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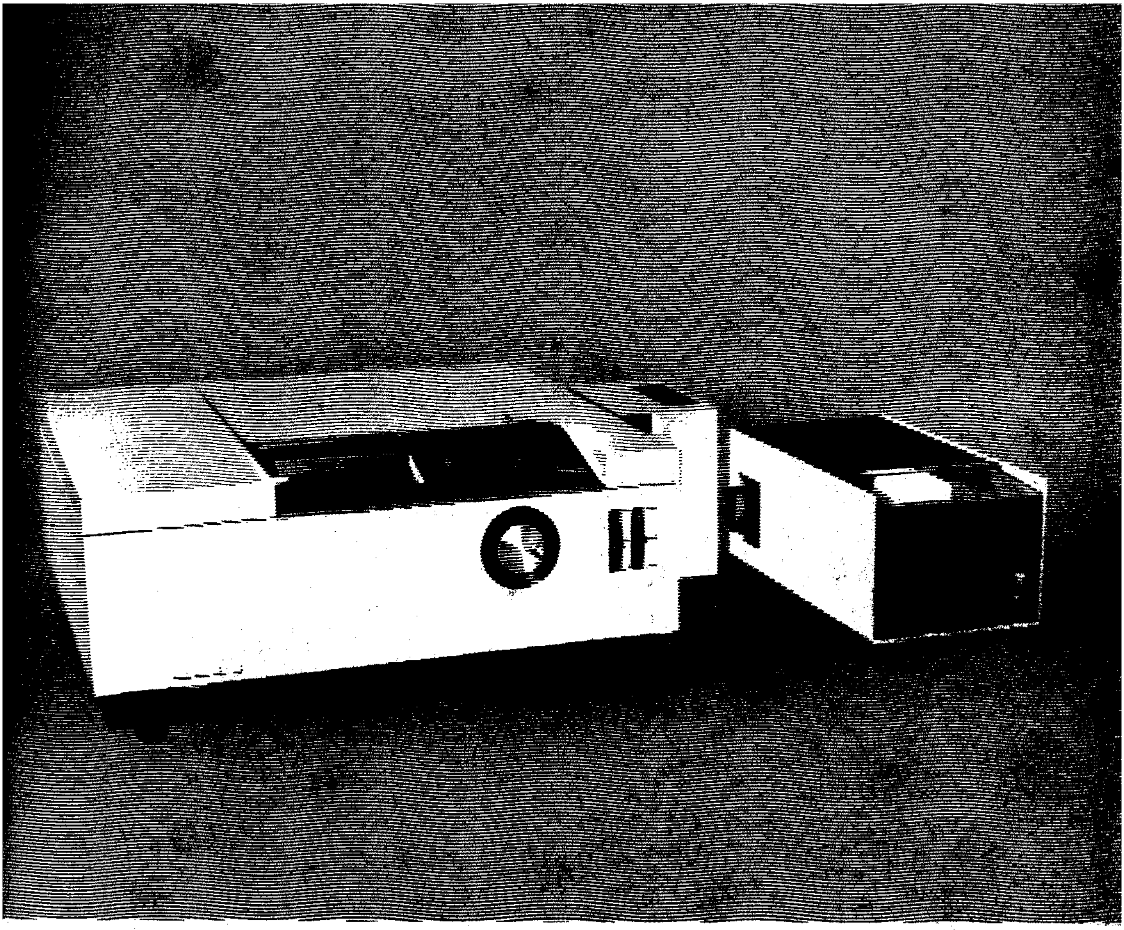

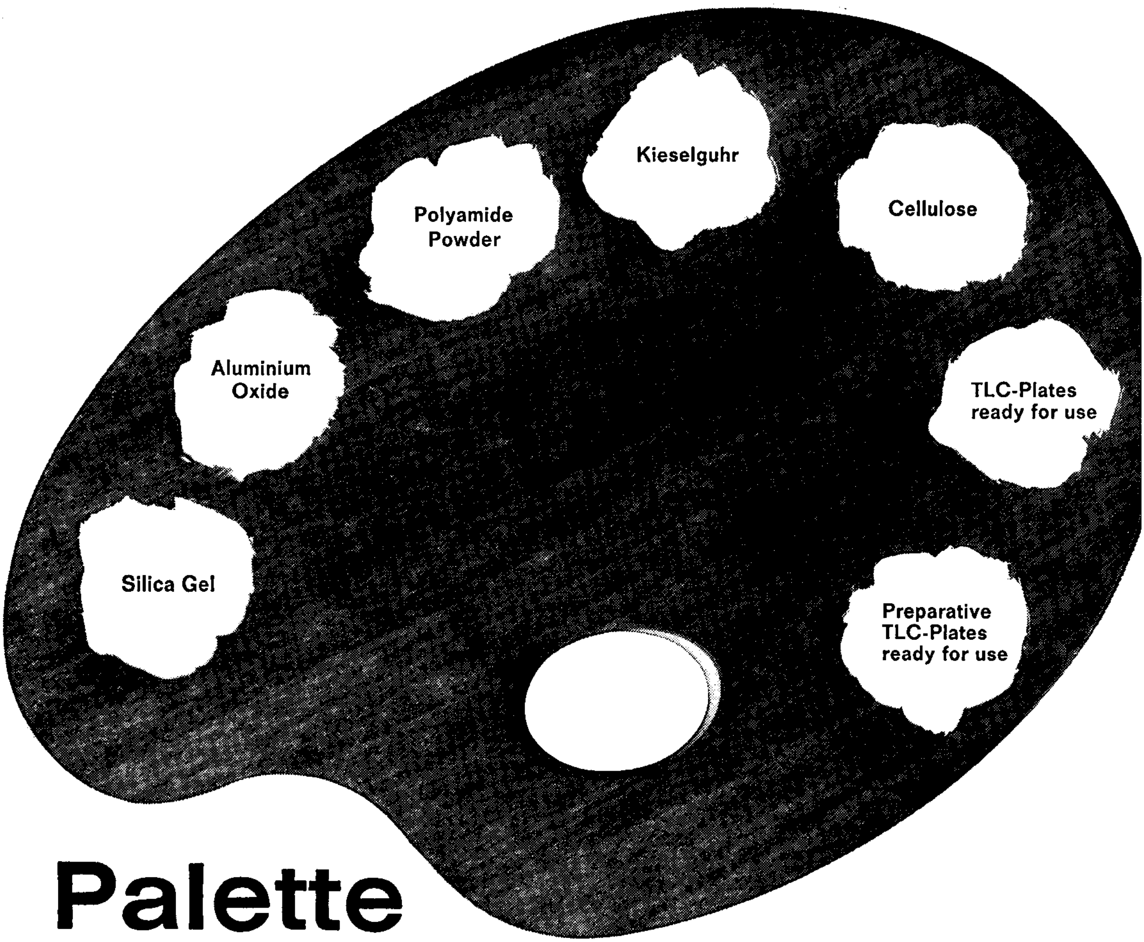
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 37, No. 3, March 1967

THE APPLICATION OF X-RAY DIFFRACTION ANALYSIS TO URANIUM CERAMICS

PART I. QUANTITATIVE ANALYSIS OF THE BINARY MIXTURE UO_2–U_3O_8

An X-ray diffraction method is proposed for the quantitative analysis of the binary mixture UO_2–U_3O_8. Diffractometer and Debye–Scherrer camera techniques were compared; the former is preferable whenever sufficient sample is available. The relative standard deviation was found to be 1%.

R. Conti, C. J. Toussaint and G. Vos,
Anal. Chim. Acta, 37 (1967) 277–283

ATOMIC ABSORPTION STUDIES ON RARE EARTH AND REFRACTORY METALS

The use of atomic absorption spectroscopy for the analysis of rare earth and refractory metals was studied. Various types of burners and fuel–oxidant mixtures were examined. The effects of organic solvents, sample solution flow rates and the use of continuous light sources on sensitivity are noted. The metals neodymium, samarium, europium, gadolinium, terbium, erbium, dysprosium, yttrium, vanadium, chromium, aluminum, and zirconium were included in this investigation.

R. J. Jaworowski, R. P. Weberling and D. J. Bracco,
Anal. Chim. Acta, 37 (1967) 284–294

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO III IN THE ORGANIC PHASE AFTER EXTRACTION WITH DI-(2-ETHYLHEXYL)ORTHOPHOSPHORIC ACID

A simple, direct colorimetric determination of thorium extracted from chloride solution with di-(2-ethylhexyl)orthophosphoric acid is described; the colour is developed in the organic phase by adding arsenazo III and then isopropanol. Two different procedures are outlined for different thorium levels; maximum absorbance occurs at 660 nm and Beer's law is obeyed within limited ranges. Molar extinction coefficients for the two methods are $4.93 \cdot 10^4$ and $8.77 \cdot 10^4$ respectively. With the more sensitive method, 0.696 μg Th/ml was determined with 0.0028 as the standard deviation. The effects of the various parameters were studied. Among 69 foreign cations tested serious interferences are U(VI), Se(IV), Ti(IV), Y and the rare earths. Of the common anions, only large amounts of sulphate interfered. Several ways of overcoming interferences are suggested, with particular reference to uranium.

Several extensions of the method are outlined; 2 p.p.b. Th in aqueous media can be determined by modifying the extraction step. The procedure also appears to be extremely sensitive for the light rare-earth elements.

E. Cerrai and G. Ghersini,
Anal. Chim. Acta, 37 (1967) 295–309

THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN ROCKS

Vanadium in rock samples is determined, after alkaline fusion of the sample, by means of its catalytic action on the oxidation of aniline to aniline black by hydrogen peroxide. If necessary, chromium can be easily extracted to prevent interference. The sensitive procedure was applied to standard granite G1 and diabase W1, and to the C.A.A.S. syenite 1; values of 16, 263 and 86 p.p.m., respectively, were obtained.

R. Fuge,
Anal. Chim. Acta, 37 (1967) 310–315

SOLVENT EXTRACTION STUDIES OF SOME COBALT(II) CHELATES

Extraction of radiolabeled cobalt(II) from aqueous solution into one or more solvents using 25 reagents was studied. Both reagent concentration and pH variation were investigated. The relevant association and partition constants for several of the better reagent–solvent systems were determined. These systems were hexanoic acid in 1-hexanol, octanoic acid in 1-octanol, and thenoyltrifluoroacetone in benzene.

G. K. Schweitzer and L. H. Howe, III,
Anal. Chim. Acta, 37 (1967) 316–324

THE PRECISE COMPLEXIMETRIC TITRATION OF URANIUM(VI)

The compleximetric reaction of uranium(VI) with EDTA has been studied. A method is described for determining uranium(VI) with PAN as an indicator and without an indicator by titration in the ultraviolet region. With the described technique, quantities of uranium varying from 12 μg to 9 mg can be determined. The coefficients of variation vary from 5 % to 0.1 %, respectively.

A. Brück and K. F. Lauer,
Anal. Chim. Acta, 37 (1967) 325–331

THE STABILITY CONSTANTS OF SOME BIVALENT METAL COMPLEXES OF α-HYDROXYISOBUTYRATE AND LACTATE

The stability constants of the lactate and α-hydroxyisobutyrate complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and UO_2^{2+} were determined by potentiometric titration. The average ligand number exceeds 2, indicating the formation of ML^+, ML_2 and ML_3^- complexes. The existence of ML_3^- complexes was confirmed by electrophoretic experiments; no polynuclear complexes were formed. α-Hydroxyisobutyrate forms stronger complexes than lactate.

H. Thun, W. Guns and F. Verbeek,
Anal. Chim. Acta, 37 (1967) 332–338

ACTIVATION OF SHORT-LIVED ISOTOPES. RAPID SEPARATION BY EXCHANGE ON MERCURY

EXCHANGE BETWEEN MERCURY AND MERCURY IONS

(*in French*)

The exchange of mercury ions and of certain organic mercury complexes with a drop of mercury was studied systematically by means of radioactive isotopes. Under defined conditions, the exchange is quantitative, very rapid and selective; most other ions remain in solution so that traces of mercury can be determined by neutron activation. Only ions with higher oxidation potentials than mercury interfere.

D. Monnier and E. Loepfe,
Anal. Chim. Acta, 37 (1967) 339–349

DIFFUSION COEFFICIENTS OF TUNGSTEN HETEROPOLYACIDS

Controlled hydrodynamics at rotating platinum and amalgamated copper electrodes were used to measure diffusion coefficients for 12-phosphotungstic and polyphosphotungstic acids in 1 M phosphoric acid. $D_{12\text{-PTA}} = 2.48 \cdot 10^{-6}$; $D_{\text{polymer}} = 2.68 \cdot 10^{-7}$ cm^2/sec, assuming only 1 tungsten atom in 12 is reduced at each diffusing entity. The phosphotungstic acids in phosphoric acid probably exist as polymers on initial formation, not greater than tetramers, rearranging to give monomers from calculations based on one reduced tungsten atom to each complex ion. Diffusion parameters of the phosphotungstic acids are compared with diffusion results of tungsten compounds from the literature obtained with dropping mercury electrodes. In all instances, low diffusion values are obtained indicating large diffusing entities.

P. Stonehart,
Anal. Chim. Acta, 37 (1967) 350–358

ANION-EXCHANGE CHROMATOGRAPHY OF ORGANIC ACIDS IN MAGNESIUM ACETATE MEDIUM

Magnesium acetate solution is a useful eluant in the separations of dibasic organic acids by anion-exchange chromatography. The following acids were separated: oxalic, tartronic, malic, glucaric, galactaric, tartaric and maleic acids. The eluate was analyzed automatically using chromic acid oxidation.

K. S. Lee and O. Samuelson,
Anal. Chim. Acta, 37 (1967) 359–363

SEPARATION OF RHENIUM(VII) FROM MOLYBDENUM(VI) AND MANY OTHER ELEMENTS BY ANION EXCHANGE

A method is described for the selective separation of μg and mg amounts of rhenium(VII) from molybdenum(VI) and many other metal ions by means of the strongly basic anion-exchange resin Dowex 1-X8. The separation is based on the preferential elution of molybdenum by a 90% (v/v) methanol – 10% 6 *M* nitric acid mixture; rhenium and a few other elements are retained while molybdenum and most other metal ions including Fe(III), Ca, Mg, Mn, U, Cu, V, etc., are practically unadsorbed. After elution of the adsorbed rhenium with 70% (v/v) tetrahydrofuran–30% 9 *M* hydrochloric acid, the rhenium is determined spectrophotometrically by a modified thiocyanate method.

J. Korkisch and F. Feik,
Anal. Chim. Acta, 37 (1967) 364–369

SEMIQUANTITATIVE AUTORADIOGRAPHIC DETERMINATION OF CARBON-14 ACTIVITY IN THE pC RANGE BY MEANS OF THE RING OVEN

(in German)

The use of the ring-oven method for the semiquantitative autoradiographic determination of ^{14}C-labelled compounds is described. Satisfactory results can be obtained in the activity range 9.2–460 pC/μl (exposure times of 122–2 h) with special commercial films.

H. Weisz and D. Klockow,
Anal. Chim. Acta, 37 (1967) 370–373

MICRODETERMINATION OF COPPER USING DITHIOOXAMIDE CRAYONS AND THE RING-OVEN TECHNIQUE

A method for the microdetermination of copper in air pollution investigations, using a dithiooxamide crayon and the ring-oven technique is presented. The limit of detection for the method is 0.04 μg, and the quantitative determination is applicable in the range of 0.05 to 0.5 μg of copper. The method is free from interferences that might be of significance in the study of air samples.

P. W. West and L. R. M. Pitombo,
Anal. Chim. Acta, 37 (1967) 374–378

SIMULTANEOUS DETERMINATION OF TRACE CONCENTRATIONS OF SATURATED AND α,β-UNSATURATED CARBONYL COMPOUNDS IN ORGANIC SYSTEMS

A method for the simultaneous determination of trace concentrations of saturated and α,β-unsaturated carbonyl compounds in complex systems is presented. Carbonyl as the alkaline 2,4-dinitrophenylhydrazone is determined spectrophotometrically at 2 selected wavelengths of 480 and 426 nm. The apparent total carbonyl concentration is obtained from prepared calibration curves at the selected wavelengths based on known concentrations of *n*-heptaldehyde. From the observed relative response of known concentrations of *n*-heptaldehyde and 2-ethyl-2-hexenal, the true concentration for saturated and α,β-unsaturated carbonyl is obtained by a simple calculation. The method has been used extensively for alcohol systems ranging up to tetracontanol but is equally useful for hydrocarbons, aromatic oxygenates and hydrocarbons, petroleum distillates and kerosenes, organic acids and esters, and some ethers.

D. E. Jordan,
Anal. Chim. Acta, 37 (1967) 379–390

SPOT TEST DETECTION OF SULFIDE IN MINERALS

(Short Communication)

F. L. Chan,
Anal. Chim. Acta, 37 (1967) 391–393

THE DETERMINATION OF NITROGEN IN BERYLLIUM WITHOUT DISTILLATION

(Short Communication)

J. K. Bundy and G. C. Goode,
Anal. Chim. Acta, 37 (1967) 394–397

THE PALLADIUM(II) COMPLEX OF PICOLINEALDEHYDE 2-QUINOLYLHYDRAZONE

(Short Communication)

R. E. Jensen and R. T. Pflaum,
Anal. Chim. Acta, 37 (1967) 397–400

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

(Short Communication)

J. C. Guyon and C. C. Clowers,
Anal. Chim. Acta, 37 (1967) 401–402

LIQUID–LIQUID EXTRACTION BY TRI-ISO-OCTYLAMINE IN METHYL ISOBUTYL KETONE FROM AQUEOUS HYDROCHLORIC ACID

(Short Communication)

M. Y. Mirza, M. Ejaz, A. R. Sani, S. Ullah, M. Rashid and G. Samdani,
Anal. Chim. Acta, 37 (1967) 402–404

FLUORIMETRIC DETERMINATION OF THORIUM WITH FLAVONOL

(Short Communication)

R. S. Bottei and A. S. D'Alessio,
Anal. Chim. Acta, 37 (1967) 405–409

ION-EXCHANGE SEPARATION AND FLUORIMETRIC DETERMINATION OF TUNGSTEN IN STEELS

(Short Communication)

R. S. Bottei and A. Trusk,
Anal. Chim. Acta, 37 (1967) 409–412

A SIMPLE SODIUM THERMIONIC DETECTOR FOR ORGANIC HALOGEN AND PHOSPHORUS COMPOUNDS

(Short Communication)

G. G. Guilbault and C. Herrin,
Anal. Chim. Acta, 37 (1967) 412–414

ALKYL-8-QUINOLINOLS

(Short Communication)

T. Rudolph, J. P. Phillips and H. Puckett,
Anal. Chim. Acta, 37 (1967) 414–417

THE APPLICATION OF X-RAY DIFFRACTION ANALYSIS TO URANIUM CERAMICS

PART I. QUANTITATIVE ANALYSIS OF THE BINARY MIXTURE UO_2–U_3O_8

R. CONTI*, C. J. TOUSSAINT AND G. VOS
Analytical and Mineral Chemistry Section, Euratom,
CCR-Ispra (Italy)

(Received August 8th, 1966)

The growth of the nuclear technology for power applications, has stimulated the evaluation of ceramics of uranium as fuel materials. These ceramics have interesting characteristics, such as good irradiation stability, high neutron utilisation and high melting point[1,2]. A proper study of these materials requires analytical methods for determining their composition. Much work involving X-ray diffraction has been done for other materials, *e.g.* determination of copper in brass[3], metallic platinum in platinum–alumina catalysts[4], retained austenite in steels[5], quantitative analysis of mixed fertilisers[6], but the only application to nuclear materials seems to occur in a study of a mixture of uranium carbides by ATODA *et al.*[7].

The present work was limited to a direct determination without use of an internal standard, because the composition was only biphasic. In this investigation the possibility of determining UO_2 in U_3O_8 and *vice-versa* using the X-ray diffractometer and the Debye–Scherrer camera, was studied.

EXPERIMENTAL

Apparatus and operating conditions

The apparatus used was a standard Philips diffractometer, including a proportional counter, and pulse-height discrimination. For the photographic measurements, a large Debye–Scherrer camera (diameter 114.83 mm with an entry collimator of 0.5 mm) was employed. The sample was introduced in a capillary tube with a diameter of 0.2 mm. The intensities were measured with the Siemens type A photometer and the Joyce–Loeb microdensitometer M K III B. A complete list of the equipment and instrumental conditions is given in Table I. The X-ray diffractometer analysis requires a minimum amount of 3 g of sample and the time for a single determination (excluding the grinding time) is about 1 h; for the Debye–Scherrer technique, the minimum sample size is only 1 mg and the time requirement is *ca.* 5 h.

Sample preparation

KLUG AND ALEXANDER[8], in discussing the statistical factors to be considered for the case of quartz powders, mention that the crystallite size must be less than 5 μ to achieve a 1% reproducibility in the intensity measurements. Therefore the

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* Present address: Faculté des Sciences d'Orsay.

TABLE I

APPARATUS AND INSTRUMENTAL CONDITIONS

X-Ray diffractometer	*Debye–Scherrer technique*
Cu tube with Ni filter	Camera diameter: 114.83 mm
50 kV — 20 mA	Collimator: 0.5 mm
Divergence and scatter slit: 1°	Sample capillary: 0.2 mm
Receiving slit: 0.2 mm	Exposure time: 4 h
Proportional counter	Microdensitometers: Siemens type A
Counting time: 100 sec	Joyce–Loeb M K III B
Pulse-height discrimination	

samples were ground in a mill (Siebtechnik-Mill) for 2 h. It was found that grinding powders under carbon tetrachloride to avoid the oxidation of UO_2 in U_3O_8 was unnecessary. Measurements of the stoichiometry of an UO_2 sample before and after grinding for 2 h without carbon tetrachloride, gave the same value (2.130) for the ratio O:U. This long period of grinding was used mainly because it seems to be a very effective means of minimizing preferred orientation errors[9]. In order to reduce further any possible orientation errors and also to facilitate sample mounting, "lakeside" (a mixture of natural resins) was added to the samples in an amount about 20% of their weight.

The samples used for the calibration curves were UO_2 (O:U=2.130) and U_3O_8 (O:U=2.680) obtained from Merck. The ratio O:U was determined by coulometry. Several diagrams for uranium oxides with different stoichiometry were recorded and did not give any notable difference in the peak intensity and peak position, between a $UO_{2.000}$ sample and a $UO_{2.130}$ sample for samples of the same origin. Nevertheless, in the case of UO_2 samples obtained by electrolysis and fused UO_2 samples, prepared by high-frequency heating, a higher intensity was obtained. This is probably due to the fact that in these cases mainly small single crystals are formed. A more accurate study of this point is in progress.

After grinding, the particle size of the samples and of the powders used to set up calibration curves, was between 15 and 30 μ. These powders were obtained by sieving with a series of "precision micromesh" sieves ASTM 161–160 T. Some smaller particles, with a crystallite size of 5–7 μ were also obtained, but the quantity was too small for practical use. The samples were packed in the rectangular sample holder.

Reproducibility

Diffractometer technique. A reproducibility test was made by preparing 10 specimens of a 50% UO_2–50% U_3O_8 sample of particle size 15–30 μ, and measuring by manual counting the peak intensities of the reflections chosen as analytical lines. The ratio of the peak intensities was calculated. The average deviation of a single determination from the mean value was found to be ±2%. The effect of particle size on the intensity and reproducibility was studied by taking several fractions of a UO_2 sample, measuring the intensity of the (111) peak and calculating the mean standard deviation. The results are shown in Fig. 1. (The observed UO_2 intensities were normalized so that the highest corresponded to 100.) The observed decrease in peak intensities with increasing crystallite size for the fraction with particle size >20 μ is probably due partially to extinction and partially to the specimen packing density. A comparison of the reproducibility obtained with the stationary specimen and by rotating the specimen in its own plane, showed only slightly better results for the latter method. This is in disagreement with the results of DE WOLF *et al.*[10], who found an improvement by a factor of about 8 in their work on silicon powders (30–50 μ).

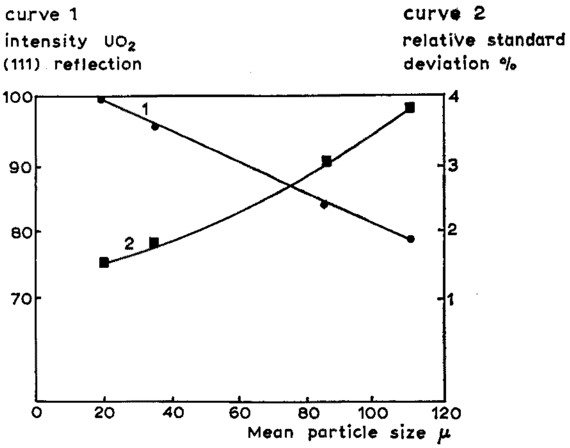


Fig. 1. Effect of particle size on intensity and reproducibility of the (110) reflection of UO_2.

Debye–Scherrer technique. Ten photographs of the same sample (50% UO_2–50% U_3O_8) were taken, without changing the specimen for each exposure. The relative standard deviation of the ratio of the peak intensities measured with a Siemens Type A photometer, was 4.7%.

RESULTS

Calibration curves and precision

The (110/011) reflection of U_3O_8 and the (111) reflection of UO_2 were chosen as analytical lines in this study. The (100) reflection of U_3O_8 was not utilized, because the addition of lakeside caused an amorphous band in that region. Figure 2 shows a portion of the X-ray diffractometer pattern of a U_3O_8 sample containing about 7% UO_2. A background measurement at $2\theta = 24°$ for the U_3O_8 and $2\theta = 30°$ for the UO_2 was subtracted from the peaks. In order to reduce instrumental and packing errors, the ratios of the intensities were compared with the weight ratios, using the diffractometer technique. For the calibration curve covering 0–10% UO_2 in U_3O_8, it was found that better results were obtained by directly comparing the peak intensities with the percentages. As an example, the curves for the 0–90% U_3O_8 and those for the 0–10% UO_2 concentration ranges using the diffractometer are given in Figs. 3 and 4 respectively. After the calibration curves had been established, the precision was checked by analysing several synthetic samples. These samples were analysed on different days; the results obtained (Table II) are considered very satisfactory. The calibration curve for 0–100% UO_2 in U_3O_8 obtained by the Debye–Scherrer method is given in Fig. 5.

