridines, pour analyse qualitative, chromatographie ou spectrophotométrie. Il y a formation d'un complexe coloré, réactif/dérivé pyridine (en proportion 1:1) en solution aqueuse. L'intensité et la stabilité de la couleur varient avec le pH.

ZUSAMMENFASSUNG

Trinatriumpentacyanoaminoferrat wird als Tüpfelreagenz, chromatographische Sprühmittel oder als spektralphotometrisches Reagenz für Pyridine vorgeschlagen. Ein gefärbter Komplex des Reagenzes und des Pyridinderivates wird in wässriger Lösung gebildet. Die Intensität und Stabilität der Farbe variiert mit dem pH-Wert.

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Anal. Chim. Acta, 40 (1968) 437–442

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A DIFFERENTIAL SPECTROFLUORIMETRIC DETERMINATION OF ADRENALINE AND NORADRENALINE

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(Received July 27th, 1967)

The fluorimetric determination of adrenaline and noradrenaline is usually carried out by oxidation of the catecholamines to adrenochrome or noradrenochrome, whereafter these derivatives are converted to fluorescent lutines by addition of alkali in an oxygen-free solution. The mechanism of the oxidation is complex and

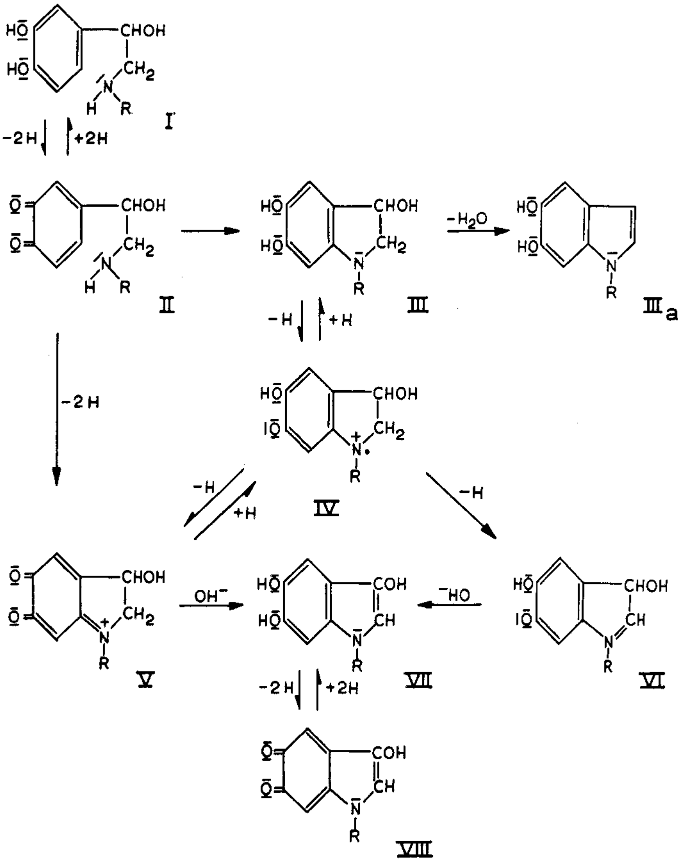


Fig. 1. Reactions occurring during the oxidation of adrenaline or noradrenaline. R = CH_3 → adrenaline; R = H → noradrenaline.

not completely elucidated. The reactions occurring during oxidation of these amines are summarized in Fig. 1.

Reaction mechanism

VON EULER[1] suggested the same oxidation mechanism for adrenaline and noradrenaline. The compounds IIIa, V and VII have been isolated and identified by GREEN AND RICHTER[2], HARLEY-MASON[3] and HEACOCK[4], whereas II, III, IV, VI and VIII are hypothetical. HARLEY-MASON[3] postulates VI as a precursor of VII. This is based on the fact that structure VI has a specific ultraviolet spectrum and is not stable in an alkaline solution. The compounds V and VI are formed via the semiquinone IV, shown as a free radical. He also assumes that the adrenochromes V in alkaline solution are immediately transformed to their trihydroxyindole derivatives VII. EHRLÉN[5] and HARRISON[6] showed that the fluorescence is produced by the 3,5,6-trihydroxyindoles (VII).

The trihydroxyindoles (VII) can be oxidized in alkaline solution (pH 14) to the corresponding non-fluorescing *o*-quinones (VIII)[3,7] by hexacyanoferrate(III) as

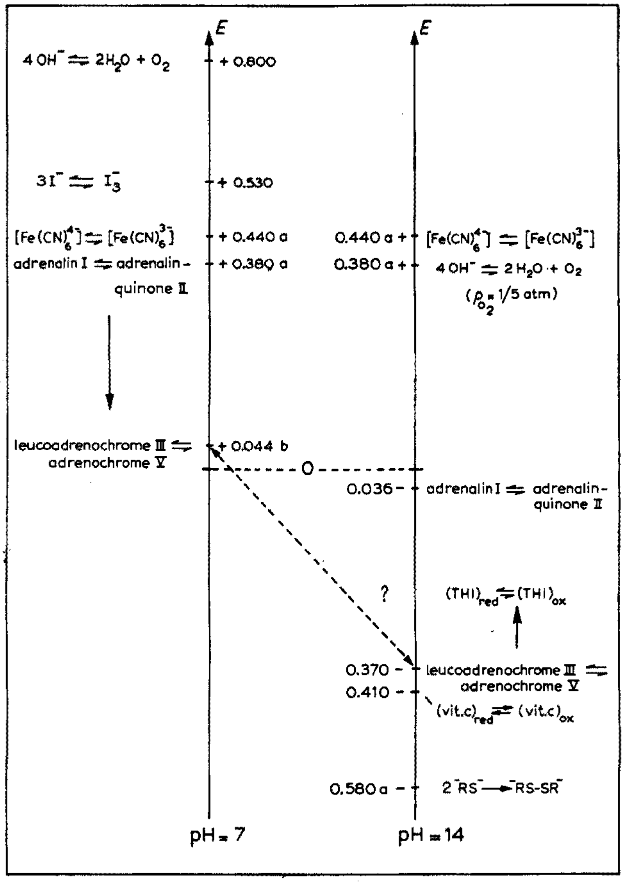


Fig. 2. Oxidation potentials at pH 7 and 14 for the different redox systems which occur during the oxidation of the amines. [a] Value taken from CLARK[8]; [b] Value taken from WIESENER[9].

well as by dissolved oxygen. The addition of ascorbic acid reduces the amount of dissolved oxygen as well as the excess of hexacyanoferrate(III), whereas the reduction of the *o*-quinone structure (VIII) is a function of time. These considerations lead to the assumption that the oxidation potential for the redox system trihydroxyindole$\rightleftharpoons$*o*-quinone must lie between the values of the hexacyanoferrate(III)/hexacyanoferrate(II) and the ascorbic acid/dehydroascorbic acid systems.

The oxidation potentials of the systems involved are shown in Fig. 2.

GADDUM AND SCHILD[10] suggest that not only the trihydroxyindole derivatives but also the 2,3,5,6-tetrahydroxy-N-methylindoles are fluorescent substances formed by the action of air on diluted alkaline solutions of adrenaline and noradrenaline.

HARLEY-MASON[3] mentions that an oxidative cyclization II→V is also possible whereas UDENFRIEND[11] excludes the structure IIIa.

DIFFERENTIAL ESTIMATION

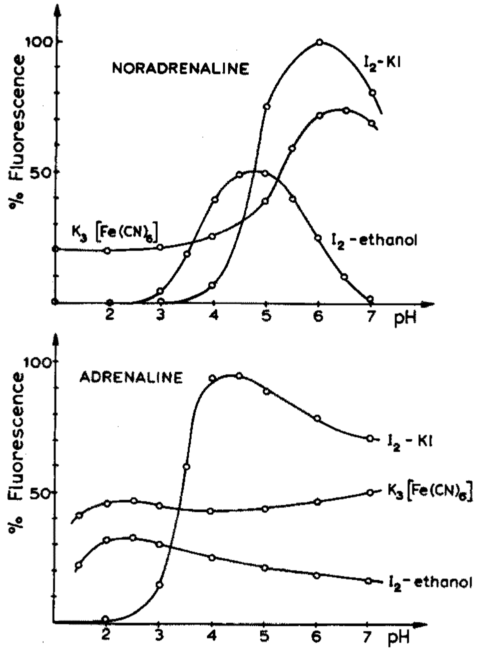
The fact that there is very little difference between the fluorescence spectra of adrenaline and noradrenaline is the reason why the differential estimation of the two amines has been the subject of so many investigations.

Among the often-used methods are those of ANTON AND SAYRE[12], VON EULER AND LISHAJKO[13], LUND[14] and FLEMING *et al.*[15]. The oxidation technique of ANTON AND SAYRE is performed with potassium hexacyanoferrate(III) at two different pH values: pH 2 for adrenaline and pH 6.8 for both adrenaline and noradrenaline. VON EULER AND LISHAJKO oxidize with hexacyanoferrate(III) at pH 6.2 and determine the fluorescence at two different wavelengths: 490 and 540 nm. However, when the VON EULER method is used, important errors can occur if the concentration ratio of adrenaline to noradrenaline differs considerably from unity. LUND oxidizes adrenaline at pH 3.5 and noradrenaline at pH 6.5 by means of the triiodide complex, whereas FLEMING *et al.* oxidize the catecholamines by means of alcoholic solutions of iodine.

In the present work, the different oxidizing agents for both amines were compared as a function of the pH. Figure 3 shows the results of experiments carried out with adrenaline and noradrenaline solutions (1 μg/ml), oxidized respectively with potassium hexacyanoferrate(III), triiodide and iodine in an ethanolic solution. From these results it can be seen that the oxidation with iodine in ethanol seems to be very reliable for the differential estimation of adrenaline and noradrenaline at pH 2 and 5 respectively. The oxidation of the latter is negligible at pH 2, and shows a maximum at pH 5, whereas the former shows only a slight maximum at pH 2.

Recently, MERRILS[16] and ROBINSON AND WATTS[17] have worked out a differential method in which they measure the combined fluorescence from both amines after oxidation with hexacyanoferrate(III) in alkaline ascorbate solution whereas the fluorescence of noradrenaline alone is measured in a separate sample, one minute after addition of alkaline thioglycolate. The time–fluorescence curves for the adrenaline and noradrenaline (0.1 μg/ml) systems in thioglycollic acid solutions (1% into 10 *N* sodium hydroxide) are given in Fig. 4. This curve shows a rapid decrease to zero fluorescence for the adrenaline system while the noradrenaline fluorescence decreases relatively slowly. The fluorescence of noradrenaline is determined immediately after the decay of the adrenaline fluorescence (*ca.* 1 min). As the decrease rate of the noradrenaline fluorescence is very high at this moment, large errors are possible.

It was found in this work that a freshly prepared mixture of 1% cysteine, 0.01% thioglycollic acid and 5% ethanol in 10 *N* sodium hydroxide has a very favorable effect compared with the reagent proposed by ROBINSON AND WATTS[17], as shown in Fig. 5. The fluorescence of adrenaline is reduced to zero after 15 min while the noradrenaline fluorescence remains virtually constant during 10 min. The



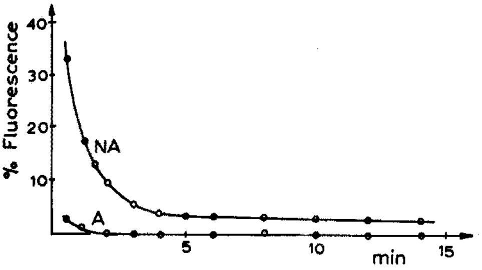
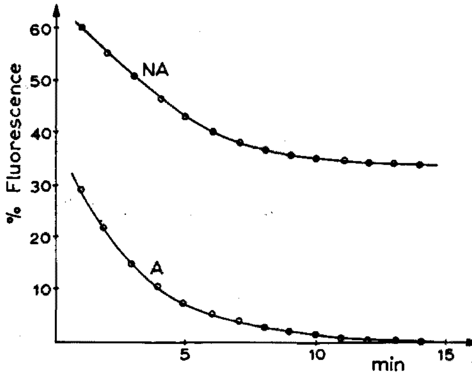


Fig. 3. Fluorescence as a function of pH for different oxidants.

Fig. 4. Influence of thioglycollic acid on the fluorescence of adrenaline and noradrenaline.



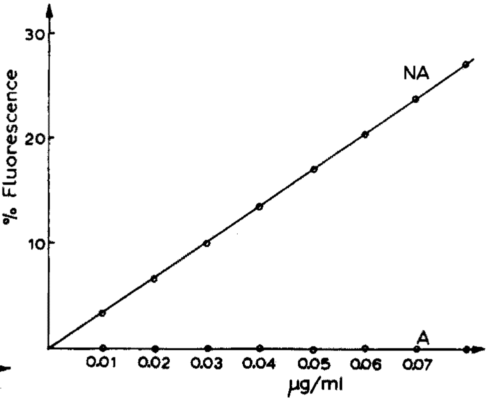


Fig. 5. Influence of the cysteine–thioglycollic acid–ethanol stabilizer on the fluorescence of adrenaline and noradrenaline.

Fig. 6. Fluorescence/concentration relation of both amines.

fluorescences for adrenaline and noradrenaline measured after 15 min as a function of concentration are given in Fig. 6.

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III). 0.25% in water.

0.5 M phosphate buffer, pH 7.0. Adjust a 1 *M* potassium dihydrogen phosphate solution to pH 7 by means of 1 *N* sodium hydroxide and dilute to 0.5 *M* with water.

Alkaline ascorbate. Prepare a mixture of 10 mg of ascorbic acid, 0.1 ml of water and 5 ml of 10 *N* sodium hydroxide fresh daily.

Cysteine–thioglycollic acid–ethanol mixture. Prepare a solution containing 1% cysteine, 0.01% (v/v) thioglycollic acid (80%) and 5% (v/v) ethanol in 10 *N* sodium hydroxide; prepare fresh daily and centrifuge before use.

Procedure

Determination of adrenaline + noradrenaline. To 0.2 ml of catecholamine solution in 0.01 *N* hydrochloric acid, add 0.017 ml of phosphate buffer pH 7 (resulting pH 6.8) and 0.02 ml of hexacyanoferrate(III) solution. After 1 min, add 0.2 ml of alkaline ascorbate and 0.5 ml of water. Shake and measure the fluorescence at excitation and fluorescence wavelengths of 409 nm and 520 nm respectively *versus* a blank solution obtained by omitting the hexacyanoferrate.

Determination of noradrenaline. Follow the above procedure but use the cysteine–thioglycollic acid–ethanol mixture instead of alkaline ascorbate as stabilizer and measure the fluorescence 15 min later.

Calculations

Noradrenaline. Assuming that the concentration of adrenaline is x_A, that of noradrenaline x_N and that of the internal standard of noradrenaline n, then:

$$x_A + x_N = X_1 \qquad x_A + x_N + n = X_2$$

As in this case the fluorescence is only due to noradrenaline, then

$$x_N = nX_1/(X_2 - X_1)$$

Adrenaline. If the fluorescence values are represented by Y and the concentration of the internal standard of adrenaline by a, then:

$$\begin{array}{ll} x_A + x_N = Y_1 & x_A + x_N = Y_1 \\ x_A + x_N + n = Y_2 & x_A + x_N + a = Y_3 \\ Y_2 - Y_1 = n & Y_3 - Y_1 = a \end{array}$$

The fluorescence due to x_A is equal to Y_1 from which has to be deduced the fluorescence due to x_N: $Y_1 - F(x_N)$. As x_A is given by:

$$x_A = a[Y_1 - F(x_N)]/(Y_3 - Y_1)$$

and $F(x_N)$ by:

$$F(x_N) = \frac{(Y_2 - Y_1)x_N}{n} = \frac{Y_2 - Y_1}{X_2 - X_1} \cdot X_1$$

substitution of this value gives the formula:

$$x_A = \frac{Y_1 - \{(Y_2 - Y_1)/(X_2 - X_1)\} \cdot X_1}{(Y_3 - Y_1)/a}$$

Table I shows the results of 3 different ratios of the two amines. In these experiments the values $a = n = 0.1$ μg were always maintained. The standard error (s) and standard deviation (σ_x) found for noradrenaline were respectively 0.007 μg and 0.003 μg on mixtures containing nominal quantities of 0.050 μg noradrenaline and 0.030 μg adrenaline.

TABLE I

DETERMINATION OF ADRENALINE AND NORADRENALINE

Concentration (µg/ml)	X_1	X_2	Y_1	Y_2	Y_3	x_N	x_A
N 0.050 A 0.030	15	47	23	47	60	0.047	0.031
N 0.030 A 0.080	10	42	37	62	73.5	0.031	0.080
N 0.080 A 0.020	24	54	26	51	60	0.080	0.018

SUMMARY

A simple, sensitive method for the differential fluorimetric determination of 0.01–1 μg/ml amounts of adrenaline and noradrenaline is proposed. Oxidation is best done with potassium hexacyanoferrate(III) at pH 6.8. The fluorescent derivatives of adrenaline and noradrenaline, and of noradrenaline alone, are stabilized respectively with alkaline ascorbate or with cysteine–thioglycollic acid mixture, and the fluorescence is measured at 409 and 520 nm respectively.

RÉSUMÉ

On propose une méthode simple et sensible pour le dosage fluorimétrique différentiel de l'adrénaline et de la noradrénaline (en quantités: 0.01–1 μg/ml). L'oxydation s'effectue à l'aide d'hexacyanoferrate(III) de potassium. Les dérivés fluorescents de l'adrénaline et de la noradrénaline sont stabilisés respectivement par un ascorbate alcalin ou par un mélange cystéine–acide thioglycolique. La fluorescence est mesurée respectivement à 409 et 520 nm.

ZUSAMMENFASSUNG

Eine einfache und empfindliche Methode zur differentiellen fluorimetrischen Bestimmung von 0.01–1 μg/ml Adrenalin und Noradrenalin wird vorgeschlagen. Die Oxydation geschieht am besten mit $K_3[Fe(CN)_6]$ bei pH 6. Nachdem die fluoreszierenden Derivate von Adrenalin und Noradrenalin sowie von Noradrenalin allein mittels basischer Ascorbat- bzw. Cystein-Thioglykolsäure stabilisiert worden sind, wird die Fluoreszenz bei 409 und 519 nm gemessen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CATION ANALYSIS BY THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY

PART II. THE DETERMINATION OF COPPER, NICKEL AND ZINC

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(Received July 15th, 1967)

Although reflectance spectroscopy has found some inorganic and physical applications[1-4], surprisingly little use has been made of the technique in the analysis of cations resolved by chromatographic procedures. Reliable methods have been devised for the determination by means of spectral reflectance of the components of mixtures of dyes[5] and of amino acids[6] resolved on thin-layer plates, and similar procedures have been applied successfully to the analysis of chemical species which absorb in the ultraviolet[7].

Numerous methods have been developed for the analysis of cations by means of thin-layer chromatography[8,9]. As with paper, quantitative techniques involve either a direct examination of the separated components, such as a comparison of the sizes of spots, or an elution of the resolved species from the substrate followed by the analysis of the eluant by some conventional means. Recently, FREI AND RYAN[10] employed the spectral reflectance technique to determine cobalt, nickel and copper following their separation on chromatoplates. Because the rubeanic acid employed as the chromogenic reagent is non-specific, however, use of this procedure is limited to systems where the opportunities for interference are minimal.

This difficulty can be avoided by a judicious selection of chromogenic reagents such that only the ion under investigation will react to form a colored product with a particular reagent. To determine the feasibility of such an approach in the analysis of mixtures of inorganic cations, it was decided to develop a procedure for the determination of copper, nickel and zinc, three ions which play an important role in various processes occurring in biological systems and natural waters.

EXPERIMENTAL

All reagents used were of analytical grade or comparable purity. Nitrate salts of the cations, Cu^{2+}, Ni^{2+} and Zn^{2+}, were used in the form of aqueous stock solutions and contained 3.177 g/l, 2.937 g/l and 3.269 g/l respectively of the metal. These stock solutions were applied as spots by means of a 10-μl Hamilton microsyringe.

A Desaga-Brinkmann Model SII applicator was employed to coat the 20 × 5 × 0.35 cm plates with a 17:3 water–MN-cellulose powder 300 (Macherey, Nagel and

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Co.; 516 Düren, Germany) mixture. The height of the applicator gate was set at 0.50 mm.

After the plates had been dried for 30 min at 75° in a mechanical convection oven, they were developed by the ascending technique with the use of a 1:3 12 *N* hydrochloric acid–1-butanol mixture until traces of iron found to be present in the adsorbent had been displaced to the top of the plate. These pretreated plates were then dried, spotted with test solution, dried again with compressed air, and developed as before with the hydrochloric acid–1-butanol mixture. The developed plates were dried for 30 min at 75°, sprayed with the appropriate chromogenic reagent or reagents, and again dried for 20 min at 75°.

Spray reagents employed consisted of 1 part of 29% ammonia to 9 parts of a 1% solution of dimethylglyoxime in 95% ethanol for nickel; a 1:2 mixture of 20% aqueous hydroxylamine hydrochloride and a saturated solution of neocuproine in absolute alcohol for copper; and a 1:5 mixture of a 1% aqueous solution of potassium ferricyanide and a saturated solution of 3,3′-dimethylnaphthidine in absolute alcohol for zinc. The dimethylglyoxime, neocuproine and 3,3′-dimethylnaphthidine were obtained from the J. T. Baker Chemical Co., K and K Laboratories, and the City Chemical Corp., respectively.

The resolved cations were identified by means of their reflectance spectra, which were recorded with the use of a Beckman Model DK-2 Spectrophotometer fitted with a standard reflectance attachment. Samples for this purpose were prepared by carefully excising spots from the developed plates and placing them in a windowless reflectance cell on top of *ca.* 40 mg of cellulose removed from the plate under examination.

A Beckman Model DU Spectrophotometer, similarly fitted with a reflectance attachment, was employed in the quantitative studies. In these studies, spots were removed from the developed plates along with enough adsorbent to make up an analytical sample weighing 40±0.1 mg. This sample was then ground in a small agate mortar for three sequences of 30 sec each to insure homogeneity and relatively uniform particle size. Between sequences the mixture was loosened from the body of the mortar with a spatula. The sample was then packed in the windowless cell mentioned above and its reflectance at the absorption maximum of the compound in question was measured. Except for the fact that the openings were only 16 mm in diameter, the reflectance cells employed in this study were identical with cells described earlier[11]. In all cases, reference standards consisting of adsorbent from the plate under investigation were prepared in the same manner as the analytical sample.

RESULTS AND DISCUSSION

Identification of the resolved cations

Excellent resolution was achieved with the use of the chromatographic procedure outlined above; R_F values of 0.09, 0.51 and 0.87 were obtained for the nickel, copper and zinc cations, respectively.

The chromogenic reagents employed were selected on the basis of the stability of the color generated by their application, their sensitivity, and their specificity for the cation in question. All three formed colored products which underwent no change with time when stored over calcium chloride out of direct light. Two of them, dimethylglyoxime for nickel[12] and neocuproine for copper[13,14], have found wide analytical application because of their high sensitivity. The zinc analysis was achieved by means of a modified turbidimetric procedure[15] which depends upon the oxidation by potassium ferricyanide of 3,3'-dimethylnaphthidine to give a blue-violet colored *p*-quinoidal diimine[16]. The intensity of the color of this product, which is adsorbed on the insoluble zinc ferrocyanide formed simultaneously, is such that it has been used as the basis for a method designed to detect microquantities of zinc[17]. In any event, the use of these 3 chromogenic reagents in the context of this research not only made it possible to detect amounts of nickel, copper and zinc as low as 0.014, 0.023 and 0.029 μg, respectively, but also resulted in the formation of adsorbed colored products whose reflectance spectra were unique enough to permit their ready identification. The spectra obtained (Fig. 1) had absorption maxima at 448 nm for copper, 540 nm for nickel, and 565 nm for zinc. The spectrum of the nickel–dimethylglyoxime complex adsorbed on the cellulose powder was identical with that obtained by VAECK[18] for the complex adsorbed on paper.

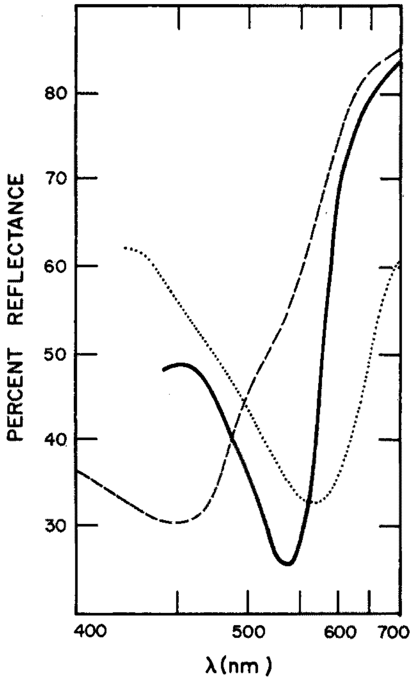

Fig. 1. Reflectance spectra obtained for 0.1 μg-at of copper (---), nickel (—) and zinc (...) cations adsorbed on cellulose and sprayed with the appropriate chromogenic reagent.

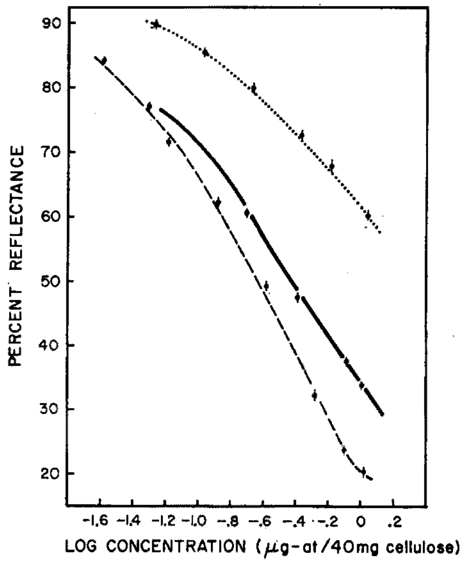

Fig. 2. Percent reflectance at the absorption maxima of the colored products formed by copper (---), nickel (——) and zinc (...) as a function of the logarithm of the concentration of the cations.

When the three chromogenic reagents were tested for selectivity, the results obtained (Table I) indicated the advantages afforded by the use of a specific rather than a nonspecific reagent in the analysis of cations resolved on thin-plates. Since only copper of the 13 cations tested gave a color reaction with neocuproine, use of this particular reagent involved no special precautions to avoid interferences. Dimethylglyoxime was almost as selective, forming a colored product only with cobalt and copper in addition to nickel. The migration rates of the cobalt and copper spots relative to the nickel spot are such, however, that not only does neither reaction represent a possibility of interference but both reactions can be prevented from taking place by the simple expedient of masking the chromatoplate appropriately while the chromogenic reagent is being applied. The 3,3′-dimethylnaphthidine, on the other hand, though the most suitable substance found for the zinc analysis, was the least selective of the 3 chromogenic reagents. Not only were colored products obtained with 9 other cations in addition to zinc, but the R_F values obtained for tin, cadmium and iron were such as to preclude the determination of zinc in mixtures containing any of these 3 cations. An even less desirable situation obtains when a less selective reagent such as rubeanic acid or dithizone is employed. Dithizone, for example, reacts to give a colored product with 11 of the cations listed in Table I. As a result, because of the overlapping that is experienced when relatively large amounts of the various cations are chromatographed, it is usually not only not possible with the use of dithizone to determine zinc in the presence of tin, cadmium and iron, but it is also not possible to determine copper in the presence of lead and bismuth, or nickel in the presence of silver and manganese. Another disadvantage that accrues to the use of dithizone as a chromogenic reagent is the decreased sensitivity that results from the color that it imparts to the adsorbent which is subsequently employed as a standard in the measurement of the reflectance of the analytical sample. 3,3′-Dimethylnaphthidine does not suffer from this drawback.

TABLE I

R_F VALUES AND COLOR REACTIONS OBTAINED FOR CATIONS ADSORBED ON MN-CELLULOSE

Cation	*R_F value*	*Color reactions*		
		Neocuproine	*Dimethylglyoxime*	*3,3′-Dimethylnaphthidine*
Silver	0.00	None	None	None
Aluminum	0.04	None	None	None
Chromium	0.07	None	None	None
Nickel	0.09	None	Red	Purple
Manganese(II)	0.16	None	None	Violet
Lead	0.30	None	None	Violet
Cobalt	0.41	None	Brown	Violet
Copper	0.51	Yellow	Brown	Violet
Bismuth	0.56	None	None	Violet
Tin	0.80	None	None	Violet
Zinc	0.87	None	None	Purple
Cadmium	0.90	None	None	Violet
Iron(III)	0.93	None	None	Violet

Although the above discussion pertains to resolutions achieved on cellulose plates, it is also possible to achieve similar results for the same cations separated on silica gel and alumina plates by modifying existing chromatographic procedures[10,19] appropriately. For example, using neocuproine as the chromogenic reagent and alumina plates, one can determine copper in the presence of the other 12 cations listed in Table I without encountering any difficulties. If the nonspecific dithizone is substituted for the neocuproine, however, it is not possible to determine copper in the presence of cobalt, mercury and zinc.

Determination of the resolved cations

Once a procedure had been arrived at for the location and identification of copper, nickel and zinc cations following their resolution on cellulose thin-plates, an effort was made to devise a method for their determination by the application of spectral reflectance. Calibration plots for the cations adsorbed on cellulose powder were prepared by applying different concentrations of each cation as spots to thin-layer plates, which were then developed, dried and readied for the measurement of reflectance according to the procedure outlined in the experimental section. When the percent reflectance at the absorption maxima for the different cations adsorbed on MN-cellulose was graphed as a function of the concentrations, the plots obtained for all 3 cations were the smooth curves usually encountered in reflectance work. Three such dilution series were run for copper, and 4 for nickel and zinc, at different times during this research. The average standard deviation observed in the readings obtained for any given concentration of any of the cations amounted to 0.23 reflectance unit. Since this approximates the maximum precision provided by the application of spectral reflectance to thin-layer chromatography[7], the preparation of a new calibration curve for each set of determinations appears to be unnecessary.

When the quantitative data are cast in the form percent reflectance *versus* the logarithm of concentration, as is done in Fig. 2, the optimum concentration range for maximum accuracy, which corresponds to the straight-line portion of the curve where the slope is greatest, is emphasized. By employing this slope in conjunction with the error expression $\%$ error $=2.303\ d(\log c)/dR$, it is also possible to estimate the percent error in the analysis that would derive from an error amounting to 1% R[20]. The optimum range and the probable percent error that were deduced in this manner for the analysis of copper, nickel and zinc adsorbed on cellulose are listed in Table II.

TABLE II

OPTIMUM RANGE AND PROBABLE ERROR IN THE DETERMINATION OF CATIONS ADSORBED ON MN-CELLULOSE

Cation	*Optimum range*		*% Analysis error/ error of 1%R*
	Reflectance (%R)	*Concentration (µg/40 mg adsorbent)*	
Copper	30–75	3.2–39.0	−5
Nickel	30–70	4.9–58.7	−7
Zinc	60–80	14.0–75.2	−8

The precision that can be attained when the above procedure is employed in the determination of copper, nickel and zinc was arrived at by running through the analyses with 5 replicate samples of each cation. As may be seen in Table III, the reflectance readings obtained for optimal concentrations of the various cations ad-

TABLE III

REPRODUCIBILITY OF % REFLECTANCE OBTAINED FOR REPLICATE SAMPLES OF CATIONS ADSORBED ON MN-CELLULOSE

Cation	*Concentration (μg)*	*Mean value (%R)*	*Standard deviation*
Copper	16	48.4	±0.56
Nickel	7	65.3	±0.30
Zinc	26	72.6	±0.70

sorbed on cellulose were found to have standard deviations ranging from 0.30 to 0.70 reflectance unit. If these data are used in conjunction with the analysis error data included in Table II, deviations of this order are found to correspond to deviations of 2.1, 2.8 and 5.6% in the determination of nickel, copper and zinc, respectively.

SUMMARY

A method has been developed whereby micro quantities of copper, nickel and zinc resolved on cellulose chromatoplates can be analyzed *in situ* by means of reflectance spectroscopy. Copper and nickel were determined in the presence of 11 other cations without any interference by employing neocuproine and dimethylglyoxime, respectively, as chromogenic reagents. In the case of zinc, the use of 3,3'-dimethylnaphthidine was equally successful except in the presence of tin, cadmium and iron. Deviations to be expected when the procedure is employed routinely to determine nickel, copper and zinc, were estimated to be 2.1, 2.8 and 5.6%, respectively.