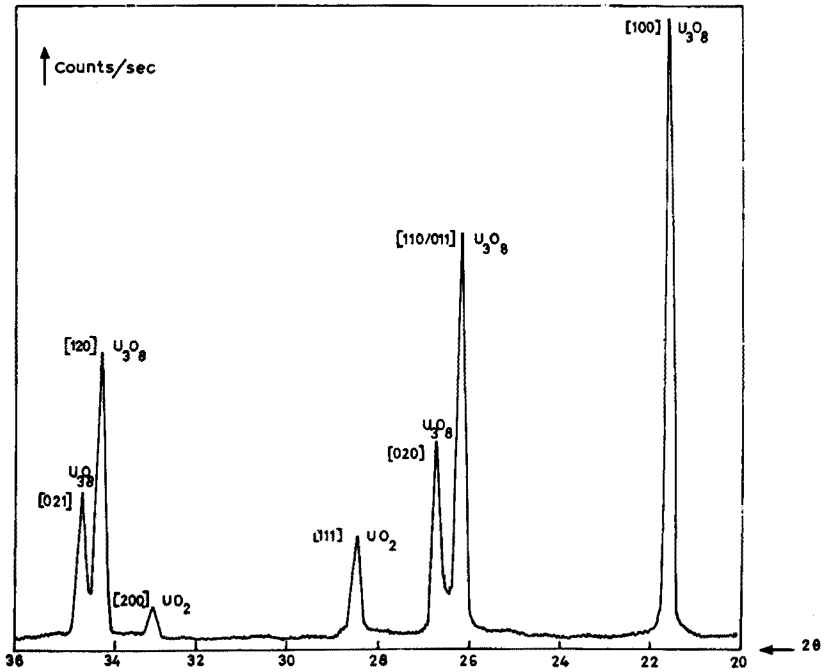
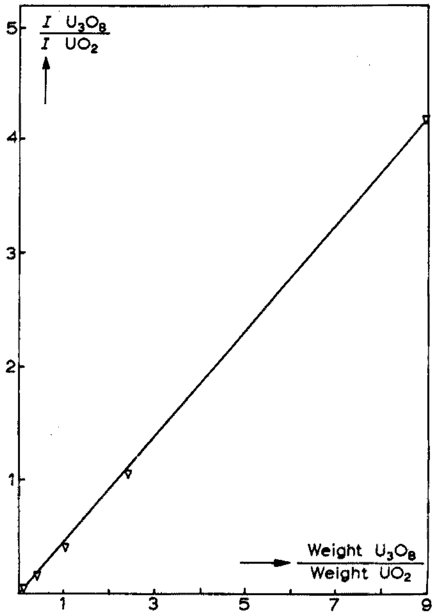


Fig. 2. X-ray diffractometer chart record obtained from a sample of U_3O_8 containing 7% of UO_2. Scanning speed: 1/2°/min. Full scale: $2 \cdot 10^3$ cps.



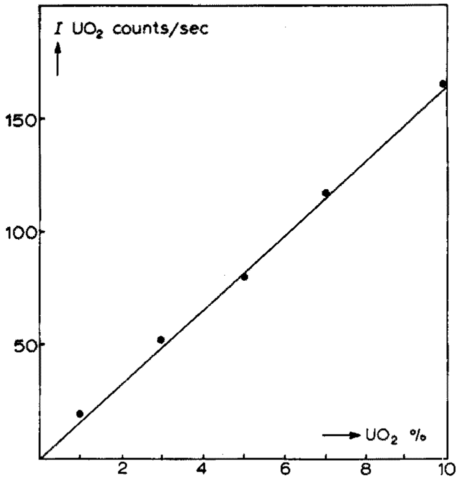


Fig. 3. Calibration curve for the determination of U_3O_8 in UO_2. Concentration range: 10–90%.

Fig. 4. Calibration curve for the determination of UO_2 in U_3O_8. Concentration range: 0–10%.

TABLE II

COMPARISON BETWEEN THEORETICAL AND FOUND VALUES DETERMINED BY THE X-RAY DIFFRACTION METHOD

Composition (%)	*Found (%)*	*Average (%)*	*Relative error (%)*
U_3O_8 : 80.0	80.4, 79.0, 79.3	79.6	1.2
U_3O_8 : 60.0	61.5, 60.6, 61.0	61.0	0.85
UO_2 : 8.0	7.7, 7.8	7.75	1.2
UO_2 : 4.0	4.3, 4.2	4.25	1.3

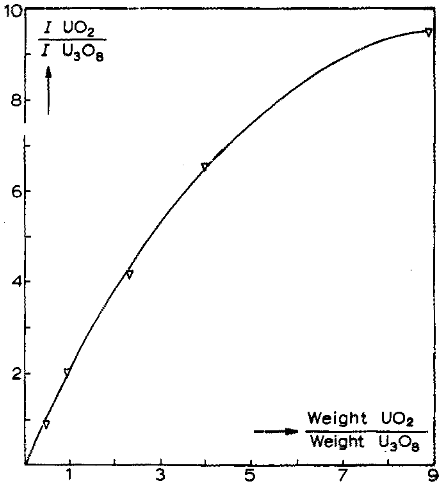


Fig. 5. Calibration curve for 0–100% UO_2 in U_3O_8 with the Debye–Scherrer camera.

Limit of detection

For the X-ray diffractometer measurements, the minimum composition detectable, LD, may be defined as the concentration, C_a, which yields an intensity of the peak height above the background equal to 3 standard deviations of the background intensity. Thus

$$LD = \frac{3\,C_a\sqrt{BT}}{P\cdot T}$$

where P is the intensity of the peak in counts per sec after the subtraction of the background, B is the intensity of the background in counts per sec, T is the counting time in sec, and C_a the concentration of the compound which has to be determined. The limit of detection of UO_2 in U_3O_8 was calculated for a counting time of 100 sec, while the intensities of the peak and background were obtained from two samples containing 1% UO_2.

The effects of some instrumental parameters on the limit of sensitivity of UO_2 was studied. From the results in Table III, it can be concluded that eliminating the β filter gave only a slight increase in sensitivity. The effect of changing the divergence

TABLE III

EFFECT OF DIFFERENT EXPERIMENTAL CONDITIONS ON THE LIMIT OF SENSITIVITY OF UO_2 IN U_3O_8

Divergence slit Scatter slit	*Receiving slit*	*Limit of detection calculated (%)*
1°–1°	0.2 mm with β filter	0.057
1°–1°	0.2 mm without β filter	0.053
4°–4°	0.2 mm with β filter	0.025

and scatter slits from 1° to 4° is quite remarkable. The lowest limit of detectability (*ca.* 0.02%) found with the diffractometer method is much better than the limit of about 1% using the Debye–Scherrer camera.

The limit of sensitivity for U_3O_8 in UO_2 was studied by using the (100) reflection, 4° divergence and scatter slits and 0.2-mm receiving slit, without the β Ni filter; the calculated limit of detection from three 0.8% U_3O_8 samples (pressed into disks)was found to be 0.075%. To verify if this calculated limit corresponded to the practical limit, a sample containing 0.15% U_3O_8 was prepared and the limit of detection calculated; the result found was about 0.085%, which is of the same order of magnitude as the calculated value.

CONCLUSION

The determination of UO_2 in U_3O_8 powders and *vice-versa*, by X-ray diffraction gives satisfactory results. The diffractometer technique should be preferred to the Debye–Scherrer camera, because of its better reproducibility, shorter analysis time and lower limit of detection. However, the latter method is the only one which can be employed when only small quantities of samples are available.

We wish to thank the European Community of Atomic Energy (EURATOM) which gave a scholarship to one of us (R.C.) for this work. We are grateful to Mr. DENIS for the chemical analysis, to Professor A. MICHEL for his direction of these investigations and to Mr. H. LAURENT, Director of the Analytical Chemistry Division.

SUMMARY

An X-ray diffraction method is proposed for the quantitative analysis of the binary mixture UO_2–U_3O_8. Diffractometer and Debye–Scherrer camera techniques were compared; the former is preferable whenever sufficient sample is available. The relative standard deviation was found to be 1%.

RÉSUMÉ

On propose une méthode par diffraction aux rayons-X pour l'analyse quantitative de mélanges binaires UO_2–U_3O_8. Les deux techniques, diffractomètre et caméra Debye–Scherrer sont comparées. La première est préférable si l'on peut disposer de suffisamment d'échantillon. La déviation standard relative est de 1%.

ZUSAMMENFASSUNG

Es wird eine Röntgenbeugungs-Methode zur quantitativen Analyse binärer UO_2–U_3O_8-Mischungen vorgeschlagen. Diffractometer und Debye–Scherrer-Kamera werden verglichen. Das erstere ist vorzuziehen, wenn genügend Probe verfügbar ist. Die relative Standardabweichung betrug 1 %.

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ATOMIC ABSORPTION STUDIES ON RARE EARTH AND REFRACTORY METALS

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Until recently, atomic absorption spectroscopy could not be used for analytical determination of the rare earth metals and many "refractory" metals because of the inability of available burners to produce sufficient ground-state atoms. This group of elements, unless they are excited in a very-high-temperature reducing atmosphere, form stable oxides which reduce the population of ground-state atoms. The slot burners and total-consumption burners previously available could not produce the required environment. Now, as a result of the work of KNISELY, D'SILVA AND FASSEL[1] in developing a pre-mix, total consumption oxygen–acetylene burner, and of AMOS[2] in developing a pre-mix, laminar flow nitrous oxide–acetylene burner, there are available 2 units capable of producing an abundance of ground-state atoms of most of the rare earth and refractory metals.

The present study was undertaken to compare the performance of the KNISELY and AMOS burners and to evaluate their performance with respect to the standard laminar flow air–acetylene burner which is used in most atomic absorption work. Furthermore, to investigate the changes in ground-state atom population with different solvents, the metal solutions were prepared in aqueous, alcohol, and acetone media. Also studied were the effect of sample solution flow rate, the use of continuous light sources, and the distribution of absorbing species in the flame using "pinhole" optics.

The metals neodymium, samarium, europium, gadolinium, terbium, erbium, dysprosium, yttrium, vanadium, chromium, aluminum, and zirconium were included in the investigation.

EXPERIMENTAL

Equipment

The following equipment was used in this investigation: Atomic Absorption Spectrophotometer Model 214 (Perkin-Elmer Corp.), Burner Atomizer (Perkin-Elmer Corp.), Syringe Pump, Model 234-2 (Sage Instruments Inc.), oxygen–acetylene burner, KNISELY type[3], nitrous oxide burner head, AMOS type[1] (Techtron Pty. Ltd.), and air–acetylene burner head (Techtron Pty. Ltd.).

Standard preparation

A stock solution containing 1000 μg/ml of metal is prepared by dissolving a weight of metal oxide, metal chloride, or metal which gives 1.00 g of the metal in

10 ml of any appropriate acid (preferably hydrochloric acid) and diluting to 1 l. Aqueous standards are prepared by diluting aliquots of the stock solution to obtain the required concentrations. Organic solution standards are prepared as follows: pipette 100 ml of the aqueous stock solution into a beaker and evaporate to less than 20 ml. Add 80 ml of ethanol, 80 ml of methanol or 50 ml of acetone and dilute to 100 ml with water. These yield 1000 μg/ml standards in solutions of 80% alcohol or 50% acetone. Additional standards are prepared by diluting aliquots of these standards with the appropriate organic solution to obtain the desired concentrations.

Analytical procedure

The atomic absorption analyses were run at the operating conditions listed in Table I. Burner height and gas pressure were adjusted for each solvent system and burner to obtain maximum absorption.

The use of organic solvents is known to increase sensitivity in analysis for most elements in both flame emission and absorption spectrophotometric methods. This effect is attributed to a variety of causes including (*1*) decreased surface tension which in turn increases the rate of sample feed, (*2*) faster and more efficient atomization, (*3*) increased flame temperature, and (*4*) a higher incidence of carbon-bearing species in the flame. To obtain a better insight into the contribution of the organic additives and to select the best solvent system for each type of burner, standard solutions were prepared in water and in 3 of the most commonly used organic solvents: ethanol, methanol and acetone. The organic solvent–water ratios were chosen to allow maximum concentration of solvent with minimum risk of precipitation of the metals at high concentration levels. The 50% acetone–water ratio was chosen because of the inability to obtain stable flames with the nitrous oxide–acetylene burner at higher acetone concentrations. Standard solutions of aluminum, chromium, europium, erbium, and neodymium were prepared in each of the 4 solvent systems. Aqueous and alcohol solution standards were prepared for the remaining elements: zirconium,

TABLE I

INSTRUMENT OPERATING CONDITIONS

Element	*Hollow-cathode current (mA)*	*Wavelength (Å)*	*Slit (mm)*	*Photomultiplier current (V)*
Al	12	3092.7	0.1	700
Cr	20	4254.3	0.1	500
V	20	3185.4	0.1	600
Zr	15	3601.2	0.15	600
Eu	14	4594.0	0.1	600
Er	20	4190.7	0.1	500
Nd	20	4924.5	0.1	500
Y	20	4128.3	0.1	500
Dy	20	4077.9	0.1	500
Sm	20	4841.7	0.1	500
Gd	15	4262.1	0.05	600
Tb	15	4356.8	0.1	600

vanadium, yttrium, dysprosium, terbium, gadolinium, and samarium. Their initial concentrations differed by factors of 10 (*e.g.* 1, 10, 100, 1000 μg/ml). The solutions were analyzed using the 3 burner–fuel gas systems: (*1*) AMOS laminar flow nitrous oxide–acetylene system, (*2*) KNISELY total consumption oxygen–acetylene system, and (*3*) Techtron laminar flow air–acetylene system. Data on absorption and on sample flow rates were recorded for each element and solvent system.

In an additional experiment a syringe pump was used to control the sample flow rate in order to determine the effect of flow rate on absorption. Additional aluminum standards were used in this test, and they were prepared in 90% organic mixtures in order to enhance any effect due to flow rate.

In the study of spectral continua the Model 214 was modified by removing the hollow-cathode holder and focusing the light from the various spectral sources on the beam splitting mirror. A 60 rev./min chopper was inserted between the source and the mirror to modulate the light source.

RESULTS AND DISCUSSION

Burners

The principal difference between the laminar flow burners and the total consumption burner is the manner in which the sample is aspirated into the flame. The laminar flow burners incorporate an atomizer design[4] in which the sample is aspirated into a mixing chamber which effectively separates the large droplets from the fine spray. Because of this design only 5–10% of the aspirated solution finally reaches the flame. This is in contrast to the total consumption burner in which all of the aspirated solution reaches the flame. However, this benefit of total sample excitation is partially overcome by a marked difference in sample solution flow rate between the 2 aspiration systems. In this investigation the sample flow rates for the total consumption burner varied between 1 and 2.5 ml/min and for the laminar flow burners they varied between 5 and 10 ml/min depending on solution composition and the element studied.

There are other considerations which also tend to minimize this advantage of total sample consumption. These include the relative time that the sample remains in the flame and the optical path length through the flame. The time the sample remains in the flame is dependent on the gas flow required to produce a stable flame. Because the flame front propagation rate is very high (flame velocity 1130 cm/sec) for an oxygen–acetylene flame, the total consumption burner requires a high gas flow to produce stable burning and the residence time of a sample droplet in the flame is short. In contrast, the flame velocity for the nitrous oxide–acetylene flame is only 180 cm/sec and for the air–acetylene flame only 120 cm/sec. This decrease in flame velocity for the laminar flow burners allows the sample particles a much longer residence time in the flame which in turn encourages the formation of ground-state atoms.

The length of the analytical flame is also an important difference between the 2 systems since increasing flame length generally leads to increased sensitivity. The design of the total consumption burner produces a small circular flame about 1 cm in diameter while the laminar flow burners have flame lengths from 5 to 10 cm. Some authors[1,3] increased the effective flame length of the total consumption burner by using 3 or more burners in series or a multi-pass optical arrangement.

The physical differences between the laminar flow and total consumption burners and the combustion reactions which occur in their flames make a variety of excitation conditions available. To determine which set of conditions yields the best results for the rare earth and refractory metals group, a series of standard solutions were analyzed using the 3-fuel gas–burner systems. The relative efficiencies of the 3 systems may be seen by comparing the sensitivities listed in Tables II and III. The sensitivities were calculated by dividing the concentration of the most diluted standard by its absorption. The data in Tables II and III clearly show the increase in sensitivity obtained with the AMOS nitrous oxide–acetylene burner over that obtained with either of the other burners. In addition, the instrument noise caused by flame instability and the audible noise of the flame are greatly reduced when the nitrous oxide burner is used. The reduction of flame noise results in a decrease in background fluctuations and a corresponding decrease in the detection limits. "Detection limit" in this case is that concentration (μg/ml) which gives an absorption equal to twice that of the average background fluctuations. An attempt to use nitrous oxide in place of oxygen with the total consumption burner failed because the flame propagation rate is much slower with nitrous oxide–acetylene mixture and the gas flow rate corresponding to a stable flame was too low to aspirate any sample solution into the flame. The use of a syringe pump to introduce sample was attempted to overcome this, but it resulted in extinguishing the delicate nitrous oxide–acetylene flame produced with the total consumption burner.

TABLE II

SENSITIVITIES[a] IN AQUEOUS AND ORGANIC SOLUTIONS

Element	*Solutions*	N_2O–C_2H_2	O_2–C_2H_2	Air–C_2H_2
Al	Aqueous	2.5	5	ND[b]
	80% MeOH	1	5	ND
	80% EtOH	1	5	ND
	50% Acetone	1.5	5	ND
Cr	Aqueous	1.5	5	1
	80% MeOH	0.6	10	0.5
	80% EtOH	0.6	7	0.5
	50% Acetone	0.6	3.5	0.5
Eu	Aqueous	7	8	3
	80% MeOH	2	20	2.5
	80% EtOH	1.5	5	2.5
	50% Acetone	2	3	7
Er	Aqueous	5.5	120	ND
	80% MeOH	2	55	ND
	80% EtOH	2	40	ND
	50% Acetone	2.5	50	ND
Nd	Aqueous	100	200	ND
	80% MeOH	22	200	ND
	80% EtOH	20	100	ND
	50% Acetone	40	200	ND

[a] Sensitivities μg/ml per 1% absorption.
[b] Not detected at 1000 μg/ml.

Solvents

The advantage of using an organic solvent medium can be seen from the data in Tables II and III. In all cases the sensitivities obtained with the organic solutions were better than those obtained with the aqueous solution. This is an expected result and has been observed by many other authors. However, when the sample solution flow rates responsible for these sensitivities were compared, in all cases the aqueous solution produced the highest flow rates. The data are recorded in Table IV. This result is in contrast with the theory that organic solvents increase the rate of sample feed and thereby increase sensitivity. More efficient atomization and vaporization and a hotter, reducing flame are probably the more important contributions of the organic solvents.

TABLE III

SENSITIVITIES IN ALCOHOL AND AQUEOUS SOLUTIONS

Element	*Solutions*	*Burner–fuel gas*		
		AMOS N_2O–C_2H_2	KNISELY O_2–C_2H_2	*Standard* Air–C_2H_2
Y	Aqueous	20	300	ND[a]
	80% MeOH	4	120	ND
Dy	Aqueous	10	30	ND
	80% MeOH	4	50	ND
Sm	Aqueous	45	100	ND
	80% MeOH	20	100	ND
Gd	Aqueous	100	2000	ND
	80% MeOH	30	1000	ND
Tb	Aqueous	65	250	ND
	80% MeOH	25	200	ND
V	Aqueous	3	100	300
	80% MeOH	17	30	400
Zr[b]	Aqueous	65	ND	ND
	80% MeOH	120	ND	ND
Zr[c]	Aqueous	20	—	—

[a] Not detected at 1000 µg/ml.
[b] Cl^- solution.
[c] 2% HF added.

As mentioned previously, the sample solution flow rates for the total consumption burner varied between 1 and 2.5 ml/min, and for the laminar burners between 5 and 10 ml/min. These flow rates are controlled by the fuel gas pressures and the physical characteristics of the atomizer. To determine the effect of higher flow rates on the sample absorption, a syringe pump was used to force more solution through the aspirator. Little effect was found with either the AMOS or Standard laminar flow burners, but increases up to a factor of 2 were obtained with the KNISELY total consumption burner. Table V shows the increased absorption obtained when the

TABLE IV

SAMPLE SOLUTION FLOW RATES

Element	*Solution*	*Solution flow rate (ml/min)*	
		AMOS *burner*	KNISELY *burner*
Al	Aqueous	9	2.2
	80% MeOH	5.5	1.8
	80% EtOH	4.8	1.5
	50% Acetone	6.0	2.0
Cr	Aqueous	9.2	2.5
	80% MeOH	6.0	1.8
	80% EtOH	4.6	1.1
	50% Acetone	5.7	1.7
Eu	Aqueous	9.0	2.3
	80% MeOH	5.1	1.6
	80% EtOH	4.6	1.1
	50% Acetone	5.7	1.6
Er	Aqueous	7.8	1.9
	80% MeOH	5.6	1.5
	80% EtOH	4.4	0.9
	50% Acetone	4.6	1.5
Nd	Aqueous	6.5	1.8
	80% MeOH	5.0	1.4
	80% EtOH	3.7	1.2
	50% Acetone	4.5	1.6
Y	Aqueous	5.9	1.8
	80% MeOH	5.4	1.7
Dy	Aqueous	4.6	2.0
	80% MeOH	4.4	1.5
Sm	Aqueous	7.5	2.0
	80% MeOH	7.1	1.4
Gd	Aqueous	10.0	—
	80% MeOH	7.7	—
Tb	Aqueous	10.0	2.0
	80% MeOH	7.8	1.6
V	Aqueous	9.2	1.9
	80% MeOH	7.7	1.6
Zr	Aqueous	10	—
	80% MeOH	8	—

syringe pump was used to feed the sample into the total consumption flame. This dependence of the total consumption burner on solution flow rate was investigated further using aluminum standards prepared in 90% organic solutions to enhance any effect. The data are plotted in Fig. 1 as solution flow rate *vs.* % absorption. With the 90% acetone solution the absorption obtained with the aspirated flow rate is very close to the maximum attainable. However, the absorption is greatly dependent on solution flow rate, and small changes in aspiration rates can give large errors in analysis. The aqueous solution aspiration rate is also shown to yield an absorption close to the maximum attainable, and the aqueous solutions are not very dependent on solution flow rate. Unfortunately aqueous solutions do not yield as much sensitivity as acetone solutions. The 90% alcohol solution shows increasing absorption with increasing flow rate up to about 3.5 ml/min. Above this flow rate, large droplets of solution could be seen spraying out of the flame. However, the best sensitivities obtained with the KNISELY total consumption burner, even with a 90% acetone solution, could not compare with those obtained using the AMOS laminar flow burner. Therefore, the AMOS burner was used throughout the remainder of this investigation.

TABLE V

EFFECT OF SAMPLE FLOW RATE ON ABSORPTION[a]

Element	*Solution*	*Aspirated flow rate*	*% Absorption*	*Syringe pump flow rate*	*% Absorption*
Al 100 μg/ml	Aqueous	2.2	12	3.4	13
	80% EtOH	1.5	10	3.4	19
	50% Acetone	2.0	15	3.4	18
Eu 100 μg/ml	Aqueous	2.3	12.5	3.4	13.5
	80% EtOH	1.1	9.0	3.4	21.0
	50% Acetone	1.6	19.0	3.4	26.0
Cr 100 μg/ml	Aqueous	2.5	20.5	3.4	21.5
	80% EtOH	1.1	15	3.4	28
	50% Acetone	1.7	15	3.4	20.5
Er 1000 μg/ml	Aqueous	1.9	22	3.4	18
	80% EtOH	0.9	32	3.4	54
	50% Acetone	1.5	35	3.4	45

[a] KNISELY total consumption burner.

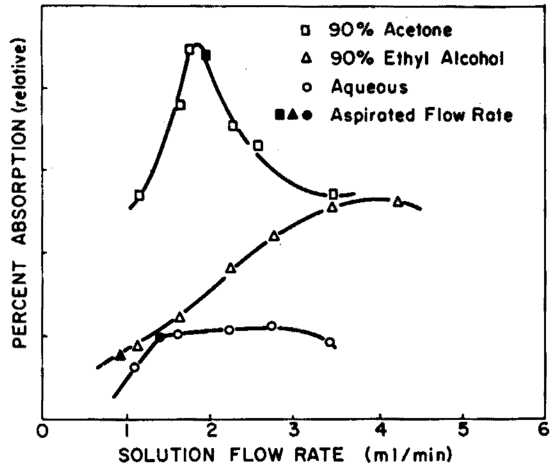

Fig. 1. Effect of solution flow rate on aluminum absorption obtained with the KNISELY burner.

A complete set of standards in 80% alcohol solution was prepared for each element over a hundred-fold concentration range. The data, when expressed in absorption *vs.* concentration plotted on log–log coordinates, yielded straight-line plots over the concentration ranges listed in Table VI.

TABLE VI

LINEAR RANGE OF CONCENTRATION CURVES

Element	*Concn. range (µg/ml)*	*Element*	*Concn. range (µg/ml)*
Al	1–100	Dy	1–100
Cr	0.5–50	Sm	10–1000
Eu	1–100	Gd	10–1000
Er	1–100	Tb	10–1000
Nd	10–100	V	1–100
Y	1–100	Zr[a]	20–1000

[a] 2% HF aqueous solutions.

Matrix effect

All the data to this point had been obtained from analyzing pure solutions of the elements. To determine the effect of a matrix on the rare earth metals, an alcohol solution of yttria (Y_2O_3, 10 mg/ml) was prepared. Small amounts of the individual rare earths were added to it, and the solutions were analyzed. Enhancements of 3 to 4 times their normal absorptions were found for europium, erbium, dysprosium, terbium, samarium, and neodymium; only gadolinium showed little or no effect from the added matrix. Analyzing europium in the presence of milligram amounts of gadolinium showed the same enhancement effect. This type of effect which has been noted before[2], is attributed to the presence of a large concentration of an easily ionizable substance in the flame which inhibits the ionization of the other elements present. As a result, their ground-state atom populations and consequently their absorptions are increased.

The yttria used in this study had been analyzed by mass spectrographic and emission spectrographic methods and was found to contain traces of rare earths. Table VII compares the results obtained by atomic absorption using the method of

TABLE VII

COMPARISON ANALYSIS OF YTTRIA

(Results in p.p.m. Solutions for atomic absorption were 80% MeOH)

Element	*Mass. spec.*	*Spectrographic "A"*	*Spectrographic "B"*	*Spectrographic "C"*	*Atomic absorption*	*Sensitivity in yttria*[a]
Er	100	290	100–1000	300	310	20
Dy	300	500	100–1000	170	650	18
Tb	15	—	100–1000	ND	ND<200	110
Eu	1	40	—	ND	10	8
Nd	25	70	—	ND	ND<100	130

[a] Sensitivity calculated by: (µg/ml per 1% absorption)/(0.05 g/ml Y_2O_3).

addition with those obtained by the other spectrographic methods. The emission spectrographic results were obtained independently by 3 different laboratories. Table VII also shows the sensitivities in yttria for the rare earth elements. Detection limits are approximately 1/5 the sensitivity figures. The difference in sensitivities when compared with Tables II and III points out one of the limitations of working with a matrix. This effect is due to the maximum concentration of sample (g/ml) which can be held in solution and which will not precipitate and clog the aspirator or burner slit during sample excitation. This concentration is usually between 0.01 and 0.1 g/ml, and its effect is to reduce the effective sensitivities to 1/100 and 1/10 those reported in literature.

Pinhole effect

A recent paper by RANN AND HAMBLY[5] concerning the distribution of atom. in atomic absorption flames discusses a technique for obtaining increased absorptions They used a pinhole aperture (1 mm in diameter) to permit the observation of only that portion of the light from the hollow-cathode lamp which passes through the region of the flame containing the highest proportion of ground-state atoms. With this technique they obtained a 6-fold increase in absorption against that obtained by conventional methods when they analyzed chromium solutions. We found no appre-

TABLE VIII

SENSITIVITIES WITH CONTINUA AS SPECTRAL SOURCES

Element	*Neon discharge lamp*	*Argon discharge lamp*	*Beckman H_2 lamp*	*Beckman W lamp*	*Sylvania alkali metal lamp*[a]	*Sylvania sun lamp*[b]	*Sylvania sun lamp N_2O–C_2H_2 burner*
Zr[c]	—	—	ND[d]	ND	—	—	—
Ni	—	—	ND	ND	—	—	—
Fe	—	—	ND	ND	—	—	—
Mn	—	—	ND	ND	—	ND	—
Pb	—	—	ND	ND	—	—	—
Cu	ND	ND	ND	ND	—	ND	—
Ag	—	—	ND	ND	—	ND	—
Ca	ND	ND	50	65	—	125	110
Cr	—	—	ND	ND	—	ND	—
Sr	22	ND	40	65	—	100	100
Ba	—	—	30	ND	—	ND	300
Na	13	ND	30	25	18	40	140
Li	13	ND	30	65	50	30	40
K	ND	ND	ND	ND	500	ND	ND
Nd	—	—	—	—	—	—	ND
Sm	—	—	—	—	—	—	ND
Eu	—	—	—	—	—	ND	80
Gd	—	—	—	—	—	—	ND
Tb	—	—	—	—	—	—	ND
Dy	—	—	—	—	—	—	300
Er	—	—	—	—	—	—	500

[a] Sylvania discharge lamp with alkali metal halides.
[b] Sylvania "Sun Gun" 1000 W tungsten filament iodine cycle lamp.
[c] 2% HF solution.
[d] Not detected at 1000 μg/ml.

ciable increases in absorption when solutions of chromium or vanadium were analyzed using the nitrous oxide–acetylene flame and a similar pinhole aperture. This is probably due to 2 differences in our systems. First, the nitrous oxide–acetylene flame is much smaller in cross-section than the air–acetylene flame (2 mm *vs.* 5 mm) resulting in a much higher proportion of the flame being seen by the photomultiplier. Secondly, the optics of our system focus the hollow-cathode emission into the flame giving a diameter of the light beam at the plane of the pinhole of approximately 5 mm compared to a 25-mm diameter light beam used by RANN AND HAMBLY.

Continuous light sources

In the past year much interest has been raised in the use of spectral continua as primary sources in atomic absorption spectroscopy. We investigated a number of continuous sources including an experimental alkali halide discharge lamp made at our laboratories. Air–acetylene and nitrous oxide–acetylene laminar flow burners were used in the investigation, and the results are shown in Table VIII. The sensitivities obtained are less sensitive by a factor of 100 than those obtained with conventional hollow cathodes. SLAVIN[6] in a recent paper states that one of the primary requirements for using spectral continua is a spectrophotometer with a resolution of 0.2 Å. The best resolution obtainable with our instrument is 2 to 3 times this figure, and this may explain the lack of sensitivity.

CONCLUSIONS

In summary, the AMOS laminar flow burner using nitrous oxide–acetylene as fuel produces a sufficient quantity of ground-state atoms to allow sensitivities of 1 to 100 μg/ml for all the rare earth and refractory metals tested. The AMOS burner outperforms the KNISELY total consumption oxygen–acetylene burner, but this is probably due more to the differences in flame length rather than to the flame reaction. R. N. KNISELY, at the 1965 Eastern Analytical Symposium, announced the development of an oxygen–acetylene laminar flow slot burner. It would be interesting to compare the sensitivities obtained with this burner with those of the AMOS burner.

The use of organic solvents enhanced the sensitivities of the elements in the flame, but this was found not to be due to an increased sample solution flow rate as the flow rates decreased with the use of organic solvents. The enhancement is probably due to a combination of factors including increased atomization and vaporization of the sample and a hotter more reducing flame.

A forced increase in sample solution flow rate resulted in higher sensitivities obtained with the total consumption burner, but even these were less than those obtained with the AMOS laminar flow burner.

Yttrium oxide enhanced the signal from the rare earth solutions, but due to the limitations of solubility the calculated sensitivities for the rare earth metals in yttrium oxide were lower than those obtained for pure solutions.

SUMMARY

The use of atomic absorption spectroscopy for the analysis of rare-earth and refractory metals was studied. Various types of burners and fuel–oxidant mixtures were examined. The effects of organic solvents, sample solution flow rates and the use of continuous light sources on sensitivity are noted. The metals neodymium, samarium, europium, gadolinium, terbium, erbium, dysprosium, yttrium, vanadium, chromium, aluminum, and zirconium were included in this investigation.

RÉSUMÉ

On a effectué une étude sur l'utilisation de la spectroscopie par absorption atomique pour le dosage des terres rares et des métaux réfractaires. On a examiné divers types de brûleurs et de mélanges de gaz, de même que l'influence des solvants organiques, du débit de l'échantillon à analyser et de l'emploi de sources lumineuses continues. Métaux examinés: néodyme, samarium, europium, gadolinium, terbium, erbium, dysprosium, yttrium, vanadium, chrome, aluminium et zirconium.

ZUSAMMENFASSUNG

Die Verwendung der Flammenabsorptionsspektroskopie für die Analyse von Nd, Sm, Eu, Gd, Tb, Er, Dy, Y, V, Cr, Al und Zr wurde untersucht. Verschiedene Brennertypen und Brennstoffgemische wurden geprüft. Die Einflüsse organischer Lösungsmittel, die Fliessgeschwindigkeit der Probelösungen und kontinuierlicher Lichtquellen auf die Empfindlichkeit werden festgestellt.

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SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO III IN THE ORGANIC PHASE AFTER EXTRACTION WITH DI-(2-ETHYLHEXYL)ORTHOPHOSPHORIC ACID

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Selectivity in spectrophotometric determinations can often be considerably enhanced by preferential extraction of the coloured species into a suitable organic phase before measurement, the pertinent colour being separated from other non-extractable interfering species. This method exploits the potentiality of selective extraction merely within the range of the previously developed colours, and it is obviously effective provided that an appropriate organic solvent is available. Interferences can obviously also be removed by a preliminary separation by means of ion exchange resins or liquid–liquid extraction. Generally, the required element is finally determined in the eluate from the resin bed or in the solution obtained from back-extraction of the organic phase. Where a liquid–liquid extraction is possible for the selection of ions concerned, it is obviously better if the colour can be directly developed in the organic phase after the required ion has been isolated. Such methods have advantages of rapidity and possible increase in sensitivity due to volume reduction, and they offer wide possibilities due to the selectivity and flexibility of modern classes of organic extractants.

The well-known organic extractant, di-(2-ethylhexyl)orthophosphoric acid (HDEHP), has been extensively applied, with particular attention to the separation of rare earths. Because of the great potentiality of this extractant, a systematic study is being performed in this laboratory of the direct organic-phase determination of various metals after extraction from an aqueous phase. In a previous paper the organic-phase spectrophotometric determination of iron(III) with thiocyanate after extraction with HDEHP from chloride solutions was described[1].

In this paper the extremely sensitive chromogenic reagent, arsenazo III, is considered. In preliminary tests a solution of this reagent in 95% ethanol was added to HDEHP solutions containing several cations extracted from chloride solutions; among the results obtained (see p. 397), the thorium-arsenazo III colour was taken into account, because of the great importance of thorium in the chemistry of elements of nuclear interest. The analytical utilization of arsenazo III, first exploited in 1959, has been reviewed by SAVVIN[2,3], who pointed out its high sensitivity for quinquevalent and quadrivalent ions, and its satisfactory selectivity for thorium, zirconium and uranium. Thorium from various sources has generally been determined with arsenazo III in an aqueous medium, *e.g.* after a pre-separation with KU-2 cation-exchange resin[4] from titanium, zirconium and rare earths[4]. However, KUZNETSOV AND SAVVIN[5] also considered the so-called extraction-photometric method, in which the coloured thorium–arsenazo III complex was extracted from the aqueous phase into butyl or amyl alcohol in the presence of diphenylguanidine chloride, before the final measurement.

Later examples of the use of arsenazo III for thorium spectrophotometry are those reported by ONISHI[6] for a mixture of thorium and zirconium, in which the latter is masked with oxalic acid, by UPOR *et al.*[7] for thorium in rock samples also in the presence of titanium and uranium, and by ABBEY[8] for rock samples, the colour being developed in a perchlorate medium.

EXPERIMENTAL

Equipment and reagents

The spectrophotometric determinations were carried out with a Uvispek spectrophotometer (Hilger & Watts, London), glass optics, and 1-cm glass cuvettes.

The liquid–liquid extractions were carried out in glass separatory funnels, shaken with an electrically operated shaker. The stopcocks were greased with Dow Corning high vacuum grease (silicone lubricant).

The di-(2-ethylhexyl)orthophosphoric acid (HDEHP) (mol.wt., 322.42; density, 0.87) was obtained from the Virginia-Carolina Chemical Co. (Richmond, U.S.A.), and arsenazo III from Fluka (Switzerland).

To prepare stock solutions of thorium, analytical-grade thorium nitrate (Merck, Germany) was used. Solutions about 0.1 *M* were prepared in 0.1 *M* hydrochloric acid, and standardized gravimetrically[9]. Other solutions were obtained by suitable dilution.

Hydrochloric acid, cyclohexane and isopropanol were RP products supplied by C. Erba (Milan). All the other chemicals used were of analytical grade.

HDEHP was used in a cyclohexane solution. Since the commercial extractant contained appreciable amounts of iron as an impurity, solutions of the required molarity were shaken with equal volumes of 6 *M* hydrochloric acid until no iron was left in the organic phase, when tested by adding a potassium thiocyanate solution in ethanol to an aliquot of the organic phase[1]. Three 6 *M* hydrochloric acid treatments were usually sufficient. The cyclohexane layers were washed twice with an equal volume of water, and then equilibrated by shaking with twice their volume of hydrochloric acid solutions at the same concentrations as those from which thorium had to be extracted.

All experiments were carried out at room temperature, *i.e.*, 24 ± 1°.

Development of the colorimetric procedures

Low acidity method. Although thorium is known[10,11] to be completely extracted by suitably concentrated HDEHP from acidic solutions up to 10 *M* in hydrochloric acid, a 0.1 *M* hydrochloric acid solution was chosen as the aqueous phase for initial testing, the organic phase being a 0.5 *F* HDEHP solution in cyclohexane, previously equilibrated with 0.1 *M* hydrochloric acid. A volume ratio of 1:1 was chosen with a 3-min shaking time; extraction of thorium into HDEHP was found to be practically instantaneous, so that extraction for 3 min was maintained throughout this work, unless otherwise specified.

The absorbance of the thorium–arsenazo III complex increases, the higher the reagent concentration in the solution[2]. Unfortunately, arsenazo III is only slightly soluble in 95% ethanol, which was used in the preliminary tests, the solubility being almost completely due to the water content of the alcohol. Moreover, when the nearly saturated arsenazo III–alcohol solution was added to the cyclohexane solution for the colour development, precipitation of the reagent occurred. Thus, an aqueous solution of arsenazo III was considered to be the best way to achieve good sensitivity, provided that complete homogeneity of the final organic solution and the aqueous arsenazo III layer could be attained by the addition of a suitable alcohol.

Methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, and isobutanol were tested; the best results were given by isopropanol. When 2 ml of the aqueous arsenazo III solution were added to 10 ml of a 0.5 *F* HDEHP solution in cyclohexane, a clear solution was obtained on dilution to 25 ml with this alcohol. Absolute ethanol promoted turbidity when small amounts of water were present in the cyclohexane phase, whereas isopropanol gave a clear solution even though an extra 0.5 ml of water was present in the final solution.

In view of these results, the preliminary method for the extraction of thorium and the colour development was as follows: 20 ml of a 0.1 *M* hydrochloric acid solution containing a known amount of thorium were extracted for 3 min with 20 ml of a 0.5 *F* HDEHP solution in cyclohexane, previously equilibrated. After the layers had separated, 10 ml of the organic phase were transferred into a 25-ml volumetric flask, and 2 ml of an aqueous solution of arsenazo III (0.155 mg/ml) were added; the mixture was then diluted to volume with isopropanol, a clear coloured solution being obtained after vigorous shaking.

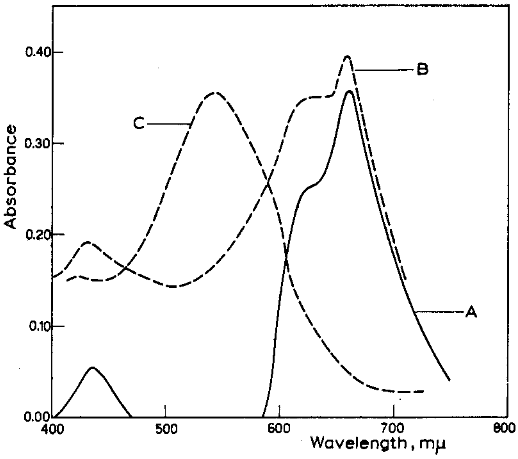


Fig. 1. Absorption spectrum of the thorium–arsenazo III colour developed in organic solution, against the reagent blank (Curve A) and against water (Curve B). Curve C is the spectrum of the reagent blank against water.

The absorption spectrum shown as curve A of Fig. 1 was obtained with an initial aqueous solution containing 20 μg thorium/ml; the colour was read against a blank prepared in the same way, starting from thorium-free 0.1 *M* hydrochloric acid.

The absorbance peak at 600–700 nm is very similar to that reported[2,7] for the thorium–arsenazo III complex in an aqueous phase; the small peak between 400 and 500 nm was also found in the aqueous phase, although not reported in the literature. The spectrum was checked by measuring the colour of both the thorium and the blank solutions against water (Fig. 1, curves B and C). From these spectra the wavelength of 660 nm was chosen as the most suitable for the colorimetric determinations.

The stability of the colour was then investigated; the results obtained showed that the colour reached a maximum after 5 min and was stable for 20 min after development.

The colour of the thorium–arsenazo complex increased as the HDEHP concentration was raised from 0.1 *F* to 1.0 *F*; however, the increase in absorbance as read on the spectrophotometer was not due to an actual increase in the absorbance of the complex, but to a decrease in the absorbance of the blank solutions. No satisfactory explanation of this behaviour was found.

The absorbance of the colour in the organic phase was independent of the hydrochloric acid concentration in the initial aqueous phase.

The behaviour of the complex as a function of the arsenazo concentration was in agreement with literature data[2], the intensity of the colour at a given acidity being enhanced as the amount of arsenazo present was raised.

In obtaining a calibration curve, the best results were obtained with a saturated aqueous solution of arsenazo, but, because of the slow dissolution of the reagent, a concentration less than saturated was preferred, namely 310 μg/ml, which could be attained by shaking for 30 min. Thorium was extracted from 0.1 *M* hydrochloric acid, the extractant being 1.0 *F* HDEHP in cyclohexane. Figure 2 shows that the complex follows Beer's law up to 5 μg/ml of thorium in the initial aqueous phase, *i.e.* 2 μg/ml in the final solution.

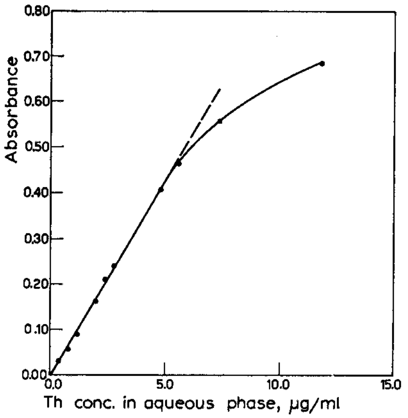


Fig. 2. Calibration curve for the standard procedure involving the development of the colour by the "low acidity" method.

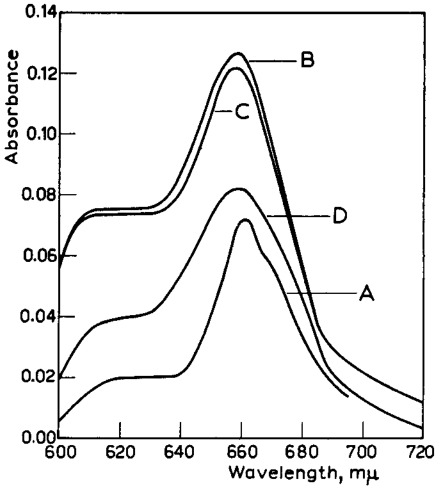


Fig. 3. The influence of the addition of acids in the organic phase on the spectrum of the Th–arsenazo colour; 0.850 μg/ml Th extracted; colour developed with the low acidity method (Curve A), or by adding 1 ml of arsenazo III solution and 1 ml of concentrated HCl (B), $HClO_4$ (C), and CH_3COOH (D).

The molar extinction coefficient was $4.93 \cdot 10^4$, which is at the lower end of the range of molar extinction coefficients that are expected from arsenazo III as a reagent for multivalent ions in aqueous solution[1].

High acidity method

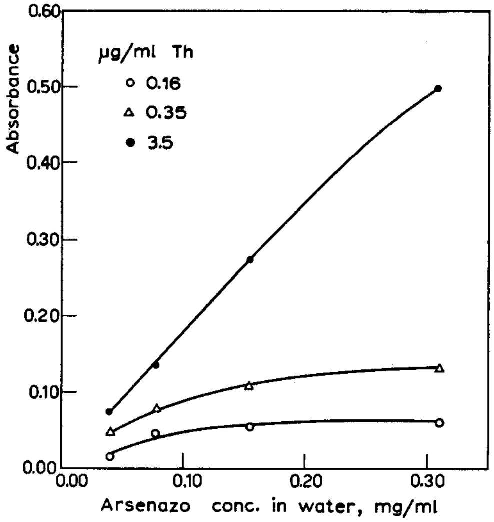
Since a considerable enhancement of the colour intensity can be achieved by increasing the acidity of the medium in which the colour is developed[2,11], the effect of increased acidity of the organic phase on the above "low acidity" method was studied. For this purpose 1 ml of arsenazo solution (0.310 mg/ml) was added, instead of 2 ml, followed by 1 ml of concentrated hydrochloric acid (12.5 *M*). The absorption spectrum of this solution, read against the corresponding blank, is shown in Fig. 3 (curve B). A comparison of the maximum of this curve with that of the curve obtained with the same amount of thorium by the "low acidity" method (curve A), proves the enhanced sensitivity of the method. The addition of other concentrated acids was also examined. The enhancing effect of 11.7 *M* perchloric acid (curve C) was less than that of hydrochloric acid (curve B), but greater than that of 17.5 *M* acetic acid (curve D); the addition of 14.5 *M* nitric acid caused the disappearance of the colour.

The effect of the various parameters was therefore investigated with the addition of hydrochloric acid, and this was termed the "high acidity" method.

With this method, the colour intensity reached a maximum in less than a minute and remained practically stable for at least 20 h. Precision could, however, be enhanced by measuring the absorbance after a fixed short time from mixing.

In contrast to the low acidity method, the concentration of HDEHP had practically no influence on the colour intensity, at least in the range 0.1–1.0 *F*. The hydrochloric acid concentration in the aqueous phase before extraction had no effect on the colour absorbance in the range 0.01–10.0 *M*.

The influence of the concentration of arsenazo is shown in Fig. 4 for 3 different



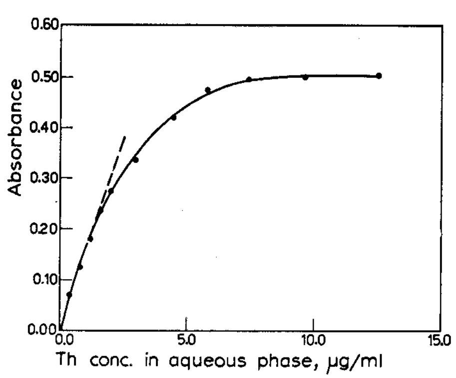


Fig. 4. The influence of the concentration of arsenazo III on the colour developed with the high acidity method, at 3 Th concentration levels in the final solution, as reported in the figure.

Fig. 5. Calibration curve for the standard procedure involving the development of the colour with the high acidity method.

thorium concentrations. It is clear that the amount of arsenazo must be as high as possible, especially when high thorium concentrations are involved. Nevertheless, as in the low acidity method, the 310 μg/ml solution of the reagent was felt to be the most convenient (see also p. 398).

These tests of the high acidity method involved the addition of 1 ml of 12.5 *M* hydrochloric acid to the organic phase. However, further tests showed that hydrochloric acid concentrations from 6 to 12.5 *M* had practically the same effect on the colour, while the addition of less concentrated acid lowered the absorbance of the thorium–arsenazo complex; concentrated hydrochloric acid (12.5 *M*) was chosen as simplest.

The calibration curve obtained is shown in Fig. 5. It should be pointed out that this curve held for any hydrochloric acid and HDEHP concentrations in the extraction step, at least in the ranges 0.1–10 *M* and 0.1–1 *F*, respectively. In this high acidity method, Beer's law was followed only up to 1.5 μg/ml of thorium in the initial aqueous phase, *i.e.* 0.6 μg/ml in the final solution.

The molar extinction coefficient of the high acidity method was considerably higher than that of the low acidity method, being $8.77 \cdot 10^4$, which is very satisfactory, although less than the value (130,000) reported[2] for the thorium–arsenazo complex in strongly acidic aqueous medium. It must be remembered that both the arsenazo content and the acidity of the medium in the organic phase, cannot reach the optimal values attainable in aqueous media.

A comparison of the calibration curves shown in Figs. 5 and 2 shows that the higher sensitivity of the high acidity method in the lower thorium range is lost for higher concentrations of thorium, where the low acidity method is more suitable. The results in Fig. 4 indicate that the flattening of the curve in Fig. 5 is due to insufficient reagent.

As already mentioned, all the experiments were carried out at room temperature, *i.e.* 24 ± 1°. Further tests showed that the mean variation of the optical density per ° was -0.9% in the temperature range 18°–35°.

Investigation on the coloured complex

As already pointed out, the molar extinction coefficients of the coloured thorium–arsenazo III complexes formed in both the procedures described above, are lower than the value found for the thorium–arsenazo complex in aqueous solution. The method of continuous variations was therefore applied to check if the molar ratio of metal to arsenazo III was the same in all cases. Figure 6 shows the results obtained for the complex developed in slightly and strongly acidic organic media. Similar results were obtained when lower or higher total concentrations than that mentioned were used. The mole ratio between thorium and arsenazo III in the complex is thus 1:2, which is the same as previously reported[2] for the complex developed in aqueous media. Thus, the lower molar extinction coefficient in the organic phase is only due to the different environmental conditions, and not to the formation of a different complex.

The effect of diverse ions

Table I shows the results obtained when foreign ions were added to a 0.1 *M* hydrochloric acid solution containing 0.800 μg of thorium per ml, the thorium being extracted with a 1.0 *F* HDEHP solution in cyclohexane. Thorium was finally determined by the high acidity procedure, by means of the equation obtained from the

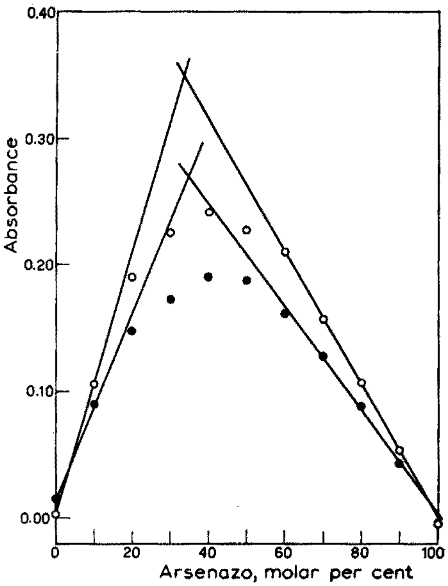


Fig. 6. The method of continuous variations applied to the coloured complex of thorium–arsenazo III, obtained with the low (●) and high (○) acidity methods. Total (reagent + cation) concentration: $1.55 \cdot 10^{-8}$ moles per ml in the final solution.

straight portion of the curve shown in Fig. 5: Abs. $= 0.151 \cdot c$ where c is the concentration in μg/ml of thorium in the initial aqueous solution. The effect of 69 foreign cations was investigated, added as the chlorides in much greater amounts than the amount of thorium to be determined. For some cations, different amounts were added; in some cases the presence of an interfering species could be tolerated in low concentration.

As a general rule, cations which are not extracted into the organic phase by HDEHP under these conditions, do not interfere in the thorium determination. Nevertheless, a slight error is given by the presence of Mg^{2+}, Sr^{2+} and Pt^{2+}; Ru^{3+} and Se^{4+}, although extracted only as traces, cause a 10% error. Among the ions which are partially or completely extracted by HDEHP, Ti^{4+}, Y^{3+} and the rare earths cause the highest errors, even when only 0.5 μeq/ml is present.

The above investigation of interferences was carried out by extracting thorium from 0.1 *M* hydrochloric acid, since these conditions were used in most of the preliminary work. However, some cations which are extracted by HDEHP at low hydrochloric acid concentrations, are no longer extracted at higher acidities. Table II shows the results obtained when foreign cations were added to a 6 *M* hydrochloric acid solution containing 0.800 μg/ml of thorium, and thorium was extracted with a 0.5 *F* HDEHP solution in cyclohexane; under such conditions the calibration of the high acidity method remains valid. Thirteen cations were taken into account, chosen among the ones which had given some interferences when thorium was extracted from 0.1 *M* hydrochloric acid. A comparison of Tables II and I shows that Mg^{2+}, Ca^{2+}, Y^{3+}, and the rare earths lighter than terbium no longer interfere while the interference of the heaviest rare earths and of Sr^{2+} is greatly lowered.