RÉSUMÉ

Une méthode est proposée pour le microdosage de cuivre, nickel et zinc par chromatographie sur couche mince et spectroscopie par réflexion. On peut ainsi doser cuivre et nickel en présence de onze autres cations, sans interférence, en utilisant respectivement néocuprine et diméthylglyoxime, comme réactif chromogénique. Dans le cas du zinc, la 3,3'-diméthylnaphtidine donne de bons résultats sauf en présence d'étain, de cadmium et de fer. Les écarts sont estimés pour nickel, cuivre et zinc, à 2.1, 2.8, et 5.6%, respectivement, lorsque cette méthode est appliquée en série.

ZUSAMMENFASSUNG

Es wurde eine Methode entwickelt, bei der Mikromengen Kupfer, Nickel und Zink auf Zellulose-Chromatographierplatten an Ort und Stelle mit der Reflektionsspektroskopie analysiert werden können. Kupfer und Nickel wurden in Gegenwart von 11 anderen Kationen ohne Störungen mit Neocuproin bzw. Dimethylglyoxim bestimmt. Für das Zink erwies sich 3,3'-Dimethylnaphthidin als im gleichen Masse geeignet ausser in der Gegenwart von Zinn, Cadmium und Eisen. Bei der routinemässigen Bestimmung von Nickel, Kupfer und Zink wurden Abweichungen von 2.1, 2.8 bzw. 5.6% gefunden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XII*. ANODIC WAVES OF MONOALKYLDITHIOCARBAMATES AND THEIR REACTIONS WITH HEAVY METALS

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Analytical polarographic methods are commonly based on waves corresponding to reduction or oxidation of the electroactive particle, but anodic waves which correspond to the formation of a mercury compound at the surface of the dropping mercury electrode are also useful[1-3]. In connection with earlier work on the anodic waves of sulphur compounds[4] as well as studies on monothiocarbamates and dithiocarbamates[5] and with respect to the application of this group of compounds as pesticides[6], the polarographic behaviour of some monoalkyldithiocarbamates was studied. As in other practical applications of polarography, it is essential to elucidate the course of the electrode process, at least in principle, because only then is it possible to anticipate the role of other components of the supporting electrolyte. A fundamental study was very important in the present case, because the effects of adsorption and the composition of the compounds formed depend on the reaction medium. The types of process governing the various waves and the chemical reactions involved were therefore studied. As the anodic wave corresponds to a chemical reaction between a particular form of the dithiocarbamate and mercury ions, it was of interest to compare information on the structure of the mercury compound from polarographic data with that obtained for reactions with heavy metals.

Reports on the polarography of monoalkyldithiocarbamates are rather limited in number and scope; only dithiocarbamates derived from amino acids have been studied[7,8]. At high pH values, the compounds give a single wave, which is split into two waves below pH 10. Based only on logarithmic analysis of these waves it was assumed[7,8] that the anodic wave corresponds to a one-electron process. Some of the features of the polarographic waves of monoalkyldithiocarbamates and the possibility of using these waves for analytical purposes have been indicated in a preliminary report[9].

EXPERIMENTAL

Apparatus

Polarographic curves were recorded using a Polariter PO4 (Radiometer,

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* Part XI: *Collection Czech. Chem. Commun.*, 22 (1957) 929.

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Copenhagen) in conjunction with a Kalousek vessel with a saturated calomel electrode. The dropping electrode used had the following characteristics: out-flow velocity $m = 1.59$ mg sec^{-1}, drop-time $t_1 = 3.6$ sec at the potential of the saturated calomel electrode and at a mercury pressure $h = 68$ cm in 0.1 M potassium chloride.

Controlled-potential electrolysis was carried out with a dropping mercury electrode in 0.5–2.0 ml of solution stirred by the falling drops. A vessel designed by MANOUŠEK[10] with a reference electrode separated by sintered glass and an agar bridge saturated with potassium nitrate and with a device to keep the level of the fallen mercury constant was used. The potential during electrolysis was kept constant manually, by means of a potentiometer.

A Unicam SP 800 spectrophotometer was used to record the spectra. A Pye-Dynacap pH meter was used with a glass electrode to measure pH. The pH values of the solutions were checked after the polarographic electrolysis had been carried out.

Chemicals

Monoalkyldithiocarbamates I–III (R-NHCSS$^{(-)}$ Na$^+$; I, R=$C_2H_5^-$; II, R=CH_3^-; III, R=$C_4H_9^-$) were prepared by the following procedure.

To 0.1 mole of the appropriate amine was added 6 g of sodium hydroxide (0.15 mole) dissolved in the minimum amount of water. The reaction mixture was cooled and 7 ml of carbon disulphide (0.11 mole) was added slowly. The solution was heated under vacuum to remove most of the water. Acetone was added to extract the dithiocarbamate. To the filtered acetone extract, ether was added to crystallize out the dithiocarbamate, which was then filtered off, redissolved in acetone or ethanol and again precipitated with ether.

These compounds decompose slowly on standing and re-crystallisation was necessary once a fortnight. The water of crystallisation was determined by loss of weight at 78° *in vacuo*. Each compound was a dihydrate. Melting points were: I, 99°; II, 88°; III, 64–66° (decomp.), uncorrected.

Aqueous 0.01 M stock solutions of sodium monoalkyldithiocarbamates made up in distilled water, borate buffer (pH 9.3) or 0.01 M sodium hydroxide showed about 10% decomposition after storage at 2° for 3 days. This reaction proceeded especially quickly in 0.01 M sodium hydroxide solution where a white precipitate was formed, probably a disulphide resulting from autoxidation. Hence, small quantities of stock solution in distilled water were prepared daily.

Buffer solutions and all other supporting electrolytes were prepared from AnalaR-grade chemicals.

Experimental techniques

In polarographic studies, 10 ml of the buffer or other supporting electrolyte was deoxygenated by a stream of nitrogen, then the appropriate volume (usually 0.5 ml) of the stock solution was added, and, after a brief flush with nitrogen, the current–voltage curve was recorded.

For logarithmic analysis, polarographic curves were recorded automatically at a slow rate of scanning (100 mV/min) to reduce the effects of hysteresis of the recording instrument.

To study the reaction of dithiocarbamates with metal ions, various amounts of a stock solution (0.004 M) of the metal salt were successively added to buffered

$4.85 \cdot 10^{-4}$ M dithiocarbamate solutions and the i–E curves were recorded after each addition.

For the millicoulometric determination of the number of electrons transferred (n), 0.5–2.0 ml of the solution of the examined compound in a suitable supporting electrolyte was transferred to the cell[10] and the capillary was positioned so that its tip was just under the surface of the solution. The solution was deoxygenated, the i–E curve recorded and a potential (usually corresponding to the limiting current) selected. The solution was discarded and replaced by the same quantity of a fresh solution. A voltage corresponding to the chosen potential was taken off the potentiometer and the change of current with time at this potential was recorded at a slow chart speed. After 10–20% conversion had been achieved by electrolysis (which required 30–60 min), the electrolysed solution was replaced by the supporting electrolyte alone, in which the condenser current was recorded in order to correct the measured limiting current.

The logarithm of the current was plotted as a function of time and from the slope (d log$i$/dt) of the resulting straight line the value of n was calculated from:

$$n = \{4.5 \cdot 10^{-9}\ (i_d)_0\} / \{cv\ (\mathrm{d} \log i/\mathrm{d}t)\}$$

where $(i_d)_0$ is the limiting current at $t = 0$, c the molar concentration and v the volume (in ml). The method was tested by determining n for thallium(I) and cadmium(II). The average reproducibility was better than ±5%.

For the identification of the electrolysis products the same basic procedure was followed, but instead of the continuous i–t record, polarographic i–E curves were recorded at intervals. After electrolysis for 24 h, polarographic curves and U.V. spectra were recorded.

RESULTS

Polarographic behaviour

Because the polarographic behaviour of all straight-chain monoalkyldithiocarbamates studied was found to be similar, it was considered appropriate to choose monoethyldithiocarbamate (I) as a representative compound for a more detailed study.

Effect of pH. The ethyl derivative (I) shows in hydroxide solutions one well-developed anodic wave (i) (Fig. 1). At concentrations above $6 \cdot 10^{-4}$ M this is accompanied by an adsorption pre-wave i_A (Fig. 2) at a potential only slightly different from wave i. Below pH 11 the wave i is accompanied by another adsorption pre-wave i_a which is observed at concentrations greater than $1 \cdot 10^{-4}$ M. Above pH 11 this pre-wave merges with the wave i. Below pH 8, the main wave (i) is split into two waves ($[i_1 + i_a]$ and i_2), the ratio of which remains constant and is practically 1:1. The sum of the waves ($i_1 + i_2$) is constant over the entire pH range studied and is equal to the height of the wave i in hydroxide solutions. In acidic solutions the more positive wave i_2 is indistinct because of its closeness to the current corresponding to the dissolution of the mercury in the supporting electrolyte. Wave i_2 is also complicated by adsorption effects.

The separation of waves i_1 and i_2 is best understood from the pH-dependence of the half-wave potentials (Fig. 3). The half-wave potential of wave i_2 shifts with

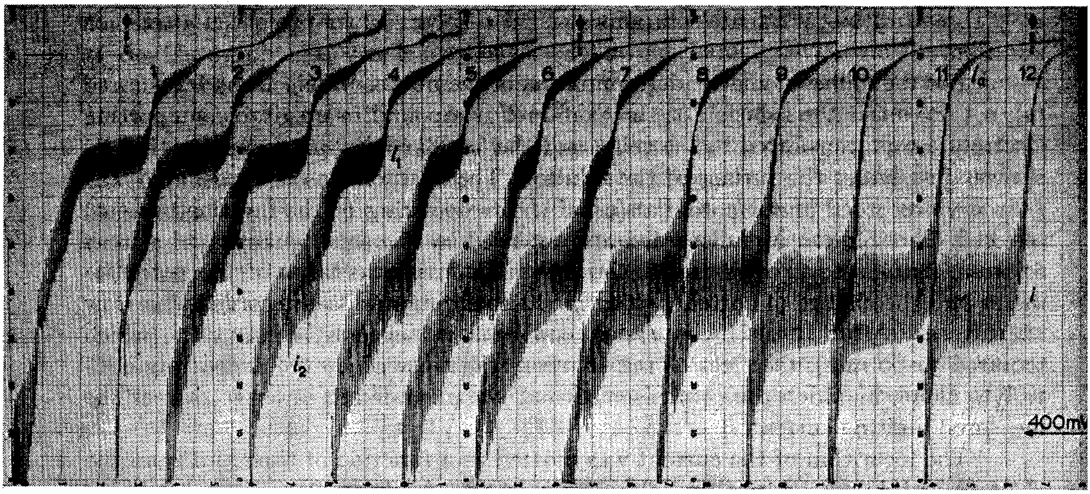


Fig. 1. The effect of pH on the waves of sodium ethyldithiocarbamate. $5 \cdot 10^{-4}$ M sodium ethyldithiocarbamate, Britton–Robinson buffers (pH shown on polarogram). Curves recorded from -1.0 V towards more positive potentials, $h = 68$ cm.

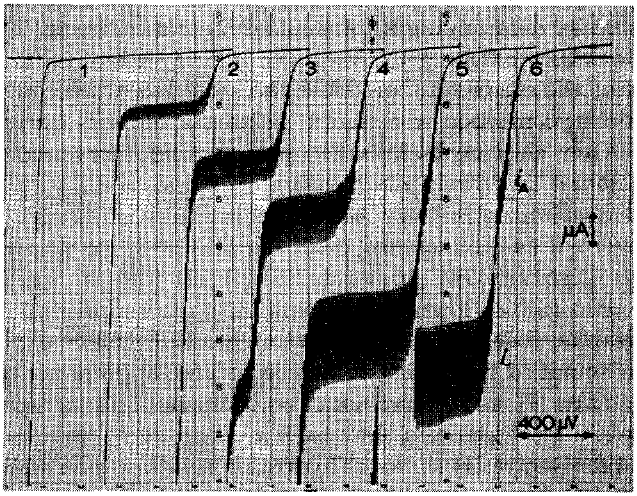


Fig. 2. The effect of concentration on the waves of sodium ethyldithiocarbamate. 0.1 M NaOH concentration of sodium ethyldithiocarbamate: (1) 0; (2) 2.0; (3) 3.9; (4) 5.8; (5) 9.9; (6) 11.5 ($\cdot 10^{-4}$ M). Curves recorded from -1.0 V towards more positive potentials, $h = 50$ cm.

increasing pH towards more negative potentials with a slope of 0.067 mV/pH, whereas that of wave i_1 remains practically constant. When the half-wave potential of wave i_2 approaches -0.3 V at which wave i_1 appears, both waves merge into wave i, the half-wave potential of which is shifted by 0.057 mV/pH to more negative potentials in a similar manner to wave i_2. The half-wave potential of wave i_a changes with pH only below pH 3 (Fig. 3), and at higher pH values is practically pH-independent. This causes waves i_a and i to merge above pH 11. A difference in shifts of half-wave potential can also explain why the wave i_A is not separated from the total wave i below pH 13.

Whereas the height of the adsorption pre-wave i_a increases with increasing concentration only up to about $1 \cdot 10^{-4}$ *M* and then becomes constant, the sum of (i_a+i_1) and of $(i_a+i_1+i_2)$ are both linearly proportional to concentration (Fig. 4a) up to a concentration at $8 \cdot 10^{-4}$ *M*; this was proved in acetate buffer, pH 4.7, and phosphate buffer, pH 6.9.

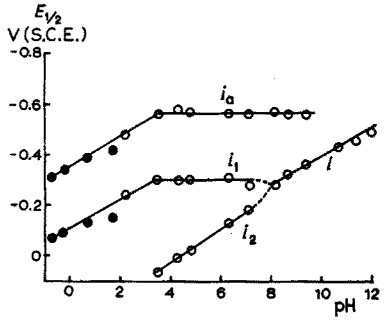


Fig. 3. The pH dependence of the half-wave potentials of the waves of sodium ethyldithiocarbamate. ○ = Britton–Robinson buffers (see Fig. 1). ● = H_2SO_4 solutions.

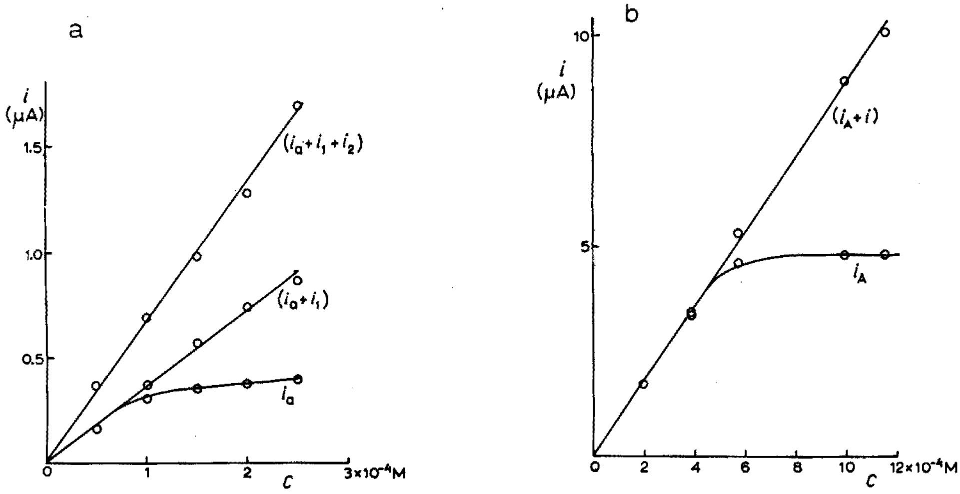


Fig. 4. The dependence of the height of the waves of ethyldithiocarbamate on concentration. (a) Phosphate buffer pH 6.9, (b) 0.1 *M* NaOH.

The height of wave i_A limits at about $6 \cdot 10^{-4}$ *M* (Fig. 4b) whereas the total height of waves i_A+i in 0.1 *M* sodium hydroxide solution is a linear function of concentration of ethyl derivative I up to $1.2 \cdot 10^{-3}$ *M*.

The half-wave potential of the wave i is shifted to more positive values with increasing concentration of the dithiocarbamate I. A similar direction of shifts was observed for other compounds[3] forming slightly soluble mercury compounds.

With increasing concentration of dithiocarbamate a decrease of the anodic current due to reaction of hydroxyl ions with mercury was observed. In 0.1 *M* sodium hydroxide solution, $5.8 \cdot 10^{-4}$ *M* in dithiocarbamate I (curve 4, Fig. 2), the hydroxyl wave is similar in height to wave i_1; at still higher concentrations of the ethyl derivative (I) no wave for hydroxyl ions was observed (Fig. 5). In 0.01 M sodium hydroxide solution the hydroxyl ion wave disappears at a lower dithiocarbamate concentration.

Logarithmic analysis of the wave of I in $5 \cdot 10^{-4}$ M solution in a Britton–Robinson buffer (pH 10.8) gave a reasonably straight line for the plot of $\log[(i_d - i)/i]$ against potential, with a slope of -0.050 V.

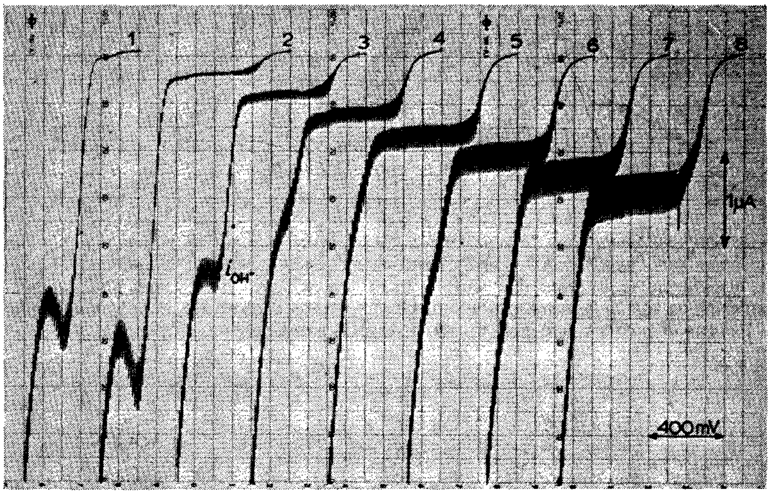


Fig. 5. The effect of the presence of ethyldithiocarbamate on the anodic wave due to hydroxide ions. 10 ml 0.1 M NaOH. Concentration of ethyldithiocarbamate: (1) 0; (2) 1.0; (3) 2.0; (4) 2.9; (5) 3.8; (6) 4.8; (7) 5.7; (8) 6.6 ($\cdot 10^{-4}$ M). Curves recorded from -0.7 V towards more positive potentials (except curve 1; from -0.3 V), $h = 50$ cm.

The effect of adsorption on the wave i_a was proved at concentrations greater than $2 \cdot 10^{-4}$ M by the linear proportionality of the wave height (i_a) to the height of the mercury column. The linear dependence of ($i_a + i_1$) and ($i_a + i_1 + i_2$) on the square root of the height of the mercury column indicates that these processes are diffusion-controlled.

No reduction waves were obtained over the whole pH range (0–13) studied. Below pH 7 a shift of the current corresponding to hydrogen evolution from the buffer towards more positive potentials indicated that catalytic hydrogen evolution was taking place. However, this current was not separated from the current of the supporting electrolyte and no developed reduction wave was observed in any of the solutions studied.

Number of electrons transferred. Comparison of the anodic waves with waves of benzophenone and of nitrobenzene at pH 9.2 (borate buffer) indicated that the wave i in alkaline solutions corresponds to a two-electron process and that the waves i_1 and i_2 at lower pH values correspond to two successive one-electron uptakes. A comparison of the heights of the waves of compounds I and II with the waves of diethyldithiocarbamate in $1.95 \cdot 10^{-4}$ M solutions at pH 9.2 showed ratios of 1.97 and 2.22 respectively. As the total height of the waves of diethyldithiocarbamate corresponds to a one-electron process[11], the transfer of two electrons for monoalkyldithiocarbamates was verified.

Millicoulometrically a value of $n=1.87$ was found with a $5 \cdot 10^{-4}$ *M* solution of the *n*-butyl derivative (III) in an acetate buffer (pH 5.7) and $n=1.89$ with a $1 \cdot 10^{-3}$ *M* solution of compound III in a phosphate buffer (pH 6.9). The millicoulometric determination of *n* at high pH values was prevented by the consecutive reaction of the electrolysis product (p. 466). The values found at the limiting current of wave i_1 were $n=0.70$ at $5 \cdot 10^{-4}$ *M* in an acetate buffer (pH 4.7) and $n=0.91$ at $1 \cdot 10^{-3}$ *M* in a phosphate buffer (pH 6.9).

Structural effects. The behaviour of the methyl (II) and butyl (III) derivatives was completely analogous to that of ethyldithiocarbamate (I). The presence of waves i_a, i_1, i_2 and i was proved in all cases. The character of the adsorption pre-waves was analogous, the ratio $(i_a+i_1):i_2$ remaining practically 1:1 in all cases. The structural changes in this limited group had little effect on the half-wave potential. In 0.1 *M* sodium hydroxide solution the approximate values of the half-wave potentials (-0.47 V for methyl (II), -0.49 V for ethyl (I) and -0.50 V for *n*-butyl (III) dithiocarbamate, all *vs.* S.C.E.) are in sequence and show the differences that would correspond to a modified Taft equation $\Delta E_{\frac{1}{2}}=\varrho_{\pi,R}^* \sigma_X^*$ for reaction constant $\varrho^* \approx 0.2$ V. It is interesting that even in this case—as for some other anodic processes—the value of the reaction constant is positive.

Controlled-potential electrolysis

Controlled-potential electrolysis of solutions of compound III at the potential of the limiting currents of waves i_1 or i_2 at lower pH values resulted in a regular decrease of the limiting current with time during the electrolysis. No precipitate was observed when the electrolysis was carried out at the limiting current of wave i_1.

On the contrary, in 0.1 *M* sodium hydroxide solution, when electrolysis was

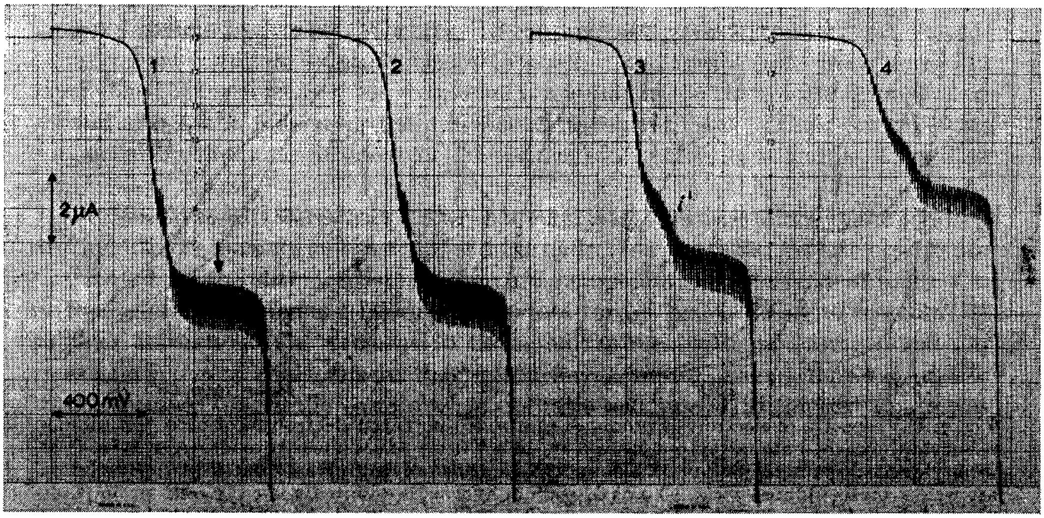


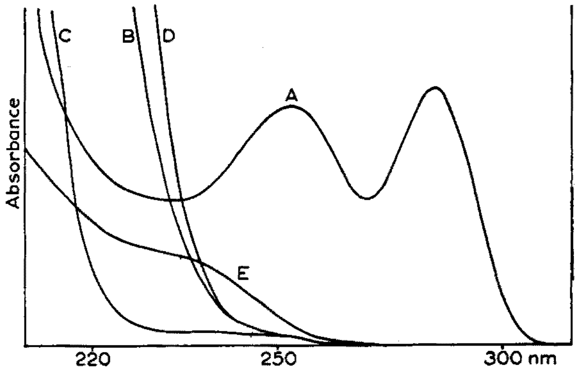
Fig. 6. Change of polarographic curves with time during controlled-potential electrolysis of sodium *n*-butyldithiocarbamate ($1 \cdot 10^{-3}$ *M*) in 0.1 *M* NaOH. Volume of solution = 2.0 ml; time of the start of recording of the curve: (1) 0; (2) 55 min; (3) 7 h 25 min; (4) 17 h. Applied potential = -0.3 V corresponds to the limiting current (arrow). Curves recorded from -1.0 V towards more positive potentials.

carried out at the potential corresponding to the limiting current of wave *i* of compound III, the height of wave *i* remained practically constant for several hours and only then decreased (Fig. 6). During the electrolysis, a new wave *i'* appeared at a potential about 0.15 V more positive than wave *i*. The relative height of this wave increased during the electrolysis (compare curves 3 and 4, Fig. 6). A solution of the butyl derivative (III) kept under the same conditions, but without applying the potential, showed that cleavage of III by a chemical reaction in the bulk of solution during electrolysis was insignificant. A black precipitate formed during the electrolysis was proved to be mercury sulphide by the action of acid. The electrolysed solution liberated the characteristic odour of an isothiocyanate.

In the solution after electrolysis for 24 h, where the total height of the waves was still about 20% of the original height, no ultraviolet bands due to dithiocarbamate were observed (Fig. 7). Calculation has shown that 1% of the original amount of compound (III) would still be apparent from the U.V. spectrum.

The "end absorption" of the electrolysed solution at 228 nm (curve B, Fig. 7) was shifted compared with sodium hydroxide (215 nm, curve C, Fig. 7). Similar end absorption was observed in the presence of carbonate (curve D, Fig. 7). When the electrolysed solution was acidified the end absorption was shifted to a shorter wavelength and a band at 240 nm was apparent (curve E, Fig. 7). Similarly, during electrolysis in a borate buffer (pH 9.2) a black precipitate was formed and a shoulder was present in the U.V. spectrum at 240 nm. Formation of carbon disulphide was demonstrated by the presence of a small band at 320 nm and of a polarographic reduction wave at -1.1 V, which diminished after bubbling nitrogen through the solution.

Reactions with metal ions. Addition of cadmium ions to the solution of sodium ethyldithiocarbamate (I) in 0.1 *M* sodium hydroxide solution resulted in a decrease



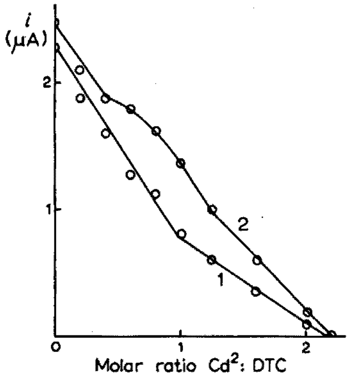


Fig. 7. U.V. spectra of electrolysis products. Controlled-potential electrolysis of $1 \cdot 10^{-3}$ *M* sodium *n*-butyldithiocarbamate carried out for 24 h at -0.3 V in 0.1 *M* sodium hydroxide. (A) $1.25 \cdot 10^{-4}$ *M* *n*-butyldithiocarbamate in 0.012 *M* sodium hydroxide before electrolysis (diluted 8 ×); (B) solution after electrolysis (diluted 2 ×); (C) 0.05 *M* sodium hydroxide (diluted 2 ×); (D) soln. as in (C) in presence of sodium carbonate; (E) soln. as in (B) acidified by hydrochloric acid.

Fig. 8. Addition of a solution of cadmium ions to sodium ethyldithiocarbamate. To 10 ml of $5 \cdot 10^{-4}$ *M* sodium ethyldithiocarbamate in 0.1 *M* sodium hydroxide $4 \cdot 10^{-3}$ *M* cadmium sulphate was successively added. Currents corrected for dilution. (1) Height of anodic wave (*i*) of dithiocarbamate; (2) total height of anodic waves.

of the anodic wave of ethyldithiocarbamate. A white precipitate appeared initially, but when the ratio of cadmium(II):dithiocarbamate exceeded 1:2, the precipitate turned yellow if the pH of the reaction mixture was sufficiently high. Simultaneously a new, small anodic wave formed at more positive potentials (at about −0.3 V). When the ratio of cadmium(II):dithiocarbamate reached 1:1, the slope of the dependence of the first wave on cadmium concentration changed (Fig. 8). With further increases in cadmium concentration the total height of the anodic waves decreased and the anodic waves vanished when the concentration ratio was about 2 Cd^{2+}:1 dithiocarbamate. No cathodic waves corresponding to soluble complexes were observed.

This behaviour can be tentatively explained by the assumption that the white precipitate initially formed is the compound $Cd(dithiocarbamate)_2$. The yellow precipitate is attributed to cadmium sulphide, formed from the compound $Cd(dithiocarbamate)_2$ and further cadmium ions. It is assumed that in this reaction the ethylmonothiocarbamate ion is formed, which is responsible for the formation of the anodic wave[12] at −0.3 V. Further addition of cadmium ions results in the cleavage of the monothiocarbamate with further formation of cadmium sulphide.

This interpretation seems to be confirmed by the result of a large-scale experiment, which showed that $5 \cdot 10^{-5}$ moles of sodium ethyldithiocarbamate react with $1.1 \cdot 10^{-4}$ moles of cadmium ions. In this reaction the formation of $0.94 \cdot 10^{-4}$ moles of cadmium sulphide was proved gravimetrically. This yellow precipitate, when decomposed by hydrochloric acid, liberated hydrogen sulphide. In the solution thus formed, $1.01 \cdot 10^{-4}$ *M* cadmium(II) was found polarographically. The other reaction products were not identified.

In attempts to isolate the product assumed to be the 1:1 complex, the existence of which was indicated by the intersection in Fig. 7, solutions of cadmium(II) ($1 \cdot 10^{-3}$ moles) and dithiocarbamate ($1 \cdot 10^{-3}$ moles) were reacted in the presence of $2 \cdot 10^{-3}$ moles of sodium hydroxide. When the white precipitate was extracted with chloroform, yellow cadmium sulphide began to precipitate rapidly from the chloroform layer. The U.V. spectrum of the compound remaining in the chloroform layer showed a band at 235 nm, indicating the presence of isothiocyanates[13]. Their presence was supported by the pungent odour of the residue after chloroform had been distilled off.

Similar results were observed when mercury(II) ions were added to the solution of ethyldithiocarbamate ions in 0.1 *M* sodium hydroxide solutions. A white precipitate (attributed to the dithiocarbamate-mercury compound) was formed initially. On further addition of mercury(II) this precipitate turned black, owing to mercury(II) sulphide formation. The decrease in the anodic waves with increasing metal ion concentration was analogous to that found for cadmium, except that the anodic wave decreased practically to zero when the ratio mercury(II):dithiocarbamate was about 3:2.

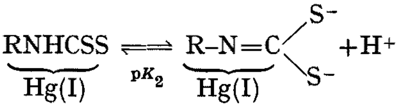
Somewhat different results were observed when lead ions were added to a solution of ethyldithiocarbamate in a borate buffer (pH 9.3). A white precipitate was formed and the anodic wave of ethyldithiocarbamate decreased practically to zero when the ratio of lead(II):dithiocarbamate reached 1:2. The composition of the white precipitate is therefore $Pb(dithiocarbamate)_2$. Addition of further lead ions slowly turned the precipitate black.

DISCUSSION

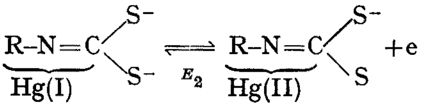
The two one-electron diffusion-controlled processes corresponding to waves i_1 and i_2 can be formulated by scheme (A)–(D):

$$\underbrace{\text{RNHCSS}^-}_{\text{H}^+} \underset{pK_1}{\rightleftharpoons} \text{RNHCSS}^- + \text{H}^+ \tag{A}$$

$$\text{RNHCSS}^- + \text{Hg} \underset{E_1}{\rightleftharpoons} \underbrace{\text{RNHCSS}}_{\text{Hg(I)}} + \text{e} \tag{B}$$



(C)



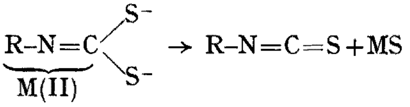
(D)

The wave i_1 at potential E_1 corresponds to processes (A) and (B), and wave i_2 at potential E_2 to processes (C) and (D). The shift of the half-wave potential of wave i_1 indicates that the value of pK_1 for the ethyl derivative I is about 3.5. This is in good agreement with the pK value of 3.10 for monocyclohexyl and 2.95 for isopropyl dithiocarbamates obtained[5] from kinetic data. The pH independence of the half-wave potential of wave i_1 above pH 4 indicates that the electroactive form is identical with the form of dithiocarbamate predominating in the solution.

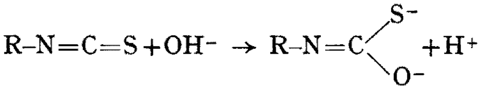
The shift of the potential of wave i_2 indicates that the value of pK_2 is greater than 12. This is consistent with the alkaline decomposition of monoalkyldithiocarbamates. It is assumed[14] that this reaction takes place with the formation of R–N=CSS^{2-}, and that it can be observed only at pH about 14. The pK_a value of the uncomplexed species RNHCSS^- is therefore greater than 14. Even when a shift toward smaller pK_a values can be expected for the complex species in reaction (C), the effect seemingly is not sufficient to shift it below 12. The slopes of the pH dependences of the half-wave potentials of wave i_1 below pH 3 and of wave i_2 over the whole pH range are consistent with the values expected for a reversible one-electron process accompanied by a transfer of one proton.

The electrode reactions (A) and (B) corresponding to wave i_1 are analogous to the reaction of metal salts with monoalkyldithiocarbamates at lower pH values, as was shown for the reaction of lead ions in a borate buffer. Even though the participation of the nitrogen atom in the mercury bonding cannot be excluded, the bond to two sulphur atoms can be considered as more probable.

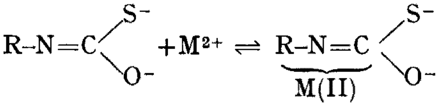
The actual form of the mercury compound resulting in reaction (D) is not known. The experimental results nevertheless indicate that the compound formed is unstable and undergoes further changes in alkaline media. A possible decomposition scheme for a complex of a metal (M) can be formulated as follows:



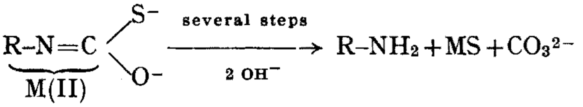
$$\underbrace{\text{R–N=C}}_{\text{M(II)}}\begin{matrix}\diagup S^- \\ \diagdown S^-\end{matrix} \rightarrow \text{R–N=C=S} + \text{MS} \tag{E}$$



$$\text{R–N=C=S} + \text{OH}^- \rightarrow \text{R–N=C}\begin{matrix}\diagup S^- \\ \diagdown O^-\end{matrix} + \text{H}^+ \tag{F}$$



$$\text{R–N=C}\begin{matrix}\diagup S^- \\ \diagdown O^-\end{matrix} + \text{M}^{2+} \rightleftharpoons \underbrace{\text{R–N=C}}_{\text{M(II)}}\begin{matrix}\diagup S^- \\ \diagdown O^-\end{matrix} \tag{G}$$



$$\underbrace{\text{R–N=C}}_{\text{M(II)}}\begin{matrix}\diagup S^- \\ \diagdown O^-\end{matrix} \xrightarrow[\text{2 OH}^-]{\text{several steps}} \text{R–NH}_2 + \text{MS} + \text{CO}_3{}^{2-} \tag{H}$$

The formation of metal sulphides, isothiocyanates and carbonates as predicted by this scheme was proved.

The scheme (A)–(F) explains the behaviour in controlled-potential electrolysis of derivative I in 0.1 M sodium hydroxide solution. The delay in the decrease of the limiting current can be explained by the cleavage of the electrolytically formed complex $[\text{RNCSS}^{2-}]\text{M(II)}$ according to reactions (E) and (F). In the latter, monoalkyl monothiocarbamate is formed. This compound is known to give anodic waves[12]; these waves will resemble, both in their heights and potentials, the waves of monoalkyldithiocarbamates and hence it would not be surprising if in a mixture of mono- and dithiocarbamates, one wave is formed. During the initial stages of electrolysis the rate of formation of the monothiocarbamate is just sufficient to supply enough depolariser to keep the limiting current practically unchanged. As the conversion of dithiocarbamate into monothiocarbamate becomes more complete, the anodic wave decreases. The rate of the interposed chemical reaction (F) governs the rate of the controlled-potential electrolysis.

Reaction (F), as was shown previously[15], is first order in hydroxyl ions. Hence at lower pH values (pH 6.9) the regeneration of an electroactive species (with similar electrochemical properties to the original compound) cannot affect the controlled-potential electrolysis, which therefore follows a simple course.

The actual course of the decomposition may be more complex than shown in reactions (E)–(H). This is indicated by the formation of carbon disulphide during electrolysis at pH 9.2. It was also not established whether the two waves observed during electrolysis in 0.1 M sodium hydroxide (Fig. 6) both belong to the monothiocarbamate or if one belongs to another intermediate.

It was necessary to exclude the possibility that the wave i_2 corresponds to mercury sulphide formation rather than to a reaction of RN=CSS^{2-}. Comparison of the half-wave potentials of wave i_2 with that of sulphide ions indicates that the sulphide wave is 150 mV more negative. Moreover, the sulphide wave[16] shows a markedly different pH dependence of half-wave potentials to wave i_2. Furthermore, the formation of the white precipitate attributed to [RNCSS]M(II) (even when isolation was impossible) indicated that reaction (E) and the subsequent reactions may be fast, but, under the conditions studied, not so fast as to convert the primary product formed after the transfer of the second electron into sulphide ion during the drop-life. Hence the process differs from that observed recently[17] for thiourea in acidic solution.

The anodic waves of monoalkyldithiocarbamates corresponding to a two-electron over-all process differ in principle from the vast majority of organic sulphur compounds, which give one-electron anodic waves[1-3]. Among other exceptions the waves of thiourea[18-20] and of thiobenzamide[21] can be mentioned. In the latter case benzonitrile, mercury(II) sulphide and some benzamide were isolated from the controlled-potential electrolysis products.

For a two-electron process at potential E_2, it is possible, apart from the scheme (A)–(D) corresponding to a system of consecutive reactions, to devise another scheme, in which the reaction at potential E_2 would be competitive with that depicted in equations (A) and (B). Such a scheme would involve the formation of mercury(II) and reaction with the anion of dithiocarbamate. The change in the wave-height i_2 during controlled-potential electrolysis at the limiting current of i_1 cannot be used here as a diagnostic tool[22] because the formation of a slightly soluble salt such as the product of (B) will result in a decrease of wave i_2 for both competitive and consecutive reactions. On the other hand, a competitive process requires that the same species reacts with uni- and bivalent mercury ions. This in turn would indicate the same shape of the pH-dependence of the half-wave potentials. The different shape of this dependence for waves i_1 and i_2 indicates that a competitive process, at least of the considered type, is less probable than the consecutive process (A)–(D).

Two types of adsorption processes affect the polarographic curves. Wave i_a, with a limiting current value of about 0.4 μA, corresponds to a surface covered by a single molecule of about 50–100 Å^2 (depending on the composition of the compound). Wave i_A, observed in sodium hydroxide solution, reaches a limiting value of 5 μA and corresponds to a surface of 5–10 Å^2 per molecule. If the composition of the mercury compound remains the same, it can be concluded that either the wave i_a corresponds to a monolayer and i_A to a multilayer formation or, perhaps more probably, the wave i_a corresponds to a film in which the molecules are oriented flat at the surface and the wave i_A to a film in which they are perpendicular and only "anchored" by the functional grouping. Such an observation has been made and a similar interpretation offered for waves of other sulphur compounds[22-26]. The effect of wave (i_A+i) on the waves of hydroxyl ions (Figs. 2 and 5) indicates that the film of mercury compounds with alkyldithiocarbamates in alkaline media is difficult to penetrate.

Because the results obtained for monoalkyldithiocarbamates are in good general agreement with those reported[7,8] for dithiocarbamoyl carboxylic acid, it seems that the observed behaviour is characteristic for a wide range of compounds with the grouping $-NHCSS^-$.

The authors thank Professor R. Belcher for his interest. D. J. H. thanks Professor M. Stacey for the provision of a research grant and P.Z. the Science Research Council for a provision of a Senior Visiting Fellowship.

SUMMARY

Monoalkyldithiocarbamates give two anodic polarographic waves, corresponding to a one-electron and a two-electron process. A reaction scheme is proposed. The unusual behaviour observed during controlled-potential electrolysis in sodium hydroxide media is interpreted as a chemical reaction of the primary electrolysis product; the species formed gives a wave similar to the original compound. Different adsorption phenomena are probably caused by varying orientation of the mercury compound on the electrode surface. The adsorbed layer formed in sodium hydroxide solution is so close-packed that it prevents hydroxyl ions from penetrating and thus giving an anodic wave. For analytical purposes, 0.1 *M* sodium hydroxide is the most suitable supporting electrolyte; linear calibration graphs can be obtained over the range $5 \cdot 10^{-5}$–$1 \cdot 10^{-3}$ *M*.

RÉSUMÉ

Les monoalkyldithiocarbamates donnent deux vagues polarographiques anodiques, correspondant à un et à deux électrons. Un schéma de la réaction est proposé. Le comportement observé au cours de l'électrolyse à potentiel contrôlé en milieu hydroxyde de sodium est interprété: réaction chimique du produit d'électrolyse primaire. Divers phénomènes d'adsorption sont probablement causés par une orientation variable du composé de mercure sur la surface de l'électrode. La couche adsorbée formée dans la solution d'hydroxyde de sodium est si compacte qu'elle empêche la pénétration des ions hydroxyles et fournit ainsi une onde anodique. Pour l'analyse, l'hydroxyde de sodium 0.1 *N* est l'électrolyte de base qui convient le mieux. Des graphiques linéaires de calibrage sont obtenus de $5 \cdot 10^{-5}$ à $1 \cdot 10^{-3}$ *M*.

ZUSAMMENFASSUNG

Monoalkyldithiocarbamate ergeben zwei anodische polarographische Stufen, welche einem Einelektronen- und einem Zweielektronenprozess entsprechen. Ein Reaktionschema wird vorgeschlagen. Das Verhalten, welches man während der Elektrolyse mit kontrolliertem Potential im Natriumhydroxid-Medium beobachtet, wird mit Hilfe einer chemischen Reaktion des primären Elektrolyseproduktes interpretiert. Die gebildeten Spezies ergeben eine Stufe, die der der ursprünglichen Verbindung ähnlich ist. Unterschiede in Adsorptionsphänomena können durch variierende Orientierung der Quecksilberverbindung auf der Elektrodenoberfläche erklärt werden. Die adsorbierte Schicht welche in Natriumhydroxidlösung gebildet wird, is so dicht, dass sie ein Eindringen der Hydroxylionen verhindert und so ihre anodische Stufe unterdrückt. Für analytische Zwecke ist 0.1 *M* NaOH der am meisten geeignete Grundelektrolyt. Lineare Eichkurven können im Bereich von $5 \cdot 10^{-5}$ bis $1 \cdot 10^{-3}$ *M* erhalten werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE CALCULATION OF INDICATOR ERROR IN OXIDATION–REDUCTION TITRATIONS

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(Received August 1st, 1967)

The proper choice of an indicator for a titration can be made most reliably by examining the error obtained when a given indicator is used. If this indicator error (often referred to as "titration error") is fairly low, the indicator is suitable for the titration in question. Standard texts of titrimetric analysis[1,2] and chemical indicators[3] devote separate chapters to the problem of indicator error and a monograph was published some 30 years ago[4], dealing quite extensively with this question. In these and other texts, one can find precise, quantitative derivations for indicator errors in acid–base, precipitation and complexation titrations, but only brief references are made to oxidation–reduction titrations, without any quantitative treatment at all. This probably arose because few reversible oxidation–reduction indicators were available when the texts were written. Nowadays, when there is a large choice of oxidation–reduction indicators, the problem of indicator error needs to be examined more quantitatively.

The indicator error arises because the colour change of the indicator does not occur at the equivalence-point potential of the titration in question, *i.e.*, the *equivalence-point potential* (E_{equ}) and the *end-point potential* (E_{end}) are not the same. The amount of titrant needed to shift the potential of the system from the end-point potential to the equivalence-point potential is a measure of the (absolute) titration error. This error, depending on the nature of the titration, might be either positive or negative.

In the derivations given below, it is assumed that both the reactant and titrant, as well as the indicator systems are thermodynamically reversible, thus their potentials can be described by the Nernst equation as follows:

$$E_r = E_r{}^0 + \frac{0.06}{N_r} \log \frac{[\text{Ox}_r]}{[\text{Red}_r]}$$

$$E_t = E_t{}^0 + \frac{0.06}{N_t} \log \frac{[\text{Ox}_t]}{[\text{Red}_t]}$$

and

$$E_i = E_i{}^0 + \frac{0.06}{N_i} \log \frac{[\text{Ox}_i]}{[\text{Red}_i]}$$

where the symbols *r*, *t* and *i* refer to the reactant, titrant and indicator systems respectively, and the E^0 values are the formal oxidation–reduction potentials of the systems involved. Note that the concentrations [Ox] and [Red] refer to the unhydrated ions (*e.g.* Mn^{7+} and Mn^{2+}); these very often are replaced by others (*e.g.* MnO_4^-) with the

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assumption of the occurrence of a hydration equilibrium (*e.g.* $Mn^{7+} + 4H_2O \rightleftarrows MnO_4^- + 8H^+$), and as a result of this the hydrogen ion concentration at the appropriate power is included into the argument of the logarithm, while (logarithms of) water concentration and equilibrium constant are included into the formal potential. For the sake of simplicity, the above equations are used in the deductions. This is, in fact, a correct procedure because oxidation–reduction titrations are generally carried out at a constant pH, when (the logarithm of) the hydrogen ion concentration, as another constant, can also be included into the value of formal potential. The value of the latter at the given pH has to be taken when calculations are made.

As mentioned above, the indicator error arises because the values of end-point potential (E_{end}) and equivalence-point potential (E_{equ}) are not identical. The equivalence-point potential can be calculated from the following expression[5,6]

$$E_{\mathrm{equ}} = (N_r E_r^0 + N_t E_t^0)/(N_r + N_t) \qquad \text{(in V)}$$

and depends entirely on the characteristics of the reactant and titrant systems. Here N_r and N_t are the numbers of electrons taking part in the corresponding electrode reactions (otherwise, the stoichiometric numbers, by which the titration reaction is expressed, are not explicitly included). The end-point potential depends on the characteristics of the indicator and can be expressed as

$$E_{\mathrm{end}} = E_i^0 \pm 0.06/N_i \qquad \text{(in V)}$$

Note that in the above equation the sign is negative for an oxidimetric titration but positive for a reductimetric titration.

A closer examination of the question of indicator error shows that different considerations must be applied for oxidimetric ($E_t^0 > E_r^0$) and reductimetric ($E_t^0 < E_r^0$) processes, and even the relative positions of end-point and equivalence-point potentials ($E_{\mathrm{end}} > E_{\mathrm{equ}}$ or $E_{\mathrm{end}} < E_{\mathrm{equ}}$) will influence the deduction process. There are four possible combinations of these cases; one combination is considered in detail below while the results of the other three are simply tabulated.

It is customary to deduce two types of formulae for the indicator error[1,2]. The *precise* expression is generally rather complicated, and in some cases it is necessary to use this. An *approximate* expression might be easier to handle. For the derivation of the precise expression, the fact that the reactions lead to an equilibrium is taken into consideration, *i.e.* the small, but finite equilibrium concentration of the reactant at the equivalence point is not regarded as "untitrated" substance, and is therefore not included in the expression. The simpler expression is derived on the simple assumption that at the equivalence point the concentrations of both the reagent and titrant ion are negligible. Results of calculations show that the differences between the two values are negligible if the error itself is rather high (over 1%), but higher if the error itself is low (under 0.05%). But, even in the latter case the magnitude of the result is the same. Since indicator errors of this magnitude are really more or less negligible, in fact the use of the approximate expressions does not lead to false conclusions if the application or rejection of a given indicator has to be decided.

Let us consider a reductimetric titration ($E_r^0 > E_t^0$), where the oxidized form of the reactant is titrated with the reduced form of the titrant. The reaction equation in almost all cases can be expressed as

$$N_t \mathrm{Ox}_r + N_r \mathrm{Red}_t \rightarrow N_r \mathrm{Ox}_t + N_t \mathrm{Red}_r$$

(If the stoichiometry is other than this, *i.e.* there is a change of mole numbers in the redox half-cell reactions in question, which is very seldom the case, the final expressions are slightly modified, but can be easily obtained by a similar deduction to the one which follows.) It is assumed that the end-point precedes the equivalence point ($E_{\text{end}} > E_{\text{equ}}$ for reductimetric titrations), *i.e.* some of the Ox_r remain untitrated.

PRECISE EXPRESSION

The absolute error is equal to the concentration of the untitrated $[\text{Ox}_r]$ in the solution at the end-point. This is equal to the actual concentration at the end-point minus the equilibrium concentration at the equivalence point:

$$[\text{Ox}_{r\ \text{end}}]-[\text{Ox}_{r\ \text{equ}}]$$

For practical purposes, the value of the relative error is more telling than that of the absolute error. To obtain this, the absolute error must be divided by the total concentration of the reactant. This can be expressed in many ways. The most convenient form is to use the concentration of the reduced form of the reactant which has been built up during the course of the titration. The value either at the end-point or at the equivalence point can be used, if they agree within say 10%. Thus, it can be assumed that

$$[\text{Red}_{r\ \text{end}}]=[\text{Red}_{r\ \text{equ}}]=[\text{Red}_r]$$

and $[\text{Red}_r]$ can be used for both the end-point and the equivalence-point value. Thus the percentage relative error will be

$$\Delta\% = 100\,\frac{[\text{Ox}_{r\ \text{end}}]-[\text{Ox}_{r\ \text{equ}}]}{[\text{Red}_r]} = 100\,\frac{[\text{Ox}_{r\ \text{end}}]}{[\text{Red}_r]} - \frac{[\text{Ox}_{r\ \text{equ}}]}{[\text{Red}_r]}$$

The potential-controlling system in this case is the reactant system; thus, the end-point potential and equivalence-point potentials can be expressed as

$$E_{\text{end}} = E_r{}^0 + \frac{0.06}{N_r}\log\frac{[\text{Ox}_{r\ \text{end}}]}{[\text{Red}_r]}$$

and

$$E_{\text{equ}} = E_r{}^0 + \frac{0.06}{N_r}\log\frac{[\text{Ox}_{r\ \text{equ}}]}{[\text{Red}_r]}$$

If these are rearranged, then:

$$\frac{[\text{Ox}_{r\ \text{end}}]}{[\text{Red}_r]} = 10^{N_r(E_{\text{end}}-E_r{}^0)/0.06}$$

and

$$\frac{[\text{Ox}_{r\ \text{equ}}]}{[\text{Red}_r]} = 10^{N_r(E_{\text{equ}}-E_r{}^0)/0.06}$$

From these, the percentage relative error can be expressed:

$$\Delta\% = 100\,\{10^{N_r(E_{\text{end}}-E_r{}^0)/0.06} - 10^{N_r(E_{\text{equ}}-E_r{}^0)/0.06}\} =$$

$$100\,\frac{10^{N_rE_{\text{end}}/0.06} - 10^{N_rE_{\text{equ}}/0.06}}{10^{N_rE_r{}^0/0.06}}$$

TABLE I

EXPRESSIONS OF THE PRECISE VALUE OF PERCENTAGE (RELATIVE) INDICATOR ERROR ($\Delta\%$)

Type of titration / *Titration finished*	*Reductimetric* $E_r^0 > E_t^0$	*Oxidimetric* $E_t^0 > E_r^0$
Before the equivalence point	$E_{\mathrm{end}} > E_{\mathrm{equ}}$ $100\,\dfrac{10^{N_rE_{\mathrm{end}}/0.06} - 10^{N_rE_{\mathrm{equ}}/0.06}}{10^{N_rE_r^0/0.06}}$	$E_{\mathrm{equ}} > E_{\mathrm{end}}$ $100\,\dfrac{10^{-N_rE_{\mathrm{end}}/0.06} - 10^{-N_rE_{\mathrm{equ}}/0.06}}{10^{-N_rE_r^0/0.06}}$
After the equivalence point	$E_{\mathrm{equ}} > E_{\mathrm{end}}$ $100\,\dfrac{10^{-N_tE_{\mathrm{end}}/0.06} - 10^{-N_tE_{\mathrm{equ}}/0.06}}{10^{N_tE_t^0/0.06}}$	$E_{\mathrm{end}} > E_{\mathrm{equ}}$ $100\,\dfrac{10^{N_tE_{\mathrm{end}}/0.06} - 10^{N_tE_{\mathrm{equ}}/0.06}}{10^{N_tE_t^0/0.06}}$

Analogous expressions can be obtained by similar treatment for the other possible variations. These expressions are shown in Table I.

APPROXIMATE EXPRESSION

For the approximate expression it is assumed that there is no measurable concentration of the (oxidized form of the) reactant at the equivalence point in the solution. Thus, the absolute error is equal to the concentration of the reactant at the end-point: $[\mathrm{Ox}_{r\ \mathrm{end}}]$, and the relative error is $[\mathrm{Ox}_{r\ \mathrm{end}}]/[\mathrm{Red}_r]$.
Since

$$E_{\mathrm{end}} = E_r^0 + \frac{0.06}{N_r} \log \frac{[\mathrm{Ox}_{r\ \mathrm{end}}]}{[\mathrm{Red}_r]}$$

by rearrangement it is possible to obtain:

$$\Delta\% = 100 \times 10^{N_r(E_{\mathrm{end}} - E_r^0)/0.06}$$

Similar expressions obtainable for other cases are summarized in Table II.

EXAMPLES

These calculations have been used to find a suitable indicator for titrations of oxidizing and reducing agents with ascorbic acid via the hexacyanoferrate(III)–hexacyanoferrate(II) system[7-9]. The choice lay between variamine blue and 2,6-dichlorophenolindophenol.

(*1*) What is the indicator error if hexacyanoferrate(III) ions are titrated with ascorbic acid at pH 6, using variamine blue indicator? The following data are obtainable from the literature[10].

$$N_r = 1;\ E_r^0 = +0.44\ \mathrm{V};\ N_t = 2;\ E_t^0 = +0.10\ \mathrm{V};\ E_{\mathrm{end}} = 0.35\ \mathrm{V}.$$

TABLE II

EXPRESSIONS OF THE APPROXIMATE VALUE OF PERCENTAGE (RELATIVE) INDICATOR ERROR ($\Delta\%$)

Type of titration *Titration finished*	*Reductimetric* $E_r^0 > E_t^0$	*Oxidimetric* $E_t^0 > E_r^0$
Before the equivalence point	$E_{\mathrm{end}} > E_{\mathrm{equ}}$ $100 \times 10^{N_r(E_{\mathrm{end}}-E_r{}^0)/0.06}$	$E_{\mathrm{equ}} > E_{\mathrm{end}}$ $100 \times 10^{-N_r(E_{\mathrm{end}}-E_r{}^0)/0.06}$
After the equivalence point	$E_{\mathrm{equ}} > E_{\mathrm{end}}$ $100 \times 10^{-N_t(E_{\mathrm{end}}-E_t{}^0)/0.06}$	$E_{\mathrm{end}} > E_{\mathrm{equ}}$ $100 \times 10^{N_t(E_{\mathrm{end}}-E_t{}^0)/0.06}$

The equivalence-point potential:

$$E_{\mathrm{equ}} = \frac{0.44+2\times 0.10}{3} = 0.213\ \mathrm{V}$$

The indicator error with the *precise expression*:

$$\Delta\% = 100\,\frac{10^{0.35/0.06} - 10^{0.213/0.06}}{10^{0.44/0.06}} = 100\,\frac{691800-3631}{21880000} = 3.1\%$$

The same result is obtained when the *approximate expression* is used.

$$\Delta\% = 100 \times 10^{(0.35-0.44)/0.06} = 100 \times 0.031 = 3.1\%$$

Thus, the indicator error is rather high, and variamine blue is not suitable for indication. At higher pH values the indicator error would be lower, but pH 6 is the highest value at which variamine blue can be practically used.

(2) The indicator error can be calculated, if hexacyanoferrate(III) ions are titrated with ascorbic acid in the presence of 2,6-dichlorophenolindophenol indicator; in this case the titration can be made at pH 7. The following data are obtainable[10]: $N_r=1$; $E_r^0= +0.44$ V; $N_t=2$; $E_t^0= +0.07$ V; $E_{\mathrm{end}}=0.22$ V. The equivalence-point potential is

$$E_{\mathrm{equ}} = \frac{0.44+2\times 0.07}{3} = 0.19\ \mathrm{V}$$

The indicator error with the *precise expression*:

$$\Delta\% = 100\,\frac{10^{0.22/0.06} - 10^{0.19/0.06}}{10^{0.44/0.06}} = 100\,\frac{4677-1419}{21880000} = 0.0146\%$$

The *approximate expression* leads to a different result:

$$\Delta\% = 100 \times 10^{(0.22-0.44)/0.06} = 100 \times 0.000213 = 0.021\%$$

The magnitude of these results is, however, the same, and both are very low, which shows that the indicator error is really negligible.

It should be noted that the calculation of the values of the type 10^x is very simple and is based on the relationship:

$$\log_{10} 10^x = x \text{ (by definition)}$$

Thus, one calculates x (the exponent), and reads the antilog from tables or a slide rule.

SUMMARY

Both precise and approximate expressions are derived for the indicator error in oxidation–reduction titrations. Examples are given of the use of these expressions for the choice of the best indicator in titrations with ascorbic acid.

RÉSUMÉ

On a calculé l'erreur due à l'indicateur dans les titrages d'oxydo–réduction. Des expressions sont données permettant de choisir l'indicateur le meilleur pour le titrage de l'acide ascorbique.

ZUSAMMENFASSUNG

Für die Berechnung des Indikatorfehlers bei Redoxtitrationen werden sowohl genaue als auch Näherungsausdrücke abgeleitet. Für die Verwendung dieser Ausdrücke zur Wahl des besten Indikators für die Titration mit Ascorbinsäure werden Beispiele angegeben.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CHELATING RESINS FOR THE CONCENTRATION OF TRACE ELEMENTS FROM SEA WATER AND THEIR ANALYTICAL USE IN CONJUNCTION WITH ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received October 16th, 1967)

Ordinary anion and cation exchangers are of very limited use for the analytical concentration of trace elements from sea water. Only lithium can usefully be concentrated by cation exchange[1,2], and only zinc, cadmium, bismuth, gold(III) and thallium(III) are amenable to concentration by anion exchange as their chloroanions[3,4]. The recent advent of commercial chelating resins, mainly based on iminodiacetic acid-substituted cross-linked polystyrene, makes it possible to concentrate trace elements from sea water and separate them from the major components. Most of the published work on these resins has been directed towards their physical chemistry[5,6] and little has so far appeared on their use in analytical chemistry. The uptake of a number of elements such as Cu, Fe(III), Zn, Cd, Ni, Co and Zn from distilled water has been studied by a number of workers[7,8], and IMOTO[9] has used a chelating resin in the determination of manganese in a concentrated brine. KUEHN AND HERING[10] have claimed that they were able to reduce the concentrations of Mn, Fe, Zn, Al, Ti, Cd, Co, Ni, Cu, Ag, Ta, Bi, Ba, Sc and Mg in sodium chloride below the limits of spectrographic detection by use of a similar resin. However, it is unlikely that the resins could be used to separate the trace elements from one another[11]. The present paper describes an investigation of the efficiency with which various trace elements can be concentrated from sea water by means of such resins, and the subsequent determination of a number of them by atomic absorption spectrophotometry.

EXPERIMENTAL

Two different resins, both of the iminodiacetic acid type, were used in this investigation.

(1) Chelex-100 (Bio Rad Laboratories, Richmond, California) with a particle size range of 50–100 mesh. This is a purified form of Dowex A-1 resin; it was found that the two resins behaved identically. The resin is stable under both acid and alkaline conditions, but changes its particle size very markedly as its counter-ion is changed. This swelling and contraction caused difficulty in maintaining a reasonable flow rate through columns. This difficulty was greatly accentuated when attempts were made to use resin of finer mesh size (100–200). Columns were packed freshly before use. The flow rate was not allowed to exceed 5 ml/min since the exchange rate of the resin was rather slow.

(2) Permutit S1005 (an experimental resin kindly supplied by the Permutit Company, Ltd.) with a mesh size of 10–20. This resin did not change its dimensions as the counter-ion was changed. It had a rapid exchange rate, and flow rates of up to 10 ml/min could be used. However, the resin was not as stable chemically as the Chelex resin, and this limited the strength of the eluting agents that could be used with it to nitric acid normalities of less than 5 *N* and to ammonia strengths of less than 4 *N*.

The resins in their hydrogen form, were packed into 12-mm diameter glass tubes to give a column length of 6 cm. Aliquots (1 l) of 0.5 μ membrane-filtered sea water were spiked with *ca.* 1 μC of radio-isotopes of the appropriate trace element (generally in carrier-free condition, and if not, containing less than 0.5 μg/μC of carrier). For elements, for which suitable radio-isotopes were not available (Al, Ni, Cu, Mo, V, U, Th, Re and P) the sea water aliquots were spiked with microgram amounts of the natural form of the element. The spiked samples were adjusted to a pH value of 7.6 (or any other desired value) and allowed to pass through the columns at a suitable flow rate. The columns were then washed with 20 ml of water. The washings and percolate were combined and analyzed for the trace element, either radiochemically or photometrically, as appropriate, in order to determine its retention. The columns were then eluted with successive 5-ml volumes of 2 *N* acids or 4 *N* ammonia in order to recover the trace element from the resin. The recovery of the trace element was again assessed radiochemically or photometrically.

RESULTS

The results of experiments using Chelex 100 are shown in Table I. In general, the Permutit S1005 resin gave similar results, except that manganese was only retained with 60% efficiency at the optimum pH of 9.0 on the S1005 resin, whereas it was completely retained by the Chelex resin at this pH value.

The resins can only be used for the uptake of trace elements from sea water and non-saline waters over a restricted range of pH values. The lower limit is pH 5.0, below which uptake falls off rapidly. The upper limit for sea water is set by the precipitation of calcium and magnesium which commences at *ca.* pH 9.1. Many of the trace elements examined were taken up efficiently from sea water at its natural pH (7.7–8.2). However, molybdenum, tungsten, vanadium and rhenium could only be chelated quantitatively at pH 5–6. Bismuth, manganese, indium, yttrium and the rare earths were retained most effectively at pH 9.0. Caesium, uranium(VI), phosphorus (PO_4^{3-}) and arsenic (AsO_4^{3-}) were not taken up at all in the pH range tested. The readily hydrolyzable elements iron, chromium, aluminium, tin and titanium were adsorbed either with low efficiency, or not at all, probably because of hydrolysis.