TABLE I

DETERMINATION OF THORIUM IN THE PRESENCE OF FOREIGN IONS

(Th extracted from 0.1 *M* HCl; high acidity standard procedure)

Ion added	*Concn. of foreign ion before extn. (μeq/ml)*	*Weight ratio of foreign ion to Th before extn.*	*Th found (μg/ml)*	*Error (%)*
Nil	—	—	0.800	Nil
Li^+	5.0	43	0.800	Nil
Na^+	5.0	144	0.806	+0.8
K^+	5.0	244	0.800	Nil
Rb^+	5.0	531	0.806	+0.8
Cs^+	5.0	831	0.800	Nil
NH_4^+	5.0	112	0.800	Nil
Be^{2+}	66.7	375	0.700	−12.5
	6.7	37	0.774	−3.2
Mg^{2+}	5.0	76	0.825	+3.1
	0.5	8	0.774	−3.2
Ca^{2+}	5.0	125	0.921	+15
	0.5	12	0.818	+2.3
Sr^{2+}	5.0	271	0.838	+4.8
	0.5	27	0.781	−2.4
Ba^{2+}	5.0	430	0.800	Nil
Sc^{3+}	5.0	94	0.800	Nil
Y^{3+}	10.1	375	2.960	+270
	1.0	37	1.635	+104
Rare earths from La^{3+} to Lu^{3+}	6.5–5.1	375	2.800–2.950	+250
	0.6–0.5	37	1.510–2.800	+89 to 250
Ti^{4+}	25.0	375	0.530	−34
	2.5	37	0.590	−26
Zr^{4+}	5.0	142	0.880	+10
	0.5	14	0.787	−1.6
Hf^{4+}	2.1	117	0.746	−6.7
	0.2	12	0.787	−1.6
V^{3+}	5.0	106	0.940	+17
	0.5	11	0.806	+0.8
V^{4+}	5.0	80	1.136	+41
	0.5	8	0.834	+4.2
V^{5+}	5.0	64	0.780	−2.5
	0.5	6	0.780	−2.5
Nb^{5+}	5.0	116	0.806	+0.8
Cr^{3+}	5.0	108	0.806	+0.8
Cr^{6+}	5.0	54	0.813	+1.6
Mo^{6+}	5.0	100	0.800	Nil
W^{6+}	5.0	191	0.800	Nil
Mn^{2+}	5.0	172	0.873	+9.1
	0.5	17	0.800	Nil
Re^{7+}	5.0	166	0.794	−0.8
Fe^{3+}	5.0	116	0.824	+3.0
	0.5	12	0.820	+2.5
Co^{2+}	5.0	184	0.800	Nil
Ni^{2+}	5.0	184	0.806	+0.8

TABLE I (continued)

Ion added	*Concn. of foreign ion before extn. (μeq/ml)*	*Weight ratio of foreign ion to Th before extn.*	*Th found (μg/ml)*	*Error (%)*
Ru^{3+}	5.0	170	0.890	+11
	0.5	17	0.806	+0.8
Rh^{3+}	5.0	170	0.800	Nil
Pd^{2+}	5.0	266	0.794	−0.8
Os^{5+}	6.0	284	0.960	+20
	0.5	24	0.800	Nil
Ir^{4+}	5.0	300	0.800	Nil
Pt^{4+}	5.0	305	0.742	−7.2
	0.5	30	0.833	+4.1
Cu^{2+}	5.0	198	0.806	+0.8
Au^{3+}	2.5	205	0.760	−5
	0.2	20	0.786	−1.7
Zn^{2+}	5.0	203	0.800	Nil
Cd^{2+}	5.0	350	0.794	−0.8
Hg^{2+}	5.0	625	0.806	+0.8
B^{3+}	5.0	22	0.806	+0.8
Al^{3+}	33.5	375	0.800	Nil
Ga^{3+}	12.9	375	0.776	−3.0
In^{3+}	7.8	375	0.800	Nil
Tl^{3+}	1.0	85	0.800	Nil
Si^{4+}	5.0	44	0.786	−1.7
Ge^{4+}	5.0	113	0.800	Nil
Sn^{4+}	5.0	186	0.833	+4.1
	0.5	19	0.814	+1.7
As^{3+}	5.0	156	0.800	Nil
As^{5+}	5.0	94	0.767	−4.1
	0.5	9	0.820	+2.5
Sb^{5+}	5.0	152	0.794	−0.8
Bi^{3+}	5.0	435	0.806	+0.8
Se^{4+}	5.0	124	0.874	+9.3
Se^{6+}	5.0	82	0.800	Nil
Te^{4+}	5.0	200	0.794	−0.8
ClO_4^-	1000	—	0.800	Nil
NO_3^-	1000	—	0.800	Nil
SO_4^{2-}	2000	—	0.810	+1.7

The extraction of thorium from hydrochloric acid solutions more concentrated than 6 M avoids the interference from some other elements. Furthermore, ions which are extracted only in trace amounts but still interfere in the thorium determination, may be substantially eliminated from the organic phase by stripping once or twice with concentrated solutions of hydrochloric acid, as in the case of uranium(VI) (see below).

Another way to eliminate interferences is to extract thorium from aqueous media other than chloride (see below). For example, 5.0 μeq per ml of Ca^{2+} or Mn^{2+} gave no error in the determination of 0.800 μg/ml of thorium when it was extracted

TABLE II

THE DETERMINATION OF THORIUM IN THE PRESENCE OF FOREIGN IONS

(Th extracted from 6 M HCl; high acidity standard procedure)

Ion added	*Concn. of foreign ion before extn. (μeq/ml)*	*Weight ratio of foreign ion to Th before extn.*	*Th found (μg/ml)*	*Error (%)*
Nil	—	—	0.800	—
Mg^{2+}	5.0	76	0.794	−0.8
Ca^{2+}	5.0	125	0.806	+0.8
Sr^{2+}	5.0	271	0.814	+1.7
Y^{3+}	10.1	375	0.800	Nil
La^{3+}	6.5	375	0.800	Nil
Sm^{3+}	6.0	375	0.806	+0.8
Eu^{3+}	5.9	375	0.806	+0.8
Gd^{3+}	5.7	375	0.800	Nil
Tb^{3+}	5.6	375	0.950	+18
Dy^{3+}	5.5	375	1.244	+37
Ho^{3+}	5.4	375	1.412	+42
Lu^{3+}	5.1	375	1.664	+60

TABLE III

THE DETERMINATION OF THORIUM IN THE PRESENCE OF URANIUM(VI)

(Extraction: 1.0 F HDEHP in cyclohexane; 1:1 phase ratio. High acidity method)

(a) 0.1 M HCl containing 0.800 μg/ml Th. Shaking time 10 min

U^{6+}, μg/ml	—	0.12	0.23	0.35	0.46	0.58	0.65	0.71	0.82	0.94
abs.	0.121	0.120	0.121	0.122	0.121	0.120	0.122	0.121	0.124	0.129

(b) 0.1 M HCl containing 0.730 μg/ml Th. Shaking time 2 min

U^{6+}, μg/ml	—	0.30	0.60	0.90	1.05	1.15	1.35	1.50
abs.	0.109	0.107	0.107	0.110	0.109	0.111	0.118	0.120

(c) 10 M HCl containing 0.730 μg/ml Th. Shaking time 10 min

U^{6+}, μg/ml	—	1.0	2.0	2.9	3.9	4.9
abs.	0.113	0.113	0.112	0.113	0.116	0.121

(d) 10 M HCl containing 0.800 μg/ml Th. Shaking time 2 min

U^{6+}, μg/ml	—	2.95	4.7	5.9	7.0	8.8	10.0
abs.	0.121	0.121	0.120	0.122	0.125	0.129	0.134

from 0.1 M perchloric acid or 0.1 N sulphuric acid respectively, and determined by the high acidity method.

Literature data on solvent extraction with HDEHP[10,13,14] provide useful guides to the choice of the most suitable aqueous media for the extraction in order to eliminate given interferences.

With regard to common anions, a slight interference is shown only by high concentrations of sulphate; nitrate and perchlorate ions do not interfere even at 1 M concentrations.

The effect of uranium

The effect of uranium(VI) in the solution from which thorium is to be extracted was studied with particular attention. When the arsenazo III–thorium colour is developed in strongly acidic aqueous solution, no interference is shown by the uranium(VI), since only uranium(IV) gives stable complexes with the reagent under such conditions[2]. In our case, however, such high acidities were not attainable and more than 7 μg/ml of uranium interfered.

When about 1.0 μg/ml of thorium was extracted by 1.0 *F* HDEHP from a 0.1 *M* hydrochloric acid solution, more than 1 μg U/ml interfered with the thorium determination. The time of the liquid–liquid contact was important, since uranium reaches the extraction equilibrium more slowly than thorium; thus the shorter the shaking, the higher the amount of uranium that could be tolerated in the aqueous phase. From Table III (a, b) it can be seen that shaking for 2 min instead of 10 min raised the tolerable uranium amount from 0.7 μg/ml to 1.1 μg/ml. Better results (Table IIIc, d) were obtained when thorium was extracted from 10 *M* hydrochloric acid: up to 3 or 7 μg U/ml were tolerated when the extraction time was 10 or 2 min, respectively.

To eliminate the interference of greater amounts of uranium, a suitable back-extraction process was necessary. This was best accomplished by partial stripping of the HDEHP phase with 10 *M* hydrochloric acid; thorium, owing to its very high extraction coefficient[10], remained in the organic phase.

Tests were made with an initial solution 10 *M* in hydrochloric acid and containing 0.730 μg Th/ml and 118 μg U/ml, which was first contacted with a 1.0 *F* HDEHP solution in cyclohexane. The organic phase was then scrubbed with equal volumes of fresh 10 *M* hydrochloric acid. After the fifth scrubbing, the residual uranium no longer interfered in the determination of thorium. The results obtained with another 3 contacts showed that no thorium was lost in the aqueous phases. It was also shown that, when the uranium content was doubled, 6 stripping steps completely eliminated its interference in the determination of 0.92 μg Th/ml.

The addition of nitrate to the organic solution lowers the absorbance of both the uranium and thorium complexes, the effect being stronger for uranium. However, the uranium interference could not be eliminated in this way, since the amount of nitrate necessary to mask appreciable amounts of uranium had too great an effect on the absorbance of the thorium complex. The addition of EDTA masked uranium efficiently, but caused turbidity in the case of thorium.

STANDARD PROCEDURES

Use HDEHP solutions in cyclohexane that have been previously shaken for 10 min with twice their volume of a hydrochloric acid solution of the same molarity as that of the solution from which thorium has to be extracted (*i.e.* 0.1 *M* to 10 *M*).

Procedure for >6 μg Th/ml (low acidity method)

Amounts of thorium up to 12 μg/ml can be determined. Shake 20 ml of an equilibrated 1.0 *F* HDEHP solution with 20 ml of the solution containing thorium for 3 min. Pipette 10 ml of the organic layer from the funnel into a 25-ml volumetric flask, add 2 ml of aqueous arsenazo III solution (0.310 mg/ml), and dilute to volume with isopropanol. Read the absorbance after 10 min at 660 nm, against a blank prepared by adding arsenazo and isopropanol to 10 ml of the equilibrated HDEHP solution.

The calibration curve is reported in Fig. 2. When isopropanol is added, the various phases present in the flask do not mix unless vigorously shaken: it is possible to leave the unmixed reagents for several hours, counting the time of colour development from the moment of complete mixing.

Procedure for <6 µg Th/ml (high acidity method)

Shake 20 ml of an equilibrated 1.0 *F* HDEHP solution with 20 ml of the solution containing thorium for 3 min. Pipette 10 ml of the organic layer into a 25-ml volumetric flask, add 1 ml of the above arsenazo III solution and 1 ml of 12.5 *M* hydrochloric acid, and dilute to volume with isopropanol. Read at 660 nm against a blank obtained from the equilibrated HDEHP solution, at any time from less than a minute to many hours. The calibration curve is reported in Fig. 5.

Eleven measurements on the same aqueous solution obtained with the high acidity procedure applied to independent extracts, gave a thorium content of 0.693 µg per ml, with a standard deviation of 0.0046. If a higher precision is required, measurement at a fixed short time after colour development is recommended. When the absorbance was measured just after obtaining a homogeneous final solution, the average result for the aqueous solution mentioned just above, was 0.696 µg of Th per ml, with a standard deviation of 0.0028.

EXTENSIONS OF THE METHOD

Extraction from other media

The procedures described above could be applied to 1.0 *F* HDEHP solutions containing thorium extracted from a nitrate, sulphate or perchlorate medium. Beer's law was followed in the low thorium concentration range. When thorium was extracted from 5 *M* nitric acid or 0.1 *M* sulphuric acid, molar extinction coefficients of $4.0 \cdot 10^4$ and $6.1 \cdot 10^4$ were found for the low acidity and high acidity methods respectively. When the medium was 1 *M* in perchloric acid, the molar extinction coefficients for the 2 procedures were $4.1 \cdot 10^4$ and $7.4 \cdot 10^4$ respectively.

Although these procedures involving the extraction of thorium from other media than chloride cause decreased sensitivity, they may be advantageous when certain interferences have to be avoided.

The procedures of colour development in the organic phase can be applied to thorium extracted with reagents other than HDEHP. When the high acidity method was applied to a 5% tri-*n*-octyl phosphine oxide solution in cyclohexane containing thorium extracted from 7 *M* hydrochloric acid, the calibration curve obtained at 660 nm followed Beer's law up to 0.45 µg Th/ml of the final solution, with a molar extinction coefficient of $9.5 \cdot 10^4$.

Improvement of sensitivity

The lowest concentration of thorium in the initial aqueous solution, which can be determined by the methods described, can be further decreased by increasing the volume ratio between the aqueous and the organic phases.

As far as the 1.0 *F* HDEHP–0.1 *M* HCl system is concerned, very high phase volume ratios do not involve any danger of losses of thorium from the organic phase, because of the high extraction coefficient. However, since the colorimetric procedure does not require the complete recovery of the organic phase, the calculation of the thorium concentration in the aqueous phase is made through a nominal phase ratio derived from the initial volumes; the extent to which the volume ratio in the extraction can be raised is limited by the reproducibility of the volume decrease of the organic phase, which is caused by slight dissolution in the aqueous phase.

However, it was found that volume ratios as high as 50:1 caused no significant volume reduction, so that results can be read from the standard calibration curve with a fairly good precision, taking into account the nominal phase ratio. Obviously, the best results would be obtained by preparing a complete calibration curve pertinent to the phase ratio chosen.

The range of the method is limited by the low solubility of arsenazo III in water, and by the low amount of aqueous solution which can be added to the organic phase. The increased sensitivity obtained by addition of hydrochloric acid in the development step could be amalgamated with the improved sensitivity obtained by adding more arsenazo III (see Fig. 4) if 2 ml of an acidic solution of the reagent were used for colour development. Since the solubility of arsenazo in aqueous solution decreases with increasing acidity, a suitable compromise appeared to be the addition of 2 ml of a saturated solution of the reagent in 3 *M* hydrochloric acid. When the standard procedure was thus modified, the calibration curve obtained followed Beer's law up to 2.5 µg Th/ml in the initial aqueous solution, with a molar extinction coefficient of $1.0 \cdot 10^5$.

Because of the very slow dissolution of arsenazo III in acidic solutions, the saturated reagent solution in 3 *M* hydrochloric acid is best obtained by acidification of the aqueous solution. This step involves the precipitation of the excess reagent and this developing method is recommended only when its high sensitivity is necessary.

Application of this modified colour development to 1.0 *F* HDEHP solutions containing thorium extracted from 0.1 *M* hydrochloric acid solutions with aqueous: organic phase volume ratios of 50:1 allowed the determination of as little as 2.0 µg of thorium per liter of aqueous solution with a standard deviation of 0.13.

Extension to other metals

The coloured reaction products obtained by the addition of arsenazo III to organic solutions containing cations extracted from a suitable aqueous phase can be used for a rapid colorimetric determination of thorium, which is less affected by interferences than the analogous aqueous methods. The determination of thorium was chosen from among several colour reactions observed with various cations in a preliminary investigation of HDEHP–cyclohexane extracts. Cation concentrations were of the order of $1 \cdot 10^{-4}$ mg/ml in the final solution. Among the elements tested, thorium, lanthanum, and europium turned the violet reagent colour to deep green; zirconium, bismuth, iron(III), and calcium modified the reagent colour to some extent; uranium(VI), lutetium, lead, copper, strontium, and barium gave no coloured reactions.

The standard procedures established for thorium were subsequently applied to some of the above cations. Zirconium gave a colour with a low molar extinction coefficient for both procedures, but very encouraging results were obtained with light rare earths. The molar extinction coefficients of some rare earth–arsenazo III complexes obtained by the low acidity procedure are shown in Table IV, together with results obtained by BUDĚŠÍNSKÝ AND HAAS[15] by means of dicarboxyarsenazo III in aqueous solution, a method claimed by the authors to be the most sensitive colorimetric method of determining rare earths. However, the arsenazo III method suggested here appears to be even more sensitive for the light rare earths and this method is now being investigated in detail.

TABLE IV

THE MOLAR EXTINCTION COEFFICIENTS OF SOME RARE EARTH COMPLEXES OF ARSENAZO III IN ORGANIC MEDIUM

(Rare earths extracted with 1.0 *F* HDEHP in cyclohexane from 0.1 *M* HCl; colours developed with the low acidity procedure)

Rare earth	*Molar extinction coefficient* $\cdot 10^{-4}$	
	Arsenazo III	*Dicarboxyarsenazo III*[15]
La^{3+}	6.7	6.63
Ce^{3+}	7.5	7.25
Pr^{3+}	8.8	7.56
Nd^{3+}	9.4	8.02
Sm^{3+}	10.4	8.20
Eu^{3+}	9.2	8.24
Gd^{3+}	9.1	8.35
Tb^{3+}	8.2	8.40
Dy^{3+}	5.8	8.38
Ho^{3+}	1.5	8.57
Lu^{3+}	0.05	8.48

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SUMMARY

A simple, direct colorimetric determination of thorium extracted from chloride solution with di-(2-ethylhexyl)orthophosphoric acid is described; the colour is developed in the organic phase by adding arsenazo III and then isopropanol. Two different procedures are outlined for different thorium levels; maximum absorbance occurs at 660 nm and Beer's law is obeyed within limited ranges. Molar extinction coefficients for the two methods are $4.93 \cdot 10^4$ and $8.77 \cdot 10^4$ respectively. With the more sensitive method, 0.696 μg Th/ml was determined with 0.0028 as standard deviation. The effects of the various parameters were studied. Among 69 foreign cations tested, serious interferences are U(VI), Se (IV), Ti(IV), Y and the rare earths. Of the common anions, only large amounts of sulphate slightly interfered. Several ways of overcoming interferences are suggested, with particular reference to uranium.

Several extensions of the method are outlined; 2 p.p.b. Th in aqueous media can be determined by modifying the extraction step. The procedure also appears to be extremely sensitive for the light rare-earth elements.

RÉSUMÉ

Les auteurs proposent une méthode simple pour le dosage colorimétrique direct du thorium, extrait d'une solution chlorhydrique, à l'aide de l'acide di-(2-éthylhexyl)orthophosphorique. La couleur est développée dans la solution organique en ajoutant une solution d'arsénazo III et de l'isopropanol ayant le maximum d'absorbance à 660 nm. Deux méthodes standards ont été mises au point pour diverses concentrations de thorium. Les coefficients d'extinction molaire sont respectivement $4.93 \cdot 10^4$ et $8.77 \cdot 10^4$. Avec la méthode la plus sensible 0.696 µg/ml de thorium ont été déterminés avec une déviation standard de 0.0028. On a examiné l'influence de divers paramètres. Entre 69 cations étrangers étudiés, U(VI), Se(IV), Ti(IV), Y et terres rares gênent. Parmi les anions courants, seules de fortes concentrations de sulfates gênent.

ZUSAMMENFASSUNG

Es wird eine einfache spektralphotometrische Bestimmung von Thorium beschrieben, bei der mit Di-(2-äthylhexyl)orthophosphorsäure aus chloridhaltiger Lösung extrahiert und die Farbe im organischen Lösungsmittel mit Arsenazo-III entwickelt wird. Für unterschiedliche Konzentrationsbereiche werden 2 verschiedene Verfahren vorgeschlagen, die beide das Absorptionsmaximum bei 660 nm verwenden und die in Grenzen das Beersche Gesetz befolgen. Die molare Extinktionskoeffizienten betragen $4.93 \cdot 10^4$ bzw. $8.77 \cdot 10^4$. Mit der empfindlicheren Methode wurden 0.696 µg Th/ml mit einer Standardabweichung von 0.0028 bestimmt. Von 69 untersuchten Fremdkationen, gaben ernsthafte Abweichungen U(VI), Se(IV), Ti(IV), Y und seltene Erden. Die gewöhnlichen Anionen stören nur in grossen Konzentrationen. Verschiedene Wege zur Beseitigung der Störungen werden vorgeschlagen unter besonderer Berücksichtigung des Urans. Eine erweiterte Methode gestattet es, bis zu 2 p.p.b. Th im wässrigen Medium zu bestimmen. Die Methode ist sehr empfindlich zur Bestimmung der leichten seltenen Erden.

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THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN ROCKS

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Relatively few photometric methods have been applied to the determination of vanadium in rocks. The element is usually determined by emission spectrography and, more recently by neutron activation and X-ray fluorescence analysis. Of the photometric methods which have been applied, the method of SANDELL[1] is by far the most widely used. In this method, the rock is fused with sodium carbonate, and vanadium(V) is separated from the other constituents of the leach with 8-hydroxyquinoline and chloroform before the final determination as phosphotungstovanadic acid.

More recent spectrophotometric methods suggested for this determination in rocks involve ultraviolet spectrophotometry[2], and spectrophotometry with a complex of nicotinohydroxamic acid[3] or diaminobenzidine, after perchloric and hydrofluoric acid attack of the sample and removal of the interfering elements by cation exchange[4].

In the present paper, the method proposed by NISHIDA[5] for the determination of sub-microgram quantities of vanadium, using the catalytic action of vanadium on the oxidation of aniline by hydrogen peroxide, is applied to rocks.

Aniline is very sensitive to oxidation and even on exposure to air it turns brown and resinifies. A large number of oxidation products can be formed with different oxidizing agents by varying the reaction conditions. The oxidation of aniline in the presence of an oxygen carrier (*e.g.* vanadium(V) and other transition elements) and a dehydrating agent produces the intensely coloured dye, aniline black, by a series of condensation reactions[6,7]. It is necessary to heat the reaction mixture to produce the dye but overheating causes the colour to fade. Heating at 100° for 8 min is sufficient to develop the colour of the dye without causing further oxidation. This time is critical to within ±15 sec.

The absorption spectrum of the aniline black dye in sulphuric acid is characterised by a broad absorption band with an absorption maximum between 436 nm and 440 nm. The quantity of dye formed, and therefore the colour intensity, is directly proportional to the concentration of vanadium up to 0.2 μg. To obtain some measure of the reproducibility of the colorimetric procedure, 10 replicate spectrophotometric determinations on a sample containing the equivalent of 100 p.p.m. V, were performed. The results obtained gave a value of 100±2 p.p.m. for the sample.

The sensitivity of the method is such that very small quantities of samples are required. Even in rocks with as little as 1 p.p.m. vanadium, a 100-mg sample is sufficient for the determination.

INTERFERING ELEMENTS

As other transition elements interfere by acting as oxygen carriers in the formation of aniline black, the rock is taken into solution by an alkaline fusion, which renders most of the other transition metals insoluble. Leaching of the fusion cake effects a separation of vanadium from all other ions except chromate, permanganate, borate, phosphate, aluminate, silicate, arsenate, molybdate, tungstate and the halogens. However, small quantities of iron in a colloidal state sometimes pass through the filter. Evaporation to low bulk and a second filtration are necessary to remove the iron. Of the ions listed above, permanganate is selectively reduced by ethanol to manganese dioxide, and of the remainder only chromate interferes by oxidizing the aniline black in the presence of sulphuric acid. No interference was recorded from 2% P_2O_5 or 100 p.p.m. Mo, W, B, As, Sb, or Sn, in the determination of 10 p.p.m. V.

It was found that chromium only interferes when present in 5-fold excess over vanadium, in rocks where the latter element is present in concentrations below 100 p.p.m. In rocks where the vanadium content is above 100 p.p.m., a 10-fold excess of chromium can be tolerated. Usually chromium only exceeds vanadium by such amounts in certain ultrabasic rocks and chromite schists, etc. In the cases where the chromium content is high enough to interfere it is necessary either to extract the vanadium or to lower the chromium content to an acceptable level. The latter course was chosen for simplicity. Chromium may be extracted as perchromic acid which is formed when the dichromate ion is treated with hydrogen peroxide. BROOKSHIER AND FREUND[8] studied the extraction with ethyl acetate and concluded that extraction was complete at pH 1.7 ± 0.2 below 20° after treatment with 0.02 M hydrogen peroxide. Perchromic acid is very unstable in water so that the acid must be extracted immediately, as its stability in ethyl acetate is far greater than in water.

EXPERIMENTAL

Apparatus

An Optica CF 4 single beam spectrophotometer equipped with 1-cm stoppered glass cells.

Reagents

Fusion mixture. Mix intimately, 4 parts of AR sodium carbonate and one part of AR magnesium oxide.

Aniline reagent, 0.2% (w/v). Dissolve 0.1 g of AR aniline in 50 ml of concentrated sulphuric acid. Prepare freshly every week.

Stock vanadium solution, 50 µg V/ml. Dissolve 0.1148 g of AR ammonium metavanadate in distilled water and dilute to 1 l.

Standard vanadium solution, 0.1 µg V/ml. Dilute 1 ml of the above vanadium solution to 500 ml.

Construction of the calibration curve

Take 0, 0.5, 1, 1.5 and 2 ml of the standard solution and dilute to 2 ml. Treat these solutions as described below (colorimetric procedure).

PREPARATION OF ROCK SAMPLES

Weigh out 0.1 g of the powdered rock sample into a 10-ml nickel crucible, and mix intimately with 0.6 g of fusion mixture; heat for 20 min at about 900°. Cool the crucible and add 1–2 drops of ethanol and almost fill the crucible with water. Heat the crucible on a water bath at 100° for about 10 min, then remove the crucible and break up the fusion cake with a glass rod to aid the solution of the vanadate. Replace the crucible on the water bath and heat for a further 10 min. Cool the crucible in an ice bath and filter the contents through a highly retentive filter paper (*e.g.* Whatman No. 542), previously washed in hot 1% sodium carbonate solution, into a 50-ml beaker. Wash the crucible and filter with ice-cold 1% sodium carbonate solution. Evaporate the solution slowly to *ca.* 10 ml.

If it is suspected that the rock has a high chromium content remove the excess of chromate ion as indicated below. If the rock does not contain an excess of chromium, or after the excess has been removed, filter the ice-cooled solution through a washed filter into a 50-ml graduated flask, washing the beaker and filter with cold sodium carbonate solution. Make up to volume with distilled water.

The procedure now depends on the probable vanadium content of the rock. If it is suspected that the vanadium content is less than 100 p.p.m. (*e.g.* acid igneous rocks), then the solution is sufficiently dilute. However, if the rock is thought to contain between 100 and 500 p.p.m. vanadium then the solution should be diluted by a factor of five. For vanadium contents of between 1000 and 500 p.p.m. V (as in some basic rocks) the solution is diluted by a factor of 10.

THE REMOVAL OF EXCESS CHROMIUM

Transfer the rock solution to a 250-ml separating funnel, dilute to about 40 ml and neutralize with *N* sulphuric acid to methyl orange indicator. Add a further 1 ml of acid and swirl the funnel to remove most of the carbon dioxide. The volume of solution in the funnel should now be about 50 ml.

Add 75 ml of ethyl acetate and place the separating funnel in the refrigerator for about 30 min. To the cold solution add 1 ml of 3.8% (w/v) hydrogen peroxide and shake vigorously for 30 sec. Remove the aqueous layer and repeat the extraction twice with 15-ml portions of ethyl acetate. Evaporate the aqueous layer to near dryness and filter it into a 50-ml graduated flask as above. It is not necessary to remove completely the hydrogen peroxide as a slight excess of this reagent does not affect the subsequent colorimetry.

COLORIMETRIC PROCEDURE

Pipette 1 ml of the rock solution into a 20-ml stoppered test-tube and dilute to 2 ml. Cool the sample in water and carefully add 10 ml of concentrated sulphuric acid. Pipette 0.5 ml of 3% (w/v) hydrogen peroxide into the cold solution, and then add 0.5 ml of aniline reagent. Homogenise the contents of the tube and heat at 100°±2° for exactly 8 min. Cool the tube and measure the optical density, at 438 nm, in a stoppered glass cell, against distilled water in the reference cell. The colour of the dye is stable for at least 2 h. A reagent blank with each group of determinations is essential since the aniline reagent darkens on keeping. This blank is carried out on a fusion blank as in the colorimetric procedure.

If the rock is expected to contain less than 10 p.p.m. vanadium then 2 ml of the rock solution should be used.

RESULTS

The above method was applied to the determination of vanadium in some standard rock samples. The results (Table I) showed good agreement with those of other methods. Most of the quoted results for these standards have been obtained by spectrographic analysis.

Fleischer and Stevens[9] suggest that the more recent values for G1 indicate a lower value than had previously been proposed; they tentatively suggest that the correct value is in the region of 16 p.p.m. Taylor and Kolbe[10] quote 15 p.p.m. while the most recent published analysis for vanadium in G1, that by Chan and Riley[4], suggests a value of 17.2 ± 0.9 p.p.m.

The value obtained for W1 is slightly higher than the suggested value which is based mainly on spectrographic results. The value for syenite 1 is very close to the mean and median values quoted by Webber[11].

The method was also applied to the determination of vanadium in some other

TABLE I

DETERMINATION OF VANADIUM IN THE STANDARD ROCK SAMPLES G1, W1, AND SYENITE 1

Rock sample	*V found (p.p.m.)*	*Literature values (p.p.m.)*	*Reference*
U. S. Geol. Survey Standard granite G1	16	11–24 Suggested average "perhaps 16"	9
U. S. Geol. Survey Standard diabase W1	263[a]	120–320 Suggested average 240	9
C.A.A.S. Standard syenite 1	86[b]	50–150 Mean value 87 Median value 88	11

[a] Average of 10 determinations. Standard deviation 5.6.
[b] Average of 10 determinations. Standard deviation 2.5.

TABLE II

DETERMINATION OF VANADIUM IN SOME ANALYSED ROCK SAMPLES

Rock sample	*V found (p.p.m.)*	
	Present method	*Comparison method*
Amphibolite 1	250	241[a]
Amphibolite 2	341	316[a]
Granite 1	25	24[a]
Granite 2	1	2[b]
Basic rock	352	340[b]
Shale	109	120[a] 110[c]

[a] Spectrographic analyses performed by Mr. G. M. Power, University of Keele.
[b] Spectrophotometric analyses by the phosphotungstate method.
[c] X-ray fluorescence analysis performed by Mr. E. J. Raynor, University of Reading.

rock samples which had previously been analysed by other methods. The results (Table II) again showed good agreement with the analyses by other methods.

Two artificial rock solutions were made up to contain the equivalent of 5,000 p.p.m. chromium and 5 and 10 p.p.m. vanadium respectively. The chromium was separated as described above, and the vanadium was determined in the extracted aqueous layer. The results obtained were slightly high in both cases (Table III).

TABLE III

ARTIFICIAL ROCK SAMPLES CONTAINING LARGE QUANTITIES OF CHROMIUM

Sample	*V present (p.p.m.)*	*Cr present (p.p.m.)*	*V found (p.p.m.)*
1	10	5000	10.4
2	5	5000	5.5

In general, the method gave satisfactory results for all the rock samples analysed. Since such a small sample can be used for the determination it is likely that the method could readily be applied to the determination of vanadium in small quantities of separated minerals.

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SUMMARY

Vanadium in rock samples is determined, after alkaline fusion of the sample, by means of its catalytic action on the oxidation of aniline to aniline black by hydrogen peroxide. If necessary, chromium can be easily extracted to prevent interference. The sensitive procedure was applied to standard granite G1 and diabase W1, and to the C.A.A.S. syenite 1; values of 16, 263 and 86 p.p.m., respectively, were obtained.

RÉSUMÉ

On propose une méthode pour le dosage du vanadium après fusion alcaline de l'échantillon. Elle est basée sur l'action catalytique du vanadium sur l'oxydation de l'analine en noir d'aniline par le peroxyde d'hydrogène.

ZUSAMMENFASSUNG

Die spektralphotometrische Bestimmung von Vanadin in Gesteinsproben wird beschrieben. Die Probe wird alkalisch aufgeschlossen und durch die katalytische Wirkung des Vanadins eine Oxydation des Anilins zum Anilinschwarz mit Wasserstoffperoxid erzielt. Falls erforderlich, kann das Chrom zur Vermeidung von Störungen leicht extrahiert werden.

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SOLVENT EXTRACTION STUDIES OF SOME COBALT(II) CHELATES

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Cobalt(II) extractions

Some of the reagents which have been reported as extractants for cobalt(II) are oxine[1], benzoylacetone[2], thenoyltrifluoroacetone[3], dithizone[4,5], diethylammonium diethyldithiocarbamate[6], 1-nitroso-2-naphthol[7-9], 1-(2-pyridylazo)-2-naphthol[10-12], cupferron[13], and N-benzoyl-N-phenylhydroxylamine[14]. Very few studies appear to have been made concerning the equilibria or use of either aromatic or aliphatic carboxylic acids in the extraction of cobalt(II). GINDIN *et al.*[15] have carried out a few experiments involving the extraction of aqueous cobalt(II) into kerosene containing various mixtures of aliphatic monocarboxylic acids.

The purpose of the present study is to conduct a search for reagents which extract cobalt(II) well at moderately low pH values and give good, reproducible data. First the reagents listed above were examined. Then, in light of GINDIN's success, a number of carboxylic acids were examined. These were salicylic acid, 3-hydroxy-2-naphthoic acid, benzilic acid, anthranilic acid, 2-thiophenecarboxylic acid, 2-naphthoic acid, 1-pyrenebutyric acid, nonanoic acid, octanoic acid, heptanoic acid, hexanoic acid, 4-methylpentanoic acid, pentanoic acid, butanoic acid, 9-octadecenoic acid, and 10-hendecenoic acid. In 8 cases in which the chelating reagent was a liquid immiscible with water, it also served as the organic solvent. In most other instances, one or more solvents were used with each reagent; those employed were chloroform, benzene, 1-butanol, methyl isobutyl ketone, 2-octanol, nitrobenzene, methyl propionate, isoamyl alcohol, 1-octanol, and 1-hexanol.

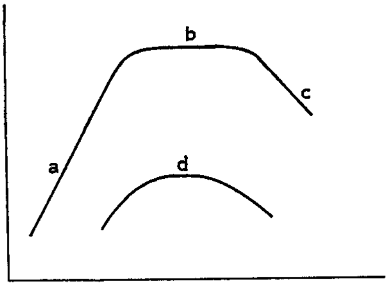

Fig. 1. Idealized solvent extraction curves for cobalt(II).

A solvent extraction system, typical of the ones mentioned above, is made up of (*1*) an organic phase presaturated with 0.1 *M* aqueous sodium perchlorate and containing a known concentration of chelating reagent HR (such as oxine), and (*2*) an aqueous phase presaturated with the organic solvent and containing cobalt(II) as the perchlorate in a concentration no more than one-tenth that of HR plus enough sodium perchlorate to make the ionic strength up to 0.1. In such a system the distribution coefficient D, which is the ratio of the total cobalt concentration in the organic phase to that in the aqueous phase, is, as a rule, experimentally determined as a function of pH. Presentation of such data as plots of log D *versus* pH often results in curves of the type abc as illustrated in Fig. 1. A theoretical approach to the treatment of these data has been given by SCHWEITZER[16].

EXPERIMENTAL PROCEDURES

Cobalt-60 in hydrochloric acid was obtained from Oak Ridge National Laboratory. The chloride was converted to the perchlorate by 3 successive evaporations with perchloric acid. From the product a stock solution was prepared. All the chemicals employed were either reagent grade or were purified by distillation procedures. Tap water containing alkaline permanganate was fractionally distilled. The resulting water was made gas-free by boiling for 5 min. All the 2-phase systems were made by equilibrating previously prepared aqueous 0.1 M sodium perchlorate with the desired organic solvent. The presaturated phases were then used to prepare the desired solutions.

Experiments conducted in a nitrogen atmosphere were performed in the following way. The above two-phase system was saturated with nitrogen, and subsequently the chelating reagent was introduced into the organic phase. After the phases were prepared for equilibration, the upper one was marked with a label. Nitrogen was continuously passed through the system during the adjustments in pH. Before equilibration, the evaporated organic solvent was replaced to the indicated level.

The distribution of cobalt(II) between the phases was measured by means of the radiolabeled ^{60}Co. Adjustments in pH were made with sodium hydroxide and perchloric acid. The total concentration of cobalt was 10^{-6} to 10^{-7} M. The volume of each of the 2 phases was 7 ml. After their separation, an aliquot of each phase was removed, and its activity was measured with a Tracerlab scaler equipped with a well scintillation detector. The pH values were measured on a Beckman H-2 pH meter equipped with Beckman miniature electrodes. The pH equipment was frequently standardized with buffers accurate to ± 0.02 pH units. All experiments were carried out at $27.5 \pm 0.5°$. Equilibrium in almost all cases was found to have been reached within 10 h, except when specific mention is made about longer equilibrations.

For two of the chelating reagents, the products of K (the association constant of HR) and P (the organic/aqueous partition coefficient of HR) were determined by a two-phase titration of the 0.1 M sodium perchlorate/chelating reagent–organic solvent system. The organic/aqueous distribution ratio of the chelating reagent may be given by $d=[\mathrm{HR}]_o/([\mathrm{R}]+[\mathrm{HR}])$ where the subscript o indicates the organic phase, and the unsubscripted brackets refer to the aqueous phase. Charges on ionic species have been omitted for simplicity in the above relation and hereafter. This relation may readily be seen to be represented by the equation $d=KP[\mathrm{H}]$, when P is large as compared to $KP[\mathrm{H}]$. If the reaction between the standard sodium hydroxide and chelating reagent is complete, then the *d* values are given by $([HR_1]_o - [R]_o)/[R]$, where $[HR_1]_o$ is the initial reagent concentration in the organic phase before contact with the water phase and [HR] is negligible as compared to [R]. The slopes of log *d* against pH plots of the experimental data attained values of −1, thereby agreeing with the presumed relation for *d* and directly yielding the *KP* products.

RESULTS

Log *D versus* pH curves of the types illustrated by Fig. 1 are represented in Table I in terms of the curve type and shape. The general type of the curve is indicated by the letters in Table I which refer to those in Fig. 1; then there is given the constant slope region of the rising portion, the $\mathrm{pH}_{\frac{1}{2}}$ which is the pH for log *D* equal to 1, the

TABLE I

EXTRACTION DATA

	System[a]	*Curve type*	*Rising slope*	*pH*$_{\frac{1}{2}}$[b]	*Maximum log D*	*pH of maximum log D*	*Reproducibility*
1	$10^{-0.5}$ *M* oxine in chloroform	ab	1	—	2.4	3.0–10.0	Poor
2	$10^{-1.0}$ *M* oxine in chloroform	ab	3	2.5	2.3	4.1–10.0	Poor
3	$10^{-1.5}$ *M* oxine in chloroform	abc	1.5	3.2	1.8	4.9–9.6	Poor
4	$10^{-2.0}$ *M* oxine in chloroform	abc	2	4.0	1.9	5.3–9.3	Poor
5	$10^{-1.0}$ *M* oxine in benzene (10–16 days shaking)	abc	5	2.6	1.8	3.7–7.2	Fair
6	$10^{-0.5}$ *M* benzoylacetone in benzene	ab	2	6.4	1.3	9.0–10.5	Poor
7	$10^{-1.0}$ *M* benzoylacetone in benzene	ab	2	6.7	1.6	8.2–11.0	Poor
8	$10^{-1.5}$ *M* benzoylacetone in benzene	ab	2	7.6	1.1	9.4–11.0	Poor
9	$10^{-2.0}$ *M* benzoylacetone in benzene	ab	2	7.7	1.1	9.4–11.0	Poor
10	$10^{-0.5}$ *M* thenoyltrifluoroacetone in 1-butanol	abc	2	2.8	3.0	4.9–6.1	Fair
11	$10^{-1.0}$ *M* thenoyltrifluoroacetone in 1-butanol	abc	2	3.2	2.8	5.0–6.2	Fair
12	$10^{-1.5}$ *M* thenoyltrifluoroacetone in 1-butanol	ab	2	3.6	2.3	5.5–8.5	Fair
13	$10^{-2.0}$ *M* thenoyltrifluoroacetone in 1-butanol	ab	2	3.8	2.1	5.3–8.1	Fair
14	$10^{0.0}$ *M* thenoyltrifluoroacetone in benzene (in N_2 atmosphere)	ab	2	3.9	2.6	7.5–8.0	Good
15	$10^{-0.5}$ *M* thenoyltrifluoroacetone in benzene (in N_2 atmosphere)	ab	2	4.6	1.7	6.6–7.0	Good
16	$10^{-1.0}$ *M* thenoyltrifluoroacetone in benzene (in N_2 atmosphere)	ab	2	5.1	1.5	7.0–7.5	Good
17	$10^{-1.5}$ *M* thenoyltrifluoroacetone in benzene (in N_2 atmosphere)	ab	2	5.6	1.3	7.4–8.0	Good

TABLE I (*continued*)

	System[a]	*Curve type*	*Rising slope*	$pH_{1/2}$[b]	*Maximum log D*	*pH of maximum log D*	*Reproducibility*
18	$10^{-2.0}$ *M* thenoyltrifluoroacetone in benzene (in N_2 atmosphere)	ab	2	6.1	1.1	7.4–8.0	Good
19	$10^{-3.0}$ *M* dithizone in benzene	d	0.5	—	2.0	3.6–6.6	Poor
20	$10^{-3.0}$ *M* diethylammonium diethyldithiocarbamate in chloroform	abc	1	3.4	2.4	7.4–8.6	Poor
21	$10^{-1.0}$ *M* 1-nitroso-2-naphthol in benzene	d	0.7	—	2.9	2.2–4.2	Poor
22	$10^{-1.3}$ *M* 1-(2-pyridylazo)-2-naphthol in benzene	d	0.4	—	1.8	4.0–5.5	Poor
23	$10^{-2.0}$ *M* cupferron in water in contact with chloroform (shaken by hand 5 min)	abc	2	3.4	2.3	5.4–6.2	Poor
24	$10^{-1.0}$ *M* N-benzoylphenylhydroxylamine in chloroform	abc	1	5.0	1.9	7.0–8.0	Poor
25	$10^{-2.0}$ *M* salicylic acid in benzene	b	—	—	−2.8	1.5–13.1	Good
26	$10^{-1.0}$ *M* salicylic acid in methylisobutylketone	d	1	—	−1.3	6.1–7.0	Good
27	$10^{-1.0}$ *M* 3-hydroxy-2-naphthoic acid in methylisobutylketone	abc	1.6	5.6	0.9	6.8–7.0	Fair
28	$10^{-1.5}$ *M* 3-hydroxy-2-naphthoic acid in methyl isobutyl ketone	abc	1.2	6.6	0.1	6.8–7.8	Fair
29	$10^{-2.0}$ *M* 3-hydroxy-2-naphthoic acid in methyl isobutyl ketone	abc	1.1	—	−0.7	6.9–8.4	Fair
30	$10^{-2.5}$ *M* 3-hydroxy-2-naphthoic acid in methyl isobutyl ketone	ab	1.1	—	−1.5	6.3–9.0	Poor
31	$10^{-1.0}$ *M* benzilic acid in methyl isobutyl ketone	d	1	—	−0.7	6.9–8.1	Fair
32	$10^{-1.0}$ *M* anthranilic acid in chloroform	ab	0.8	—	−2.7	5.5–6.5	Fair
33	$10^{-1.0}$ *M* anthranilic acid in methyl isobutyl ketone	bc	None	—	−2.0	1.1–5.0	Fair
34	$10^{-1.0}$ *M* 2-thiophene-carboxylic acid in methyl isobutyl ketone	b	None	—	−1.7	2.6–10.0	Poor
35	$10^{-1.0}$ *M* 2-naphthoic acid in 2-octanol	abc	2	6.6	0.5	7.5–8.7	Good
36	$10^{-1.5}$ *M* 1-pyrene-butyric acid in methyl isobutyl ketone	abc	2	8.2	0.6	8.5–8.6	Fair
37	$10^{0.8}$ *M* nonanoic acid in contact with water	abc	2	3.1	2.3	4.8–5.1	Good
38	$10^{0.8}$ *M* octanoic acid in contact with water	ab	2	4.5	2.1	5.9–6.3	Good
39	$10^{0.8}$ *M* heptanoic acid in contact with water	ab	2	4.5	2.0	5.7–6.2	Good
40	$10^{0.9}$ *M* hexanoic acid in contact with water	ab	2	4.3	1.4	5.1–5.8	Good

continued on the next page

TABLE I (*continued*)

	System[a]	*Curve type*	*Rising slope*	*pH*$_{\frac{1}{2}}$[b]	*Maximum log D*	*pH of maximum log D*	*Reproducibility*
41	$10^{0.9}$ *M* 4-methylpentanoic acid in contact with water	ab	2	—	−0.7	4.1–4.4	Good
42	$10^{1.0}$ *M* pentanoic acid in contact with water	ab	2	4.0	0.6	4.6–4.9	Good
43	$10^{-1.0}$ *M* butanoic acid in water in contact with 2-octanol	b	—	—	−2.3	2.5–11.2	Poor
44	$10^{0.5}$ *M* 9-octadecenoic acid in contact with water	ab	2	4.8	2.2	7.5–8.0	Good
45	$10^{0.7}$ *M* 10-hendecenoic acid in contact with water	ab	2	4.7	0.6	5.3–5.8	Good
46	$10^{-1.0}$ *M* octanoic acid in nitrobenzene	ab	1	—	−1.5	7.2–8.0	Fair
47	$10^{-1.0}$ *M* octanoic acid in methyl propionate	ab	0.8	—	−1.4	7.6–7.8	Poor
48	$10^{-1.0}$ *M* octanoic acid in methyl isobutyl ketone	ab	1	—	−0.9	8.0–9.0	Good
49	$10^{-1.0}$ *M* octanoic acid in chloroform	ab	1.3	—	−0.3	7.8–8.7	Fair
50	$10^{-1.0}$ *M* octanoic acid in isoamyl alcohol	ab	2	6.6	1.6	7.8–9.4	Good
51	$10^{-1.0}$ *M* octanoic acid in 1-hexanol	ab	2	6.6	2.0	8.8–9.8	Good
52	$10^{-1.0}$ *M* octanoic acid in 1-octanol	abc	2	6.5	1.8	8.1–8.8	Good
53	$10^{0.5}$ *M* octanoic acid in 1-octanol	ab	2	4.7	1.9	6.1–6.4	Good
54	$10^{0.0}$ *M* octanoic acid in 1-octanol	ab	2	5.3	1.9	6.5–6.9	Good
55	$10^{-0.5}$ *M* octanoic acid in 1-octanol	ab	2	5.9	1.9	7.5–7.8	Good
56	$10^{-1.5}$ *M* octanoic acid in 1-octanol	ab	2	7.0	1.1	8.1–8.9	Good
57	$10^{-2.0}$ *M* octanoic acid in 1-octanol	ab	2	7.4	0.4	8.2–8.9	Good
58	$10^{0.5}$ *M* hexanoic acid in 1-hexanol	ab	2	4.8	1.3	6.2–6.7	Good
59	$10^{0.0}$ *M* hexanoic acid in 1-hexanol	ab	2	5.5	1.1	6.8–7.4	Good
60	$10^{-0.5}$ *M* hexanoic acid in 1-hexanol	ab	2	6.2	0.7	7.4–8.6	Good
61	$10^{-1.0}$ *M* hexanoic acid in 1-hexanol	ab	2	7.1	0.1	7.4–8.8	Good

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[a] All aqueous phases were 10^{-6} to 10^{-7} *M* in radiolabeled cobalt(II) perchlorate and $10^{-1.0}$ *M* in sodium perchlorate.

[b] pH$_{\frac{1}{2}}$ is the pH for *D* equal to 1.

maximum log *D*, and the pH range of the maximum log *D*. Table I also indicates whether the reproducibility of the data was good, fair, or poor. The reproducibility of each of the log *D versus* pH curves was considered in terms of the deviation of the log *D* values from the curve, assuming the pH to be known without error. When the log *D* deviations along the curve were within ±0.2, within ±0.4, or greater than ±0.4, the reproducibility of the data was considered to be good, fair, or poor, respectively.

Referring to Table I, systems 1 through 4 (oxine in chloroform) extract cobalt(II) well at low pH values and show a high plateau, *i.e.*, section b of Fig. 1 appears at about a log *D* of 2, but the data showed poor reproducibility. Very little improvement in reproducibility was observed in system 5 when benzene was used as a solvent, even for longer equilibration times. Almost the same may be said about systems 6–9 (benzoylacetone in benzene) and systems 10–13 (thenoyltrifluoroacetone in 1-butanol). It is to be noted that a plot of log *D versus* log [R] for system 5 gives a slope of 3, suggesting that cobalt(III) is being extracted (CoR_3 dominating the organic phase). However, when benzene is used as a solvent for thenoyltrifluoroacetone (systems 14–18), the data are good, especially when the extractions are conducted in a nitrogen atmosphere.

Systems 19 through 24 involve the use of dithizone, diethylammonium diethyldithiocarbamate, 1-nitroso-2-naphthol, 1-(2-pyridylazo)-2-naphthol, cupferron, and N-benzoylphenylhydroxylamine. Each of these reagents extracts cobalt(II) well at low pH values and exhibits a high plateau, but in all cases the reproducibility of the data is poor.

In systems 25–36 a numbeı of aromatic carboxylic acids are considered as possible extractants. Different solvents were used in attempts to raise the plateau. Also variations in the structure about the carboxyl group were made in an effort to enhance the extractions. For example, phenyl, naphthyl, and pyrenyl groups were tried. Then hydroxyl, amino, and sulfur sites adjacent to the carboxyl group were tried. The best extractions resulted with 3-hydroxy-2-naphthoic acid in methyl isobutyl ketone as shown in systems 27–30. The highest plateau appeared in system 27 at a log *D* value of 0.9. A more favorable plateau would be one at a log *D* of 2. However, the curves indicated that the data were either fair or poor, and no basic analysis could be made.

In systems 37–45 a number of aliphatic carboxylic acids are considered as extractants. Since all of these acids, with the exception of butanoic acid, were liquids and immiscible with water, they were used undiluted in order to serve as both reagent and solvent. Nonanoic, octanoic, and heptanoic acid (systems 37–39) show plateaus at a log *D* of about 2. The plateau is somewhat lower for hexanoic acid (system 40); it is much lower for 4-methyl-pentanoic acid (system 41), an isomer of hexanoic acid. For pentanoic acid (system 42), the plateau is lower than that for hexanoic acid but higher than that for 4-methylpentanoic acid. Essentially, no extraction was seen in system 43 (butanoic acid in water in contact with 2-octanol). System 44 indicates that 9-octadecenoic acid extracts cobalt(II) about as efficiently as do nonanoic, octanoic, and heptanoic acids. On the other hand, 10-hendecenoic acid (system 45) is about as effective an extractant as pentanoic acid. Among the reagents described above, octanoic and hexanoic acid showed the most reproducible log *D versus* pH curves with sufficiently high plateau.

Systems 46–52 consider a number of solvents for octanoic acid. The alcohols (systems 50–52) were the only ones which exhibited high plateaux. 1-Octanol (systems 52–57) appeared to give the best data. 1-Hexanol was found to be a suitable solvent for hexanoic acid. These data are described in systems 58–61.

Among the curves presented in systems 1–61, the log *D versus* pH curves for thenoyltrifluoroacetone in benzene (systems 14–18), octanoic acid in 1-octanol (systems 52–57), and hexanoic acid in 1-hexanol (systems 58–61) exhibited the most reproducible data with sufficiently high plateaus. These systems have been analyzed in detail. The results of these analyses are given below.

Log P values for octanoic acid in 1-octanol systems were obtained from the experimentally determined log KP values and the log K value reported in the literature[17]. For reagent concentrations of $10^{-2.0}$, $10^{-1.0}$, $10^{-0.5}$, and $10^{0.0}$ M, the value of log P was found to be 2.9. This indicated, as was expected for dilute solutions in oxygenated solvents[18], that there was negligible polymerization of the chelating reagent. However, the log P value for the $10^{0.5}$ M system was found to be 2.5; when undiluted octanoic acid ($10^{0.8}$ M) was used, the log P value was observed to be 2.1. The lower P values seen with the two highest concentrations of octanoic acid ($10^{0.5}$ and $10^{0.8}$ M) possibly arise because the role of octanoic acid as a solvent becomes important.

In light of these observations, the cobalt(II) species for the octanoic acid in 1-octanol extraction systems which showed constant P values (systems 52, 54–57) were identified. Referring to curve type ab of Fig. 1 and to the aqueous phase species, Co was found to predominate on the rising portion a; CoR was seen to appear along the changing portion between a and b; and CoR_2 was observed to dominate along the plateau region b. The organic species CoR_2 was seen to predominate throughout curve type ab of Fig. 1. A distribution relation, which includes all these species, is

$$D = [CoR_2]_o/([Co] + [CoR] + [CoR_2]) \tag{1}$$

Substitution of constants leads to

$$D^{-1} = K_{20}^{-1}P_{20}^{-1}[R]^{-2} + K_{20}^{-1}P_{20}^{-1}C_{10}[R]^{-1} + P_{20}^{-1} \tag{2}$$

where K_{20} is the association constant of CoR_2, P_{20} is the organic/aqueous partition constant of CoR_2, and C_{10} is the association constant of CoR. By proper curve fitting procedures, the values of $K_{20}^{-1}P_{20}^{-1}$, $K_{20}^{-1}P_{20}^{-1}C_{10}$, and P_{20}^{-1} were obtained from a plot of log D against log [R]. The resulting values of log P_{20}, log K_{20}, and log C_{10} were found to be 1.8, 2.9, and 1.1, respectively.

The log P values for the hexanoic acid in 1-hexanol systems were obtained from the experimentally determined log KP values and the log K value reported in the literature[19]. For reagent concentrations of $10^{-1.0}$, $10^{-0.5}$, $10^{0.0}$ and $10^{0.5}$ M, the value of log P was found to be 2.1, indicating, as was anticipated[18], that there was negligible polymerization of the chelating agent. On the other hand, the log P value for undiluted hexanoic acid ($10^{0.9}$ M) was found to be 1.6. This lower P value probably is due to the difference in the solvents, 1-hexanol and hexanoic acid.

Accordingly, in those hexanoic acid in 1-hexanol systems which showed the constant P values (systems 58–61), the cobalt(II) species were identified, and their relevant partition and association constants were determined. The aqueous species Co, CoR, CoOH, CoR_2 and CoROH were found to successively describe the rising, changing, and plateau region of curve type ab illustrated by Fig. 1. For this situation the over-all distribution may be styled:

$$D = [CoR_2]_o/([Co] + [CoR] + [CoOH] + [CoR_2] + [CoROH]) \tag{3}$$

Insertion of constants results in

$$D^{-1} = K_{20}^{-1}P_{20}^{-1}[R]^{-2} + K_{20}^{-1}P_{20}^{-1}C_{10}[R]^{-1} + K_{20}^{-1}P_{20}^{-1}C_{01}[R]^{-2}[OH] + P_{20}^{-1} + K_{20}^{-1}P_{20}^{-1}C_{11}[R]^{-1}[OH] \tag{4}$$

where C_{01} is the association constant of CoOH, C_{11} is the association constant of CoROH, and other terms have their previous meaning. By proper curve fitting procedures, the values of $K_{20}^{-1}P_{20}^{-1}$, $K_{20}^{-1}P_{20}^{-1}C_{10}$, $K_{20}^{-1}P_{20}^{-1}C_{01}$, P_{20}^{-1} and $K_{20}^{-1}P_{20}^{-1}C_{11}$ were obtained from this relation. Separation of the over-all values led to the individual log values of P_{20}, K_{20}, C_{10}, C_{01} and C_{11}, which were found to be 1.2, 1.6, 0.0, 6.4 and 7.6, respectively. It is to be noted that the value of 6.4 found for $\log C_{01}$ agrees with that reported in the literature[20].