Nitric acid (25 ml of 2*N*) proved to be the most generally useful reagent for removing cationic species from the resins, and has the advantage that it is easy to remove subsequently. However, it was not very effective for the elution of either bismuth or thorium, and these elements were most satisfactorily eluted with 20 ml of 2 *N* perchloric acid and 20 ml of 2 *N* sulphuric acid respectively. Cobalt was not removed at all by 2 *N* nitric acid but could be completely eluted with 20 ml of 2 *N* hydrochloric acid. Ammonia (10 ml of 4 *N*)was an efficient eluting agent for vanadium(V), molybdenum(VI), tungsten(VI) and rhenium(VII), which were scarcely eluted at all with acid reagents. Silver, mercury, chromium and tin were very strongly retained

TABLE I

DATA ON ADSORPTION AND ELUTION OF TRACE ELEMENTS FROM SEA WATER WITH CHELEX-100 (50–100 MESH) AND 20 ml OF ELUTING AGENT

	pH for adsorption	*Retention* (%)	*Eluant*	*Total recovery* (%)
Aluminium	7.6	0	—	0
Arsenic (AsO_4^{3-})	7.6	0	—	0
Barium	5.0[a]	25	2 N HNO_3	25
Bismuth	9.0[a]	100	2 N $HClO_4$	100
Cadmium	7.6	100	2 N HNO_3	100
Caesium	7.6	0	—	0
Cerium (Ce^{3+})	9.0[a]	100	2 N HNO_3	100
Chromium (Cr^{3+})	5.0[a]	25	2 N HNO_3	10[b]
Cobalt	7.6	100	2 N HCl	100
Copper	7.6	100	2 N HNO_3	100
Indium	9.0[a]	100	2 N HNO_3	100
Lead	7.6	100	2 N HNO_3	100
Manganese	9.0[a]	100	2 N HNO_3	100
Mercury (Hg^{2+})	7.6	85	2 N HNO_3	40[b]
Molybdenum (MoO_4^{2-})	5.0[a]	100	4 N NH_4OH	100
Nickel	7.6	100	2 N HNO_3	100
Phosphorus (PO_4^{3-})	7.6	0	—	0
Rhenium (ReO_4^-)	7.6	90	4 N NH_4OH	90
Scandium	7.6	100	2 N HNO_3	100
Selenium (SeO_4^{2-})	7.6	0	—	0
Silver	7.6	100	2 N HNO_3	90[b]
Thallium (Tl^+)	7.6[a]	50	2 N HNO_3	50
Thorium	7.6	100	2 N H_2SO_4	100
Tin (Sn^{4+})	7.6	85	2 N HNO_3	60[b]
Tungsten (WO_4^{2-})	6.0[a]	100	4 N NH_4OH	100
Uranium (UO_2^{2+})	7.6	0	—	0
Vanadium (VO_3^-)	6.0[a]	100	4 N NH_4OH	100
Yttrium	9.0[a]	100	2 N HNO_3	100
Zinc	7.6	100	2 N HNO_3	100

[a] Optimum pH value.
[b] Maximum percentage removable from resin.

by the resin and no reagent was found which would elute them completely. Complete (99–100%) recoveries of Bi, Cd, Co, Cu, In, Mn, Mo, Ni, Pb, Re, Sc, Th, W, V, Y, Zn and the rare earth elements could thus be obtained at their natural concentrations from sea water when Chelex-100 was used. Their separation from the major cations of sea water is satisfactory since both the acid and the ammonia eluates on evaporation yield only comparatively small residues. Thus, the 30-ml 2 N nitric acid and the 20-ml 4 N ammonia eluates were found to contain 80 and 1.8 mg Na, 1 and 0.3 mg K, 2.3 and 0.2 mg Ca, and 0.3 and 0.02 mg Mg respectively.

The chelating resins thus provide a convenient technique for the analytical concentration of many of the more interesting trace elements from sea water and other natural waters. After concentration, the elements can be determined by sensitive physico-chemical methods, such as spectrophotometry, flame photometry, polarography or neutron activation.

The chelating ion-exchange concentration procedure can be used to concentrate trace elements from much larger volumes of sea water than can be conveniently handled by solvent extraction. This is a particular advantage where the concentration of the element sought is very low, or where the sensitivity of the method available for its determination is poor. The use of the concentration technique, in conjunction with atomic absorption spectrophotometry, for the determination of zinc, cadmium, copper, nickel and cobalt in sea water is described below. Analogous techniques could be developed for the estimation of other trace elements such as vanadium, manganese and molybdenum.

In addition to their analytical application, it was thought that the resins might be of use for the preparation of sea water free from biologically essential trace metals for work with marine organisms. However, it was found that sea water which had been passed through columns of the resins and then enriched with chelated trace metals would not support the growth of even hardy species of phytoplankton, presumably because it contained toxic materials dissolved from the resin.

DETERMINATION OF COPPER, ZINC, CADMIUM, NICKEL AND COBALT IN SEA WATER

Despite its advantages of specificity and high sensitivity, atomic absorption spectrophotometry does not seem to have been much used for the determination of trace metals, occurring in sea water at concentrations below 10 μg/l. The claim of FABRICAND *et al.*[12] to have been able to estimate manganese, iron, copper, nickel and zinc must be treated with reserve, in view of the fact that the sensitivity which they found is *ca.* 100 times that attained by other workers using this technique. It is thus probable that it is necessary to concentrate trace elements from sea water before they can be determined in this way. For this purpose BURRELL[13] has used coprecipitation with iron(III) hydroxide. BROOKS *et al.*[14] have concentrated copper *ca.* 100 fold from sea water by extracting it with methyl isobutyl ketone after reaction with ammonium pyrrolidine dithiocarbamate. The organic extract was sprayed into the flame of an atomic absorption spectrophotometer; this increased the sensitivity for copper *ca.* 4½ times over that obtainable by spraying an aqueous solution. Unfortunately, the sensitivity of this type of technique is limited by the fact that it is not feasible to increase the ratio of the volume of sea water to that of solvent to more than 100:1. Many of the biologically important trace elements occur in ocean waters at concentrations below 0.5 μg/l, which are too low to be determined accurately by this method. If chelating ion exchange is used for the preliminary concentration, there is no limit, within reason, to the volume of sample which can be used. With a 10-l sample it is simple to obtain a 2000-fold enrichment of a number of trace metals and subsequently to determine them consecutively by atomic absorption spectrophotometry.

The elements copper, nickel, cobalt, zinc and cadmium were selected for investigation since they are retained quantitatively by Chelex-100 and can be readily eluted completely. In order to enhance the sensitivity of the procedure it was thought desirable to evaporate the eluate to dryness and to dissolve the trace metals in an organic solvent before determining them by atomic absorption spectrophotometry. After comparison of the sensitivity enhancement obtained with a number of different solvent systems, 90% acetone, 0.01 *N* with respect to nitric acid was chosen. With this solvent, sensitivities (compared with aqueous solutions) were increased by 3, 2, 4, 4 and 3 times for Co, Cd, Cu, Zn and Ni respectively. Linear relationships were found between flame absorbance and concentration up to at least 8 μg/ml.

Equipment

A Techtron AA4 atomic absorption spectrophotometer with digital output was used in the experimental work. Running conditions of the hollow-cathode lamps were those recommended by the manufacturers. The burner was run on coal gas–air and the optimum operating conditions were found empirically for each element.

All glass and silica apparatus should be allowed to stand overnight filled with a 1:1 mixture (by volume) of concentrated nitric and sulphuric acids.

Ion-exchange column

Digest Chelex-100 ion-exchange resin (50–100 mesh) 3 times at room temperature with excess 2 *N* nitric acid. Wash the resin thoroughly with redistilled water and fill a 1.2-cm diameter exchange column to a depth of 6 cm with it. After use wash the resin with 200 ml of redistilled water to prepare it for use again.

Reagents

Distilled water and nitric acid should be redistilled through a silica still. Acetone should be redistilled in an all-glass apparatus.

Standard solutions

Dissolve 1.00 g each of copper, nickel, cobalt, zinc and cadmium in a slight excess of an appropriate acid and dilute each solution to 1 l. Dilute 10-ml aliquots of these solutions to 100 ml with acetone. The resultant solutions contain 100 μg of the element/ml; use them to prepare working standards containing 1.0–5.0 μg of the metals/10 ml, each solution being 90% with respect to acetone.

Determination of trace elements in sea water

Filter sea water samples through a 0.5-μ membrane filter and allow 10-l aliquots to pass through the column of Chelex-100; the flow rate should not exceed 300 ml/h. If only zinc, copper and nickel are to be determined, 1-l aliquots are sufficient. Wash the column with 250 ml of water and reject the washings. Elute copper, nickel, zinc and cadmium with 30 ml of 2 *N* nitric acid and then elute cobalt with 20 ml of 2 *N* hydrochloric acid. Place the eluates in 50-ml silica conical flasks, cover with silica bubble stoppers and evaporate to dryness on a hot plate at low temperature. Add to each flask, by means of a pipette, 1 ml of 0.1 *N* nitric acid and when the residue has dissolved add 9 ml of acetone. Determine copper, nickel, cadmium and cobalt in the appropriate solution using the atomic absorption spectrophotometer and the resonance lines at wavelengths of 3247, 2318, 2287 and 2406 Å respectively. Dilute 1 ml of the acetone solution from the 2 *N* nitric acid eluate to 5 ml with 90% aqueous acetone and use the resultant solution for the determination of zinc using the 2137 Å zinc resonance line. Determine the reagent blank for the method in the same manner using sea water which has been stripped of trace elements by passage through a column of Chelex-100. Calibrate the instrument in the range 0.5–2.5 μg with standard solutions of the elements in 90% acetone; 90% acetone is used as a blank for the calibration.

Results

In order to evaluate the precision of the method, replicate analyses (4) were carried out for all 5 trace elements on sea water from the Menai Straits. These showed the presence of 4.86±0.06 µg Cu/l; 4.1±0.1 µg Ni/l; 3.88±0.03 µg Zn/l; 0.060±0.001 µg Cd/l and 0.12±0.01 µg Co/l. In order to check the accuracy of the procedure, trace elements were stripped from a large volume of sea water by passage through a 10 × 2 cm column of Chelex-100. Aliquots (10 l or 1 l) of this water were spiked with known amounts of copper, zinc, cadmium, nickel and cobalt and analysed. The results of these experiments (Table II) show that recoveries of added trace metals, at levels approximating to their sea water concentrations, are satisfactory.

TABLE II

RECOVERY OF TRACE ELEMENTS FROM SPIKED SAMPLES OF STRIPPED SEA WATER

Vol. of sample (l)	*Zinc (µg)*		*Copper (µg)*		*Nickel (µg)*		*Cobalt (µg)*		*Cadmium (µg)*	
	Added	*Found*	*Added*	*Found*	*Added*	*Found*	*Added*	*Found*	*Added*	*Found*
1	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—	—
1	2.0	1.9	2.0	2.0	2.0	1.8	—	—	—	—
1	4.0	4.0	5.0	4.8	4.0	4.0	—	—	—	—
1	6.0	6.0	10.0	9.9	6.0	5.9	—	—	—	—
1	8.0	7.9	—	—	—	—	—	—	—	—
10	—	—	—	—	—	—	0.00	0.00	0.00	0.00
10	—	—	—	—	—	—	0.40	0.40	0.10	0.10
10	—	—	—	—	—	—	0.60	0.61	0.30	0.31
10	—	—	—	—	—	—	0.80	0.81	0.50	0.51
10	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00
10	10.0	9.9	10.0	9.9	10.0	10.1	0.10	0.11	0.10	0.10
10	30.0	29.8	30.0	30.0	30.0	30.0	0.30	0.28	0.30	0.28
10	50.0	49.9	50.0	50.0	50.0	50.2	0.50	0.52	0.50	0.48

The authors wish to thank the Permutit Company Ltd. for supplying their experimental resin S1005.

SUMMARY

An investigation has been made of the uptake of trace elements from both distilled water and sea water by the chelating ion-exchange resins Chelex-100 and Permutit S1005. The resins retained the following elements with an efficiency of *ca.* 100%: Ag, Bi, Cd, Cu, In, Pb, Mo, Ni, rare earths, Re (90% only), Sc, Th, W, V, Y and Zn. Manganese was retained quantitatively only by the Chelex resin. The following elements are removed with 100% efficiency by means of 2 *N* mineral acids: Bi, Cd, Co, Cu, In, Ni, Pb, rare earths, Sc, Th, Y and Zn. Ammonia (4 *N*) completely removes molybdenum, tungsten, vanadium and rhenium. The resins have been used in conjunction with atomic absorption spectrophotometry for the simultaneous determination of zinc, cadmium, copper, nickel and cobalt in sea waters.

RÉSUMÉ

Une étude est faite sur l'utilisation de résines chélatantes échangeuses d'ions Chelex-100 et Permutite S1005 pour l'analyse de traces dans l'eau distillée et l'eau de mer. Les résines retiennent les éléments suivants avec un rendement de près de 100%: Ag, Bi, Cd, Cu, In, Pb, Mo, Ni, terres rares, Re (90% seulement), Sc, Th, W, V, Y et Zn. Le manganèse est retenu quantitativement par la résine Chelex seulement. Les éléments suivants sont élués avec 100% de rendement, au moyen d'acides minéraux 2 *N*: Bi, Cd, Co, Cu, In, Ni, Pb, terres rares, Sc, Th, Y et Zn. L'ammoniaque 4 *N* permet d'éluer complètement molybdène, tungstène, vanadium et rhénium. Les résines ont été utilisées conjointement avec la spectrophotométrie par absorption atomique pour le dosage simultané du zinc, du cadmium, du cuivre, du nickel et du cobalt dans l'eau de mer.

ZUSAMMENFASSUNG

Es wurde untersucht, inwieweit sowohl aus destilliertem Wasser als auch aus Seewasser Spurenelemente durch chelatbildende Ionenaustauscherharze Chelex-100 und Permitit S1005 aufgenommen werden. Die Harze halten folgende Elemente fast vollständig zurück: Ag, Bi, Cd, Cu, In, Pb, Mo, Ni, Seltene Erden, Re (90%), Sc, Th, W, V, Y und Zn. Mangan wird quantitativ nur durch Chelex-100 zurückgehalten. Bi, Cd, Co, Cu, In, Ni, Pb, Seltene Erden, Sc, Th, Y und Zn werden vollständig mit 2 *N* Mineralsäuren zurückgewonnen, Mo, W, V und Rh mit 4 *N* Ammoniak. Die Harze wurden in Verbindung mit der atomaren Absorptionsspektralphotometrie zur gleichzeitigen Bestimmung von Zn, Cd, Cu, Ni und Co im Seewasser verwendet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANALYSE ISOTOPIQUE DE L'AZOTE PAR SPECTROMETRIE OPTIQUE, POUR DE FAIBLES TENEURS EN ^{15}N

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(Reçu le 20 juin, 1967)

On connait l'importance des molécules marquées à l'azote-15 dans les études de biologie, de médecine et de physico-chimie. En particulier, des engrais marqués avec cet isotope sont souvent employés en agronomie. Pour des raisons économiques, des quantités importantes étant nécessaires à ce genre d'études, les biologistes n'utilisent, le plus souvent, que des molécules azotées dont le taux d'enrichissement en isotope-15 est faible: en général, la teneur isotopique est comprise entre 1 et 2 atomes de ^{15}N pour 100 atomes d'azote. Rappelons que l'abondance naturelle de l'isotope de masse 15 est voisine de $0.36_{6}\%$. C'est donc entre ces valeurs qu'une méthode de dosage est la plus utile: nous limiterons notre étude à cette gamme de concentrations isotopiques.

Parmi les méthodes d'analyse, la spectrométrie de masse est naturellement la mieux adaptée à ce genre de mesure. Cependant, toujours pour des raisons économiques et parce que les spectromètres optiques se trouvent plus fréquemment dans les laboratoires, on les emploie souvent pour effectuer ces dosages isotopiques. La précision est alors généralement un peu moins bonne; cet inconvénient n'est pas très grave pour la plupart des études agronomiques, qui ne nécessitent qu'une précision de quelques pour cent.

L'utilisation de la spectrométrie optique pour le dosage isotopique de l'azote est bien connue depuis le travail de HOCH ET WEISSER[1], qui a été développé par divers auteurs[2-6]; on trouvera un historique dans l'article de MEIER de 1962[4]. Pour plusieurs raisons, il nous a cependant paru nécessaire de procéder à un nouvel examen des possibilités de la spectrométrie d'émission appliquée à la détermination de l'azote-15: le domaine de concentration isotopique compris entre 0.36 et 2 atomes de ^{15}N pour 100 atomes d'azote n'a été, en effet, que sommairement étudié; cela s'explique par les difficultés expérimentales rencontrées; la plus importante est liée à l'existence d'un fond spectral important: pour l'abondance naturelle, ce fond est égal ou supérieur à l'intensité de la bande attribuable à la molécule ^{14}N^{15}N**, quelque soit le couple de bandes d'analyse utilisé.

D'autre part les conditions opératoires n'ont pas été suffisamment précisées et varient beaucoup d'un auteur à l'autre; en particulier, le choix du couple de bandes servant à l'analyse dépend naturellement de l'appareillage et des interférences avec les bandes d'éventuelles impuretés; or avec des spectromètres de type semblable, tous deux équipés de prisme de quartz, GORBUNOV ET SAGOREC[3] avaient choisis en

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* C.E.A. Saclay, S.I.S., France.

** Dans la gamme de concentrations isotopiques qui nous intéresse, la quantité relative de molécules $^{15}N_2$ est si faible qu'aucune bande attribuable à cette molécule ne peut être décelée sur nos spectres.

1955 la transition 2→0 du système de transition électronique $C(^3\Pi_u)\leftrightarrow B(^3\Pi_g)$ de l'azote comme couple de bandes d'analyse, alors que MEIER[4], en 1960, utilisait la transition 1→0*.

Il est donc nécéssaire d'effectuer une étude complémentaire, particulièrement pour le domaine de concentrations qui nous intéresse, où les dosages sont difficiles à effectuer, surtout si l'on veut opérer rapidement.

On indiquera d'abord sommairement l'appareillage utilisé, puis on examinera successivement les couples de bandes isotopiques pouvant servir à cette analyse; comme il n'est pas possible d'éliminer totalement tous les gaz étrangers en dosage de routine, on choisira le couple de bandes qui sera le moins affecté par la présence de traces d'impuretés. Enfin, on présentera une série de résultats quantitatifs qui seront discutés et confrontés à ceux de la spectrométrie de masse.

PARTIE EXPÉRIMENTALE

Appareillage et échantillons

La présence d'un isotope de masse 15 dans la molécule d'azote provoque un déplacement isotopique relativement important de certaines bandes du spectre. Pour le système de transitions électroniques $C(^3\Pi_u)\leftrightarrow B(^3\Pi_g)$, ces déplacements sont +6.10, +3.60, −3.64, −8.35 et −7.27 Å respectivement pour les transitions 2→0, 1→0, 0→1, 0→2 et 0→3 (*cf.*, par exemple, réf. 4); seule la transition 0→0 ne présente naturellement qu'un déplacement isotopique très faible (+0.11 Å). Le pouvoir de résolution nécessaire pour séparer les bandes attribuables aux molécules $^{14}N_2$ et $^{14}N^{15}N$ n'est que de 1000 environ, dans le cas le plus défavorable, exception faite de la transition 0→0; les spectrographes de dispersion moyenne permettent donc d'effectuer l'analyse isotopique de l'azote.

Nous disposions d'un appareil Hilger et Watts, modèle E 742, équipé d'un prisme de quartz; nous l'avons modifié pour faciliter et accélérer les mesures quantitatives: cette transformation a été décrite par ailleurs[7]; le détecteur placé derrière la fente de sortie était un photomultiplicateur RCA 1 P 28, dont le signal était amplifié et enregistré.

Tous les travaux antérieurs[1–6] montrent que les lampes à décharge sans électrode, contenant de l'azote et excitées par haute fréquence, constituent des sources de lumières commodes pour effectuer cette analyse isotopique; cependant les conditions expérimentales n'étaient pas bien précisées; en particulier la fréquence de l'excitation, la forme et la matière des lampes, l'influence des impuretés sur la stabilité de la décharge et la luminance des sources ont dû être examinées au cours d'une étude préliminaire[7,8]. Nous avons utilisé une excitation à quelques dizaines de méga-Hertz, ce qui est préférable que de travailler à quelques milliers de méga-Hertz; les générateurs hautes fréquences ont été décrits précédemment[7,9,10], et les précautions indispensables pour préparer des sources stables et brillantes y ont été indiquées[7,8].

Nous avons examiné des échantillons constitués par des sels d'ammonium, des engrais azotés ou des extraits secs de plantes (maïs Columbia). L'azote est obtenu,

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* Dans un article récent, MEIER ET MUELLER[4] proposent d'utiliser les bandes de transitions 2 → 0 et 0 → 2 ou 1 → 3, mais dans des conditions expérimentales différentes.

par exemple, par action de l'hypobromite de sodium, selon la réaction de Rittenberg (*cf.*, par exemple, réf. 11), les composés azotés complexes étant préalablement transformés en sel d'ammonium par la méthode de Kjeldahl.

Pour effectuer une mesure, la prise d'échantillon de départ dépend de sa nature: pour du sulfate d'ammonium, on met en oeuvre 20 mg environ; pour des plantes, on utilise 1 gramme environ d'extrait sec*.

CHOIX DU COUPLE DE BANDES D'ANALYSE

Parmi les bandes les plus intenses du spectre de l'azote, pour le système de transition $C(^3\Pi_u) \leftrightarrow B(^3\Pi_g)$, les transitions 0→2, 1→3, 0→1, 1→0 et 2→0 ont été utilisées pour effectuer le dosage isotopique[2-6]. De tous ces travaux, il est impossible de déduire quel est le couple de bandes le mieux adapté au dosage de faibles quantités d'azote-15. Nous verrons en effet que les trois premières de ces transitions donnent des bandes qui se situent dans des régions du spectre où le fond spectral est intense; la quatrième donne des bandes qui se superposent à des bandes d'impuretés; la cinquième enfin avait été proposée dès 1955 par GORBUNOV ET SAGOREC[3] comme couple de bandes d'analyse, mais leur tentative n'avait pas été entièrement concluante, leur spectromètre étant un appareil à plaques photographiques. Au moment où nous reprenions cette étude, la transition 2→0 n'avait pas été utilisée pour effectuer le dosage isotopique de l'azote avec un photomultiplicateur comme récepteur.

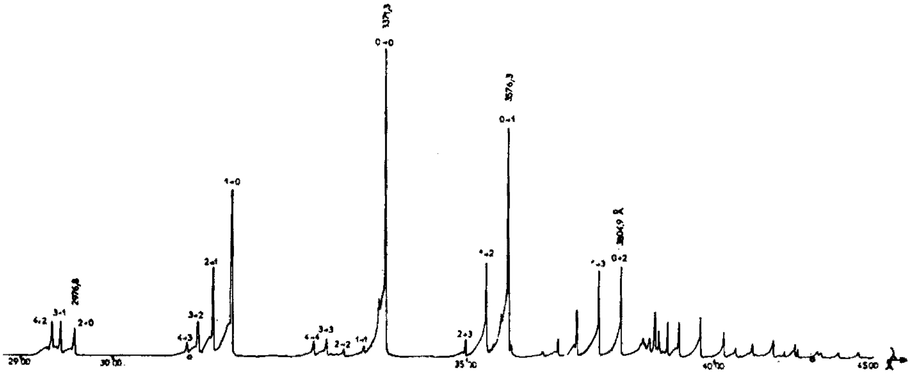

Fig. 1. Spectre de l'azote ordinaire, $^{15}N = 0.36_6\%$. $C(^3\Pi_u) \rightleftarrows B(^3\Pi_g)$. $f = 0.02$ mm; $v = 600$ mm/h; $sh = 10\,\Omega$; tension P.M. = 600 V.

Nous avons donc été conduits à faire un examen systématique de tous les couples de bandes isotopiques suffisamment intenses. Pour cela, nous avons enregistré un spectre de l'azote ordinaire de 4500 à 2500 Å (Fig. 1). En utilisant le travail de BROIDA ET CHAPMAN[2], nous avons repéré les principales bandes qui correspondent aux transitions suivantes (en partant des grandes longueurs d'onde): 0→2, 1→3, 0→1, 1→2, 0→0, 1→0, 2→1, 3→2, 4→3, 2→0, 3→1, 4→2**.

Comme nous voulons travailler avec des mélanges isotopiques d'azote pauvres

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* Récemment, FAUST[11] et MIDDELBOE ET PROKSCH[12] ont réduit la prise d'échantillon de départ à quelques μg, en effectuant l'oxydation des sels ammoniacaux par de l'oxyde de cuivre.

** Ce spectre et ces attributions sont en bon accord avec un travail récent de MEIER ET MUELLER[4].

en $^{14}N^{15}N$, il sera nécessaire de choisir une transition présentant un déplacement isotopique suffisamment grand et pour laquelle le fond spectral sous la bande correspondant à cette molécule soit aussi faible que possible (afin que les fluctuations éventuelles de ce fond n'influent pas trop sur les mesures d'abondance isotopique). Un autre critère de notre choix sera d'éviter les interférences avec des bandes provenant d'impuretés. Nous allons successivement examiner les couples de bandes correspondant aux transitions du système $C(^3\Pi_u) \leftrightarrow B(^3\Pi_g)$.

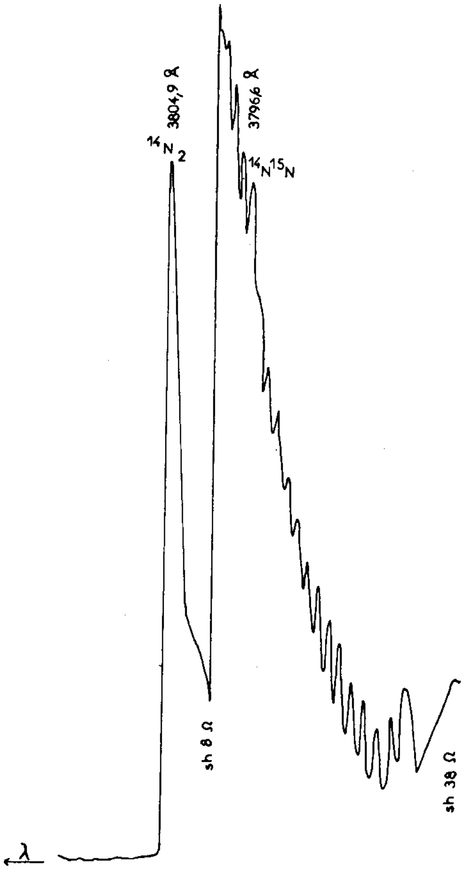

Fig. 2. Spectre de l'azote ordinaire, transition 0 → 2. $f = 0.02$ mm; v, enregistreur 600 mm/h; prisme: 6 Å/mn; tension P.M. = 700 V.

Examen du spectre de l'azote

Le spectre reproduit sur la Fig. 1 permet de procéder à un premier tri, compte tenu de la position relative des bandes dues respectivement à $^{14}N_2$ et $^{14}N^{15}N$.

Transitions conduisant à un déplacement isotopique négatif. Pour les transitions 0→1, 0→2, 1→2 et 1→3, le déplacement isotopique

$$\Delta\lambda = \lambda_{^{14}N^{15}N} - \lambda_{^{14}N_2}$$

est négatif (par exemple pour la transition 0→1 il est de −3.64 Å et pour 0→2 de −8.35). Ce déplacement négatif conduit la bande attribuable à la molécule $^{14}N^{15}N$

à se superposer à des bandes de la molécule $^{14}N_2$ comme le montre la Fig. 2 (cas de la transition 0→2). Comme la gamme de concentrations isotopiques qui nous intéresse est comprise entre 0.36 et 2%, la hauteur du fond spectral sous la bande de la molécule $^{14}N^{15}N$ atteint alors 10 à 15 fois celle de cette même bande. De plus, avec un prisme de quartz, nous sommes dans une région spectrale où la résolution n'est pas excellente: on est conduit à fermer beaucoup les fentes du spectromètre et le rapport signal sur bruit devient assez médiocre. Chacune de ces raisons est suffisante pour qu'on n'utilise pas ces transitions pour l'analyse isotopique envisagée.

Transition 0→0. Le déplacement isotopique est pratiquement nul (+0.11 Å); malgré la très forte intensité de la bande correspondante, elle est donc inutilisable pour l'analyse isotopique, avec le spectromètre dont nous disposons.

Transitions 2→1, 3→1, 3→2, 4→2 et 4→3. Elles présentent un déplacement isotopique positif; mais la proximité de bandes voisines, provenant d'autres transitions, donne un fond spectral intense à l'endroit où se place la bande attribuable à la molécule de masse 29.

Ces bandes ne sont également pas appropriées au dosage isotopique de $^{14}N^{15}N$.

Transitions 1→0 et 2→0. Finalement, il ne reste à examiner que les transitions dont les têtes de bande sont situées, pour la molécule $^{14}N_2$, à 3159.3 et 2976.8 Å. Elles présentent des déplacements isotopiques respectivement de +3.60 et 6.10 qui placent les bandes attribuables à la molécule $^{14}N^{15}N$ en avant de la tête de bande de la molécule $^{14}N_2$, à un endroit où le fond spectral est très faible: la disposition relative de ces bandes est donc, a priori, plus favorable pour effectuer le dosage isotopique de l'azote. La plus intense des deux est naturellement la bande située à 3159.3 Å correspondant à la transition 1→0 (il y a un rapport de 6 environ dans leurs intensités maximales). C'est celle qui a été le plus utilisée[2,4]; mais son déplacement isotopique est plus faible que pour la transition 2→0, dont la bande se place à une longueur d'onde plus basse (2976.8 pour la molécule de masse 28). On pourra alors utiliser des fentes plus larges, d'autant plus, qu'avec notre appareillage à optique de quartz, la résolution est meilleure dans cette région spectrale; finalement, on pourra obtenir à 2976.8 Å un signal à peu près égal à celui qui est observé à 3159.3 Å, bien que cette dernière valeur soit un peu plus proche du maximum de sensibilité de la photocathode du photomultiplicateur RCA 1 P 28.

Spectres des impuretés

Comme on veut travailler rapidement on ne pourra supprimer toutes traces de gaz étrangers; il faut donc comparer les spectres de l'azote et ceux des impuretés pour repérer le couple de bandes d'analyse qui est le moins affecté par la présence de celles-ci. Les impuretés les plus fréquentes qui accompagnent l'azote dans les lampes, sont l'eau et l'oxygène. Ces impuretés sont parfois difficiles à exciter; à la suite des travaux sur les lasers moléculaires, qui ont montré que l'azote pouvait dans certains cas transmettre son énergie à d'autres molécules (*cf.*, par exemple, réf. 13), on peut craindre que l'excitation de ces impuretés ne soit plus facile en présence d'azote; en outre, pour l'oxygène mélangé à l'azote, il se forme peut-être dans la décharge des oxydes de l'azote; les conclusions de la présente étude qualitative devront donc être vérifiées à l'aide de mélange de ces gaz et d'azote, lors de la mesure des abondances isotopiques.

Eau. La Fig. 3 représente le spectre de la vapeur d'eau à faible pression dans la région spectrale considérée*; nous y avons porté les positions des transitions 1→0 et 2→0 de l'azote. On voit qu'une bande intense de la vapeur d'eau (bande de vibration 0→0 du système $A^2\Sigma^+ \leftrightarrow X^2\Pi_i{}^+$) se superpose à la transition 1→0 de l'azote; malgré tout le soin que l'on apporte à la préparation des lampes et bien qu'on en élimine la plus grosse partie pour avoir une décharge stable[7,8], il reste toujours des traces de vapeur d'eau dans les lampes. On ne pourra donc travailler sur la transition 1→0 qu'en piégeant l'eau par de l'air liquide dans la lampe elle-même en cours de fonctionnement; c'est cette difficulté qui a conduit certains auteurs[4] à utiliser des lampes à décharge de formes compliquées. Des conclusions analogues peuvent être tirées de l'ensemble des travaux de MEIER[4].

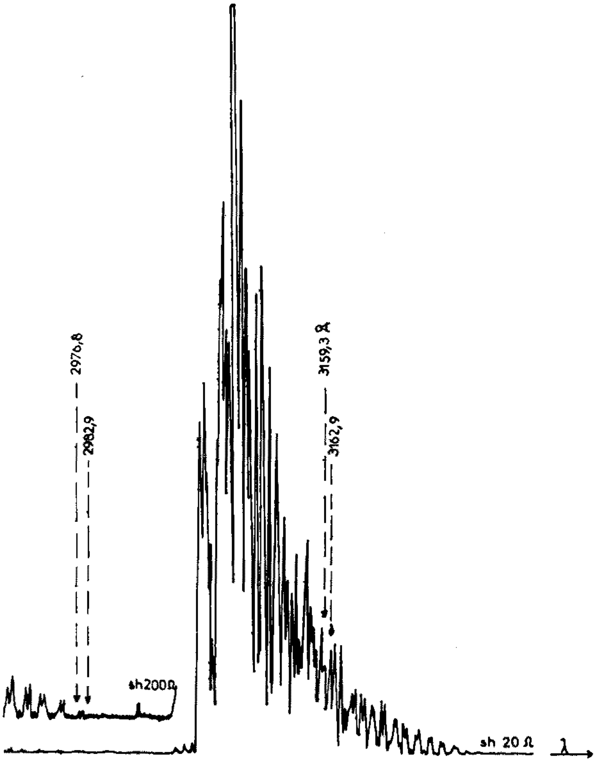

Fig. 3. Spectre de l'eau, transition 0 → 0. $A^2\Sigma^+ \rightleftarrows X^2\Pi_i{}^+$. f = 0.02 mm; v = 600 mm/h; tension P.M. = 750 V.

Dans la région des 2980 Å il n'apparaît que des bandes de très faibles intensités, en particulier à 2987 Å, qui ne se superposent pas aux bandes isotopiques de l'azote.

Oxygène. La Fig. 4 reproduit le spectre obtenu quand on remplit la lampe avec de l'oxygène à une pression de 1.5 torr environ; on y a repéré les positions des bandes de l'azote: on voit que la transition 1→0 ne doit pas être affectée par la

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* Ce spectre a dû être enregistré en plusieurs fois, la lampe devant être régénérée toutes les cinq minutes environ, en raison des instabilités de décharge signalées par ailleurs[7,8]; les rapports d'intensité des bandes ne sont donc peut-être pas rigoureusement exacts. Néanmoins ce spectre est semblable à ceux de la littérature (*cf.*, par exemple, réf. 4).

présence de l'oxygène. Par contre, une faible bande de cette molécule se superpose à la bande de l'azote située à 2976.8 Å (correspondant à la molécule $^{14}N_2$), alors qu'aucune interférence n'est à craindre pour la bande attribuable à la molécule $^{14}N^{15}N$; seule la bande située à 2976.8 Å peut donc être faiblement modifiée par la présence de l'oxygène; mais, pour la gamme de concentrations isotopiques qui nous intéresse, il s'agit de la bande isotopique la plus intense: l'influence de cette éventuelle impureté devrait être minime, d'autant plus que la bande incriminée due à l'oxygène est d'assez faible intensité, comme on peut le remarquer en comparant les Figs. 1 et 4 (compte tenu des shunts utilisés pour enregistrer chacun de ces spectres). Néanmoins, pour confirmer que la présence de traces d'oxygène ne fausse pas trop les mesures d'abondances isotopiques, nous ferons quelques mesures avec des mélanges oxygène–azote (*cf.* RÉSULTATS).

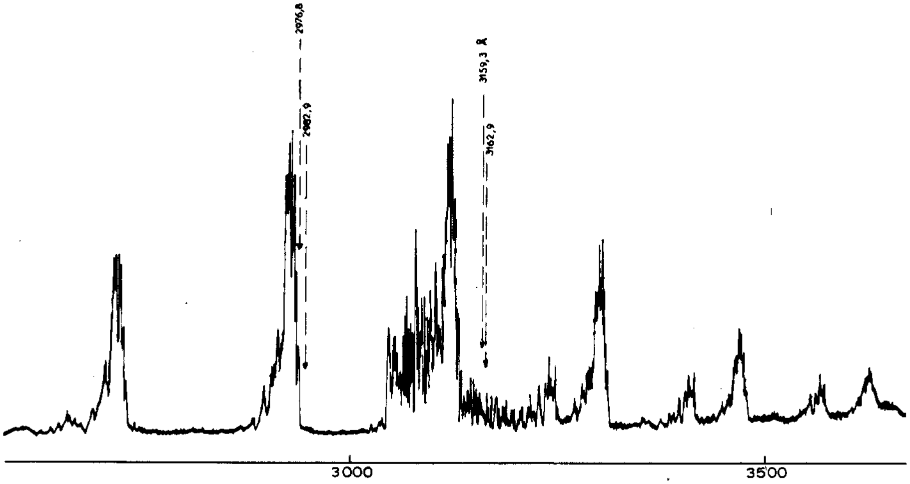

Fig. 4. Spectre de l'oxygène. $f = 0.02$ mm; $v = 600$ mm=h; sh $= 500\ \Omega$; tension P.M. $= 750$ V.

Finalement on voit qu'il est impossible de trouver un couple de bandes d'analyse parfaitement isolé; on utilisera la transition pour laquelle les impuretés auront le moins d'influence possible: les traces d'humidité adsorbée dans la lampe à décharge étant l'impureté la plus difficile à éliminer en peu de temps, c'est pour la transition $2 \rightarrow 0$ que la situation nous semble la plus favorable; très récemment MEIER[4] a confirmé ce choix; il est corroboré par les mesures effectuées avec des mélanges d'azote et de ces gaz étrangers, comme nous le verrons dans la partie réservée aux résultats.

La présence éventuelle d'ammoniac semble peu probable, le piégeage à l'air liquide étant très efficace. Par précaution nous avons néanmoins introduit de l'ammoniac dans une série de lampes; dans tous les cas, le spectre obtenu était identique à celui d'un mélange d'hydrogène et d'azote: l'ammoniac se décomposerait dans la décharge. Ce fait vient d'être confirmé[14]. D'autre part, l'ammoniac ne pouvant provenir que du ballon où a eu lieu la réaction de Rittenberg (quantité trop faible d'hypobromite), il a la teneur isotopique de l'échantillon à doser: la présence éventuelle de trace d'ammoniac ne serait donc pas gênante, si elle ne s'accompagnait d'une diminution de luminance et de stabilité; la vapeur d'eau s'introduit en effet dans la lampe en même temps que cette impureté.

MESURES DES ABONDANCES ISOTOPIQUES

Le plus souvent, nous travaillons à 2976.8 et 2982.9 Å (transition $2 \rightarrow 0$). Cependant nous rapporterons quelques exemples de mesures faites à 3159.3 et 3162.9 Å (transition $1 \rightarrow 0$), pour confirmation des observations faites ci-dessus.

Expression des résultats

La mesure des abondances isotopiques se fait simplement à partir des enregistrements des spectres; mais, comme nous voulons appliquer à des échantillons pauvres en azote-15 la technique habituelle en spectrométrie d'émission, elle ne sera pas utilisable directement, en raison de la grande différence d'intensités des deux bandes que l'on veut comparer.

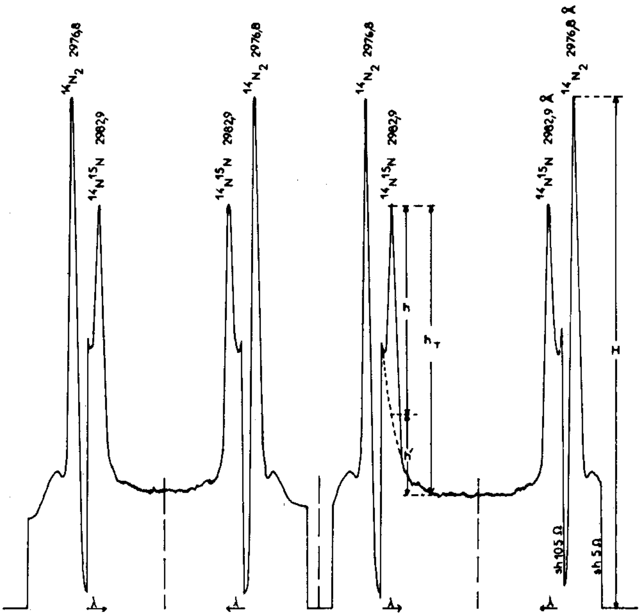

Fig. 5. Spectre de l'azote enrichi à $^{15}N = 1.12\%$, transition $2 \rightarrow 0$. $f = 0.1$ mm; v, enregistreur 600 mm/h, prisme 6 Å/mn; tension P.M. = 700 V.

Principe de la méthode classique. Nous le décrirons, par exemple, pour la transition $2 \rightarrow 0$; dans la région des 2980 Å, le spectre de l'azote se présente comme le montre la Fig. 5, qui reproduit les spectres d'un échantillon à 1.12%. On veut déterminer le rapport isotopique

R_1H = nombre de molécules $^{14}N_2$/nombre de molécules $^{14}N^{15}N$.

On admet que l'intensité I d'une bande isotopique est proportionnelle au nombre de molécules de l'espèce isotopique correspondante; il vient alors:

$$R_1H = I_{^{14}N^{14}N} / I_{^{14}N^{15}N}.$$

Enfin, on fait l'approximation que ces intensités sont proportionnelles aux hauteurs des bandes au maximum d'intensité, compte tenu des shunts utilisés pour enregistrer le spectre de chacune des deux bandes du couple de bandes d'analyse; finalement avec notre montage:

$$R_1 \# \frac{H}{h} \cdot \frac{sh.h}{sh.H}$$

où H et h sont les hauteurs des bandes correspondant respectivement aux molécules $^{14}N_2$ et $^{14}N^{15}N$ et $sh.H$ et $sh.h$ les valeurs des shunts utilisés pour enregistrer les bandes respectivement situées à 2976.8 et 2982.9 Å; on peut alors calculer le nombre d'atomes d'azote-15 pour 100 atomes d'azote-(14+15):

$$\begin{aligned} {}^{15}N\% &= \text{nombre d'atomes d'azote-15/100 atomes d'azote-(14+15)} \\ &= 100/(2R_1+1)^* \end{aligned}$$

On doit déterminer R_1H sur chaque spectre, puis calculer la valeur de $^{15}N\%$.

Détermination du rapport isotopique R_1. Il faut mesurer les hauteurs H et h aux maxima d'intensité des bandes situées à 2976.8 et 2982.9 Å. Comme dans tous les cas où l'on veut comparer les intensités de deux raies ou bandes dont le rapport est grand (rappelons que pour l'azote ordinaire, R_1 est voisin de 135.6), il y a un problème d'origine pour la moins intense.

Pour les molécules isotopiques abondantes, l'origine est bien définie: c'est le fond spectral lui-même, qui compte tenu des conditions opératoires se confond en général avec le zéro de lumière. La mesure de H est donc aisée.

Pour la bande de la molécule isotopique la moins abondante on doit, au contraire, trouver un protocole de lecture des spectres permettant de préciser le fond spectral sous cette bande. Bien qu'on ait choisi une transition pour laquelle la bande due à la molécule $^{14}N^{15}N$ se trouve du côté abrupt de la tête de bande attribuable à la molécule $^{14}N2H$, elle se superpose au pied de cette dernière (*cf.* Fig. 5). Ceci provient des largeurs de fente employées et de la largeur naturelle de ces bandes. Il faut trouver un point du spectre qui ne soit modifié ni par les variations de teneurs isotopiques, ni par la présence éventuelle de très petites bandes d'impuretés. Le

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* Le nombre d'atomes d'azote-14 est proportionnel à $2H+h$; le nombre d'atomes d'azote-15 est proportionnel à $h + 2\varepsilon$ où ε serait la hauteur de la bande attribuable aux molécules $^{15}N_2$, qui est indécelable sur nos spectres. Le nombre d'atomes d'azote-15 pour 100 atomes d'azote-14 est donné par (en n'introduisant pas les valeurs des shunts pour simplifier l'écriture):

$$\frac{^{15}N\ \%}{^{14}N} = \frac{h+2\varepsilon}{2H+h} \cdot 100 = \frac{h}{2H} \cdot \frac{1+2\varepsilon/h}{1+h/2H} \Big/ 100$$

et finalement compte tenu de la constante d'équilibre de la réaction $^{14}N_2 + {}^{15}N_2 \rightleftharpoons 2\,{}^{14}N^{15}N$:

$$^{15}N\%/^{14}N \simeq 100/2R_1$$

Habituellement on préfère donner les résultats en nombre d'atomes d'azote-15 pour 100 atomes d'azote-(14 + 15):

$$^{15}N\ \% = \frac{^{15}N}{^{14}N + {}^{15}N} \cdot 100 = \frac{100}{2R_1 + 1}$$

Dans les études biologiques, la teneur en azote-15 s'exprime souvent par $^{15}N\%$ ex. qui est le nombre d'atomes d'azote-15 pour 100 atomes d'azote-(14 + 15) qui excède l'abondance isotopique naturelle: $^{15}N\%$ ex. = $^{15}N\% - 0.36_6$.

minimum d'intensité placé entre les deux bandes d'analyse ne convient évidemment pas; il en est de même au voisinage immédiat du pied de la bande de la molécule $^{14}N^{15}N$ (principalement à cause d'une très faible bande de la vapeur d'eau à 2987 Å environ). On prend alors comme fond spectral un point situé à 2992 ± 1 Å région du spectre parfaitement claire, même en présence de quantité relativement importante d'impuretés; on mesure à 2982.9 Å la hauteur totale h_T en prenant ce fond spectral comme origine: on a:

$$h_T = h + h'$$

h' étant la hauteur du pied de la bande due à la molécule $^{14}N_2$ à 2982.9 Å. Cette dernière grandeur est évidemment proportionnelle à H compte tenu des shunts servant à mesurer ces hauteurs. On peut donc exprimer h' en pour cent de H:

$$h' = \frac{xH}{100} \cdot \frac{sh.h}{sh.H}$$

Finalement on a:

$$h = h_T - \frac{xH}{100} \cdot \frac{sh.h}{sh.H}$$

Pour déterminer le fond spectral x, on utilise des échantillons de teneurs connues, et on ne change pas les conditions opératoires tout au long d'une série de mesures. Connaissant R_1 pour ces étalons, H étant mesuré compte tenu des shunts, on peut en déduire la valeur de h. Cela permet alors de calculer la valeur de x. Ce fond spectral, exprimé en pour cent de H, servira ensuite à déterminer h à partir de h_T et de H pour les échantillons de teneurs isotopiques inconnues.

Comme nous travaillons dans un petit intervalle de concentrations isotopiques (0.36_6 à 1.5% en azote-15) et comme x est également petit, on pourra utiliser pratiquement la même valeur de x dans toute cette gamme de concentrations isotopiques, ce qui évitera de tracer des courbes d'étalonnage. On a intérêt, pour déterminer x avec le maximum de précision, à prendre un échantillon de teneur bien déterminée et donnant une valeur de h' la plus grande possible par rapport à h: l'échantillon le plus commode est naturellement l'azote naturel. Pratiquement, pour mesurer ce fond spectral, on a utilisé des échantillons d'azote ordinaire prélevés soit directement dans une bouteille d'azote comprimé, soit à partir de sels ammoniacaux traités suivant la méthode de Rittenberg.

Avant toute série de mesures d'abondance isotopique, on enregistre, dans des conditions expérimentales identiques, des spectres d'échantillons d'azote ordinaire, d'où on tire une valeur moyenne de x; cette valeur, suivant la résolution utilisée va de 0.34 à 0.40% de H; le plus souvent, pour des ouvertures de fentes de 0.1 mm (et une hauteur de fente de 20 mm) on avait $x = 0.36 \pm 0.02\%$ de H. On vérifie périodiquement qu'il n'y a pas de fluctuation anormale de x.

Présentation des résultats

Conditions expérimentales. Les spectres sont enregistrés entre 2992 et 2975 Å avec des fentes d'entrée et de sortie ouvertes à 0.1 mm de largeur; la hauteur de la fente d'entrée est comprise, selon les séries de mesure, entre 10 et 20 mm. Nos sources étant de faible diamètre, pour faciliter les réglages, on utilise une conjugaison optique de la source avec le spectrophotomètre qui donne une image assez grande sur la fente d'entrée (lentille de quartz de 6.4 cm de focale placée à 30 cm de la fente d'entrée, la source étant à 38 cm de celle-ci).

La vitesse d'enregistrement est de 6 Å par minute environ, et chaque détermination est la moyenne de trois mesures: chacune d'elle demandant environ 3 min, la durée totale d'une détermination est donc de 10 min.

Pour vérifier les conclusions émises au cours de l'étude qualitative, quelques spectres sont enregistrés avec le couple de bandes de la transition 1→0; les fentes sont alors ouvertes à 0.02 mm, les autres conditions expérimentales étant inchangées.

Résultats et comparaison avec ceux de la spectrométrie de masse. Pour confirmer le choix du couple de bandes d'analyse, on travaille d'abord dans la région des 3160 Å (transition 1→0), puis on présentera les résultats obtenus avec les bandes de la transition 2→0.

Le Tableau I rassemble quelques exemples de détermination effectués sur le couple de bandes isotopiques correspondant à la transition 1→0 (la technique de mesure étant identique à celle que l'on a décrit ci-dessus à propos de la transition 2→0). Comme on pouvait le prévoir par ce qui précède, la reproductibilité des mesures n'est pas satisfaisante (±0.03%); les différences entre valeurs mesurées et attendues sont toujours de même signe et souvent importantes (+0.02 à +0.07%). Il y a donc une erreur systématique; dans le cas le plus favorable, la précision n'est que de 10%. A la suite des travaux de MEIER[4] et des conclusions de l'examen des spectres, on peut penser que l'erreur systématique est due à la présence de traces d'eau dans les lampes. Pour effectuer le dosage avec ce couple de bandes isotopiques, il faut travailler, comme l'a fait MEIER[4] en refroidissant une partie de la source lumineuse par de l'air liquide; cela présente l'inconvénient de compliquer le montage de l'excitateur haute fréquence et, surtout, amène une diminution importante de la luminance et de la stabilité des lampes, d'où résulte un rapport signal sur bruit faible et des valeurs de R_1H peu reproductibles; nous ne les rapportons donc pas ici.

TABLEAU I

EXEMPLES DE DÉTERMINATIONS DE ^{15}N%

(Transition 1 → 0)

Echantillons	*$^{15}N\% = 100/(2\,R_t + 1)$ Valeurs*		*Différences*
	Prévues	*Mesurées*	
1	0.36_6	0.44 ± 0.03	$+0.07_4$
2	0.36_6	0.39	$+0.02_4$
3	0.36_6	0.40	$+0.03_4$
4	0.38_3	0.41	$+0.02_7$
5	0.50_6	0.52	$+0.01_4$
6	0.77_3	0.85	$+0.07_7$
7	0.79_7	0.83	$+0.03_3$
8	1.51_1	1.53	$+0.01_9$

Comme prévu, les mesures d'abondances isotopiques sont peu précises lorsqu'on effectue les mesures sur ce couple de bandes isotopiques.

Avec les deux bandes isotopiques de la transition 2→0, au contraire, on doit obtenir des résultats plus satisfaisants, la présence de traces d'eau n'étant plus aussi gênante, comme le montre les spectres de l'azote et de l'eau (Fig. 3).

Le Tableau II rassemble une série de quelques unes des valeurs de ^{15}N% que nous avons déterminées au cours de ce travail; pour comparaison, on y a joint les résultats obtenus parallèlement par spectrométrie de masse avec les mêmes échantillons.

Pour chaque série de trois mesures, la reproductibilité est de ±0.01% (nettement supérieure à celle obtenue avec la transition 1→0).

Les écarts maximaux avec les déterminations de la spectrométrie de masse sont de 3% environ pour les échantillons dont la teneur est proche de l'abondance

TABLEAU II

COMPARAISON DES RÉSULTATS OBTENUS PAR SPECTROMÉTRIE D'ÉMISSION ET PAR SPECTROMÉTRIE DE MASSE

(Transition 2 → 0)

Echantillons no.	$^{15}N\% = 100/(2R_i + 1)$		*Différences*	*x (%)*
	Spectrométrie d'émission[a]	*Spectrométrie de masse*		
1	0.36_8	(naturel)	$+0.00_2$	0.4
2	0.36_2	(naturel	-0.00_4	0.4
3	0.36_6	(naturel)	0.000	0.4
4	1.23_5	1.23_6	-0.00_1	0.4
4	1.24_1	1.23_6	$+0.00_5$	0.4
4	1.24_1	1.23_6	$+0.00_5$	0.4
5	1.520	1.51_1	$+0.00_9$	0.4
6	1.51_5	1.520	-0.00_5	0.4
6	1.52_8	1.520	$+0.00_8$	0.4
7	0.36_4	(naturel)	-0.00_2	0.34
8	0.36_5	(naturel)	-0.00_1	0.34
9	0.37_0	(naturel)	$+0.00_4$	0.34
10	0.36_1	(naturel)	-0.00_5	0.34
11	0.37_5	(naturel)	$+0.00_9$	0.34
12a	1.22_5	1.23_6	-0.01_1	0.34
12b	1.22_9	1.23_6	-0.00_7	0.34
13a	1.51_5	1.51_1	$+0.00_4$	0.34
13b	1.51_0	1.51_1	-0.00_1	0.34
13c	1.51_7	1.51_1	$+0.00_6$	0.34
14	1.15_4	1.14_5	$+0.00_9$	0.4
15	0.86_4	0.87_7	-0.01_3	0.4
16	0.77_5	0.77_3	$+0.00_2$	0.4
17	0.37_2	0.37_2	0.000	0.34
18	0.39_7	0.38_3	$+0.01_4$	0.34
19	0.49_6	0.50_6	-0.01_0	0.34
20	1.51_5	1.51_1	$+0.00_4$	0.34
21	0.81_0	0.79_7	$+0.01_3$	0.36
22	1.01_0	1.00_2	$+0.00_8$	0.36
23	0.85_5	0.85_0	$+0.00_5$	0.36
24	0.85_1	0.85_2	-0.00_1	0.36
25	0.44_0	0.44_1	-0.00_1	0.36
26	0.39_8	0.39_5	$+0.00_3$	0.36
27	1.19_2	1.19_3	-0.00_1	0.36

[a] Moyenne de 3 mesures—Ecart maximum de ces 3 mesures: $+0.01_0$.

naturelle; elle est de 1% environ pour ceux qui ont une teneur voisine de 1.5% en azote-15. On peut penser que la précision est du même ordre de grandeur. Dans tous les cas, la précision des mesures est supérieure aux 5% qui sont nécessaires pour interpréter les résultats de la plupart des études biologiques.

Dans un article récent SOMMER ET KICK[5] ont remarqué que leur technique de remplissage des lampes sans électrode provoquait des effets de mémoire. L'examen du Tableau II, où nous avons présenté les résultats dans l'ordre où les analyses ont été effectuées, montre qu'avec notre mode opératoire aucun effet de mémoire ne se manifeste. Une lampe a été remplie avec un échantillon d'azote beaucoup plus enrichi en azote-15 (environ 10%) que ceux que nous utilisons normalement; cette lampe a servi ensuite à déterminer l'abondance isotopique d'un échantillon d'azote ordinaire: aucune anomalie n'a été alors remarqué, ce qui confirme l'absence d'effet de mémoire. L'effet observé par SOMMER ET KICK[5] est probablement dû à ce que leurs sources de lumière ne semblent pas avoir été dégazées à haute température entre chaque remplissage.

La présence d'impuretés dans les lampes diminue la reproductibilité[7,8]; en outre, à l'état de microtraces, elles pourraient introduire des erreurs systématiques dans

TABLEAU III

INFLUENCE DES IMPURETÉS SUR LE DOSAGE ISOTOPIQUE DE ^{15}N%

(Transition 2 → 0)

Mélanges d'azote et de:	$^{15}N\% = 100/(2\,R_t + 1)$ *Valeurs*		*Remarques*
	Prévues	*Mesurées*	
O_2 (1% environ)	0.36_6	$0.37_0 \pm 0.01$	Lampes dégazées 10 min
	0.40_0	$0.39_5 \pm 0.01$	Lampes dégazées 10 min
	0.86_7	$0.87_3 \pm 0.01$	Lampes dégazées 01 min
	1.51_1	$1.51_0 \pm 0.01$	Lampes dégazées 10 min
O_2 (5% environ)	0.36_6	$0.36_5 \pm 0.01$	Lampes dégazées 10 min
	0.44_4	$0.43_7 \pm 0.01$	Lampes dégazées 10 min
	0.50_7	$0.50_1 \pm 0.01$	Lampes dégazées 10 min
	1.23_6	$1.23_0 \pm 0.01$	Lampes dégazées 10 min
O_2 (10% environ)	0.38_0	$0.37_0 \pm 0.02$	Lampes dégazées 10 min
	0.50_0	$0.49_0 \pm 0.02$	Lampes dégazées 10 min
	1.51_5	$1.50_8 \pm 0.02$	Lampes dégazées 10 min
O_2 (15% environ)	0.36_6	$0.34_0 \pm 0.04$	Lampes dégazées 10 min
	0.49_6	$0.47_6 \pm 0.04$	Lampes dégazées 10 min
	1.51_5	$1.48_8 \pm 0.04$	Lampes dégazées 10 min
H_2O (traces)	0.36_6	$0.35_9 \pm 0.01$	Lampes dégazées peu de temps (environ 3 min)
	1.51_1	$1.51_5 \pm 0.01$	Lampes dégazées peu de temps (environ 3 min)
	0.36_6	0.37 ± 0.03	Lampes non dégazées
	1.51_1	1.53 ± 0.03	Lampes non dégazées
H_2O ($\frac{1}{2}$% environ)	0.36_6	—	Mesures impossibles: lampes s'allumant et s'éteignant alternativement
	1.51_1	—	

les mesures. Pour cela, on réalise des mélanges d'azote et d'oxygène ou de vapeur d'eau; cela permet de préciser les quantités tolérables de ces gaz étrangers. Les résultats sont résumés sur le Tableau III: il faut des quantités importantes d'oxygène pour que la reproductibilité devienne mauvaise; cette impureté en faible quantité n'introduit pas d'erreur systématique. Il en est de même, semble-t-il, pour la vapeur d'eau, mais, comme on l'a déjà remarqué[7,8], la présence de celle-ci dans les lampes provoque une baisse importante de la luminance des sources et la décharge devient instable.

Des traces d'oxygène sont donc peu gênantes, comme le laissait prévoir l'étude qualitative; pour la vapeur d'eau, l'utilisation de la transition 2→0 permet de supprimer l'erreur remarquée sur la transition 1→0; néanmoins, pour des raisons de stabilité et de luminance des sources, il est nécéssaire de dégazer les lampes par chauffage sous vide pendant une dizaine de minutes. Ces mesures confirment donc bien les remarques faites au cours de l'étude qualitative préliminaire[7,8].

CONCLUSION

L'utilisation du couple de bandes isotopiques correspondant à la transition 2→0 du système $C(^3\Pi_u) \leftrightarrow B(^3\Pi_g)$ de l'azote permet de déterminer les teneurs en azote-15 dans des mélanges de $^{14}N_2$ et $^{14}N^{15}N$ contenant de faibles proportions de cette dernière molécule. Pour ce couple de bandes, la présence de traces des impuretés les plus courantes n'a aucune influence notable sur le dosage isotopique, dans les conditions opératoires qui ont été choisies. Avec les échantillons de diverses provenances que nous avons utilisés (sel d'ammonium, engrais et plantes), la précision des mesures (1 à 3% selon la quantité de $^{14}N^{15}N$ dans le mélange gazeux) est nettement supérieure à celle que nécessitent les études agronomiques (5 à 6%), même dans le cas de teneurs isotopiques voisines de l'abondance naturelle. Pour chaque échantillon, la durée d'analyse n'excède pas 10 minutes.

La fabrication des lampes à décharge sans électrode est simple et rapide le mode opératoire supprimant tout effet de mémoire; leur excitation par haute-fréquence, pour obtenir des sources stables et de luminance suffisante, ne nécessite pas d'appareillage compliqué: un oscillateur de petite puissance, facile à réaliser, donne entière satisfaction.

Enfin ce travail montre qu'il n'est pas indispensable de disposer d'un spectromètre perfectionné: un spectrographe classique sur lequel on monte une fente de sortie suivie d'un photomultiplicateur, pour remplacer la plaque photographique, permet d'effectuer rapidement et commodément ces analyses isotopiques avec une précision suffisante pour beaucoup d'études où l'azote-15 intervient comme traceur.

Nous tenons à remercier le Laboratoire d'Optique du Service des Isotopes Stables (C.E.N. Saclay, France) pour l'aide qu'il a bien voulu nous accorder en nous prêtant le matériel nécessaire au démarrage de ce travail, et Mr. FIEDLER pour son aimable collaboration.

RÉSUMÉ

La possibilité d'analyser un mélange gazeux des azotes $^{14}N_2$ et $^{14}N^{15}N$ par spectrométrie optique est bien connue. Cependant, pour des mélanges pauvres en azote-15 (abondances isotopiques inférieures à 2%), les méthodes proposées ne donnaient pas rapidement des résultats suffisamment précis. Dans le présent travail, on décrit les conditions opératoires permettant de déterminer les teneurs isotopiques à 3% près au voisinage de l'abondance naturelle et à 1% près lorsque l'échantillon contient environ 1.5 atomes d'azote-15 pour 100 atomes d'azote; la durée d'une détermination est de 10 minutes. On utilise un spectromètre modifié par substitution d'une fente de sortie et d'un photomultiplicateur à la plaque photographique. L'excitation des lampes à décharge sans électrode est obtenue par un champ haute fréquence. La méthode est employée avec des échantillons de départ de provenances diverses (sels ammoniacaux, engrais et plantes); dans tous les cas, la précision des dosages isotopiques est nettement supérieure à celle que nécessite la plupart des études agronomiques (5 à 6%).

SUMMARY

For mixtures of $^{14}N_2$ and $^{14}N^{15}N$ low in ^{15}N (isotopic abundances less than 2%), previous optical spectrometric methods do not produce rapid results of sufficient precision. In this paper, operating conditions are described for the determination of the isotopic content to ±3% near the natural abundance and to ±1% when the sample contains an atom ratio of ^{15}N: ^{14}N of 1.5:100. The time required for a determination is *ca.* 10 min. A spectrometer is modified by the substitution of an exit slit and a photomultiplier in place of a photographic plate. The excitation of the electrodeless discharge tube is made by a high-frequency field. The method has been applied to samples of ammonium salts, fertilisers and plant material. In all cases, the precision of the isotopic measurements was greater than that required for most agricultural studies (5–6%).

ZUSAMMENFASSUNG

Für Mischungen von $^{14}N_2$ und $^{14}N^{15}N$ in ^{15}N (Isotopenhäufigkeit weniger als 2%) ergaben frühere spektraloptische Methoden keine schnellen Ergebnisse von befriedigender Genauigkeit. In der vorliegenden Arbeit werden die Arbeitsbedingungen zur Bestimmung des Isotopengehaltes beschrieben mit einer Genauigkeit von ±3% nahe des natürlichen Vorkommens und von ±1%, wenn die Probe ein Atomverhältnis von $^{15}N:^{14}N = 1.5:100$ enthält. Die erforderliche Zeit für eine Bestimmung beträgt etwa 10 min. Das Spektrometer wird durch Hinzufügen eines Spalts und eines Photomultipliers anstelle einer fotografischen Platte abgewandelt. Die Anregung der elektrodenlosen Entladungsröhre geschieht durch ein Hochfrequenzfeld. Die Methode wurde zur Analyse von Ammoniumsalzen, Düngern und Pflanzen angewandt. In allen Fällen war die Genauigkeit der Isotopenmessungen (5–6%) grösser als es für die meisten landwirtschaftlichen Untersuchungen erforderlich ist.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE ANALYSIS OF ALUMINIUM ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY WITH SPECIAL REFERENCE TO THE DETERMINATION OF CHROMIUM AND ZIRCONIUM

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(Received August 15th, 1967)

The determination of silver, copper, zinc and magnesium in aluminium alloys by atomic absorption spectroscopy has been previously reported[1,2]. The sample was dissolved by digestion with sodium hydroxide solution; the solution was then acidified with nitric acid, suitably diluted and atomised in an air–coal gas flame. The copper determinations were unaffected by the presence of other elements but the silver, zinc, and magnesium absorbances were appreciably lowered in the presence of relatively large amounts of aluminium, although these effects could be compensated by using standard solutions containing the same concentration of aluminium as the samples to prepare calibration curves.

When this technique was applied to the analysis of commercial aluminium alloys containing elements such as silicon, titanium, chromium and manganese, the results for magnesium were invariably low. This difficulty was partially overcome by the use of the standard addition technique, but this depends on the assumption that the absorbance varies linearly with concentration over a fairly wide range. This, of course, is not necessarily true and must be checked in each separate type of alloy, thus at least trebling the number of determinations required for a single analysis. Another problem encountered in attempting to analyse commercial aluminium alloys was the difficulty associated with the atomisation of elements such as chromium and zirconium which do not show any absorption in the air–coal gas flame.

A major advance in atomic absorption spectroscopy technique over the past few years has been the use of flames which are hotter than the air–coal gas flame. The use of air–acetylene flames has increased the number of elements which can be determined to about thirty by adding metals such as molybdenum, tin, chromium, etc. Some chemical interferences were also removed in this flame, *e.g.* the effect of sodium on the determination of magnesium[3]. The refractory elements such as titanium, zirconium, silicon, etc., were added in 1965 when WILLIS[4] introduced the nitrous oxide–acetylene flames. It is now possible to determine about sixty elements by atomic absorption spectroscopy.

The increase in the level of noise on the output meter due to emission from the hotter flames, particularly when elements with resonance lines around 3000 Å are determined, is a minor drawback. SULLIVAN AND WALSH[5] have recently produced hollow-cathode tubes where the intensity of the resonance line is greatly enhanced. It was expected that the use of these lamps, apart from increasing sensitivity and improving the linearity of calibration curves, would lower the relative intensity of the flame emission thus reducing noise to a negligible amount.