With the reported values of K and P[21], the analysis of the thenoyltrifluoroacetone in benzene extractions (systems 14–18) indicated that the species CoR_2 always predominated in the organic phase. The aqueous species Co and CoR were found to describe the initial and changing region of the curves. Slope analysis indicated that along the plateau region a hypothetical species given by the formula $CoR_{1.7}(OH)_{0.3}$ seemed to predominate in the aqueous phase. An aqueous mixture of the species CoR_2 and CoROH would be a possibility consistent with this formula. An over-all expression, which includes all the species previously identified, is

$$D=[CoR_2]_o/([Co]+[CoR]+[CoR_2]+[CoROH]) \qquad (5)$$

This equation may be written

$$D^{-1}=K_{20}^{-1}P_{20}^{-1}[R]^{-2}+K_{20}^{-1}P_{20}^{-1}C_{10}[R]^{-1}+P_{20}^{-1}$$
$$+K_{20}^{-1}P_{20}^{-1}C_{11}[R]^{-1}[OH] \qquad (6)$$

upon substitution of the proper relations. As with the octanoic acid and hexanoic acid systems, over-all constants were obtained and separated into their constituent parts. The log values of P_{20}, K_{20}, C_{10} and C_{11} were found to be 2.5, 5.4, 3.3 and 11.0, respectively.

The aqueous mixture of CoR_2 and CoROH, which was assumed to predominate along the plateau regions in systems 14–18, is not the only mixture which is consistent with a hypothetical species $CoR_{1.3}(OH)_{0.7}$. Another possibility would be CoR_2 and $Co(OH)_2$. In this case the expression would be similar to eqn. (5) except with $Co(OH)_2$ in place of CoROH. The usual treatment leads to log values of P_{20}, K_{20}, C_{10} and C_{02} (the association constant of $Co(OH)_2$) equal to 2.5, 5.4, 3.5 and 15.1, respectively. The fit of an equation using these constants to the experimental data was about as good as seen for eqn. (6), but neither was entirely satisfactory. Possibly CoROH or $Co(OH)_2$ might partition. However, this is unlikely because these species would be expected to be quite hydrophilic.

SUMMARY

Extraction of radiolabeled cobalt(II) from aqueous solution into one or more solvents using 25 reagents was studied. Both reagent concentration and pH variation were investigated. The relevant association and partition constants for several of the better reagent–solvent systems were determined. These systems were hexanoic acid in 1-hexanol, octanoic acid in 1-octanol, and thenoyltrifluoroacetone in benzene.

RÉSUMÉ

On a étudié l'extraction du radiocobalt(II) marqué, en solution aqueuse, dans un ou plusieurs solvants, en utilisant 25 réactifs. L'influence de la concentration du réactif et de la variation de pH a été examinée. On a déterminé les constantes d'association et de partage pour les meilleurs systèmes réactif–solvant: acide hexanoïque dans l'hexanol-1, l'acide octanoïque dans l'octanol-1 et la thénoyltrifluoroacétone dans le benzène.

ZUSAMMENFASSUNG

Die Extraktion von radiomarkiertem Kobalt(II) aus wässriger Lösung mit einem oder mehreren Lösungsmitteln unter Verwendung von 25 Reagenzien wurde untersucht. Dabei wurde sowohl die Reagenzkonzentration als auch der pH-Wert variiert. Die Assoziations- und Verteilungskonstanten folgender Systeme wurden bestimmt: Hexanonsäure in 1-Hexanol, Octanonsäure in 1-Octanol und Thenoyltrifluoroaceton in Benzol.

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THE PRECISE COMPLEXIMETRIC TITRATION OF URANIUM(VI)

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Compleximetric determinations of uranium using disodium (ethylene dinitrilo)-tetraacetate dihydrate (EDTA) as a titrant have frequently been described. In most cases hexavalent uranium is reduced to the tetravalent state. Several reducing agents have been employed, *e.g.* ascorbic acid[1], granulated zinc in hydrochloric acid medium[2], electrolytic reduction on a mercury cathode in dilute perchloric acid[3] and formamidinesulfinic acid[4]. The indicators in these uranium(IV)–EDTA titrations were xylenol orange[1], solochrome black 6 BN[2], thoron[3] and arsenazo[4].

EDTA has been widely utilized as a volumetric agent because of its broad chelating power and the stability of the EDTA chelates. Unfortunately, the conditions for the titration of uranyl ions are less favorable than those for many other cations. The stability of the complex compound with EDTA is rather low; stability constants have been determined[5–7]. It has been shown that for the pH range 3.5–4.0, EDTA reacts with uranyl ion to form a stable salt[8]. In contrast to most other metals which react with EDTA in the proportion 1:1, the reaction ratio for uranyl ion to EDTA was found to be 2:1[8,9]. HARA AND WEST[8] have suggested a high-frequency titration employing trisodium (ethylene dinitrilo)-tetraacetate for the determination of uranyl ions[8]. They determined amounts varying from 9 to 27 mg UO_2^{2+} per determination, the errors varying from 0.40 to 0.92%.

LASSNER AND SCHARF[10] suggested a rapid titrimetric method for the determination of uranyl ion based on a visual end-point detection using PAN [1-(2-pyridylazo)-2-naphthol] as indicator. The pH of the solution to be titrated was kept close to 4.5 and the titrations were carried out in a 1:2 water–isopropanol mixture at the boiling point of the latter. In this way they determined quantities of uranium varying from 11 to 100 mg per determination, the error being not greater than ±0.3 mg.

In the investigation described in this paper a method similar to that of LASSNER AND SCHARF was used. But in order to determine accurately micro-amounts of uranium(VI) a weight titration technique, a new titration cell for photometric determinations[11], and a photometric end-point detection technique were used.

COMPLEXIMETRIC TITRATION OF URANIUM(VI) WITH PAN AS AN INDICATOR

The characteristics of the uranium–PAN complex for different media have been reported in the literature[12–14]. In the present work, the composition, structure and stability of the complex in an isopropanol–water medium at pH 4.40 were studied. Maximum absorption occurred at a wavelength of 555 nm and the composition of the complex was 1:1. The value for the apparent stability constant K determined by the modified method of ANDERSON *et al.*[15,16] as modified by MUKHERJI AND DEY[17,18], and by the method of SAKELLARIDIS[19] was respectively 4.06 ± 0.10 and 4.20 ± 0.10.

Experimental

Equipment. The titration cell had a light path of 10 cm and fitted into the normal cell-holder carriage of the CARY recording spectrophotometer, model 11–50. The addition of EDTA solution was done partially with a weight burette and partially with a Metrohm microburette E 374.

Standard uranium solution. A standard uranium solution containing about 1 mg of uranium per g of solution was prepared. An appropriate quantity of U_3O_8 (NBS-950 A) previously calcined at 850° for 1 h was dissolved in pure nitric acid. The excess of acid was removed by heating gently to near dryness. The uranyl nitrate was taken up in water and the solution was made up to a known weight. More dilute solutions were prepared by gravimetric dilution.

Standardization of the EDTA solutions. The EDTA solutions were standardized as follows. A stock solution of 0.1 M EDTA was prepared and standardized against high-purity zinc by gravimetric titration, using erio T as indicator. More dilute solutions were prepared by gravimetric dilution of this stock solution. In order to minimize the errors involved in volumetric dilutions, the gravimetric preparation of the solutions was applied where necessary, and the solutions were stored in quartz containers. The variation in the strength of the EDTA solution during 6 months was only 0.1%. Table I shows the results of the direct standardization with zinc, n denoting the number of determinations.

TABLE I

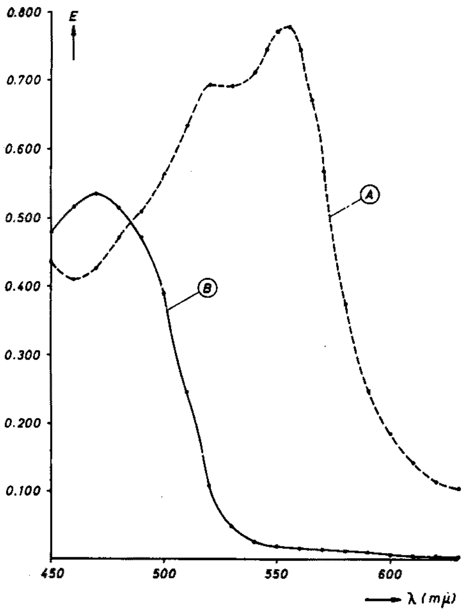
STANDARDIZATION OF EDTA SOLUTIONS WITH ZINC

EDTA (M)	*Method*	*Coeff. of variation (s %)*	*n*
0.1	Visual	0.011	11
0.01	Visual	0.08	11
0.001	Spectrophotometric	0.06	8

Choice of the wavelength for titration. Figure 1 shows the absorption curves of solutions of interest for the titration. Maximum absorbance occurs at 555 nm which corresponds to the maximum absorbance of the uranyl–PAN complex. The wavelength of 555 nm was therefore chosen for the titration.

Preparation of the titration medium. About 25 g of the standard uranium solution were dispensed into a 250-ml volumetric flask. Then 50 ml of water were added with a pipette followed by enough diluted ammonia to adjust the pH to 4.40, the volume of the solution being one-third of the total volume of the flask; 1 ml of a 0.1% solution of PAN in ethanol was added and the volumetric flask filled to the mark with isopropanol. The solution was homogenized and after a short time the volumetric flask was weighed.

Titration procedure. A portion (30 ml) of the above solution was introduced with a weight burette into the cylindrical cell provided with the cell attachment for photometric titrations. EDTA solution (0.003 *M*) was added gravimetrically in such a quantity that the end-point was nearly reached. The following final titration was done volumetrically with the same EDTA solution, using a calibrated 1-ml microburette (± 0.0003 ml). Small increments of the titrant were added stepwise and after each addition the solution was well mixed and the optical density was measured at 555 nm against a water blank. The titration was continued until sufficient points were obtained for the construction of a graph, from which the end-point was derived by the usual extrapolation technique. A curve in the vicinity of the end-point is shown in Fig. 2.



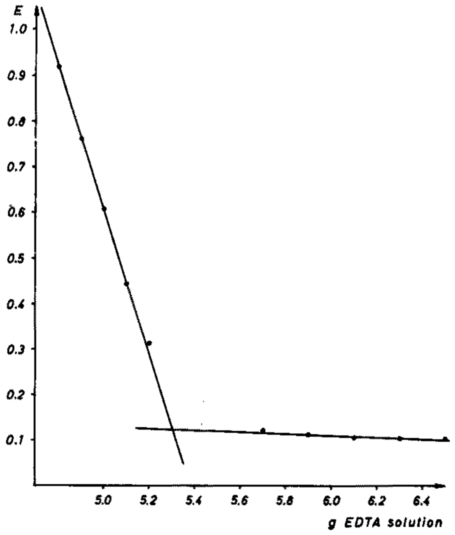


Fig. 1. Curve A: Absorption curve before the titration of an uranium solution of about 0.3 mg U/ml. The light path length of the cell was 2 cm. Curve B: The same solution with EDTA 100% titrated.

Fig. 2. Titration curve in the vicinity of the end-point. The cell contained 3 mg of uranium; the EDTA was 0.001 *M*.

Results

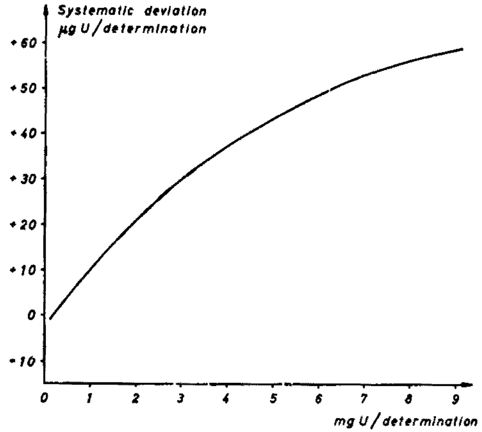
The results obtained by the described procedure are given in Table II with the coefficients of variation (s%) obtained. When a standard solution of uranium NBS-950 A was used for these titrations, systematic deviations were found as shown in Fig. 3.

It can be seen that the method has a systematic error that varies practically from zero to about +60 μg of uranium depending on the total quantity of uranium present. It is, of course, possible to eliminate this systematic deviation by using empirical factors for the strength of the EDTA solution. These would have to be determined by titrating the corresponding quantities of standard uranium.

TABLE II

RESULTS OF THE COMPLEXIMETRIC TITRATION OF URANIUM(VI) WITH PAN AS AN INDICATOR

U in cell (mg)	*s %*	*No. of determinations*	*U in cell (mg)*	*s %*	*No. of determinations*
9	0.1	10–15	0.3	0.8	10–15
3	0.2	10–15	0.12	1.2	10–15
1.5	0.3	10–15	0.065	1.8	10–15
0.6	0.5	10–15	0.012	5.0	10–15



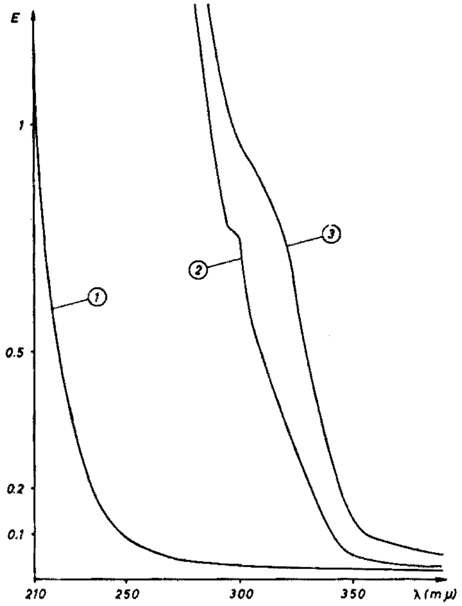


Fig. 3. Systematic deviation of compleximetric titration as a function of the amount of uranium.

Fig. 4. Absorption curves at pH 4. (1) EDTA, 10^{-3} *M*. (2) UO_2^{2+}, 10^{-3} *M*. (3) $(UO_2)Y$, 100% titrated.

DETERMINATION OF URANIUM(VI) WITHOUT AN INDICATOR BY TITRATION OF THE METAL IN THE ULTRAVIOLET REGION

In parallel with the method using PAN as indicator, a method for the determination of uranium without the addition of an indicator in the ultraviolet region was studied.

Several cations have already been determined by photometric titration with EDTA in the ultraviolet region. MALMSTADT AND GOHRBRANDT[20] determined thorium at 290 nm using a solution of a copper salt as an indicator. UNDERWOOD AND WHILHITE[21] showed that bismuth and lead could be determined simultaneously at 240 nm because of the differences in the absorption of the different metal–EDTA complexes. SWEETSER AND BRICKER[22] determined cadmium, zinc, magnesium, titanium and zirconium using a similar technique. FLASCHKA[23] studied the theory of such titrations without indicators.

Experimental

All the instruments and reagents were the same as described above for the method using PAN as an indicator.

Choice of the wavelength and pH *for the titration.* Figure 4 shows the ultraviolet spectra of the solutions of interest for the titration. The wavelength chosen for the determination was 320 nm. A comparison of titration curves at different pH values showed that the most favorable pH value for the titration was 4. At pH values below or above 4 no sharp end-point could be extrapolated from such titration curves.

Procedure. The procedure was nearly the same as for the titration with PAN as an indicator. Into a cylindrical cell (5 cm path length), 15 ml of a uranium solution containing 0.08 mg of uranium per g of solution were introduced with a weight burette; the pH of the uranium solution had previously been adjusted to 4. The strength of the titrant was 0.002 *M*. A titration curve for a quantity of 1.22 mg of uranium in the cell is shown in Fig. 5.

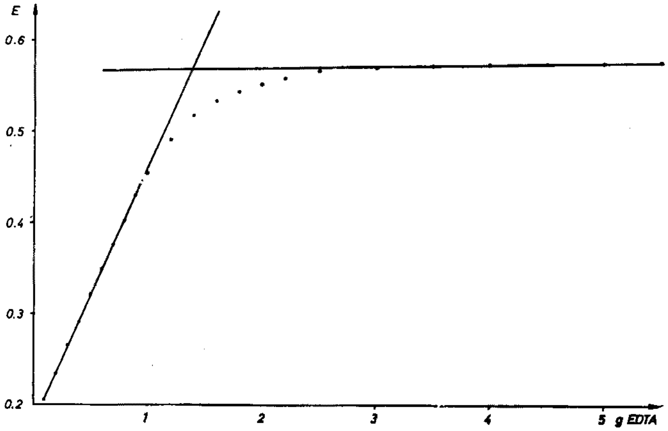


Fig. 5. Titration curve of 1.22 mg of uranium at pH 4.

TABLE III

RESULTS OF THE URANIUM TITRATION IN THE ULTRAVIOLET REGION

U(VI) given (mg)	*U(VI) found (mg)*
1.220	1.229
	1.224
	1.216

Results

For a quantity of 1.22 mg of uranium in the cell the results shown in Table III were obtained.

CONCLUSIONS

Contrary to some previous conclusions[5], the precise determination of uranium-

(VI) with EDTA is possible in the range of 12 μg to 9 mg uranium. Because of problems with the rather low dissociation constant of the U–PAN complex, it is not possible in the higher mentioned concentration range, to accept the method as an absolute one using the titer of the EDTA solution for the calculations of the uranium content. The method has to be standardized with a standard uranium sample which must lie in a limited concentration range close to the quantity that is to be determined. If this is done the method is sufficiently precise and accurate. The advantage of the method is its ease of application: per day 5 complete determinations can be done.

The authors are indebted to Mr. W. WOLTERS for much of the practical work done during the study of the compleximetric titrations of uranium with PAN as indicator, and to Mr. R. REYNDERS for his technical assistance during the investigation of the uranium–PAN complex and for most of the practical work done in the ultraviolet titration of uranium.

SUMMARY

The compleximetric reaction of uranium(VI) with EDTA has been studied. A method is described for determining uranium(VI) with PAN as an indicator and without an indicator by titration in the ultraviolet region. With the described technique, quantities of uranium varying from 12 μg to 9 mg can be determined. The coefficients of variation vary from 5% to 0.1%, respectively.

RÉSUMÉ

Les auteurs ont étudié la réaction compleximétrique de l'uranium(VI) avec l'EDTA. Une méthode est décrite pour déterminer l'uranium en utilisant le PAN comme indicateur. On détermine également l'uranium sans l'ajoute d'un indicateur en effectuant la titration dans l'ultraviolet. Avec la méthode ainsi décrite on dose des quantités d'uranium allant de 12 μg à 9 mg par détermination. Les coefficients de variation varient de 5% à 0.1% respectivement.

ZUSAMMENFASSUNG

Die komplexometrische Reaktion von Uran(VI) mit dem AeDTE wurde untersucht. Es wird eine Methode beschrieben, die sowohl die Bestimmung von Uran(VI) mit PAN als Indikator, als auch die Bestimmung ohne Indikator durch Titration im ultravioletten Bereich gestattet. Die beschriebene Methode erlaubt es, Uranmengen zwischen 12 μg und 9 mg je Einzeltitration zu bestimmen. Die prozentuale Standardabweichung schwankt je nach der bestimmten Menge zwischen 5% und 0.1%.

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THE STABILITY CONSTANTS OF SOME BIVALENT METAL COMPLEXES OF α-HYDROXYISOBUTYRATE AND LACTATE

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Stability constants of lanthanide and alkaline earth metal α-hydroxyisobutyrate complexes have previously been given in the literature[1-3]. In order to compile further data, the work described below was carried out, stability constants being determined for the complexes of this ligand with Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+} and UO_2^{2+} ions, by a potentiometric technique. The literature[4-11] contains little data on the stability constants of metal lactate complexes—most K_1 values at ionic strength $i = 0$—hence the stability constants of the lactate complexes of the above-mentioned metal ions were also determined in the same way. For all complexes K_1, K_2 and approximate K_3 values were calculated, because electrophoretic experiments with ^{65}Zn tracer indicated the existence of ML_3^- complexes.

For both ligands the sequence of increasing stability constants proved to be the same: $Mn^{2+} < Cd^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Pb^{2+} < Cu^{2+} < UO_2^{2+}$, in agreement with the well-known IRVING–WILLIAMS series[12].

CALCULATION PROCEDURE

The theoretical basis of the calculations has been described in previous papers[2,3,13]. However, for determining the potential corrections caused by changes in ionic strength, a slight modification was introduced. The previous formula, developed by SONESSON[14], $\Delta I = 0.5\, C_M \cdot \bar{n}(5-\bar{n})$, was only valid for bivalent metals up to $\bar{n} = 2$. Hence a modified formula is proposed, which for bivalent metals results in $\Delta I = 0.5\, C_M(2-\varepsilon)(3+\varepsilon)$ where $\varepsilon = |2-\bar{n}|$. As before, the experimental data were supplied to an IBM 1620 digital computer which gave $\bar{n}$, (L) and pL values. From these results K_1 and K_2 values were derived by means of BJERRUM's graphical half $\bar{n}$ method[15]. When these data were used as approximate values, more adequate constants could be computed by the least squares treatment. Furthermore, several constants were checked by FRONAEUS' graphical integration method[16].

EXPERIMENTAL

Reagents

Metal solutions. Analytical grade metals were dissolved in 6 N nitric acid. After addition of the calculated amount of perchloric acid, the solutions were evaporated to the appearance of dense white perchloric acid fumes, whereafter heating at 60° was continued until a negative test was obtained for nitric acid. All stock solutions contained nearly 25 mM metal perchlorate, about 2 to 7 mM free perchloric acid and sodium perchlorate for adjusting the ionic strength to $i = 1$.

Due to hydrolysis of the metal ion, it was impossible to determine accurately the amount of perchloric acid in the uranyl solutions. Therefore these solutions were prepared by dissolving a known amount uranyl nitrate and adding a known amount perchloric acid. As nitrate is known to have almost no complexing tendencies, no interferences are to be expected.

The small amount of perchloric acid in excess was determined by potentiometric titration in a nitrogen atmosphere. The metal ion concentrations were determined by electrolysis, except for uranyl which was determined as U_3O_8 by a gravimetric procedure[17].

Sodium perchlorate. Sodium perchlorate, Fluka analytical grade, was used. Analysis gave 99.75% purity.

Organic buffer solutions. The α-hydroxyisobutyrate and lactate solutions were prepared and analysed as described before[2,3]. Results for the buffer solutions were as follows:

α-Hydroxyisobutyrate $C^0_{\mathrm{HL}} = 1.029\ M$; $C^0_{\mathrm{NaL}} = 1.009\ M$; $\delta = 1.020$.

Lactate $C^0_{\mathrm{HL}} = 0.974\ M$; $C^0_{\mathrm{NaL}} = 1.002\ M$; $\delta = 0.972$.

As the pK values of both acids approach 4 and as the uranyl solution shows tendency to hydrolysis above pH 3–4, special buffer compositions were used for this metal ion (sodium perchlorate was added to give $i = 1$):

α-Hydroxyisobutyrate $C^0_{\mathrm{HL}} = 1.088\ M$; $C^0_{\mathrm{NaL}} = 0.4020\ M$; $\delta = 2.706$.

$C^0_{\mathrm{HL}} = 1.115\ M$; $C^0_{\mathrm{NaL}} = 0.2010\ M$; $\delta = 5.547$.

Lactate $C^0_{\mathrm{HL}} = 1.063\ M$; $C^0_{\mathrm{NaL}} = 0.4070\ M$; $\delta = 2.610$.

$C^0_{\mathrm{HL}} = 1.008\ M$; $C^0_{\mathrm{NaL}} = 0.2040\ M$; $\delta = 4.941$.

Procedures

For the potentiometric titrations the Fronaeus–Choppin arrangement with 3 half-cell compartments in series was used.

All other conditions were as before[3] ($t = 25.0 \pm 0.1°$; $i = 1$; $C_{\mathrm{M}}{}^0 = 25$ mM; $H_{\mathrm{A}} = 5$ mM; initial volume 20 ml).

For the electrophoretic experiments, 1 cm wide paper strips (Whatman no. 1) were inserted between 2 V-shaped plastic plates and the loose paper ends were dipped into the buffer solution. Two platinum wires connected to a 120-V battery acted as electrodes. The current was passed through the system for 1 h after the paper was completely saturated with ligand. Then a sufficient activity of ^{65}Zn tracer was spotted in the center of the paper strips and the electrophoresis was started. The whole system was placed in a box which was previously saturated with water vapour. After a sufficient time the strips were dried and cut into 5-mm pieces which were counted separately by a Tracerlab Superscaler, with a NaI(Tl) well-type crystal. This was sufficient to give good qualitative information about the distribution of the activity along the strip.

RESULTS

(a) Potentiometric titrations

The formation curves, representing $\bar{n}$ as a function of pL ($= -\log[L^-]$) of the metal(II) complexes with lactate and α-hydroxyisobutyrate are reproduced in Figs. 1 and 2.

Approximate values of the stability constants were obtained directly from these formation curves, using BJERRUM's half $\bar{n}$ method[15]: the logarithms of the stepwise formation constants K_1, K_2 and also K_3 for UO_2^{2+} are approximately given by the pL values at $\bar{n} = 0.5$, 1.5 and 2.5 respectively. These values, together with the constants calculated by computer, are listed in Tables I and II.

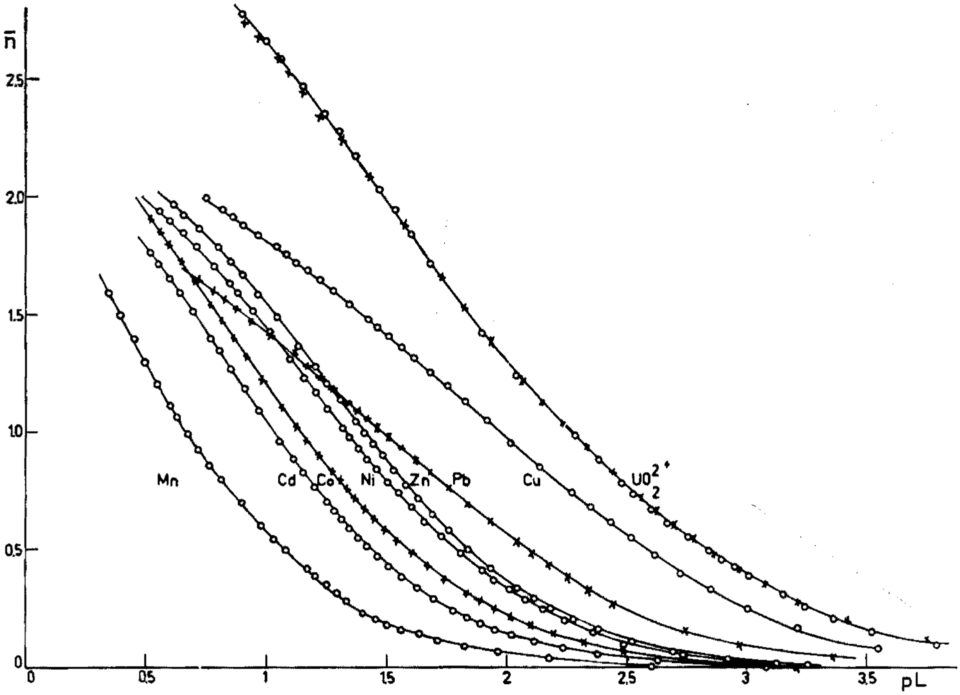

Fig. 1. Formation curves of metal(II)–lactate complex systems at 25.0° (UO_2^{2+}: o, $\delta = 4.9$ and x, $\delta = 2.6$).