This paper compares the use of the 3 types of flame for the analysis of aluminium alloys by atomic absorption spectroscopy, and reports the development of procedures for the determination of chromium and zirconium using high-intensity hollow-cathode lamps as light sources.

EXPERIMENTAL

Apparatus

The instrument used was similar to that described by BOX AND WALSH[6] except that the dispersing medium was a Zeiss monochromator (Model M4QIII). The hollow-cathode lamps were supplied by Atomic Spectral Lamps Pty.Ltd., Melbourne, Australia. A Techtron burner (Type AB4O) with a slot 50 × 0.46 mm was used in conjunction with a Techtron atomiser and spray chamber.

Reagents

All reagents used were of A.R. grade.

Standard silver, copper, magnesium or zinc solution (1 mg metal/ml). These were prepared from the spectrographically pure metal dissolved in the minimum amount of nitric acid, the solution being diluted to 1 l in a standard flask.

Standard chromium solution (1 mg Cr/ml). 1.000 g of spectrographically pure chromium was dissolved in the minimum amount of hydrochloric acid, and the solution diluted to 1 l.

Standard zirconium solutions (2 mg Zr/ml). 3.533 g of zirconium oxychloride octahydrate was dissolved in water and the solution diluted to 500 ml.

THE EFFECT OF FLAME COMPOSITION ON THE DETERMINATION OF SILVER, COPPER, ZINC AND MAGNESIUM

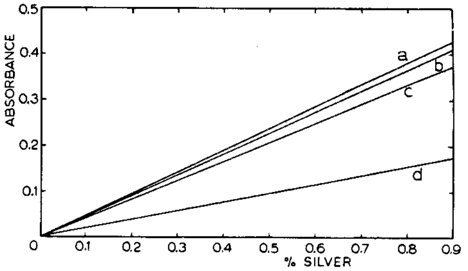
Solutions containing varying amounts of silver, copper, zinc, and magnesium were atomised and their absorbances measured in each of the 3 flames described in the introduction. The absorbances of solutions containing the same amounts of these elements plus 0.1 g of aluminium per 100 ml (*i.e.* 1000 p.p.m. of aluminium) were also measured in the 3 flames. These latter solutions also contained 2 ml of 20% sodium hydroxide (2300 p.p.m. of sodium) and 2 ml of concentrated nitric acid per 100 ml which had been used to dissolve the aluminium.

Silver

Figure 1 shows that the previously reported interference effect of aluminium on silver in the air–coal gas flame[1] does not occur in the two hotter flames. However, the sensitivity is reduced as the flame temperature increases, because of the greater ionization of the silver at the higher temperatures. The presence of 2300 p.p.m. of the more easily ionized sodium (ionization potential = 5.1 eV) and aluminium (ionization potential = 6.0 eV) has no suppressing action on the ionization of silver (ionization potential = 7.6 eV).

Copper

Figure 2 shows that the situation for copper is almost the same as that for silver, as would be expected from the closeness of their ionization potentials (copper = 7.7 eV); *i.e.* the use of hotter flames results in a similar lowering of sensitivity. Again, this is unaffected by the presence of 2300 p.p.m. of sodium and 1000 p.p.m. of aluminium.



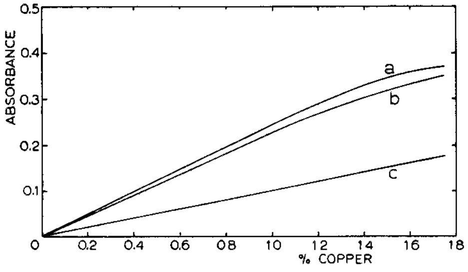
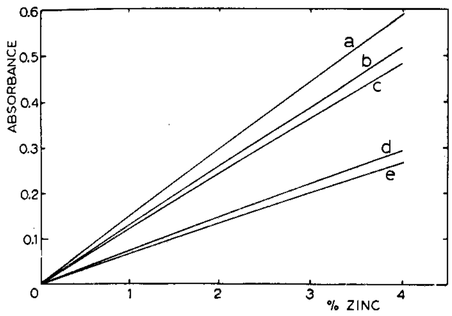


Fig. 1. Effect of flame composition and of Al on Ag absorbances. Hollow-cathode tube current 5 mA; wavelength, 328.1 nm; slit width, 0.05 mm. (a) air–coal gas without Al; (b) air–coal gas with Al; (c) air–acetylene with and without Al; (d) N_2O–acetylene with and without Al. 0.1 g sample per 100 ml.

Fig. 2. Effect of flame composition and of Al on Cu absorbances. Brass hollow-cathode tube current, 13 mA; wavelength, 324.7 nm; slit width, 0.03 mm. (a) air–coal gas with and without Al; (b) air–acetylene with and without Al; (c) N_2O–acetylene with and without Al. 0.1 g sample per 100 ml.



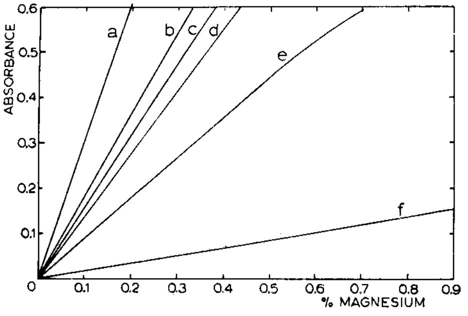


Fig. 3. Effect of flame composition and of Al on Zn absorbances. Brass hollow-cathode tube current, 13 mA; wavelength, 213.9 nm; slit width, 0.03 mm. (a) air–coal gas without Al; (b) air–acetylene with and without Al; (c) air–coal gas with Al; (d) N_2O–acetylene with Al; (e) N_2O–acetylene without Al. 0.01 g sample per 100 ml.

Fig. 4. Effect of flame composition and of Al on Mg absorbances. Hollow-cathode tube current, 6 mA; wavelength, 285.2 nm; slit width, 0.05 mm. (a) air–acetylene without Al; (b) N_2O–acetylene with Al; (c) N_2O–acetylene without Al; (d) air–coal gas without Al; (e) air–acetylene with Al; (f) air–coal gas with Al. 0.1 g sample per 100 ml.

Zinc

The high concentrations of zinc (up to 10%) in the alloys being studied necessitated the use of sample concentrations of 0.01 g per 100 ml[2]. This amount of alloy required only 0.2 ml of 20% sodium hydroxide and 0.2 ml of concentrated nitric acid for its dissolution. Figure 3 shows that once again the use of the hot flames lowers the sensitivity. The air–acetylene flame completely removes the interference caused by aluminium in the air–coal gas flame, whilst in the nitrous oxide–acetylene flame the presence of 100 p.p.m. of aluminium and 230 p.p.m. of sodium results in an enhancement of the zinc absorbance. This is understandable since the ionization potential of zinc (9.4 eV) is considerably higher than that of either sodium (5.1 eV) or aluminium (6.0 eV), so that preferential ionization of these elements would certainly occur.

Magnesium

In the case of magnesium (Fig. 4) the use of an air–acetylene flame instead of an air–coal gas flame results in a considerable increase in sensitivity. The presence of 0.1 g of aluminium dissolved in 2 ml of 20% sodium hydroxide and 2 ml of concentrated nitric acid appreciably lowers the absorbance in both flames.

The nitrous oxide–acetylene flame, on the other hand, gives magnesium absorbance values lying between those obtained with the air–coal gas and the air–acetylene flames. Further, the presence of 1000 p.p.m. of aluminium and 2300 p.p.m. of sodium results in a *ca.* 15% increase in these values. This enhancement is not completely explained in terms of preferential ionization, as the ionization potential of magnesium (7.6 eV) is not greatly different from those of aluminium and sodium.

TABLE I

EFFECT OF FLAME COMPOSITION ON MAGNESIUM DETERMINATION

(Standards contained an equivalent concentration of magnesium)

Sample	*% Magnesium*			
	Air–coal gas	*Air–acetylene*	*N_2O–acetylene*	*Certificate value*
N.R. 305	0.65	0.74	0.79	0.80
B.C.S. 216	0.47	0.49	0.53	0.53
S.S. 880	2.85	2.91	3.35	3.34
S.S. 881	2.15	2.20	2.45	2.47
S.S. 882	1.84	1.85	1.90	1.90

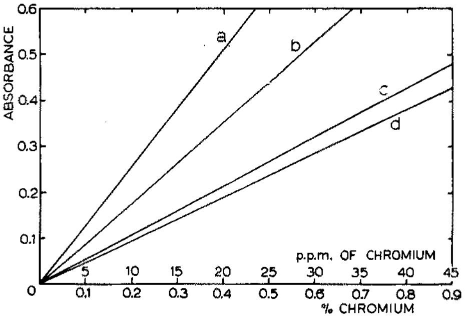
As discussed in the introduction, the accurate determination of magnesium in commercial aluminium alloys by atomic absorption spectroscopy is difficult with an air–coal gas flame. Results obtained on chemically analysed samples (Table I) show that if standards containing equivalent concentrations of aluminium to that in the samples are used to prepare calibration curves, low results are obtained when either the air–coal gas or air–acetylene flame is used, whereas when the nitrous oxide–acetylene flame is used, the figures agree very well with those obtained chemically. This is obviously due to the high temperature (*ca.* 3000°) of the nitrous oxide–acetylene flame preventing the formation of refractory compounds of magnesium with metals such as silicon, titanium, zirconium etc., as occurs in the cooler flames.

DETERMINATION OF CHROMIUM

Selection of optimum operating conditions

Tests showed that variation of the operating current of the hollow-cathode tube over the range 5 to 20 mA had little effect on the absorbance of the chromium line at 3579 Å. The effect of variation in slit width was also investigated and found to be of little significance between 0.02 and 0.10 mm. The conditions selected for use were a current of 20 mA, and a slit width of 0.10 mm (spectral slit width 10 Å).

Absorbance measurements were made on solutions containing 10, 20, 30, 40, and 50 p.p.m. of chromium using air–acetylene and nitrous oxide–acetylene flames. For 0.1 g of sample per 100 ml, these solutions corresponded to a range of 1.0–5.0% chromium. Maximum absorbance in both flames was markedly dependent on the flame composition and also on the position of focus of the hollow-cathode tube beam. Optimum conditions were obtained in luminous (*i.e.* fuel-rich) flames with the light beam focussed in the centre of the flame 1–3 mm above the burner top. The results obtained (Fig. 5) show that chromium absorbs more strongly in the nitrous oxide–acetylene flame. However, the absorbance of a 10 p.p.m. chromium solution was only about 0.1; since the expected concentration range of chromium in the alloys was 0–1%, a larger sample concentration was essential and a sample size of 0.5 g per 100 ml was chosen.



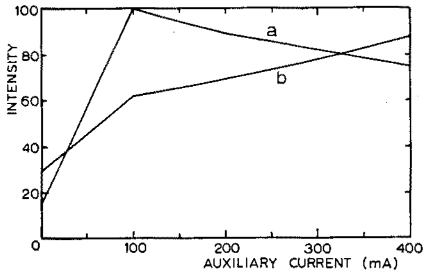


Fig. 5. Effect of flame composition, of Al, and of resonance-line intensity on Cr absorbances. Wavelength, 357.9 nm; slit width, 0.10 mm. (a) and (b) N_2O–acetylene with and without Al; (c) air–acetylene without Al; (d) air–acetylene with Al. (a) high-intensity hollow-cathode tube; (b)–(d) normal hollow-cathode tube. 0.5 g sample per 100 ml.

Fig. 6. Effect of auxiliary current on resonance-line intensity from: (a) Cr, (b) Zr high-intensity lamps.

Tests for interference

In further tests, solutions were prepared to contain chromium and 0.5 g of aluminium dissolved in 10 ml of 20% sodium hydroxide and 10 ml of concentrated nitric acid per 100 ml. The results obtained (Fig. 5) showed that the presence of aluminium and sodium depresses the chromium absorbances in the air–acetylene flame but not in the nitrous oxide–acetylene flame.

The effect of adding various other elements was studied at the 0.20, 0.60, and 1.00% chromium levels by adding the appropriate quantities of spectrographically pure metal to 0.5-g samples of super-pure aluminium dissolved in 10 ml of 20% sodium hydroxide and 10 ml of concentrated nitric acid. The following additions had no effect on the absorbances obtained in the nitrous oxide–acetylene flame: 1% silver, 4% copper, 10% zinc, 5% magnesium, 1% silicon, 1% iron, 1% manganese, 1% titanium, and 1% zirconium.

The effect of increasing the resonance-line intensity

The relatively large sample concentration (0.5 g/100 ml) results in a large salt concentration in the aspirated solution, thus the narrow-slot (0.46 mm) burner which must be used with the nitrous oxide–acetylene flame tends to clog very easily and must be cleared frequently. Another problem in using the nitrous oxide–acetylene flame was the noise generated in the photomultiplier detector by flame emission.

In an attempt to improve the sensitivity of the chromium determination so that a smaller sample could be used, and also to increase the signal-to-noise ratio at the detector, a high-intensity chromium hollow-cathode tube was tried. A 6-fold increase in resonance-line intensity was obtained at the normal operating current of 20 mA and a booster current of 100 mA. This immediately eliminated the trouble caused by the noisy flame. Increases in the booster current from 100 mA to 400 mA decreased the brightness of the resonance line slightly (Fig. 6).

Plots of absorbance *versus* concentration over the range 0 to 50 p.p.m. of chromium (Fig. 5) indicate that the use of a high-intensity chromium lamp increases the absorbance values by 40–50% (compared with the values obtained with conventional hollow-cathode lamps), but this is not enough to permit the use of smaller sample concentrations than 0.5 g per 100 ml. The following conditions were finally chosen as the most suitable for the determination of chromium in aluminium alloys.
Sample concentration. 0.5 g per 100 ml.
Light source. High-intensity chromium hollow-cathode tube.
Light source operating conditions. Normal mode 20 mA; booster current 100 mA.
Wavelength. 3579 Å.
Slit width. 0.1 mm.
Flame. A nitrous oxide–acetylene mixture with a nitrous oxide pressure of 15 psi. The acetylene pressure is adjusted to give maximum absorbance when a 20 p.p.m. chromium solution is aspirated into the flame. This occurs when the flame is slightly fuel-rich.

DETERMINATION OF ZIRCONIUM

Selection of optimum operating conditions

The most sensitive zirconium line, according to AMOS AND WILLIS[7], is at 3601.2 Å. However, tests at this wavelength showed no absorbance at all in the nitrous oxide–acetylene flame until the acetylene flow was increased so that the flame was appreciably luminous. Even then, the absorbance of a 1000-p.p.m. zirconium solution was only about 0.05. AMOS AND WILLIS[7] also reported enhanced absorption for titanium, zirconium, hafnium, and tantalum in the presence of hydrofluoric acid and so measurements were carried out on solutions containing 2% hydrofluoric acid.

A high-intensity zirconium hollow-cathode lamp was used and the results obtained were the same whether the lamp was operated with or without auxiliary electrode current. This is understandable since there are no zirconium lines—other than the one at 3601 Å—within the spectral bandpass of the monochromator at this wavelength. Increasing the normal electrode current to 20 mA and the auxiliary electrode current to 400 mA had no effect on these results. However, since increasing the electrode currents increased the intensity of the resonance line (Fig. 6) the lamp was operated at the maximum values (20 mA and 400 mA) recommended by the manufacturers. The increase in intensity over a normal lamp was then about 4-fold, resulting in a considerable improvement in the signal-to-noise ratio. All further measurements were therefore made with the lamp operated in the high-intensity mode. Plots of absorbance *versus* concentration of zirconium over the range 0–1000 p.p.m. of zirconium in 2% hydrofluoric acid solutions are shown in Fig. 7.

Increasing the slit width lowered the absorbance of the zirconium solution; a slit width of 0.02 mm was therefore used, corresponding to a spectral slit width of 4 Å.

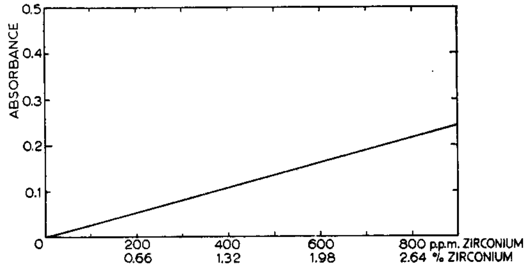


Fig. 7. Calibration curve for determination of Zr in Al alloys. High-intensity hollow-cathode tube operating conditions: normal current, 20 mA; auxiliary current, 400 mA; wavelength, 360.1 nm; slit width, 0.02 mm. N_2O–acetylene flame, 2% HF solutions. 3 g sample per 100 ml.

Tests for interferences

The percentage of zirconium in the experimental aluminium–zirconium alloys under consideration was between 1 and 6%. For a 1-g sample diluted to 100 ml, this represents a range of zirconium between 100 and 600 p.p.m. None of these alloys contained silver, hence dissolution was most easily effected in hydrochloric acid.

Absorbance measurements were made on solutions prepared by dissolving 1 g of pure aluminium in 20 ml of concentrated hydrochloric acid, adding 2 ml of concentrated hydrofluoric acid, 50.0 ml of standard zirconium solution (1 ml = 0.002 g Zr) and diluting to 100 ml with water. The average absorbance obtained was 0.020. The average absorbance of similar solutions containing no aluminium was 0.259. The difference is due to the aluminium preferentially combining with the fluoride and leaving most of the zirconium free to form zirconium oxide in the flame. The oxide is less readily decomposed than zirconium fluoride; increasing the hydrofluoric acid concentration to 4% resulted in an increase in zirconium absorbance in the presence of 1 g of aluminium per 100 ml to 0.092. The results obtained in the absence of aluminium were the same whether 2% or 4% hydrofluoric acid solutions were used. An increase in the hydrofluoric acid concentration above 4% was considered undesirable owing to the highly corrosive and hazardous nature of this acid.

Further tests (Table II) showed that for a solution containing 1000 p.p.m. of zirconium, the presence of less than 0.1 g of aluminium per 100 ml was without effect in 2% hydrofluoric acid solution, whereas in 4% hydrofluoric acid solution up to 0.5 g of aluminium per 100 ml could be tolerated. Under these conditions enough fluoride ion was present to combine with all the zirconium and aluminium. It was therefore decided that the removal of the bulk of the aluminium in a single step followed by the dissolution of the zirconium and the rest of the aluminium etc. in hydrochloric acid and hydrofluoric acid would not only avoid the depressing effects of large amounts of aluminium but also permit the use of much larger sample weights and so improve the accuracy of the proposed method.

TABLE II

EFFECT OF ALUMINIUM AND HYDROFLUORIC ACID CONCENTRATIONS ON ZIRCONIUM ABSORBANCE

g of aluminium added per 100 ml	*Absorbance of a 1000-p.p.m. zirconium solution in*		*g of aluminium added per 100 ml*	*Absorbance of a 1000-p.p.m. zirconium solution in*	
	2% HF	*4% HF*		*2% HF*	*4% HF*
0	0.259	0.259	0.6	0.146	0.222
0.1	0.259	0.259	0.7	0.119	0.161
0.2	0.252	0.259	0.8	0.086	0.145
0.3	0.222	0.252	0.9	0.043	0.116
0.4	0.190	0.256	1.0	0.020	0.092
0.5	0.164	0.259			

Tests on 3-g samples of an aluminium alloy showed that a single dissolution in 60 ml of 20% sodium hydroxide followed by centrifuging, washing the residue with hot water, and dissolving it in hydrochloric acid removed all but about 0.2–0.3 g of aluminium.

The addition of other alloying elements to 3-g samples of aluminium plus zirconium showed that copper, zinc, magnesium, iron, silicon, manganese, titanium and chromium in the quantities usually found in aluminium alloys had no effect on the absorbance of alloys containing 3, 6, and 9% of zirconium by the above procedure.

Recommended procedure for zirconium

Heat a 3-g sample with 60 ml of 20% sodium hydroxide solution until dissolution is complete. Dilute to 150 ml with hot water and centrifuge. Wash the residue 3 times with hot water, and dissolve it in 20 ml of concentrated hydrochloric acid and 4 ml of concentrated hydrofluoric acid (this step is best carried out in a platinum vessel). Cool, transfer to a standard flask and dilute to 100 ml with distilled water. Measure the absorbance due to zirconium under the following conditions.

Light source. High-intensity zirconium hollow-cathode tube operated at 20 mA in the normal mode and 400 mA auxiliary current.

Wavelength. 3601.2 Å.

Slit width. 0.02 mm.

Flame. A nitrous oxide–acetylene mixture with a nitrous oxide pressure of 20 psi. Adjust the acetylene pressure to give maximum absorption when a 1000-p.p.m. zirconium solution is aspirated into the flame. This is a very luminous flame and constant cleaning of the burner slot to remove deposited carbon is necessary.

Calibration curve. This is prepared by measuring the absorbances of solutions made by diluting appropriate quantities of standard zirconium solution with 20% hydrochloric acid–4% hydrofluoric acid solution.

Results for chromium and zirconium

Table III shows a comparison of results obtained for chromium and zirconium by the proposed atomic-absorption procedures with those obtained by classical methods. It can be seen that the figures for chromium show excellent agreement between the two methods; the zirconium results obtained by atomic absorption tend to be lower than those obtained gravimetrically, particularly in the low zirconium alloys.

TABLE III

TYPICAL RESULTS FOR CHROMIUM AND ZIRCONIUM

Sample	*% Chromium*		*% Zirconium*	
	Titrimetric	*A.A.S.*	*Gravimetric*	*A.A.S.*
1	0.25	0.25		
2	0.31	0.32		
3	0.74	0.75		
4			0.15	0.09
5			1.82	1.75
6			3.92	3.9

CONCLUSIONS

It has been demonstrated that the use of flames hotter than the air–coal gas flame makes it unnecessary to use standard solutions containing aluminium to prepare working curves for the determination of silver, copper, zinc, and chromium in aluminium alloys. Silver and zinc are best determined in an air–acetylene flame as the use of a nitrous oxide–acetylene flame results in considerable ionization of these elements. Similarly, the use of air–coal gas is recommended for the determination of copper, as the hotter flames cause a reduction in sensitivity. Chromium shows no absorbance in the air–coal gas flame, and there is interference from aluminium in the air–acetylene flame. However, a nitrous oxide–acetylene flame does not produce this interference, and also results in increased sensitivity. Calibration curves for magnesium still need to be produced using standard magnesium solutions containing aluminium even in the nitrous oxide–acetylene flame, because aluminium causes an enhancement of magnesium absorbances. The use of a nitrous oxide–acetylene flame for magnesium results in an increased sensitivity and also in the removal of the interfering effects of elements other than aluminium.

A method for the determination of chromium on the same sample as used for silver, copper, zinc, and magnesium has been developed. The use of a high-intensity hollow-cathode lamp increased the sensitivity and improved the signal-to-noise ratio.

Zirconium has also been determined by atomic absorption spectroscopy but a separate sample is necessary. The use of a high-intensity hollow-cathode lamp had no effect on the sensitivity. However, owing to the high emissivity of the fuel-rich nitrous oxide–acetylene flame, it was almost essential to use a high-intensity lamp to produce a satisfactory signal-to-noise ratio. The use of hydrofluoric acid, the required preliminary separation of aluminium, the rapid build-up of carbon at the burner slot, and the relative inaccuracy at low concentrations all tend to detract from the developed procedure. Work aimed at eradicating these disadvantages is being carried out.

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SUMMARY

The analysis of aluminium-base alloys for silver, copper, magnesium, zinc, chromium, and zirconium by atomic absorption spectroscopy is described. The use of hot flames (nitrous oxide–acetylene) allows improvements to earlier procedures for such analyses. Sensitivities are increased, interferences reduced, and the determination of more refractory elements, *e.g.* Cr and Zr, becomes possible. Hollow-cathode lamps with greatly increased resonance-line intensities are used for the determination of chromium and zirconium.

RÉSUMÉ

On décrit une analyse d'alliages à base d'aluminium pour le dosage de l'argent, du cuivre, du magnésium, du zinc, du chrome et du zirconium par spectroscopie par absorption atomique. L'emploi de flammes oxyde nitreux–acétylène permet d'augmenter les sensibilités et de réduire les interférences. Le dosage d'éléments plus réfractaires tels que Cr et Zr devient possible. Des lampes à cathode creuse avec des intensités de ligne de résonance considérablement augmentées sont utilisées pour le dosage du chrome et du zirconium.

ZUSAMMENFASSUNG

Die Analyse von Ag, Cu, Mg, Zn, Cr und Zr in Aluminiumlegierungen mittels atomarer Absorptionsspektralphotometrie wird beschrieben. Die Verwendung von heissen Stickstoffoxid–Acetylenflammen führt zu Verbesserungen gegenüber früheren Verfahren. Durch Verwendung einer Hohlkathodenlampe mit verstärkter Resonanzlinienintensität konnten Chrom und Zirkonium bestimmt werden, was früher nicht möglich war.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

An electron-microprobe study of the homogeneity of glass discs for X-ray fluorescence analysis

One of the main controversies concerning the preparation of rock samples for X-ray fluorescence analysis is whether to use a fusion technique developed from that of CLAISSE[1], or some type of pellet made with the rock powder direct. In particular, doubts have been expressed about the homogeneity of the fused discs. This study shows that the distribution in the disc of iron, one of the major rock-forming elements, is uniform on the scale dealt with in fluorescence analysis.

Experimental

A disc of a basic igneous rock was used for the test. It was prepared in the routine fashion for this laboratory, that is: fusion of the rock with four times its own weight of lithium tetraborate in a platinum–gold crucible for 15 min at 1050°, followed by casting on to an aluminium plate at 450° and cooling over a period of about 3 h. A vertical slice was cut out of the centre of the disc and embedded in Araldite, after which it was polished with carborundum and diamond paste. The specimen was then coated with carbon. The microprobe used for the analysis was built by Dr. D. T. HOPKINS of this department. It was operated at 28 kV, using an LiF 100 crystal and a scintillation counter set to detect the iron Kα radiation. Six traverses across the disc were made at 5-mm intervals (see Fig. 1). The electron beam diameter was set at 10 μ. The section was traversed at 3 cm/h, and an optical microscope built into the instrument was used for monitoring. Successive 10-sec counts were taken during the traverses, and recorded on a print-out facility.

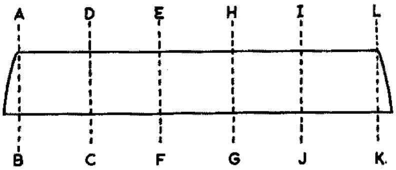

Fig. 1. Position of traverses on disc section.

Results

The measurements were first plotted on a graph relating intensity to position on the section (Fig. 2). The gross mean of the intensities was then calculated, and a histogram constructed of the points on the graph falling within a series of 5-count increments on either side of this mean (Fig. 3). Finally the normal curve representing the theoretical distribution of X-ray quanta was superimposed on the histogram. This combined figure then shows that any variation from the mean in the intensity measurements is within that attributable to counting error.

Discussion

In X-ray fluorescence analysis the areas over which integrated intensity measurements are taken are far larger than the areas irradiated in this study. Thus any variation in the iron distribution which is too small to be detected here would not be significant in fluorescence measurements, and near the edge of the disc, where layering or segregation would most probably occur, there is no more evidence of systematic variation than elsewhere.

It is hoped to continue this work with other rock types and study more of the major rock-forming elements.

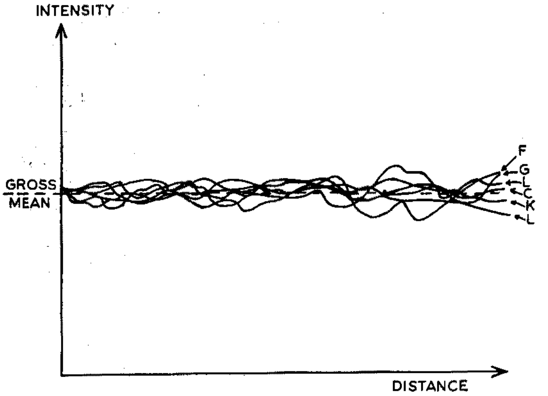

Fig. 2. Intensity profiles of traverses.

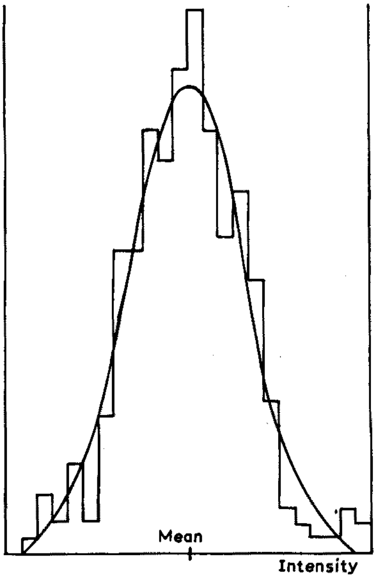

Fig. 3. Histogram of points falling within 5-count intervals from mean intensity with normal curve fitted.

The author would like to thank Dr. D. T. Hopkins and Dr. T. V. Loudon for helpful discussion and Mr. J. E. Thomas for reading the manuscript.

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(Received August 2nd, 1967)

Beam centering in a neutron generator

In the course of experiments to determine the neutron density near the target of Cockroft–Walton type accelerators used in activation analysis, it became apparent that the drift tube was not aligned in the manner necessary for the deuteron beam to strike the center of the target. To assist in the correction for beam centering, an extremely simple method, utilizing copper foil autoradiography from the (n,2n) reaction of ^{63}Cu was devised. Other workers have used target autoradiographs (as opposed to copper foil autoradiographs), requiring the removal of the target (with the exception of sealed-off neutron tubes[1]) from the accelerator and the placement of the target directly against the X-ray film. Target scanning, using a narrow (1 mm) aperture counter and associated equipment, has also been performed[2].

The proposed technique has several advantages. First, it is relatively fast; usable results have been obtained within 30 min. Second, it is very inexpensive, requiring a minimum of equipment and personnel. Third, it is unnecessary to open the vacuum system and remove the target, a time-consuming and sometimes costly operation in itself. Finally, the autoradiograph can reveal areas of serious tritium depletion in the target, thereby giving a better idea when the target should be changed.

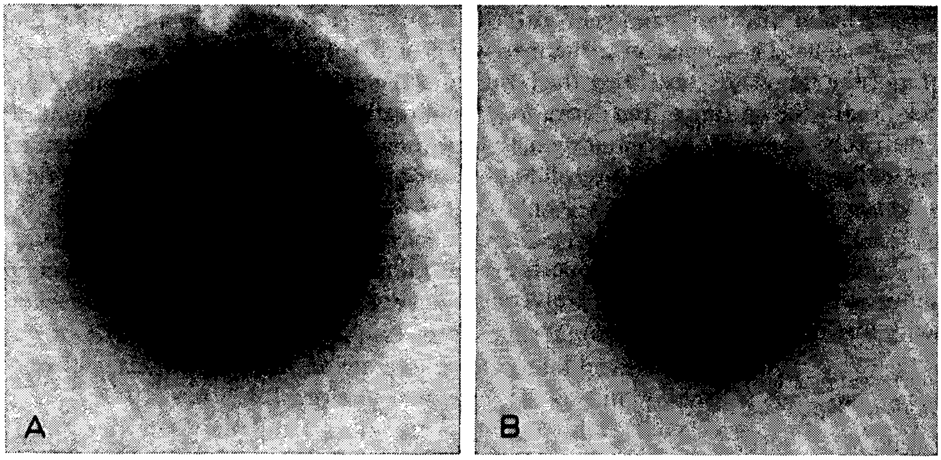

Fig. 1. Autoradiographs made by activated copper foils. (A) Deuteron beam well centered. New target. (B) Deuteron beam slightly off-center. Tritium depletion visible on upper portion of center spot.

In the copper foil autoradiograph technique, a piece of 2-mil copper foil, cut to the exact diameter of the water jacket which surrounds the tritium target, is notched slightly at two places separated by about 90°. Different style notches determine the proper orientation when the autoradiograph is viewed. The prepared foil is carefully taped to the water jacket. Although the thickness of the foil is not critical, it should be sufficiently thick to permit easy removal of the tape and subsequent handling in the darkroom. Once the foil is in place, activation may commence. Some experimentation is necessary to determine the optimum activation time, but on the Texas Nuclear Corporation and Technical Measurement Corporation accelerators used, 1-

min activation was found to give consistently good results with new targets. The accelerators were operated near maximum output during activation. The activation time will vary with parameters such as target condition, accelerating voltage, extraction, beam current, foil thickness (mass), and foil-to-target distance.

After activation, a delay of 1–5 min may be permitted, to shut down the accelerator, remove the foil, and transfer the foil to the film holder. Before the activation of the copper foil, a sheet of type KK X-ray film is placed in a film holder in a darkroom. A lead-screen radiography cassette is ideal for this. The holder is left in the darkroom, and the activated foil is brought to the darkroom and placed inside the holder, against the film. An exposure time of 15–30 min is usually adequate. Again, some experimentation may be needed to determine the combination of conditions necessary to produce the desired results.

When exposure is complete, the film is processed in accordance with instructions for the type of film used. Although it may be desirable to process the film completely and file for future reference, the film may be viewed while wet after "fixing" for 2–5 min.

Although it is well known that the beam of a neutron generator is subject to flickering across the target[2], the completed autoradiograph may be used to correct beam centering as follows: the film is taken to the generator for reference and oriented in the same manner as the copper foil during activation (the notches permit this). Since the beam direction cannot be altered once the beam enters the drift tube, the drift tube must be aligned in a manner which will permit the beam to strike the center of the target. By observing the position of the dark spot in the autoradiograph in relation to the outline of the entire foil, the direction and amount of movement of the drift tube necessary for centering may be estimated. Once the correction is made, it is usually desirable to make a second autoradiograph to see if the proper correction has been applied.

This investigation was supported by a grant from the U.S. Atomic Energy Commission to Louisiana State University for Research Participation in Nuclear Science by College Teachers (1966).

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(Received July 31st, 1967)

Determination of mixtures of mercury(II) and organomercury(II) ions by dithizone

Although mercury(II) and organomercury(II) ions can readily be determined separately, there appears to be no satisfactory method for their determination in presence of each other. Such a procedure is of particular interest in following the kinetics of mercuration processes. The methods commonly used for this analysis suffer from various inaccuracies. In one method, the higher solubility of organomercury(II) halides in inert solvents compared with the corresponding mercury(II) halides is utilized for their separation[1]. When the mixture is shaken with, *e.g.*, chloroform, the organomercury(II) compound (*e.g.*, methoxycyclohexylmercury(II) or cyclopentylmercury(II) chloride) is said to be completely extracted, and the mercury(II) in the aqueous phase may then be determined spectrophotometrically with dithizone. However, mercury(II) halides are known also to partition into inert solvents, the degree of partitioning increasing in the order chloride<bromide<iodide, so that mercury(II) halides will be coextracted to some extent. Moreover, any organomercury(II) compound remaining in the aqueous phase will interfere in the dithizone method, because organomercury(II) ions react with dithizone and form 1:1 stable dithizonate complexes[2] of the general formula RHg(HDz).

Another method[3] is based on an absorption band of mercury(II) iodide at 280 nm, where some organomercury(II) iodides do not absorb. Although this method has been applied for the determination of mercury(II) iodide in presence of the iodides of methylmercury(II), vinylmercury(II), 2-methoxycyclohexylmercury(II), cyclopropylmercury(II), etc., it cannot be successfully applied to arylmercury(II) compounds, for they also show absorbance maxima in the region of 250–280 nm[4].

BROWN *et al.*[5] utilized the different positions of the ultraviolet absorption bands of mercury(II) and some arylmercury(II) chloride complexes. They reported that phenyl-, methyl-, chloro- and methoxyphenylmercury(II) chlorides show an absorption minimum near 250 nm whereas mercury(II) chloride in the presence of excess chloride ions ($HgCl_3^-$ and $HgCl_4^{2-}$) has a much greater absorption at this wavelength owing to the broad absorption peak at 232 nm; however, they did not specify definite wavelengths where accurate measurements could be effected.

REUTOV *et al.*[6] determined mercury(II) ions in presence of benzylmercury(II) chloride by treating the solution with cadmium iodide, the excess of which was back-titrated with mercury(II) chloride; blank experiments showed that one mole of mercury(II) chloride reacts with two moles of cadmium iodide. However, preliminary tests in the present work showed that benzylmercury(II) chloride interferes to some extent in the titration of mercury(II) chloride with cadmium iodide.

GAGE[7] described another method for the determination of phenylmercury(II) (or methylmercury) and mercury(II) ions in the presence of each other. The sample solution was made strongly acidic with hydrochloric acid and extracted with benzene, and the organomercury(II) was then back-extracted into an aqueous sodium sulphide solution; eventually mercury(II) was titrated with dithizone, the total mercury content being determined on another sample. Unfortunately, in this method, only *ca.* 90% of the organomercury(II) can be extracted into benzene, and there is a possibility of carbon–mercury bond cleavage with concentrated hydrochloric acid, *e.g.* in the case of methoxycyclohexylmercury(II) chloride.

In view of the above-mentioned difficulties, the following method is suggested. It is based on the stoichiometrically different reactions of dithizone (H_2Dz) with mercury(II) and organomercury(II) ions. In slightly acidic or neutral aqueous solutions, the following reactions take place:

$$2\ H_2Dz_o + Hg^{2+} \rightarrow Hg(HDz)_{2o} + 2\ H^+ \qquad (1)$$

$$H_2Dz_o + RHg^+ \rightarrow RHg(HDz)_o + H^+ \qquad (2)$$

where the subscript o represents the organic phase.

When equimolar solutions of mercury(II) and organomercury(II) ions are mixed in varying proportions, the total concentration being kept constant, and shaken with a constant excess amount of dithizone in carbon tetrachloride, all other conditions being kept constant, the different amounts of dithizone consumed directly correspond to the total concentration of mercury(II) and organomercury(II) ions. The concentration of dithizone that reacts with both ions can accurately be determined from its maximal absorption at 620 nm and its molar extinction coefficient[8], ε_{620} (34600). Neither mercury(II) nor *o*-methoxyphenylmercury(II) dithizonate absorbs at 620 nm[9].

If A_o, A_s and A_r are the optical densities of the original dithizone solution, of the excess of dithizone left after the reaction, and of the dithizone consumed during the reaction, then, for a 1-cm cell:

$$A_r = A_o - A_s = \varepsilon_{620}\{[Hg^{2+}] + [RHg^+]\} \qquad (3)$$

By plotting A_r values against the corresponding concentrations of Hg^{2+} and RHg^+, a linear "mixed calibration curve" will be obtained and the concentration of any unknown concentration of either component can be determined from the curve by interpolation.

Thus, for an analysis, the total mercury(II) content is first determined by wet-ashing an aliquot of the mixture with concentrated perchloric acid and determining mercury(II) by the dithizone method; then equimolar solutions of mercury(II) and the organomercury(II) compound are prepared for constructing the mixed calibration curve.

Reagents

All reagents were of recognised analytical purity. Twice-distilled water from an all-glass Pyrex still was used throughout.

Purification of reagents. Technical carbon tetrachloride was purified by GEIGER AND SANDELL'S method[10]. Hydrochloric acid and ammonia solutions were purified by isopiestic distillation[11]. Oxidising agents and any traces of dithizone-reacting metals were removed from *M* perchloric acid and from 2 *M* sodium perchlorate solutions by shaking for 1 h with a strong solution of dithizone in carbon tetrachloride.

Dithizone. Solutions of AnalaR dithizone in carbon tetrachloride were shaken with dilute (1:100) ammonia solution. The aqueous phase was separated and then washed several times with the organic solvent until the washings were colourless (or until pure green). The aqueous extract was then acidified with dilute (1:100) hydrochloric acid solution in presence of fresh solvent into which dithizone was re-extracted. This procedure was repeated until the solution of dithizone reached its maximum purity as checked by the ratio of absorbancies at 620 and 450 nm ($A_{620}/A_{450}=1.7$ for 100% purity in carbon tetrachloride[9]). All the customary precautions in work with dithizone were observed[12,13].

Standard mercury(II) chloride solution (0.0195 mM) was prepared by dilution of a 1.0 m*M* stock solution of mercury(II) chloride with 0.1 *M* perchloric acid solution.

Standard o-methoxyphenylmercury(II) chloride solution (0.0195 mM) was prepared by dilution of a 0.2 m*M* stock solution of *o*-methoxyphenylmercury(II) chloride with water.

Apparatus

All absorptiometric measurements were carried out with a Zeiss PMQ II spectrophotometer. pH measurements were made with a Metrohm pH-meter.

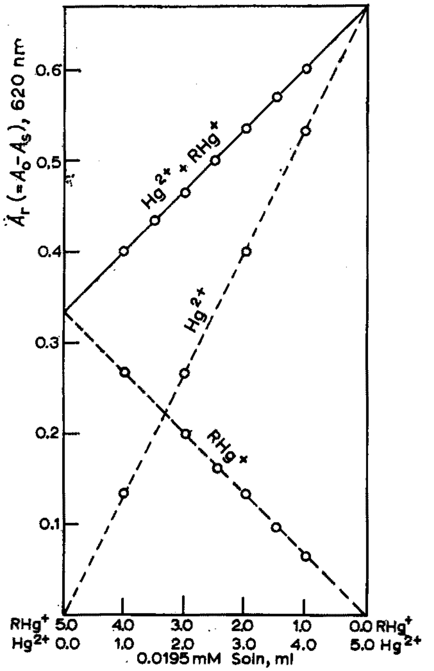

Fig. 1. Typical mixed calibration curve of mercury(II) and *o*-methoxyphenylmercury(II) ions, together with calibration curves of single ions for comparison.

Calibration curve for mercury(II) and o*-methoxyphenylmercury(II) chloride mixtures*

A series of mixtures was made up containing 10 ml of 0.03063 m*M* purified dithizone in carbon tetrachloride, 5 ml of 0.2 *M* sodium perchlorate (adjusted to pH *ca.* 2.5), *x* ml of the standard mercury(II) solution and (5−*x*) ml of the standard *o*-methoxyphenylmercury(II) solution. The phases were equilibrated for 2–3 min and then the organic layers were separated. The absorbance measurements were made in 1 cm silica cells at 620 nm.

Discussion

A typical mixed calibration curve for the determination of mercury(II) and *o*-methoxyphenylmercury(II) ions with dithizone is shown in Fig. 1 together with calibration curves of the single ions for comparison. The slopes of the curves of mercury(II) and *o*-methoxyphenylmercury(II) ions were found to be 2 and 1, which confirms the stoichiometric composition of the two dithizonates. When the concentrations of mercury(II) and the organomercury(II) ions were kept constant, the same mixed calibration curve was found to serve for the determination of various organomercury(II) ions irrespective of the nature of the organic radical. The main prerequisite needed to construct a mixed calibration curve is the determination of the pH range where the extraction of the organomercury(II) dithizonate complex is complete. If aqueous perchlorate solutions are used, the extraction into carbon tetrachloride is complete in the pH range 0.0–7.0 for the dithizonate complexes of the following phenylmercury(II) derivatives: pentafluoro-, 2-hydroxy-3-nitro-, *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *o*-hydroxy-, *p*-methoxy-, *o*-methoxy-, *o*-carboxy- and *p*-acetimino-. If mixed buffers of chloro-acetate or phosphate are used, complete extraction of these dithizonates is effected in the pH range 2.2–7.0[8].

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(Received August 20th, 1967)

Anion-exchange separation of thorium from the rare earths in an acetone–hydrochloric acid medium

Most methods of separating thorium from the rare earth elements on strongly basic anion-exchange resins are based on the different adsorption behavior of these elements from pure aqueous or mixed aqueous–organic solvent media containing nitric acid[1,2]. Under all conditions, the adsorption of thorium is invariably higher than that of the rare earths so that the latter can be eluted preferentially.

No eluting medium has so far been reported which allows this separation to be performed using hydrochloric acid systems. Both in pure aqueous hydrochloric acid of a normality ranging up to 12 N[3] and in hydrochloric acid media containing organic solvents, e.g. aliphatic alcohols, thorium and the rare earth elements show a very similar adsorption behaviour so that separations are impossible. Thus in pure aqueous hydrochloric acid media thorium and the rare earths are not retained at all by strongly basic resins[3] and when mixed aqueous–alcoholic systems are used the extent of adsorption, although appreciable, is virtually the same for both thorium and the rare earths[4]. In the earlier investigations, however, the adsorption of these elements was not measured in systems with a high hydrochloric acid concentration which also contained appreciable percentages of acetone. This has been done in the present investigation and a method has been developed for the anion-exchange separation of these elements with a hydrochloric acid medium as eluent.

Experimental

Reagents and solutions. Ion-exchange resin. The strongly basic anion-exchange resin Dowex 1-X8 (100–200 mesh, chloride form, air dried) was used for the batch and column experiments.

Standard solutions. Stock solutions of the metals were made by dissolving the chlorides, oxides or carbonates of the metals in reagent-grade conc. hydrochloric acid. EDTA (disodium salt) solutions were prepared from 0.1 *M* EDTA stock solution.

Eluent solution. 75% (v/v) acetone–25% concentrated hydrochloric acid.

Determination of the distribution coefficients. The batch distribution coefficients were determined by making up a solution of 20 mg of the element in 12.5 ml of concentrated hydrochloric acid diluted to 50 ml with the organic component, pipetting 20 ml of the solution onto 1.00 ± 0.01 g of resin, shaking vigorously for 8 h, and determining the metal ion concentrations in the equilibrated and non-equilibrated solutions using appropriate titrimetric or fluorimetric procedures.

The column distribution coefficients were determined by adding 1 mg of the element in 2 ml of solution, 75% acetone–25% conc. hydrochloric acid, to 1.00 ± 0.01 g of resin in a 0.5-cm diameter column, followed by elution with a solution of the same composition. The distribution coefficient was taken to be equal to the volume in milliliter of the maximum on the elution curve[5].

Separation of thorium from lanthanum (and some other elements)

The resin (20 g) was soaked in 20 ml of the eluent solution, transferred to a 1-cm diameter column, and washed with 50 ml of the eluent. An aliquot (5–10 ml) of the sorption solution, with the same composition as the eluent, containing thorium, lanthanum and other elements, was added to the column. After passage of the sorption solution into the bed, the resin was washed with the eluent at a rate of 0.20–0.25 ml/min, the eluate being collected in a fraction collector. The concentrations of the elements in the eluate were determined by titration with 0.001 *M* EDTA.

After the elution of the rare earths, or other elements, the thorium may be completely eluted with 75 ml of a 40% acetone–25% conc. hydrochloric acid–35% water soln.

Results

It was found that the maximum separation factor for thorium and the rare earths, defined by the equation:

$$\text{Separation factor } (\alpha) = \frac{\text{distribution coefficient of thorium}}{\text{distribution coefficient of lanthanum}}$$

occurs at the concentration of 75% acetone–25% hydrochloric acid. Distribution coefficients for various metals at this concentration are shown in Table I. Lanthanum, cerium and holmium all have approximately the same value, from which it was concluded that the rare earths could not be separated from each other under these conditions.

TABLE I

DISTRIBUTION COEFFICIENTS (*Kd*) OF VARIOUS METAL IONS AND PHOSPHATE (AS H_3PO_4) IN 75% ACETONE–25% CONC. HCl (v/v) SOLN. ON DOWEX 1-X8

Ion	Th(IV)	La(III)	Ce(III)	Ho(III)	Mn(II)	Fe(III)	Co(II)
Kd	35	4	6	6	90	<1	170
Ion	Cu(II)	Be(II)	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Zn(II)
Kd	60	1^{a}	4	1.5	1.4	<1	150
Ion	Cd(II)	Al(III)	Ga(III)	In(III)	UO_2(II)	Zr(IV)	Bi(III)
Kd	60	1^{a}	1.1	9	600	$>10^3$	>500
Ion	Cr(III)	H_3PO_4					
Kd	4^{a}	3^{a}					

[a] The *Kd* values of these ions were determined by the column method, the others by the batch distribution method.

Figure 1 shows a separation obtained with 10 mg each of lanthanum and thorium. Other runs, with different quantities of these elements in the presence of 5 mg each of metal ions with low distribution coefficients, e.g. Fe(III), Ni(II), Ca(II) and Mg(II) (see Table I), revealed a clean separation of the thorium (iron is not retained by the resin because of the Ciese-effect[6]). There was good agreement between the batch distribution coefficients and the maximum of the elution curve for each of the elements tested. Furthermore, there was no observable interference of the elements with one another's distribution coefficient, e.g. the maximum in the elution curve of lanthanum was at an elution volume of 80 ml in the presence and in the absence of Mg(II) and Ni(II).

At these concentrations of acetone and hydrochloric acid enough polymerization occurs in a few hours to turn the eluent orange. This was not found to interfere with the separation or determination of the metal ions. Phosphate ion, present as phosphoric acid, did not interfere with the separation, being eluted before and with the first part of the lanthanum.

TABLE II

DISTRIBUTION COEFFICIENTS (*Kd*) AND SEPARATION FACTORS (α) FOR Th(IV) AND La(III) IN VARIOUS ORGANIC SOLVENTS (75%) MIXED WITH CONC. HCl (25%) ON DOWEX 1-X8

Solvent	*Kd-values*		*Separation factors* (α)
	Th(IV)	*La(III)*	
Acetone	35	4	~ 9
THF	7	11	0.6
MeOH	3	1	3
EtOH	13	8	1.6
n-PrOH	44	22	2
iso-PrOH	69	43	1.6

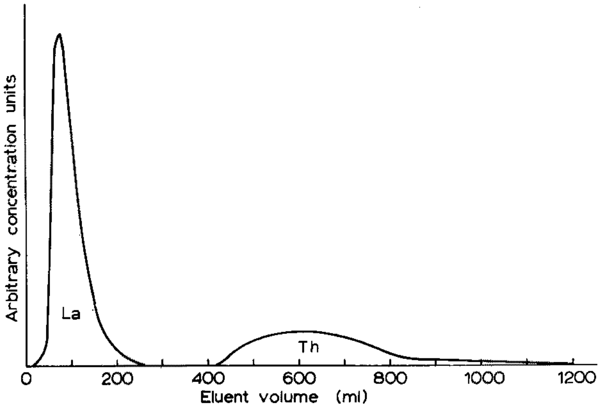

Fig. 1. Separation of La and Th on a 20-g column of Dowex 1-X8 with 75% acetone–25% conc. HCl as eluent.

When tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH), 1-propanol (*n*-PrOH), or 2-propanol (iso-PrOH) was used, it was found that the distribution coefficients of thorium and lanthanum, at a concentration of 75% organic component–25% conc. hydrochloric acid, were too similar to permit as good a separation as in the case of acetone (see Table II). The largest separation factor, α, was observed in the acetone–hydrochloric acid system.

If holmium(III) or other rare earth elements are taken in place of lanthanum, separation factors are obtained which are very similar to those shown in Table II. Consequently, a separation of thorium from the rare earth series is only possible in the acetone–hydrochloric acid medium.

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(Received July 5th, 1967)

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Voltammetric determination of cerium in concentrated phosphoric acid

Direct voltammetry is among the most simple and rapid electroanalytical methods for the determination of cerium in the concentration range 10^{-4}–10^{-3} M. The methods currently used include voltammetry with solid electrodes, e.g. platinum[1] or pyrolytic graphite[2], which are used in acid media. Classical polarography with a dropping mercury electrode is also used in suitable complexing solutions, in order to shift the $E_{\frac{1}{2}}$ value to the range of potential in which this electrode operates[3-5].

In order to determine cerium in strong acid media and in the concentration range mentioned above, a rapid voltammetric analysis with a rotating platinum electrode as indicator electrode, was applied. Voltammograms in various acids—proposed in the literature as media for cerium voltammetry—were recorded. It was soon realised that a precise measurement of the limiting current could not be made because of the serious interference resulting from the oxidation currents of platinum and water; this is a consequence of the high positive value of E_0 for the Ce^{3+}/Ce^{4+} couple in acidic media. It was found, however, that in a concentrated phosphoric acid medium the current–voltage curve is more suitable for analytical purposes than in the other media tested. In this medium the residual oxidation current due to water appears at more positive potentials, whereas the $E_{\frac{1}{2}}$ value of the Ce^{3+}/Ce^{4+} couple becomes more negative because Ce^{4+} is more strongly complexed than Ce^{3+}. The limiting oxidation current of Ce^{3+} can therefore be read precisely, while in all previous voltammetric methods the reduction current measurement for Ce^{4+} had to be preferred.

In the present paper, an analytical method for the direct determination of cerium(III) is proposed. The time and manipulation needed for quantitative chemical oxidation to the tetravalent oxidation state can thus be avoided. Two methods are suggested. In the first, a voltammogram is taken for each sample solution and the limiting current is measured; the total cerium in the sample is determined. In the second, cerium(III) is determined by measuring its limiting oxidation current at a fixed potential. Better precision can be achieved by the latter method.

Equipment and solutions

All the instruments were supplied by Metrohm AG: polarocord, type E261; stirrer, type EA682; rotating platinum electrode, type EA222; mercury–mercury(II) sulfate reference electrode, type EA 406, in saturated sodium sulfate; polarographic cell, type EA664.

Cerium(III) stock solution. Dissolve *ca.* 1 g of cerium metal (spectrographic grade) in 10 ml of concentrated perchloric acid and dilute to 100 ml with twice-distilled water. Prepare the solutions used for the calibration curve by suitable dilution with concentrated phosphoric acid (85% w/w).

Method I

Apply a potential of 0 V for 2 min to the platinum electrode in the sample solution. Slowly scan the potential in the positive direction from 0 V to +1.2 V. The half-wave potential of the cerium(III) oxidation wave is +0.45 V *vs.* the mercury/mercury(II) sulfate electrode (Fig. 1). Determine a blank before each series of measurements, using concentrated phosphoric acid, and deduct the blank value from the value for the sample.

The half-wave potentials of the cerium(IV) reduction wave and the cerium(III) oxidation wave are very similar in concentrated phosphoric acid (about +0.45 V), hence a single wave is obtained for a mixture. The wave height is proportional to the total cerium concentration (see Table I).

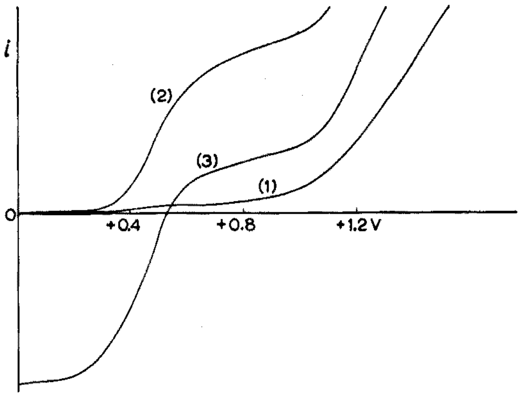

Fig. 1. Voltammograms of concentrated (1) phosphoric acid, (2) Ce^{3+} and (3) Ce^{4+}.

TABLE I

COMPARISON OF LIMITING CURRENTS OF CERIUM

Oxidation state of cerium	*Total molarity*	*Current (µA)*
Ce^{3+}	$0.98 \cdot 10^{-3}$	5.4
Ce^{4+}	$1.0 \cdot 10^{-3}$	5.6
$Ce^{3+} + Ce^{4+}$ (1:1)	$0.99 \cdot 10^{-3}$	5.5

The surface of the solid electrode affects current values, hence careful pre-treatment of the indicator electrode is needed in order to achieve small, constant residual currents. Chemical oxidizing (0.1 *M* Ce^{4+}) or reducing (0.1 *M* Fe^{2+}) treatments and electrochemical treatments were tried. The best results were achieved with an electrochemical reduction at an applied potential of 0 V.

The calibration curve obtained, when Method I was used, was a straight line passing through the origin, but the slope did not remain constant from day to day. When a standard addition technique was used, the standard deviation amounted to 3%.

Method II

Measure the limiting oxidation current of cerium(III) at a fixed potential, +0.9 V. Before measurements, store the electrode in concentrated phosphoric acid at 0 V for 15 min to reduce the oxide film, and then overnight at +0.9 V to obtain a reproducible thin oxide coating. After such a pre-treatment the electrode may be used for repeated determinations for at least 3 days. During this period it should be left connected to the polarograph at an applied potential of +0.9 V. After the pretreatment, immediately replace the solution in the cell by the sample, and measure the limiting current after 10 min. Take a blank reading before and after each sample measurement.

This overnight pre-treatment of the platinum electrodes yields reproducible results with a standard deviation of 2%. The calibration curve obtained is a straight line through the origin and can be applied for routine analysis.

Interferences

The interference of the cations which usually accompany cerium was examined. The following cations caused no interference: Fe^{3+}, Al^{3+}, Th^{4+}, Ti^{4+}, Nb^{5+}, UO_2^{2+}, Cr^{3+}, La^{3+}, Nd^{3+}, Sm^{3+}, Yb^{3+}, Eu^{3+}, alkaline and alkaline earth cations. Nitrate ions caused severe distortions of the voltammogram when the potential scanning method was applied, but did not interfere when Method II was used. Elimination of Cl^-, Mn^{2+} and Fe^{2+} is essential since they are oxidised in concentrated phosphoric acid together with cerium(III).

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(Received August 14th, 1967)

Anal. Chim. Acta, 40 (1968) 524–526

The automatic determination of manganese in silicate rocks and sediments

In the most commonly used procedure for the photometric determination of manganese in natural silicates, manganese is oxidised to permanganate. If the oxidation is carried out with periodate[1,2], the rate of oxidation is slow and it is difficult to achieve consistent colour intensities. When the oxidation is carried out with ammonium peroxydisulphate catalysed by silver(I)[3], the development of the colour is faster but the precision is still not good. The sensitivity of the permanganate method is low, hence it is unsuitable for microanalysis of separated minerals.

Formaldoxime reacts with manganese(II) in alkaline solution to produce an intense orange-red complex, the maximum molar extinction of which is *ca.* 5 times that of the permanganate ion[4]. However, iron also produces a strongly coloured complex and interferes seriously. SIDERIS[5] recommended the prior removal of iron by precipitation and RILEY AND WILLIAMS[6], in the application to silicate rocks, extracted iron and alumina as oxinates with chloroform. BRADFIELD[7] used N-(2-hydroxyethyl)-diaminoethanetriacetic acid for chelating iron in the determination of manganese in plants. GOTO *et al.*[8] used EDTA and hydroxylamine hydrochloride for the same purpose in the analysis of their materials. HENRIKSEN[9] has described an automatic method for the determination of manganese in water based on the procedure of GOTO *et al.* He claimed that small amounts of iron(II) aid the decomposition of the complex formed by the iron present in the sample. The maximum concentration of iron which could be tolerated was found to be 1.0 μg Fe/ml.

The present paper describes an automatic procedure for the determination of manganese in silicate and sedimentary rocks, in which relatively large amounts of iron are present.

Development of the method

The optimum pH range for the formation of the manganese–formaldoxime complex is 9.0–9.5[10]. In this pH range, iron(III) forms a strongly coloured complex which interferes in the determination of manganese. It was found that the suppression of iron(II) interference by addition of EDTA and hydroxylamine hydrochloride was only efficient if the actual concentration of iron present did not exceed 3 μg Fe/ml and if the Fe: Mn ratio in the sample did not exceed 1:1. Since the Fe: Mn ratios in silicate rocks can be as much as 200:1, it was found necessary to use ascorbic acid to reduce iron and complex most of the iron(II) before the addition of formaldoxime. The iron(II)–formaldoxime complex is then destroyed, before the photometric measurement, with EDTA and hydroxylamine hydrochloride. The use of hydroxylamine hydrochloride as well as ascorbic acid is necessary since the excess of ascorbic acid added earlier tends to be destroyed at pH 9.

Reagent concentration

The concentration of formaldoxime (0.005 *M*) used by GOTO *et al.*[8] was found to be insufficient to complex manganese, iron and aluminium in silicate rocks. A concentration of 0.025 *M* of formaldoxime in the final solution was found necessary for the full development of the manganese colour up to 10 μg MnO/ml. Moreover, in order to prevent iron interference, the concentration of ascorbic acid and hydroxylamine hydrochloride had to be in excess of 0.025 and 0.2 *M* respectively in the final solution if the iron concentration in the sample exceeded 20 μg Fe/ml. Although lower concentrations of hydroxylamine hydrochloride destroyed the brown-red iron complex, the resultant solution had a yellow colour which absorbed appreciably at 490 nm. The absorbance of this yellow complex at 490 nm increased non-linearly with the concentration of iron, hence accurate corrections could not be made above 10 μg Fe/ml.

When the concentration of ascorbic acid was less than 0.025 *M* in the final solution, the efficiency of the hydroxylamine hydrochloride–EDTA in destroying the iron–formaldoxime complex was impaired; the complex was not destroyed even when the concentrations of the hydroxylamine and EDTA were doubled.

Development of colour

The reduction of iron(III) by ascorbic acid was very rapid but the maximum colour of the manganese–formaldoxime complex at pH 9 was not developed until *ca.* 90 sec had elapsed; the colour was then stable for at least 4 h. The destruction of the iron(II)–formaldoxime complex was a relatively slow process and depended on both the concentration of hydroxylamine hydrochloride and the amount of iron present in the sample. When the final solution contained 0.2 *M* hydroxylamine hydrochloride, the colour due to 1 mg/ml was destroyed within 4 min and the solution then remained colourless for at least 1 h. The destruction of the iron complex had no detectable effect on the manganese–formaldoxime complex.

Reagents

Analytical-reagent grade chemicals were used throughout.

Formaldoxime solution (0.4 M). Dissolve 20 g of hydroxylamine hydrochloride in 90 ml of water and add 10 ml of 36% formaldehyde solution.

Buffer solution. Dissolve 70 g of ammonium chloride in 400 ml of water and add 600 ml of ammonia solution (s.g. 0.880).

Manganese standard solution. Prepare a stock solution containing 100 µg MnO/ml by dissolving 0.1548 g of "Specpure" manganese in 20 ml of 0.5 *N* sulphuric acid and dilute to 2 l. Prepare working standards as required.

Preparation of sample

Weigh accurately *ca.* 0.500 g of rock powder in a platinum crucible and digest overnight on a water bath with 2 ml of 60% (w/w) perchloric acid and 15 ml of 40% hydrofluoric acid. Evaporate the hydrofluoric acid on the water bath and then fume off the perchloric acid under an infrared heater until the residue is almost dry. Add a further 2 ml of perchloric acid and repeat the fuming to remove the last traces of fluoride. Add 2 ml of perchloric acid and heat until fuming commences, cool, add 20 ml of water and place the covered crucible on the water bath to aid dissolution. Dilute the solution to 500 ml.

Manual procedure

Pipette a 20-ml aliquot of the sample solution into a 50-ml graduated flask. Add 3 ml of freshly prepared 0.4 *M* ascorbic acid solution and 3 ml of formaldoxime solution and mix. Add 4 ml of buffer solution, shake and allow to stand for at least 2 min. Add 3 ml of 0.1 *M* EDTA and 4 ml of 2.2 *M* hydroxylamine hydrochloride solution, dilute to volume with water and mix well. Measure the optical density at 490 nm in 1-cm cell after at least 4 min, against a distilled water blank. Determine the reagent blank by the same procedure with the omission of the sample. Calibrate the method using 0, 1, 2 ... 10 µg MnO/ml standard solution.

Automatic procedure

The manifold for the automatic determination of manganese with the Technicon AutoAnalyzer is shown diagrammatically in Fig. 1. Aliquots of sample solution and standard calibration solutions are placed in 10-ml cups, alternating with cups of distilled water, on the sampler which is set to sample at 40 samples/h. The sample is drawn in *via* a pumping tube of 0.090″ i.d. Ascorbic acid and formaldoxime reagents are added through 0.030″ pumping tubes and mixed with the sample in a 3″ mixing coil. The ammonia/ammonium chloride buffer is then added *via* a pumping tube of 0.035″ i.d. and the mixing process is completed in a 6″ mixing coil. The time delay in this mixing coil is sufficient for the full development of the manganese–formaldoxime colour. EDTA and hydroxylamine hydrochloride solutions are then added through 0.030″ and 0.035″ pumping tubes respectively and mixing and destruction of the iron–formaldoxime complex is completed in two 6″ mixing coils. The optical density of the resultant solution is measured by means of a photo-tube colorimeter equipped with 490 nm interference filters and a 15-mm flow cell.