When 3 or 4 successive titration series of the same metal ion were done the deviations between extreme values were in general within 0.02 for log K_1 and 0.05 for log K_2. This corresponds to errors within 5 and 10% for K_1 and K_2 respectively.

In all cases except for lead (lactate) and for manganese (with both ligands) which form weaker complexes, $\bar{n}$ values higher than 2 were obtained, indicating the existence of ML_3^- complexes. However, in these pL ranges the potential measurements were not sufficiently reproducible in each of the titration series to permit an exact calculation of K_3. The values given for this last constant in Tables I and II are only approximate and can differ upto ±0.1 log unit from the exact constants.

To check the computer values, several stability constants were also determined

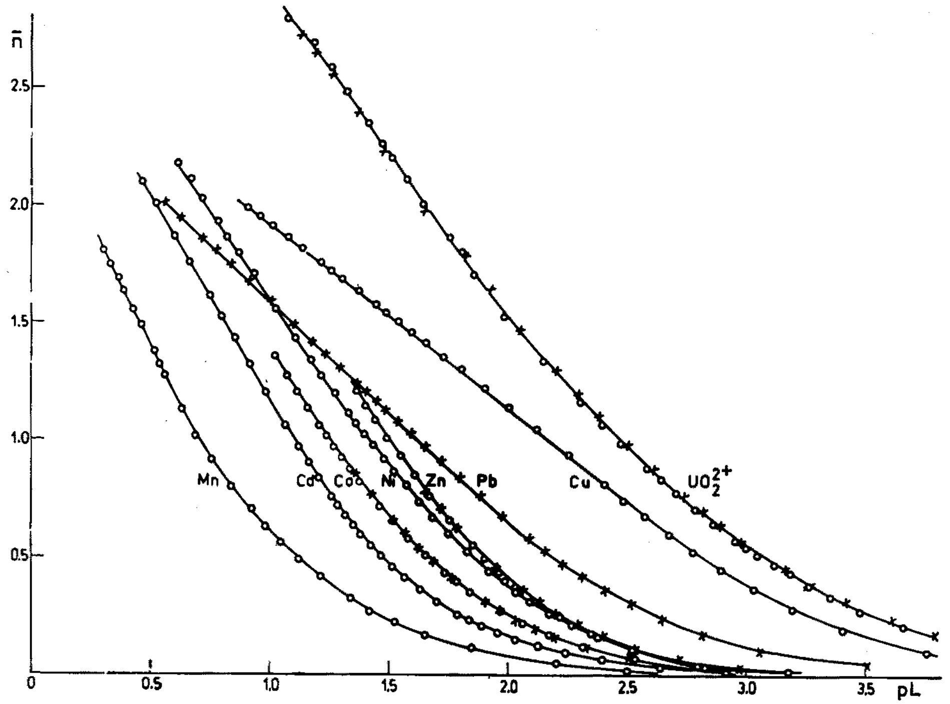

Fig. 2. Formation curves of metal(II)–α-hydroxyisobutyrate complex systems at 25.0° (UO_2^{2+}: o, $\delta = 5.5$ and x, $\delta = 2.7$; Zn, Co: x, $C_M \cong 25$ m*M* and o, $C_M \cong 12.5$ m*M*).

TABLE I

STABILITY CONSTANTS OF METAL(II)–LACTATE COMPLEXES (25.0° AND $i = 1$)

Metal ion	*Bjerrum's method*			*Computer*			
	log K_1	*log K_2*	*log K_3*	*log K_1*	*log K_2*	*log K_3*	*log β_2*
UO_2^{2+} [a]	2.84	1.85	1.14	2.76	1.67	1.34	4.43
[b]	2.86	1.86	1.11	2.77	1.68	1.32	4.45
Cu	2.58	1.40	—	2.49	1.49	~0.3	3.98
Pb	2.08	0.90	—	1.98	1.00	—	2.98
Zn	1.84	1.03	—	1.61	1.24	~0.3	2.85
Ni	1.79	0.99	—	1.59	1.08	~0.3	2.67
Co	1.59	0.81	—	1.37	0.95	~0.2	2.32
Cd	1.44	0.74	—	1.21	0.87	~0.2	2.08
Mn	1.08	0.40	—	0.92	0.54	~0.1	1.46

[a] $\delta = 4.9$.
[b] $\delta = 2.6$.

by FRONAEUS' graphical integration method[16]; agreement within the error limits was obtained.

The solubilities of the neutral α-hydroxyisobutyrate complexes of zinc and cobalt (ZnL_2 and CoL_2) being rather low, precipitation occurred above $\bar{n} = 0.8$ and 0.85 respectively, when initial metal concentrations of 25.2 m*M* for zinc and 23.45 m*M* for cobalt were used. In titration series with these metal concentrations reduced by

TABLE II

STABILITY CONSTANTS OF METAL(II)–α-HYDROXYISOBUTYRATE COMPLEXES (25.0° AND $i=1$)

Metal ion	*Bjerrum's method*			*Computer*			
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_2$
UO_2^{2+} [a]	3.07	2.01	1.33	3.01	1.82	1.55	4.83
[b]	3.09	2.02	1.31	3.03	1.83	1.53	4.86
Cu	2.80	1.54	—	2.74	1.60	~0.4	4.34
Pb	2.08	1.15	—	2.03	1.17	~0.2	3.20
Zn [c]	1.90	—	—	1.71	1.30	—	3.01
[d]	1.89	1.11	—	1.70	1.29	~0.4	2.99
Ni	1.84	1.07	—	1.67	1.13	~0.4	2.80
Co [c]	1.65	—	—	1.46	0.97	—	2.43
[d]	1.65	0.86	—	1.45	0.98	~0.3	2.43
Cd	1.46	0.79	—	1.24	0.92	~0.3	2.16
Mn	1.12	0.45	—	0.96	0.58	~0.2	1.54

[a] $\delta=5.5$.
[b] $\delta=2.7$.
[c] $C_{\mathrm{M}} \cong 25$ m*M*.
[d] $C_{\mathrm{M}} \cong 12.5$ m*M*.

half, precipitation began above $\bar{n} = 1.2$ and 1.35 respectively. For computer calculation only the $\bar{n}$ values obtained before precipitation occurred, were used.

The formation curves, being the same for $\bar{n} \leqslant 0.8$ at both metal concentrations for both zinc and cobalt, indicated that no polynuclear complexes were formed in solution. Furthermore, the agreement between the stability constants of the uranyl ion at the different δ values indicated that the degree of hydrolysis was negligible in the pH range investigated. When buffer solutions with $\delta \simeq 2.5$ were used the pH in half cell B was always between 2 and 3, except for a few points at the end of titration ($\bar{n} > 2.5$, pH $\geqslant 3$). In this pH range UO_2^{2+} is the species of uranium(VI) existing in solution[18].

(b) *Electrophoretic experiments*

The results of the migrations are summarized in Table III. From these results it follows that ML_3^- complexes are formed at a ligand concentration of 0.5 *M*, which corresponds to a pL value of 0.3 ($\bar{n} > 2$). This is in agreement with the formation curves of the Zn–α-hydroxyisobutyrate system.

No precipitation took place, as the ^{65}Zn was used in tracer concentrations.

TABLE III

ELECTROPHORETIC RESULTS FOR THE ^{65}Zn–α-HYDROXYISOBUTYRATE COMPLEX SYSTEM

Concentration (M)	*Voltage (V)*	*Current (μA)*	*Time (h)*	*Migration*	*Distance (cm)*
0.01 ($\bar{n} \cong 0.4$)	120	50	21	Cathode	3.5
0.05 ($\bar{n} \cong 1.3$)	120	300	29	Cathode	2.0
0.1 ($\bar{n} \cong 1.8$)	120	1300	24	Cathode	1.25
0.5 ($\bar{n} > 2$)	120	2000	71	Anode	7.25
1.0 ($\bar{n} > 2$)	120	3000–1200	25	Anode	1.80

DISCUSSION

From the formation curves it can be seen that the metal ions investigated form ML^+, ML_2 and ML_3^- complexes with lactate and α-hydroxyisobutyrate. However, additional evidence for the existence of ML_3^- complexes was found in electrophoretic experiments with Zn^{2+} and α-hydroxyisobutyrate.

The stabilities of the α-hydroxyisobutyrate complexes are higher than for the corresponding lactate complexes; this can be attributed to the increased inductive effect of the 2 methyl groups in α-hydroxyisobutyrate (this effect becomes also prominent in the acid dissociation constants: $K_A = 2.30 \cdot 10^{-4}$ for lactic acid, $K_A = 1.73 \cdot 10^{-4}$ for α-hydroxyisobutyric acid[3]).

For both ligands the observed sequence of increasing stability is the same: $Mg^{2+} < Mn^{2+} < Cd^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Pb^{2+} < Cu^{2+} < UO_2^{2+}$, lanthanide ions[1-3].

As in the case of alkaline earth and lanthanide metal ions, here too the $\Delta \log \beta$ for 2 adjacent metal ions was greater for α-hydroxyisobutyrate complexes than for lactate complexes.

In this sequence the position of magnesium and the lanthanide ions is rather obvious. Among the other metal ions, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} belong to the same series of transition metal ions for which the 3d shell is filled from Mn^{2+} ($3d^5$) to Zn^{2+} ($3d^{10}$). Cadmium ($4d^{10}$), because of its complete d-shell, and lead ($5d^{10}6s^2$) with its inert 6s electrons, can be compared to the transition metal ions. The uranyl ion cannot really be classified in this series, and thus it will not be considered in this discussion.

Differences in stabilities for complexes of several metal ions with the same ligand can be explained by 3 factors: ligand field stabilisation energy, electronegativity measured by the ionisation potentials, and the ionic radii. When only the transition metal ions, their second ionisation potentials and their ionic radii (see, *e.g.* PERRIN[19]) are considered, the normal sequence of stability should be

$$Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}, Zn^{2+}$$

Under the influence of the ligand field cobalt(II) ($3d^7$), copper(II) ($3d^9$) and especially nickel(II) ($3d^8$) will receive some extra stabilisation[20] in their complexes. Subject to the Jahn–Teller effect, the copper(II) complexes will be further stabilised; this also explains why the formation curves for this ion do not reveal ML_3^- complexes, as this effect encourages the binding of the first two ligand ions and opposes the binding of a third ion[20].

The stability of the zinc(II) complexes may also be a little higher than expected from the tendency for this ion to form planar complexes. This is not in contradiction with the existence of ML_3^- complexes provided that a large excess of ligand is present. From the second ionisation potentials it also follows that cadmium(II) complexes should be more stable than manganese(II) complexes.

The lead(II) complexes, not being influenced by ligand field or electronegativity effects, have a rather high stability. The radius of lead(II) indicates that it is the most readily polarised cation in this series, which might explain the greater stability of its complexes.

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SUMMARY

The stability constants of the lactate and α-hydroxyisobutyrate complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and UO_2^{2+} were determined by potentiometric titration. The average ligand number exceeds 2, indicating the formation of ML^+, ML_2 and ML_3^- complexes. The existence of ML_3^- complexes was confirmed by electrophoretic experiments; no polynuclear complexes were formed. α-Hydroxyisobutyrate forms stronger complexes than lactate.

RÉSUMÉ

Les auteurs ont déterminé les constantes de stabilité des lactate et α-hydroxyisobutyrate complexes de Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} et UO_2^{2+} par titrage potentiométrique. On a pu observer ainsi les formes suivantes ML^+, ML_2 et ML_3^-. Il ne se forme pas de complexes polynucléaires. Les complexes des α-hydroxyisobutyrates sont plus forts que ceux des lactates.

ZUSAMMENFASSUNG

Die Stabilitätskonstanten der Lactat- und α-Hydroxiisobutyrat-Komplexe mit folgenden Kationen wurden durch potentiometrische Titrationen bestimmt: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} und UO_2^{2+}. Die durchschnittliche Ligandenzahl überschritt 2, was auf die Bildung von ML^+-, ML_2- und ML_3^--Komplexen hinweist. Die Existenz des ML_3^--Komplexes wurde durch elektrophoretische Versuche bestätigt. Polynukleare Komplexe wurden nicht gebildet. α-Hydroxiisobutyrat bildet stärkere Komplexe als Lactat.

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ACTIVATION D'ISOTOPES A COURTE PERIODE. SEPARATION TRES RAPIDE PAR ECHANGE SUR LE MERCURE

ECHANGE MERCURE–IONS MERCURE

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Lors de l'activation aux neutrons d'un échantillon, il se forme à côté de l'isotope radioactif utilisé pour le dosage, des particules radioactives gênant la détermination. Dans certains cas on peut éviter leur formation par un choix judicieux du temps d'irradiation (t) et de décroissance (t'). Si l'analyse est basée sur l'activité γ de l'isotope à doser, l'établissement du spectre de cette radiation augmente la sélectivité de la mesure. Pourtant le plus souvent, ces divers moyens ne suffisent pas à éliminer tous les isotopes gênants. Il faut donc avoir recours à des séparations qui, si l'analyse est basée sur la formation d'isotopes à courte période, doivent être très rapides ce qui exclut la plupart des techniques utilisées en chimie analytique classique (échangeurs d'ions, distillation, précipitation, etc.). L'objet de ce travail est d'étudier de façon approfondie les échanges isotopiques et redox sur le mercure et sur les amalgames, des essais empiriques[1-6] ayant montré que les équilibres s'établissent très rapidement, en quelques minutes et certains même en moins d'une minute, et que les échanges peuvent être quantitatifs.

PRINCIPE DE L'ÉCHANGE

Symboles utilisés

$M_1, M_2, \ldots, M_1^{n+}, M_2^{m+}$	métaux et ions correspondants
$(Hg)M_1, (Hg)M_2 \ldots$	leurs amalgames
E_0^1, E_0^2	les potentiels redox des couples M_1^{n+}/M_1, M_2^{m+}/M_2
M_1^*, M_2^*	les isotopes radioactifs des métaux M_1, M_2

Dans un article[7] nous avons exposé les bases théoriques qui conditionnent ces échanges. En résumé, on a:

$$\text{échange isotopique}\begin{cases}(Hg)M_1 + M_1^{n+*} \rightarrow (Hg)M_1^* + M_1^{n+} & (1)\\ Hg + \tfrac{1}{2}\,Hg_2^{2+*} \rightarrow HgHg^* + \tfrac{1}{2}\,Hg_2^{2+} & (2)\end{cases}$$

$$\text{échange redox}\begin{cases}(Hg)M_1 + M_2^{m+*} \rightarrow (Hg)M_2^* + \dfrac{m}{n}\,M_1^{n+} & (3)\\ Hg + M_3^{n+*} \rightarrow (Hg)M_3^* + n/2\;Hg_2^{2+} & (4)\end{cases}$$

Ces équilibres sont fortement déplacés vers la droite, si, à volumes égaux:

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$$\left.\begin{array}{l}(M_1^{n+}) \ll (M_1)_{\mathrm{amalg}} \\ (Hg^{2+}) \ll (Hg)_{\mathrm{mét}}\end{array}\right\} \text{ pour les échanges isotopiques}$$

$$\left.\begin{array}{l}E_0^1 \; < E_0^2 \\ E_0^{\mathrm{Hg}} < E_0^3\end{array}\right\} \text{ pour les échanges redox}$$

Il est ainsi possible de faire passer, de la solution à l'amalgame, l'isotope à doser et de mesurer l'activité du mercure après séparation des phases.

La sélectivité de la méthode est encore augmentée si on effectue une *réextraction.*

(*a*) soit au moyen d'une solution renfermant une quantité d'ions inactifs de même nature que celui de l'amalgame mais en concentration suffisante pour déplacer quantitativement l'équilibre de droite à gauche (équilibre 1).

(*b*) soit au moyen d'une solution renfermant des ions M_2^{m+} dont $E_0^2 > E_0^1$

$$HgM_1^* + M_2^{m+} \rightarrow HgM_2 + \frac{m}{n} M_1^{n+*}$$

Il faut pour que la réaction soit quantitative que $E_0^2 - E_0^1 > 0.1$. D'autre part pour une bonne sélectivité il est nécessaire que la valeur de E_0^2 soit aussi proche que possible de celle de E_0^1. Dans ces conditions ne repasse en solution que l'élément M_1 à séparer (Tableau I).

TABLEAU I

EXTRACTION ET RÉEXTRACTION

E_0 *ordre croissant*	*extraction: solution → amalgame (Hg)*	*réextraction selon (a): amalgame → solution*
Li^+ − 3.0 V K^+ − 2.9 V	Pas extraction dans amalgame	Pas extraction puisqu'ils n'ont pas passé dans le mercure
Ion devant être extrait M_1^{n+} x V	Passe dans l'amalgame	Passe en solution aqueuse
Pt^{2+} + 1.2 V Au^{2+} + 1.5 V	Passent dans l'amalgame	Restent dans l'amalgame

Ont été examinés systématiquement: Cd[6], Zn[8], In[4], Tl[1], Bi[2] et Pb[4].

Bien que les auteurs cités aient constaté, lors de leurs essais de sélectivité, l'échange rapide et quantitatif entre les ions Hg_2^{2+} et Hg^{2+} et le mercure métallique, ils n'ont pas relevé la valeur analytique de ce phénomène.

L'étude systématique de l'échange isotopique mercure/ion mercure fera donc l'objet principal de ce travail.

APPAREILLAGE ET MODE OPÉRATOIRE

Dispositif d'échange

Il est utilisé pour tous les essais systématiques d'échange effectués dans ce travail.

Alors que les divers auteurs cités[1-6] ont toujours effectué l'échange au moyen d'agitateurs mécaniques ou d'agitateurs-vibreurs, nous avons développé une nouvelle technique de vibration qui parvient à réduire le temps de l'échange d'un facteur 2 à 3. L'appareillage (Fig. 1) est simple, il consiste en un vibreur Chemap du type E 1 (4) muni d'une pièce spéciale F 1/50 (5). L'échange se fait dans une ampoule de 2 à 10 ml au col élargi (1 A), permettant l'introduction rapide des réactifs. L'ampoule est fermée par soudure du col (2) et placée dans une manchette en caoutchouc de 3 cm de long (6). La partie inférieure de l'ampoule repose légèrement sur l'aile métallique du bras du vibreur (7), de sorte que les 2 liquides, étalés et de faible hauteur, se prêtent particulièrement bien aux mouvements verticaux du vibreur. Grâce à la fixation élastique de l'ampoule, le mercure se disperse en un grand nombre de fines gouttelettes et les deux phases sont rapidement et intimement mélangées. Une vis (8) permet de régler facilement l'intensité de la vibration.

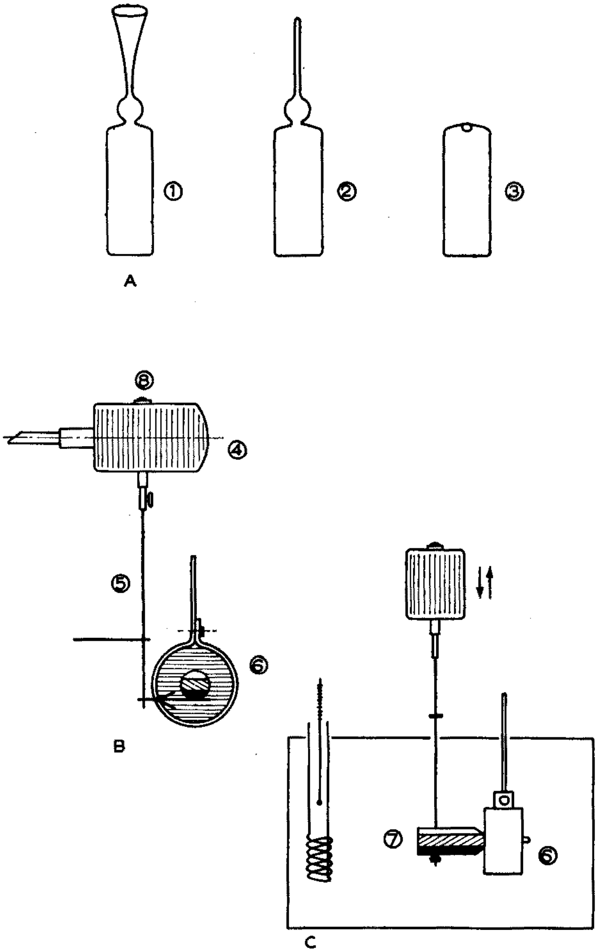

Fig. 1. (A) Ampoules d'échange de 5 ml. (B) Vue de côté de l'échangeur. (C) Vue de face de l'échangeur plongé dans un ultra-thermostat.

Outre la diminution du temps d'agitation, cette technique présente d'autres avantages:

(*1*) Pas de pertes dans les rodages ou les bouchons.

(*2*) Une séparation facile des 2 phases après l'échange: l'ampoule est ouverte au point le plus étroit (3) et renversée. La phase métallique sort par son propre poids, tandis que la quasi-totalité de la phase aqueuse reste dans l'ampoule.

(*3*) Une grande facilité de travailler en l'absence d'oxygène, si cela est nécessaire.

(*4*) La possibilité d'étudier l'influence de la variation de température en immergeant le système dans un bain-marie thermostatisé (Fig. 1C).

Réactifs

Tous les réactifs sont de qualité "puriss. p.a."; l'eau est en général bidistillée. Pour une bonne sélectivité de la méthode, le mercure doit être très pur, particulièrement en ce qui concerne les métaux susceptibles de subir des échanges isotopiques (Cu, Zn, Cd, In, Tl, Sn, Pb, Bi). Nous avons purifié, le mercure "pur" du commerce par l'acide nitrique dilué, puis effectué une bidistillation.

Mode opératoire

Dans des ampoules de 5 ml on introduit 100 à 500 μl de mercure et 2 ml d'une solution aqueuse de nitrate mercurique inactif $2 \cdot 10^{-5}$ *M*, accompagné d'un électrolyte approprié. (D'après HAISSINSKY ET COLLIN[9] la composition chimique de la phase aqueuse influence peu la vitesse de l'échange mercure/ion mercurique. Il est aussi satisfaisant en milieu acide minéral (0.1 à 2 *M*) qu'en milieu ammoniacal tamponné.) Finalement on ajoute 2 ml de la solution aqueuse d'ions mercuriques marqués (pour les essais de rendement de l'échange isotopique) *ou* d'un cation étranger marqué (pour les essais de sélectivité) dont la concentration dans le volume final est donnée dans le Tableau II. On rince avec très peu d'eau, puis on scelle l'ampoule. Pour une bonne homogénéisation, les ampoules ne sont remplies qu'à 80% de leur volume. La tige de l'ampoule est enfoncée dans la manchette de caoutchouc et l'ensemble placé de telle sorte que l'ampoule s'incline légèrement du côté de l'aile du vibreur, afin d'éviter que la goutte mercurique ne pénètre dans la tige.

TABLEAU II

ÉTUDE DE LA SÉLECTIVITÉ DE L'ÉCHANGE

(Toutes les activités sont calculées au temps $t'=0$)

Sel de M^{n+} mis en solution	*Nombre de masse de M^{n+}*	*Conc. init. (mM)*	*Q (%)*	*Sel de M^{n+} mis en solution*	*Nombre de masse de M^{n+}*	*Conc. init. (mM)*	*Q (%)*
Na_2SO_4	24	2 (−3)[a]	BF[b]	$Ga(NO_3)_3$	70	7 (−3)	<0.05
$SrCl_2$	89	5 (−4)	<0.1	$SnCl_2$	117	1 (−5)	<0.05
$MnSO_4$	56	1 (−4)	<0.2	Sb_2O_3/HCl	122	1 (−3)	BF
$FeCl_2$	59	1 (−5)	BF	$Pb(NO_3)_2$	210	5 (−4)	0.5
$Co(NO_3)_2$	60	2 (−5)	<0.1	$RuCl_3$	105	4 (−3)	BF
$Ni(NO_3)_2$	65	1 (−3)	<0.05	$Rh(NO_3)_2$	100m	8 (−3)	1.4
$CuSO_4$	64	1 (−3)	BF	$Pd(NO_3)_2$	109m	5 (−4)	0.2
$AgNO_3$	110m	1 (−5)	99.2	H_2IrCl_6	194	5 (−3)	BF
$CdSO_4$	115	1 (−3)	<0.1	H_2PtCl_6	199	4 (−5)	98.5
$In(NO_3)_3$	116	1 (−4)	1.2	$HAuCl_4$	198	5 (−3)	97.5
$ZnSO_4$	69m	1 (−4)	<0.05	$HgCl_2$	203	1 (−5)	99.9

[a] $2(-3) = 2 \cdot 10^{-3}$.

[b] BF = bruit de fond du spectromètre.

La vibration terminée, l'ampoule est ouverte à l'aide d'une lime, puis renversée. On reçoit le mercure dans un petit godet, la quasi-totalité de la phase aqueuse restant à l'intérieur de l'ampoule. Le mercure est alors lavé successivement avec les solutions suivantes: deux fois avec 5 ml d'acide nitrique 0.2 *M*, et deux fois à l'eau.

La goutte de mercure est placée dans une cupule standardisée de 8 mm de diamètre et recouverte d'une couche d'eau bidistillée de 1 cm de hauteur. Ces cupules sont facilement centrées dans le puits de la sonde d'un scintillateur.

Analyse spectrométrique

Les mesures quantitatives d'activité pour l'ensemble des essais d'échange amalgamique ont été effectuées à l'aide de l'équipement électronique suivant:

(a) Déterminations de rendement sur des solutions pures (comptage global). Une échelle décadique 1000 Scaler, Tracerlab, munie d'une sonde P-20C surmontée d'un cristal à puits NaI (Tl) 5 × 5 cm.

Une échelle décadique Single channel wellcounter, Philips avec cristal à puits NaI (Tl) 5 × 5 cm et discriminateur d'énergie à bande.

(b) Etude de sélectivité. Un spectromètre multicanaux SAM 60 (à 60 canaux) de SAIP muni d'un cristal plat NaI (Tl) 7.5 × 7.5 cm, d'une machine imprimante Burroughs et d'un enregistreur potentiométrique "MECI".

Un spectromètre multicanaux TMC 256 muni d'un cristal plat NaI (Tl) 7.5 × 7.5 cm, d'un imprimeur digital Hewlett Packard, d'un enregistreur potentiométrique 2D2-XY-Recorder, SL-Moseley Co. et d'un imprimeur à bande perforée Tally Printer, Register Corp.

Un sélecteur multicanaux SA 40 (à 400 canaux) Intertechnique muni d'un cristal plat NaI (Tl) 5 × 5 cm, d'une alimentation THT VH 20, d'un chassis de commande BK 21, d'un calculateur intermédiaire RG 23 et d'une machine imprimant ADDO-X.