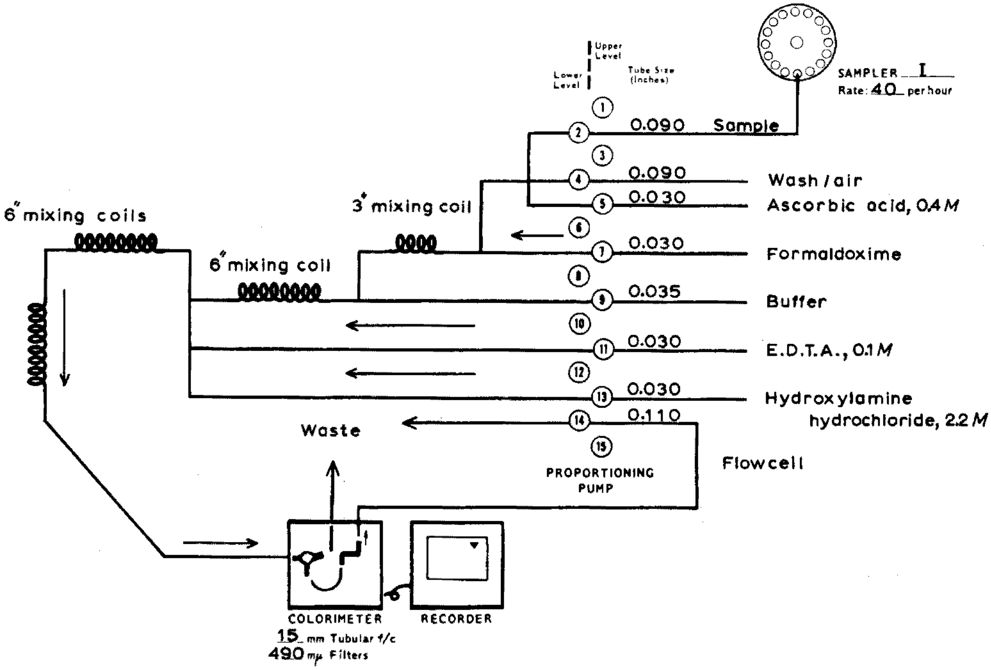

Fig. 1. Flow diagram for the determination of manganese in silicate rocks.

Calibration

A series of standard solutions containing 1, 2, 3, 4, 5 μg MnO/ ml was prepared and a calibration curve was constructed for the automatic method. Beer's law was obeyed over the concentration range of 0–10 μg MnO/ml and the molecular extinction coefficient was calculated to be 7,320 at 490 nm. Replicate determination of a known amount of manganese showed that the standard deviation of the automatic method was ±0.02 μg MnO/ml over the range of 1–6 μg MnO/ml (the equivalent of ±0.002% MnO in the rock sample). In the manual procedure, the molecular extinction coeffi-

TABLE I

EFFECT OF POSSIBLE INTERFERENCES

Element	*Optical density*
2 μg/ml MnO	0.191
2 μg/ml MnO + 10 μg/ml Fe^{3+}	0.192
2 μg/ml MnO + 100 μg/ml Fe^{3+}	0.191
2 μg/ml MnO + 1,000 μg/ml Fe^{3+}	0.193
3 μg/ml MnO	0.288
3 μg/ml MnO + 10 μg/ml Fe^{3+}	0.287
3 μg/ml MnO + 100 μg/ml Fe^{3+}	0.286
3 μg/ml MnO + 1,000 μg/ml Fe^{3+}	0.288
2 μg/ml MnO + 400 μg/ml Ca	0.193
2 μg/ml MnO + 400 μg/ml Mg	0.191
2 μg/ml MnO + 50 μg/ml P_2O_5	0.190

cient was calculated to be 7,500 at 490 nm and Beer's law was followed in the range 0–500 μg MnO.

Interference

A series of solutions containing varying amounts of iron (0–1 mg/ml) and fixed amounts of manganese were prepared and analysed using the automatic procedure described above (Table I). No detectable change in the optical density of the manganese colour was found. The effect of calcium, magnesium and phosphates on the manganese determination was also investigated (Table I). At the concentration levels at which these constituents are present in silicate rocks, no interference was found.

Accuracy of the automatic procedure

To assess the accuracy of the method, U.S. Geological Society standard rocks, G1 and W1 were analysed. The values of MnO obtained for G1 and W1 were 0.035 ± 0.002% and 0.172 ± 0.002% MnO respectively; these agree closely with the recommended values of 0.03% ± 0.01% and 0.17% ± 0.02% MnO respectively[11].

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(Received July 7th, 1967)

The absorption spectrum of phosphorus(III) iodide*

A quantitative treatment of the visible absorption spectrum of phosphorus(III) iodide was made as part of a general study of the kinetic properties of the compound. The major contaminant in terms of the optical spectrum was iodine, which, however, does not interfere in the absorption of the phosphorus(III) iodide. The mathematical treatment includes the assumption that the sample contained only phosphorus(III) iodide and iodine, and adherence to Beer's law would be taken as evidence for the validity of this assumption. As further confirmation, another procedure was used where impure phosphorus(III) iodide solution was purified by passing through a charcoal column and the resulting solution was analyzed quantitatively for phosphorus(V) after suitable oxidation.

Solvents

All solvents used were purified by standard techniques and thoroughly dried to reduce hydrolysis of the phosphorus(III) iodide.

Synthesis of phosphorus(III) iodide

Sodium iodide was refluxed with phosphorus(III) chloride in benzene for 4 h[1]. The mixture was filtered while hot and after cooling the crystals were filtered and then most of the solvent stripped from the filtrate to produce a second crop of crystals. These were combined, dried over calcium chloride at reduced pressure and stored in the same manner. The absorption spectrum of freshly prepared material showed little iodine, a melting point (61°) comparable to the literature value, and no absorption in the region where P_2I_4 was expected to absorb (228 nm).

Analysis for phosphorus

The procedure described below involves oxidation of the phosphorus(III) to phosphorus(V) with nitric acid and spectrophotometric analysis of yellow phosphomolybdate[2,3]. An aliquot of sample solution was added to 50 ml of 6 *M* nitric acid and refluxed for 1 h. The excess organic solvent and nitric acid were removed by evaporating the solution just to dryness and then the solution was transferred to a 50-ml volumetric flask with 20 ml of distilled water. Nitric acid solution (5 ml of 2.5 *M*), about 15 ml of distilled water, and 5 ml of aqueous 10% sodium molybdate solution were added, the solution was diluted to the mark with water, and the transmittance was measured on a Beckman DK-1 with 10-mm cells against a reagent solution.

Absorption spectra

Procedure I. Absorptions were measured over the range 350–650 nm on a Bausch and Lomb Spectronic 505 using 10-mm matched quartz cells with the solvent as the blank. The spectra of phosphorus(III) iodide in hexane and iodine in hexane are shown in Fig. 1. The maximum at 374 nm is attributed to phosphorus(III) iodide while that at 520 nm is due to iodine.

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* Taken in part from the M.S. Thesis of FLORENCE M. WOLTERS, John Carroll University, Cleveland, Ohio, 1964, and from the M.S. Thesis of CHI-TSANG SUN, New Mexico Highlands University, 1967.

In all the solvents employed, phosphorus(III) iodide had maximum absorption at 374 nm whereas the maximum for iodine was solvent-dependent as follows: hexane—520 nm, cyclohexane—524 nm, and carbon tetrachloride—518 nm. Iodine does not absorb at 374 nm while phosphorus(III) iodide does absorb in the region of iodine absorption. Therefore, no correction need be made at 374 nm, but the absorption of phosphorus(III) iodide must be subtracted from the iodine absorption.

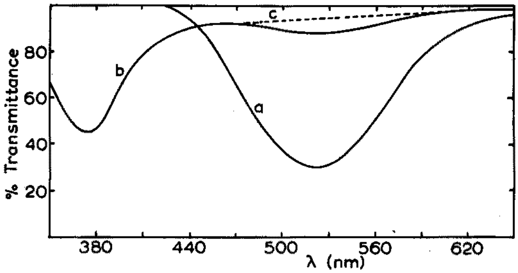

Fig. 1. Absorption spectrum of (a) I_2 in hexane, (b) $PI_3 + I_2$ due to decomposition, and (c) estimated PI_3 curve.

This procedure is justified on the grounds that freshly prepared samples of phosphorus(III) iodide showed essentially no iodine but the absorbance did not go to zero in the wavelength region studied.

Since absorbances are additive, the following procedure and notation was adopted for the analysis of spectra: $(A_T)_\lambda$, $(A_{PI_3})_\lambda$ and $(A_{I_2})_\lambda$ indicate respectively the total absorbance, the PI_3 absorbance and the I_2 absorbance at wavelength λ; C_{PI_3} and C_{I_2} indicate respectively the concentrations of PI_3 and I_2 in moles per liter; and $(\varepsilon_{I_2})_\lambda$ and $(\varepsilon_{PI_3})_\lambda$ indicate the molar absorptivity of I_2 and PI_3 at wavelength λ in l/mole-cm. At any wavelength

$$(A_T)_\lambda = (A_{PI_3})_\lambda + (A_{I_2})_\lambda \tag{1}$$

and

$$A = \varepsilon C = \log I_0/I \tag{2}$$

At 374 nm (ε_{I_2}) is essentially zero, so that the total absorbance corresponds to the PI_3 absorbance. However, since the concentration of phosphorus(III) iodide is unknown, and only the total weight of the sample is known, as a first approximation, it was assumed that this sample contained only phosphorus(III) iodide and iodine and that its composition remained unchanged throughout the analysis. At 520 nm, eqn. (1) was used to calculate the concentration of iodine in the sample by substituting eqn. (2) into eqn. (1) and rearranging:

$$C_{I_2} = \{(A_T)_{520} - (A_{PI_3})_{520}\}/(\varepsilon_{I_2})_{520} \tag{3}$$

where $(\varepsilon_{I_2})_{520}$ for the particular solvent was determined separately. The quantity $(A_{PI_3})_{520}$ was estimated by drawing a line to represent what the absorption of phosphorus(III) iodide at 520 nm might be if iodine was absent as explained above (see Fig. 1).

The concentration of iodine obtained by means of eqn. (3) was used to correct the initial weight of the sample. The weight of phosphorus(III) iodide was then the difference between the total weight taken and the weight of iodine calculated.

TABLE I

EXPERIMENTAL DATA USED IN DETERMINATION OF $(\varepsilon_{PI_3})_{374}$ BY PROCEDURE I

Sample wt. (g/l)	$(A_T)_\lambda$	$(A_{PI_3})_\lambda$	$(A_{I_2})_\lambda$	$C_{I_2}\cdot 10^4$ *(moles/l)*	$C_{PI_3}\cdot 10^4$ *(moles/l)*	$(A_{PI_3})_{374}$
Hexane (λ = 520 nm)[a]						
0.1926	0.1553	0.0756	0.0797	0.896	4.126	0.5611
0.1666	0.1335	0.0569	0.0766	0.861	3.514	0.4609
0.112	0.0569	0.0344	0.0225	0.253	2.57	0.3501
0.0843	0.0597	0.0253	0.0344	0.387	1.81	0.2330
0.0644	0.0645	0.0212	0.0433	0.487	1.26	0.1367
0.0496	0.0682	0.0253	0.0429	0.482	0.908	0.0073
Cyclohexane (λ = 524 nm)[a]						
0.0184	0.0112	0.0090	0.0022	0.024	0.432	0.0542
0.2890	0.1089	0.0588	0.0501	0.542	6.684	0.8567
0.1527	0.0719	0.0334	0.0385	0.417	3.451	0.4409
0.0796	0.0302	0.0162	0.0140	0.152	1.84	0.2201
0.1232	0.0390	0.0326	0.0064	0.069	2.949	0.3729
Carbon tetrachloride (λ = 518 nm)[a]						
0.1542	0.1038	0.0434	0.0604	0.682	3.325	0.4440
0.0812	0.0445	0.0318	0.0127	0.143	1.88	0.2753
0.2800	0.1045	0.0734	0.0311	0.351	6.585	0.9586
0.2782	0.1219	0.1630	0.0589	0.665	6.347	0.8698
0.1086	0.0674	0.0354	0.0320	0.361	2.41	0.3664
0.1446	0.0864	0.0445	0.0419	0.473	3.220	0.4314
0.0396	0.0183	0.0128	0.0055	0.062	0.923	0.1255

[a] Wavelength of maximum absorption of iodine.

TABLE II

EXTINCTION COEFFICIENTS OF I_2 AND PI_3 IN HEXANE, CYCLOHEXANE AND CARBON TETRACHLORIDE AT THE NOTED WAVELENGTHS

Solvent	*Wavelength (nm)*	$\varepsilon_{I_2}\cdot 10^{-2}$ *(l/mole-cm)*	*Wavelength (nm)*	$\varepsilon_{PI_3}\cdot 10^{-3}$ *(l/mole-cm) (Procedure I)*
C_6H_{14}	520	8.898±0.078[a]	374	1.28±0.07[b]
C_6H_{12}	524	9.237±0.029	374	1.25±0.04[c]
CCl_4	518	8.858±0.010	374	1.39±0.05[b]

[a] The deviations are absolute deviations of the mean.
[b] Average of 6 runs.
[c] Average of 5 runs.

Table I lists the experimental data and Table II the resultant molar absorptivities.

This method was modified by assuming the sample contained elemental phosphorus in addition to phosphorus(III) iodide and iodine:

$$PI_3 = \frac{1}{4} P_4 + \frac{3}{2} I_2$$

The total weight of the sample was then corrected to include both iodine and phosphorus. However, such a correction did not improve the data significantly and so is not recommended.

Procedure II. The next approach was to find a method of purifying the crude phosphorus(III) iodide and then to study its absorption spectrum. This was accomplished by passing the solution of phosphorus(III) iodide through a charcoal column (1.5 cm × 4.8 cm^2) and eluting with the same solvent. A separate experiment showed that the phosphorus(III) iodide was eluted first followed by the iodine. Aliquots of the purified solutions of phosphorus(III) iodide were used for spectrophotometric analysis and for determination of orthophosphate. With cyclohexane as the solvent, an average molar absorptivity of $1.54 \cdot 10^3 \pm 0.03$ l/mole-cm over 11 runs was found. The difference between this value and those reported in Table II is related to the different slit arrangements in the instruments used.

Passage through the charcoal column removes any phosphorus in solution so that the analysis gives the quantity of phosphorus originally present as phosphorus(III) iodide. Since the two procedures agreed in the sense that Beer's law was followed, it is concluded that the assumption made in Procedure I is valid and that this method may be used for the analysis of phosphorus(III) iodide solutions.

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(Received July 15th, 1967)

Anal. Chim. Acta, 40 (1968) 531–534

Spectrophotometric determination of uranium in organic solutions of tributyl phosphate

Tri-*n*-butyl phosphate (TBP) in a chemically inert hydrocarbon diluent is widely used for the extraction of uranium[1]. For routine analysis, the uranyl ion is usually back-extracted into an aqueous solution and then determined by a standard analytical procedure[2,3]. Two direct spectrophotometric methods have been proposed for use in organic solvents: the thiocyanate[2,4] and the dibenzoylmethane method[5,6]; the main difference from the normal reactions in aqueous media seems to be the mixing of organic samples with polar solvents like acetone, penta-ether or ethanol, followed by "color" development in a homogeneous organic–aqueous phase[7]. Such methods depend on the mutual solubility of the components and on the kinetics of the complex formation. Thus, samples containing uranium in more polar solvents like methyl isobutyl ketone or ethyl acetate can be readily analyzed by both methods, but difficulties occur if the main solvent is a paraffinic hydrocarbon. Another routine spectrophotometric procedure[8] is based on the re-extraction of uranium into an aqueous solution.

The present paper describes a new spectrophotometric method for direct determination of uranium in TBP solvents. No attempt is made to form a single organic–aqueous phase. The chromogenic reagent is added as a toluene solution, which is perfectly miscible with samples containing TBP in a hydrocarbon solvent. The method is actually based on the formation of a "mixed ligand" complex of uranyl ion with thenoyltrifluoroacetone (HTTA) and TBP. Such complexes of uranium have been investigated in connection with "synergistic" effects in solvent extraction[9–11].

Stability constants

The uranyl nitrate extracted into TBP solvents is in the form $UO_2(NO_3)_2 \cdot 2TBP$[1]. On addition of HTTA and TBP, the reaction is probably:

$$UO_2(NO_3)_2 \cdot 2TBP + 2\ HTTA + TBP \rightleftharpoons UO_2(TTA)_2TBP + 2\ TBP \cdot HNO_3$$

The formation of the "mixed ligand" complex has been proved[11] and its molal absorptivity in benzene at 332 nm found[10] to be $2 \cdot 10^4$, about three orders of magnitude higher than the value obtained for $UO_2(NO_3)_2 \cdot 2TBP$ in the same solvent.

The equilibrium constant for the above over-all reaction is difficult to derive but some information about the stability of the mixed complex can be obtained by studying the reaction

$$UO_2(TTA)_2 + TBP \rightleftharpoons UO_2(TTA)_2TBP$$

Rough estimates of the stability constants, based on spectrophotometric measurements, gave the following log K values: 4.1 for toluene media, 4.3 for benzene media and 4.4 for carbon tetrachloride media. A value of 5.7 has been reported[12] for cyclohexane media. For analytical application, toluene was chosen as a suitable solvent owing to its relatively low vapour pressure.

Composition of the chromogenic reagent

Absorption spectra of the system $UO_2(NO_3)_2$–TBP–HTTA–toluene were studied with solutions of various composition (see also ref. 10). It was concluded that absorbances should be measured at the 395-nm band, where $UO_2(TTA)_2TBP$ has a molar absorptivity of $1.9 \cdot 10^4$, and free HTTA (enol form) $2.5 \cdot 10^2$, while the absorption of TBP is negligible. If the uranium concentration in the organic solution is below $10^{-3}\ M$, an excess of $2.5 \cdot 10^{-3}\ M$ HTTA and $5.0 \cdot 10^{-2}\ M$ TBP is sufficient to convert completely the uranyl species to the mixed ligand complex.

Stability of color. Validity of Lambert–Beer law

A study of the dependence of the absorbance of an uranium-containing $2.5 \cdot 10^{-3}\ M$ HTTA + $5.0 \cdot 10^{-2}\ M$ TBP solution on time showed that maximum absorbance was achieved within 10 min, the absorbance then remaining stable for at least 100 min. The Lambert–Beer law was shown to be valid over the range 0–8 μg of uranium per ml.

Influence of impurities

The extraction of uranium with TBP is fairly selective. Optimum conditions can be obtained by regulating the pH and by addition of salting-out electrolytes and/or complexing agents before the extraction. Thus, the organic extracts for nuclear fuel reprocessing facilities, in which the main impurities—Al, Zr, Ni, Co, Fe, Cr—are present in concentrations far below that of uranium, will contain very little impurity. Plutonium and fission products are only trace components. Preliminary experiments showed that above mole ratios of U/Co(Ni) of 1.5, U/Fe of 7 and U/Zr of 25, no effect on the absorbance measurements could be detected.

Provided that the only anion present in the extract is nitrate, and that possible anionic impurities are below 1% of the nitrate content, their effect is negligible.

Although the effect of impurities can be safely neglected if extracts from nuclear fuel reprocessing are analyzed, further study would be needed before samples from ore reprocessing could be analyzed.

Reagents and apparatus

Thenoyltrifluoroacetone and tributyl phosphate (BDH Ltd.) were purified as described previously[13]. All other reagents (A.R. grade) were used without further purification.

Crystalline $UO_2(TTA)_2$ was prepared[14] and used for the determination of the stability constant of the "mixed ligand" complex.

All spectrophotometric measurements were done in a Unicam SP-500 instrument with 1-cm quartz cells.

Procedure

To a 10-ml volumetric flask, add an aliquot (10–200 μl) of the organic-solvent sample containing 10–90 μg of uranium. In a similar flask, prepare a blank with the same volume of toluene, containing the same amount of TBP as the actual sample. Dilute both solutions to volume with the reagent solution, $2.5 \cdot 10^{-3}$ M HTTA and $5.0 \cdot 10^{-2} M$ TBP in toluene. Measure the sample solution against the blank at 395 nm in 1-cm cells.

This procedure is convenient for the determination of 0.05–9 g of uranium per liter of TBP solvent. The standard error is below ±5%. With a suitable dilution technique and other optical cells, the procedure could be easily extended to a range of 0.01–100 g U per liter of TBP solvent.

Results and discussion

The method was carefully checked on many synthetic organic solutions, and then applied to routine analysis for uranium in organic streams of a small-scale nuclear fuel reprocessing facility. In this facility a "Purex" type of extraction

TABLE I

A COMPARISON OF URANIUM ANALYSES BY TWO METHODS

Samples[a]	*U found (g/l)*		*Difference (%)*
	Thiocyanate method	*HTTA–TBP method*	
HSP	74.4	76.6	+2.6
BU-1	78.0	77.5	−0.6
CW-1	0.82	0.85	+3.5
BU-4	65.8	64.8	−1.5

[a] Samples refer to organic streams of a Purex flowsheet[15].

flowsheet was used[15]. The organic solvent was 30 vol.% TBP in kerosene, and several organic streams of variable uranium, plutonium and fission product concentration were analyzed. A comparison of results obtained by the proposed method and by the previous routine method, *i.e.* back-extraction followed by the thiocyanate complex determination[2,3], is given in Table I.

The sensitivity of the new method makes it possible to take very small aliquots (10–100 μl) which is important from the point of view of radiation protection when radioactive samples are analyzed. The method is simple, rapid and suitable for routine control; and both the reagent and the colored solution formed are stable. The disadvantages of the new method are that the Lambert–Beer law holds only in a relatively narrow concentration range and that the absorbance of HTTA is considerable, so that precise compensation of HTTA absorption in the sample and blank solution is essential.

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(Received August 3rd, 1967)

Über die Möglichkeit einer extraktionsphotometrischen Eisenbestimmung mit Kristallviolett

Farbstoffe sind in der Literatur wiederholt zur Bestimmung von Metallionen herangezogen worden[1-5]. In mineralsaurer Lösung werden Farbstoffe wie Kristallviolett, Brilliantgrün, Rhodamin B, Äthylmauvein, Methylenblau, Nilblau, Neutralrot u.a. protonisiert und sind dadurch in organischen Extraktionsmitteln unlöslich. Andererseits zeigt sich im Experiment, dass nur Kationen mit dem Farbstoff reagieren, die mit der verwendeten Säure komplexe Anionen zu bilden vermögen. Diese deprotonisieren den Farbstoff, und machen ihn zusammen mit dem komplexen Anion extrahierbar. Demnach ist als Reaktionsmechanismus nahezu ausschliesslich die Bildung eines Farbstoffkation–Metallanion-Komplexes anzunehmen. Dies ermöglicht prinzipiell extraktionsphotometrische Bestimmungen von Kationen.

In einer früheren Arbeit[6] bestimmten wir auf diese Weise Thallium in biologischem Material. Da Quecksilber und Eisen auch komplexe Anionen bilden, untersuchten wir die Möglichkeit diese beiden Elemente mit Kristallviolett zu bestimmen. Die Halogenide eignen sich gut als Komplexbildner. So ist eine Quecksilber(II)-Bestimmung mit Kristallviolett in salzsaurem Medium, nach Zusatz von wenig Kaliumjodid (Bildung von $[HgJ_4]^{2-}$) möglich. Beim Eisen(III) ist die Bestimmung als $[FeCl_6]^{3-}$ in 4 N Salzsäure am günstigsten. Da Eisen(II) keine Halogenkomplexe gibt, ist es nach dieser Methode nicht bestimmbar. Etwa in der Analysenprobe vorhandenes Eisen(II) muss daher vor der Bestimmung zu Eisen(III) oxydiert werden. Als Oxydationsmittel verwendeten wir Kaliumpermanganat, dessen Überschuss mit Oxalat entfernt wird. Als Extraktionsmittel eignet sich Chloroform am besten.

Reagenzien und Geräte

Salzsäure, Chloroform, Kristallviolett, Methanol, p.A. Merck. Als Reagens dient eine Lösung von 0.05% Kristallviolett in Chloroform. Für alle Messungen wurde ein Spektralphotometer der Firma Zeiss, Type PMQ II verwendet.

Arbeitsvorschrift

Die Eichkurve wurde durch geeignetes Verdünnen einer Eisen(III)-chlorid Standardlösung (1 mg Eisen/ml) aufgestellt. In einem Schütteltrichter werden 25 ml Probelösung (0.5–4.0 mg Eisen(III) enthaltend), die zuvor auf ein pH von 1–5 gebracht worden ist, mit 25 ml 8 N Salzsäure versetzt. Man fügt 3 ml Reagenslösung hinzu und schüttelt kräftig durch. Die Chloroformschicht wird abgetrennt, und die wässrige Phase noch zweimal mit je 3 ml Chloroform extrahiert. Die organischen Extrakte werden in einem 10-ml Messkolben vereinigt und mit Methanol zur Marke aufgefüllt. Man misst die Extinktion in 5-cm Küvetten, bei 590 nm gegen einen analog hergestellten Blindwert.

Das Lambert–Beer'sche Gesetz ist im Bereich von 0.05 bis 0.4 mg Fe/ml Chloroform erfüllt. Die Empfindlichkeit der Methode beträgt 2.9 μg Fe ml^{-1} cm bezogen auf Chloroform bei einer Extinktion von 0.001.

Diskussion

Die Bestimmung beruht auf der Extraktion einer zum Eisengehalt proportionalen Menge des Farbstoffkomplexes. Der Blindwert steigt mit fallender Säurenormalität. So ist in 6 *N* Salzsäure die Chloroformphase des Blindwertes farblos, die Empfindlichkeit der Eisenbestimmung jedoch geringer. Das Absorptionsspektrum des Kristallviolettkation $\{(FeCl_6)^{3-}\}$-Komplexes unterscheidet sich im sichtbaren Bereich von dem des reinen Farbstoffes nicht, weil die das Chloroform färbende Komponente das Kristallviolettkation ist. Als Beleganalysen bestimmten wir mit der angeführten Methode den Eisengehalt eines Mineralwassers (20 mg Fe/l enthaltend) und den einer Aluminiumlegierung (0.81% Fe). Die angegebenen Eisengehalte konnten mit einem Fehler von ±0.9% bestätigt werden.

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(Eingegangen den 5. September, 1967)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEWS

E. PUNGOR, *Flame Photometry Theory*, Van Nostrand Series in Analytical Chemistry, D. van Nostrand Co., London, 1967, x+200 pp. Price 60 s.

It should be understood that this is not a book about flame photometry, but about flames. The first two chapters on flames and radical equilibria in flames occupy 78% of the book, and two short chapters deal further with flame temperature and fuels. The final two chapters are, however, specifically on flame photometry, giving a very useful 13 page account of atomisation, and five extremely meaty pages on flame emission spectroscopy and one on atomic absorption spectroscopy. The title is therefore in a measure misleading, but the flame and how it works and what goes on in it have a strong relevance to, so to phrase it, the second phase of understanding flame photometry and allied techniques. PUNGOR has contributed a succinct yet comprehensive account of present views on the subject in terms understandable to the chemist, of value not only to analytical users of flames, but also to those concerned with combustion processes and flame propagation.

E. BISHOP (Exeter)

Anal. Chim. Acta, 40 (1968) 540

Encyclopedia of Industrial Chemical Analysis, Edited by F. D. SNELL AND C. L. CLINTON, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1967, *Vol. II. General Techniques F–O*, xi+769 pp.; *Vol. III. General Techniques P–Z*, xi+845 pp.; price 340 s. each (260 s. subscription price).

These two volumes complete the first part of this Encyclopaedia. Volume II contains 31 articles on topics such as flammability, gas chromatography and magnetic susceptibility. Volume III includes 38 relevant topics between the letters P and Z, such as polarography, surface and interfacial tension, viscosity, etc., and has the index to the whole first part.

Inevitably, the treatment throughout these two volumes is uneven, and it is easy to criticize, for no two people will agree on what should be omitted. However, where instrumental methods are concerned, a prime objective in consulting a text of this nature would be to discover the general range of application of a particular technique and this information is not often given; instead, space is allotted to descriptions of commercially available apparatus which will rapidly become obsolete. There is a lack of balance in the treatment of the various themes. For example, Rheological Measurements, Fluid, are accorded 55 pages, whilst ultraviolet and visible spectrophotometry is rushed through in 27 figure-strewn pages. Separation by extraction is discussed in 33 pages, but solvent extraction in the conventional analytical sense is barely mentioned (½p.)

The treatment of classical analysis is cursory for the most part. A fairly good treatment of precipitation processes is given under Gravimetry but the sections on Redox Titrations, Indicators and Standardisation of Solutions are poor. The picture given of organic microanalysis is misleading, for a great deal happened between the Pregl methods and the introduction of automatic apparatus and much of it remains of value.

Of course, in these 1600 pages, there is a great deal that is worth reading, despite the occasional feeling of *déjà vu*, particularly in the section on pH determination. The actual production of these volumes is superb, but in proportion to the freshness of the treatment of most topics, the price seems excessive.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 40 (1968) 540–541

W. SIMON UND T. CLERC, *Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden,* Methoden der Analyse in der Chemie, Band 7, Akademische Verlagsgesellschaft, Frankfurt am Main, 1967, iv+92 S.+50 Übungsbeispiele, DM 39.

At the 1966 Gordon Conference on Analytical Chemistry, the reviewer was impressed by demonstrations of how a combination of infrared, nuclear magnetic resonance and mass spectra can result in the elucidation of the structure of simpler organic compounds. In the present volume, ultraviolet spectra are also included. The book handles the problem in the form of tables, first according to the structure and then according to the method. Most common types of organic compounds (alkanes, ethers, ketones, amines, etc.) are listed together with data obtained by all four methods. Then I.R., U.V., N.M.R. and mass spectra are reproduced and U.V. data are given for 50 substances so that some practice can be obtained. The handbook is very useful both as a teaching aid and in laboratory practice.

P. ZUMAN (Prague)

Anal. Chim. Acta, 40 (1968) 541

Advances in Electrochemistry and Electrochemical Engineering. Vol. 5. Electrochemical Engineering, Edited by C. W. TOBIAS, Interscience Publishers–J. Wiley and Son, Inc., New York, 1967, xi+325 pp., price 116 s.

This volume contains contributions on the Nickel–Cadmium Cell by C. P. C. MILNER AND U. B. THOMAS; Transport Processes in Electrolytic Solutions by J. NEWMAN; Transport Properties in Molten Salt Electrolytes by G. J. JANZ AND R. D. REEVES; Electrolysis of Nonaqueous Solutions by A. BRENNER; and Electrodeposition of Alloys by K. M. GORBUNOVA AND YU. M. POLUKAROV.

The reviews by NEWMAN and by JANZ AND REEVES are done from a largely theoretical viewpoint, whereas the others are more concerned with practical problems. Most of the reviews were completed in 1966 and are well documented. The analytical chemist should find these volumes useful in keeping up-to-date with the type of methods used in modern applied electrochemistry in terms of research and development.

P. ZUMAN (Prague)

Anal. Chim. Acta, 40 (1968) 541

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANNOUNCEMENTS

INTERNATIONAL SYMPOSIUM ON ANALYTICAL CHEMISTRY, BIRMINGHAM, 1969, JULY 21st–25th, 1969

The Midlands Section of the Society for Analytical Chemistry is organising an International Symposium at the University, Birmingham, England, over the period 21st–25th July, 1969. The programme will include invited and contributed papers covering a wide field of analytical chemistry, together with social events, a ladies' programme, etc.

Some preliminary notices gave the data of this Symposium as 6th–10th April, 1970, but this has now been changed to the above.

General information about the Symposium can be obtained from Mr. D. M. PEAKE, Research Department, Imperial Metal Industries Limited, P.O. Box 216, Witton, Birmingham 6, England. Information about the scientific programme is obtainable from Dr. W. I. STEPHEN, Department of Chemistry, The University, Birmingham 15, P.O. Box 363, England.

BIOCHEMISCHE ANALYTIK, MÜNCHEN, 1968

Biochemische Analytik ist das Thema einer gemeinsamen Tagung der Gesellschaft Deutscher Chemiker, der Gesellschaft für Biologische Chemie, der Deutschen Pharmazeutischen Gesellschaft und der Deutschen Gesellschaft für Klinische Chemie, der unter Leitung von Professor Dr. Dr. E. WERLE vom 29. April bis 2. Mai 1968 in München stattfindet. Alle wichtigen Gebiete moderner biochemischer Analytik werden in Hauptreferaten und Kurzvorträgen behandelt.

Während der Tagung findet ein internationales Symposium über "Statistische Qualitätskontrolle im analytischen Laboratorium" statt.

Verbunden mit dem Kongress ist die internationale Fachausstellung "Analytica 68", auf der Laboratoriums-Geräte und Einrichtungen gezeigt werden.

Vortragsanmeldungen und Auskünfte bei Priv. Doz. Dr. H. SCHIEVELBEIN, 8 München 15, Nussbaumstr. 20.

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PRINTED IN THE NETHERLANDS