(c) Intégration des pics photoélectriques. Le programme GAUCO du calculateur digital ZUSE de l'Institut fédéral de recherches nucléaires à Wurenlingen (occasionnellement).

Sélectivité de l'échange

D'après le mode opératoire décrit, nous avons étudié la sélectivité de l'échange mercure/ion mercurique en présence d'une vingtaine d'éléments (Tableau II).

Conditions d'échange. Composition de la phase aqueuse: (*1*) 10^{-5} *M* en nitrate mercurique inactif. (*2*) 1 *M* en ammoniaque et 0.2 *M* en chlorure d'ammonium (tampon pH = 10), ou 0.2 *M* en acide nitrique pour les ions insolubles dans ce premier milieu. (*3*) Concentration connue de l'ion étudié, activé dans notre réacteur "AGN" ou marqué par un isotope radioactif acheté dans le commerce. (*4*) Volume de la phase mercurique: 300 μl. (*5*) Volume de la phase aqueuse: 4 ml dans une ampoule de 5 ml. (*6*) Temps d'agitation: 3 min.

La méthode est rapide, sélective et quantitative pour la séparation radiochimique des ions Hg^{2+}, Hg_2^{2+}, Ag^+, Au^3 et Pt^{4+}. Certains ions, tels que le Pd^{2+} et l'Ir^{4+}, quoique réduits par le mercure, ne s'y amalgament pas. Ils restent dans la phase aqueuse sous forme de suspensions noirâtres. Lors de chaque extraction, les activités γ de l'amalgame et de la solution ont été déterminées par intégration du pic photoélectrique principal du radioisotope considéré, développé sur un des 3 spectromètres disponibles. On a notamment mesuré: A_0, l'activité initiale de la solution et A_s, l'activité restant dans la solution après un temps d'extraction t_a.

Le % d'extraction $Q(\%) = \frac{(A_0 - A_s)}{A_s} . 100$ pour $t_a = 3$ min est donné pour 22 métaux dans le Tableau II.

CINÉTIQUE DE L'ÉCHANGE ISOTOPIQUE MERCURE/ION MERCURE

Les bases électrochimiques

L'échange se fait aussi bien avec Hg^{2+} qu'avec Hg_2^{2+}. Les réactions suivantes sont possibles:

(1) phase aqueuse: ions mercureux

$$Hg_2^{2+(*)} + (Hg) \rightarrow Hg_2^{2+} + Hg^{(*)}(Hg) \tag{5}$$

(2) phase aqueuse: ions mercuriques

$$Hg^{2+(*)} + (Hg) \rightarrow Hg_2^{2+} + Hg^{(*)}(Hg) \tag{6a}$$

ou

$$Hg^{2+(*)} + (Hg) \rightarrow Hg^{2+} + Hg^{(*)}(Hg) \tag{6b}$$

(Hg) désigne l'ensemble de la phase mercurique.

A ces réactions d'échange se superpose une réaction secondaire sans effet direct sur l'échange isotopique et qui dépend du pH:

$$Hg^{2+(*)} + (Hg) \underset{pH > 1.7}{\overset{pH < 1.7}{\rightleftharpoons}} Hg_2^{2+(*)} \tag{7}$$

En milieu acide (pH = 1), l'équilibre, très rapidement atteint, tend vers une valeur constante. En milieu nitrique 0.1 *M*, les valeurs données pour $K' = (Hg_2^{2+})/(Hg^{2+})$ varient entre 88 et 130.

Les mesures cinétiques faites par HAISSINSKY ET COLLIN[10] montrent que la réaction (7) est plus rapide que les échanges isotopiques (5) et (6), ces derniers n'étant pourtant pas négligeables dans l'établissement de l'équation cinétique globale. On peut même admettre qu'en milieu acide, l'ion mercureux contrôle l'échange quel que soit l'état d'oxydation initiale du mercure en phase aqueuse. En milieu alcalin, où l'ion mercure doit être complexé par l'ammoniaque pour rester en solution, c'est toujours l'ion mercurique qui passe directement en phase métallique, l'ion mercureux n'étant pas stable. Par contre ce dernier est, à l'origine de la réaction anodique (mise en solution d'un ion mercure), quel que soit le pH de la solution. L'explication électrocinétique a été donnée par GERISCHER ET KRAUSE[11] qui, en déterminant l'ordre cinétique de la réaction électrochimique cathodique, démontrent que le mercure par oxydation donne toujours l'ion Hg_2^{2+}, ion qui, en milieu alcalin, se dismute instantanément, et on observe un dépôt noir, poudreux, de mercure amorphe ne s'incorporant plus à la goutte métallique. Les réactions électrochimiques (5) et (6a) prédominent dans l'échange isotopique mercure/ion mercure.

Essais pratiques

Volume de mercure: 300 μl. Volume de la solution: 4 ml.

Composition de la phase aqueuse: $Hg(NO_3)_2$ 10^{-5} M renfermant le traceur Hg-203, et HNO_3 0.2 M.

Température: ordinaire.

Mesures spectrométriques: Tracerlab "1000 Scaler", comptage de l'émission globale de l'énergie-γ.

Nous avons effectué une triple série d'échanges en faisant varier le temps de vibration t_a de 10 sec à 3 min. Les résultats obtenus sont représentés dans la Fig. 2.

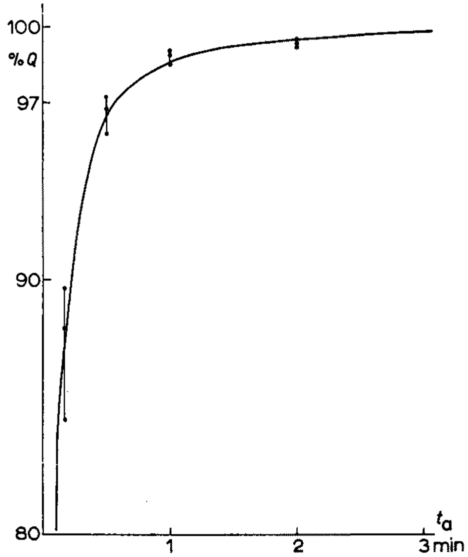

Fig. 2. Echanges isotopiques de système $Hg_{mét}/Hg^{2+}$. Vitesse d'échange en milieu HNO_3 0.2 M.

L'équation (6) montre que la cinétique de l'échange isotopique, contrôlé par le transfert de charge est en général du premier ordre. Si l'on trace les ln des valeurs moyennes $Q-Q_t$* des 3 séries effectuées sur l'ion Hg^{2+} par rapport au temps d'agitation t_a on obtient une courbe qui montre que la cinétique plus compliquée vient du fait que plusieurs réactions simultanées se produisent (voir équations (5), (6) et (7)).

Notre travail ayant avant tout un but analytique, nous n'avons pas étudié l'ordre cinétique exact de cet échange. Dans le système mercure/ion mercurique, t_a pour $Q = 97\%$, suffisant dans le cas du dosage de traces, est voisin de 45 sec.

Influence du milieu

Milieu acide. La variation de la concentration d'acide nitrique de la phase aqueuse de 0 à 2 M, pour un t_a constant de 3 min est sans influence sur le % extrait (qui est compris entre 99.4 et 99.9). Pour l'acide nitrique 3 M il diminue (98%). En remplaçant l'acide nitrique par l'acide sulfurique 1 M, puis par l'acide chlorhydrique 1 M, nous avons obtenu, pour un t_a =3 min, 99.9 resp. 99.5% d'échange. Il

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* $Q = \%$ échange pour un temps t très grand, $Q_t = \%$ échange au temps t_a.

est donc aussi quantitatif qu'en milieu nitrique. Néanmoins les précipités blancs de sulfate ou de chlorure mercureux formés lors de l'échange, s'adsorbant en partie sur la surface de la goutte mercurique, provoquent des interférences lorsque les mélanges irradiés renferment du chlore (^{38}Cl, $t_{\frac{1}{2}} = 37$ min).

Milieu alcalin. Nous avons examiné les systèmes suivants: (a) NH_3 1 *M*, NH_4NO_3 0.2 *M* (tampon standard pH = 10.15); (b) EDTA 0.01 *M* à pH 10.15; (c) KCN 0.25 *M*.

Les conditions d'échange sont les mêmes, le temps d'agitation variant de 10 sec à 3 min. Les valeurs de Q_t sont données dans le Tableau III. Chacune d'elles représente la moyenne de 2 essais identiques. La vitesse d'échange est donc très semblable à celle qui est observée en milieu non-complexé. Ce fait s'explique par la labilité des complexes mercuriques.

TABLEAU III

LES VALEURS DE Q_t (%) EN MILIEU ALCALIN

Temps d'agitation	*NH_3–NH_4NO_3 (pH 10.15)*	*EDTA à pH 10.15*	*KCN*
10 sec	93.2	84.6	77.0
0.5 min	96.1	93.7	92.5
1 min	97.7	97.4	96.9
2 min	99.2	99.2	99.0
3 min	99.95	99.95	99.9

Effet des solvants non aqueux et des complexants sur l'échange entre le mercure à l'état de métal et le mercure combiné

Les observations précédentes nous ont amené à remplacer la phase aqueuse par un solvant non aqueux, les ions mercure s'y trouvant sous forme de dithizonate $Hg(DHz)_2$ (obtenu par extraction du $Hg(NO_3)_2$, en solution aqueuse tamponnée pH 4.5 au moyen d'une solution de dithizone dans du CCl_4, l'excès de dithizone étant réextrait par une solution aqueuse alcaline).

L'extraction avec une goutte de mercure en fonction du temps de vibration est:

temps	10 sec	30 sec	1 min	2 min	3 min
% Q	80.0	91.4	95.5	92.4	99.5

Ainsi ni la phase organique ni le fait que le mercure est très fortement complexé ($K_c = 10$) ne diminue sensiblement la vitesse d'extraction (v.p. 345). Ce fait permet de douter des assertions de certains auteurs qui attribuent un caractère covalent aux liaisons mercure–azote des complexes. Dans ces essais nous avons éliminé l'oxygène des solutions aqueuses par N_2 afin d'éviter l'oxydation du dithizonate lors de l'agitation et la formation d'un oxyde de mercure qui gêne l'échange.

Il est évident que dans ces échanges, la labilité des complexes joue un rôle plus important que la stabilité.

Etude analytique de la séparation et du dosage du mercure organique

Les derniers résultats ci-dessus nous ont incités à étudier le comportement de certains dérivés organiques du mercure, lors de l'extraction au moyen d'une goutte de mercure.

Pour les premiers essais nous avons choisi le sel disodique, trihydraté, du dibromohydroxymercurifluoresceine cristallisé (Na_2DHMF), soluble dans l'eau et dans l'éthanol, dont 6.68 mg ont été irradiés pendant 15 min par un flux de $2.7 \cdot 10^{12}$ n/cm/sec. Les principaux isotopes formés lors de cette activation sont: ^{24}Na $t_{\frac{1}{2}} = 15$ h; ^{80}Br $t_{\frac{1}{2}} = 18.5$ min; ^{80m}Br $t_{\frac{1}{2}} = 4.5$ h; ^{82}Br $t_{\frac{1}{2}} = 35.9$ h; ^{197}Hg $t_{\frac{1}{2}} = 65$ h.

Les essais préliminaires de sélectivité ont montré que le sodium et le brome restent quantitativement dans la solution lors de l'échange. Mais ils gênent la mesure des activités A_0 et A_s du mercure-197 dans la solution. Pour palier cet inconvénient nous avons, dans une même opération, irradié un échantillon de Na_2DHMF et une solution de nitrate de mercure renfermant une même quantité de mercure (étalon externe).

Solution de base: 6.68 mg de Na_2DHMF ont été dissous dans 100 ml d'eau (solution A), 2.84 mg de $Hg(NO_3)_2 \cdot H_2O$ ont été dissous dans 100 ml d'acide nitrique 0.1 M (solution B). Les 2 solutions de base contiennent donc 50 μg de mercure par 3 ml de solution.

Conditions d'échange: ampoule de 5 ml; phase mercurique: 100 μl; phase aqueuse: 3 ml de solution A resp. B; température ordinaire; temps d'agitation: variable pour la solution A, 3 min pour la solution B.

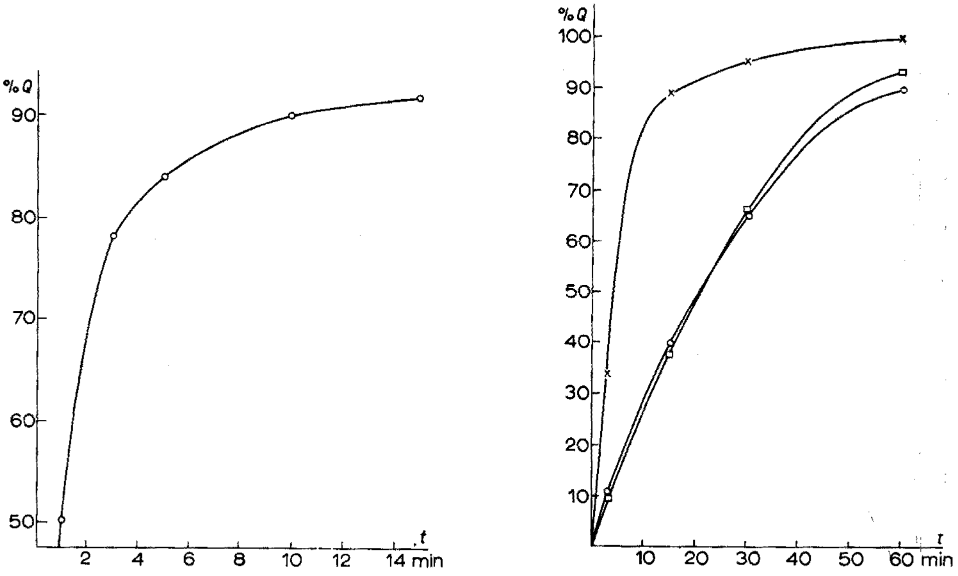

Fig. 3–4. Echanges isotopiques entre $Hg_{mét}$ et Hg_{org}: Fig. 3, du Na_2DHMF; Fig. 4, du *p*-chloromercuribenzoate de sodium. (○), produit IIa à 20°; (□), produit IIb à 20°; (×), produit IIa à 70°.

L'examen de la courbe d'extraction, dont chaque point représente la moyenne de 3 essais identiques, donnée dans la Fig. 3, montre qu'il y a échange, mais celui-ci est beaucoup plus lent que dans les cas étudiés jusqu'ici. La courbe présente un palier pour un rendement qui ne dépasse pas 92%, même après 2 h d'extraction. Il y a 2 interprétations possibles de ce phénomène:

(I) La liaison R–Hg (R = partie organique de la molécule) est détruite lors de l'irradiation, ce qui reviendrait à une ionisation du mercure. Cette hypothèse n'explique pas le ralentissement de l'échange.

(II) Sous l'influence de l'oxygène renfermé dans l'ampoule, de faibles quantités de mercure métallique s'ionisent. Le mercure organique subirait avant de passer dans la goutte de Hg un échange intermoléculaire avec des ions mercuriques.

Etude du comportement du mercure dans l'acide p-*chloromercuribenzoique*

Les essais ont été faits sur les solutions des 2 échantillons de ce composé, l'un synthétisé au centre d'Amersham (GB) avec du mercure marqué préalablement (produit IIa), l'autre provenant de la maison Aldrich Chemical Co. (produit IIb) ayant été activé 30 min dans le réacteur Saphir (flux $2.7 \cdot 10^{12}$ n/cm²/sec avec formation de mercure-197).

Conditions d'échange. Ampoule 5 ml; Hg 100 μl; phase aqueuse: 3 ml d'une solution renfermant soit 0.1137 mg de IIa, soit 0.107 mg de IIb, plus 1 ml d'un tampon ammoniacal pH 10; température ordinaire (et 70° pour IIa).

Les résultats sont portés dans la Fig. 4.

On constate: (1) que les produits IIa et IIb se comportent de façon identique ce qui montre que IIa n'a pas subi d'altération (pas de rupture R–Hg) dans le réacteur; (2) que la température a un effet important sur la vitesse d'échange qui est de toute façon beaucoup plus faible qu'avec les ions mercure; (3) que ce dernier n'est quantitatif qu'à 70°.

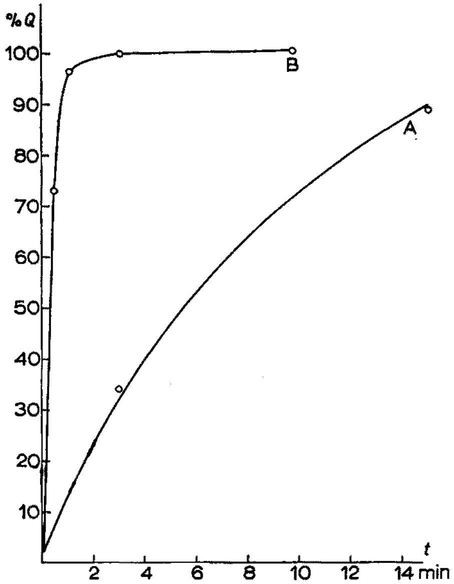

Fig. 5. Influence du mercure ionisé sur la vitesse de l'échange isotopique entre $Hg_{mét}$ et Hg_{org} du *p*-chloromercuribenzoate de sodium à 70°. (A), sans entraineur; (B), 10^{-2} *M* en $Hg(NO_3)_2$.

Une série de travaux sur les substitutions organiques de INGOLD[12] et LOCKART[13] ont permis d'expliquer ce phénomène d'échange entre ions mercure et mercure organique. Il en découle que l'addition en grand excès d'ions mercure inactifs à la solution doit d'abord permettre l'échange rapide ions mercure–mercure organique radioactif en phase aqueuse, l'ion radioactif libéré passant ensuite dans le mercure dont on mesure l'activité. Les résultats de tels essais sont donnés dans la Fig. 5.

Ainsi la présence d'un ion entraineur rend l'extraction quantitative et rend possible un dosage très sélectif, très rapide et non destructif du mercure de certains composés organiques du mercure par activation aux neutrons.

Nous remercions le Fonds National Suisse, grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

Une étude systématique de l'échange des ions mercure, et du mercure de certains composés organiques, avec goutte de mercure a été effectuée au moyen d'isotopes radioactifs de cet élément. Dans certaines conditions (concentrations, température, électrolyte de base, etc.) cet échange est quantitatif, très rapide et sélectif. La plupart des autres ions métalliques restant en solution, ceci permet un dosage de traces de mercure par activation aux neutrons. Les divers facteurs intervenant dans la vitesse de l'échange ont été examinés. Seuls les ions ayant un potentiel ox–red supérieur à celui du mercure passent dans le mercure.

SUMMARY

The exchange of mercury ions and of certain organic mercury complexes with a drop of mercury was studied systematically by means of radioactive isotopes. Under defined conditions, the exchange is quantitative, very rapid and selective; most other ions remain in solution so that traces of mercury can be determined by neutron activation. Only ions with higher oxidation potentials than mercury interfere.

ZUSAMMENFASSUNG

Der Austausch von Quecksilberionen und bestimmten organischen Quecksilberkomplexen mit einem Quecksilbertropfen wurde mit Hilfe von radioaktiven Isotopen systematisch untersucht. Unter definierten Bedingungen ist der Austausch qualitativ, sehr schnell und selektiv. Die meisten anderen Ionen bleiben in der Lösung zurück, so dass Spuren von Quecksilber mit der Neutronenaktivierungsanalyse bestimmt werden können. Es stören nur Ionen mit höherem Oxydationspotential als das Quecksilber.

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DIFFUSION COEFFICIENTS OF TUNGSTEN HETEROPOLYACIDS

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In a previous publication[1] it was shown that tungstate ions in excess phosphoric acid, forming phosphotungstic acids, may be reversibly reduced at mercury, platinum and rhodium electrodes according to the equation:

$$WO_4^{2-} + e^- \rightleftarrows WO_4^{3-} \qquad E_0 = +0.216 \pm 0.002 \tag{1}$$

On rhodium and platinum, the interfering reversible hydrogen reaction may be suppressed by saturating the electrolyte with carbon monoxide. Owing to the various structures of the heteropolyacids formed, both the diffusion characteristics and electrode reaction kinetics are modified. In particular, KENNEDY[2] suggested that for the 12-phosphotungstic acid (12 atoms of tungsten to 1 atom of phosphorus), only between 1 and 2 tungsten atoms on the complex was reduced. Two other prominent phosphotungstic acids exist in solution with W:P ratios of 9:1 and 3:1. For the 9-phosphotungstic acid (9-PTA), KENNEDY indicates reduction of 5 of the tungsten atoms in the complex, while no data are reported for the 3-phosphotungstic acid. The chloro complex was investigated by LINGANE AND SMALL[3] and a diffusion coefficient has been reported by REZNIK AND KOVALENKO[4]. Additional data have been reported for the reduction of tungstate complexed with tartrate[5] and oxalate[6,7] using dropping mercury electrodes.

In order to evaluate the reduction mechanisms of complexed tungstates and their ionic structures, more precise diffusion data were needed than had previously been reported in the literature. To this end, diffusion limited reduction currents were measured for phosphotungstic heteropolyacids in phosphoric acid using a rotating disc apparatus as well as computing diffusivities with dropping mercury electrodes. An examination of the reactions of the chloro complex was also carried out at mercury electrodes to examine the differing diffusivities reported.

EXPERIMENTAL

Rotating disc apparatus

The rotating disc apparatus is shown in Fig. 1. The shaft for the disc was machined from a stainless steel tube to 1/2″ outside diameter with 3/16″ inside diameter. It was found that the heavy wall tubing was needed to prevent whipping of the shaft at high rotational speeds (>3000 rev./min) which had been experienced with a similar shaft with 1/4″ outside diameter. Bearing surfaces were mounted using 2 ball races (Fafnir MS3K) with a $5\frac{1}{2}$″ separation of the races. The bearing assembly

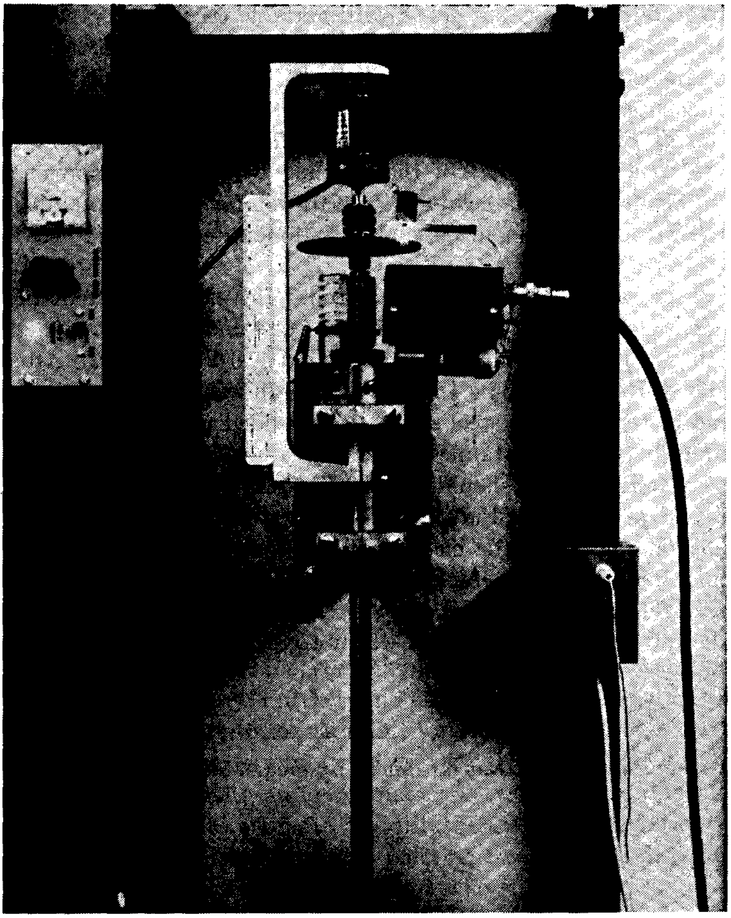

Fig. 1. Rotating disc apparatus.

was contained within a brass bearing support with threaded retaining caps for disassembly. Electrical contacts to the disc electrode were provided using copper rings (3/4″ o.d.) insulated from the metal shaft with a threaded polymethylmethacrylate collar at the top of the shaft. Insulated contact wires were soldered to the inside of the copper rings and passed through precision drilled holes in the side of the metal shaft and were soldered directly to wire contacts on the disc electrodes. Phosphor bronze rubbing contacts were then mounted on a polymethylmethacrylate support to make electrical contact to the copper rings. As an added precaution against contact noise, both the copper rings and the phosphor bronze contactors were gold plated. At the top of the shaft a 1/4 × 28 N.F. thread was machined to accept a brass timing disc and collar. The timing disc was 3″ diameter by 1/16″ thick, having 100 precision holes (1/32″ dia.) drilled on a circle $2\frac{1}{4}$″ diameter. Not only did the timing disc allow precise determinations for the rotational speed of the shaft but acted as a flywheel, helping to maintain a constant speed of the shaft. Into the threaded top of the timing disc collar was inserted a flexible coupling with a neoprene joint to attach the driving motor to the rotating assembly. The motor was a d.c. servo unit with a tachometer winding and a control system for constant speed with variable torque (Electrocraft E-150, 0–10,000 rev./min). The motor was mounted on the inside face of a narrow cut 10" aluminum "U" beam with the opposite face of the "U" beam machined to fit around the brass bearing support. In this way, a convenient rigid bracket was formed for maintaining alignment of the motor with the shaft. The total assembly was mounted to a concrete structural support of the building with a 6" section of a 4" × $3\frac{1}{2}$" aluminum "I" beam. Two collars with $2\frac{1}{2}$" separation for fitting around the brass bearing support were mounted on a leveling plate and mounted to the "I" beam with 4 bolts.

The disc electrodes were prepared as metal rods and either inserted into machined Kel-F cylinders 1/2" o.d. and machined holes 0.002" under size or moulded in a press at 250° with 100 lb/inch^2 using micropulverized Kel-F (3M-6061). After mounting the electrodes in Kel-F, a female $\frac{1}{4}$ × 28 N.F. thread was cut in the plastic to mount it on the end of the stainless steel shaft. As an added precaution against leakage of the electrolyte between the stainless steel shaft and the plastic electrode support, a groove was cut in the mating shoulder of the Kel-F to accept a $\frac{1}{4}$" neoprene ring which was compressed on tightening the plastic to the shaft.

Before mounting on the shaft, the electrodes and the plastic support were polished to a mirror finish using a 2" diameter polishing support.

Final balancing of the shaft was carried out with the electrode in position, such that excentricity of the top of the plastic mount was not greater than ±0.0005" on the diameter.

Timing

The rotational speed of the shaft was measured by means of a timing disc with 100 perforations mounted on the shaft. A light beam from a pre-focussed lamp passed through the perforations in the timing disc and was sensed by a photo-diode (Electro-Nuclear Laboratories, Inc., PD 9000-1). The changing d.c. potential was capacitatively coupled to an operational amplifier (Heath Kit) and the pulse frequency counted for 10 seconds with a digital electronic scalar (Baird-Atomic). The circuit is shown in

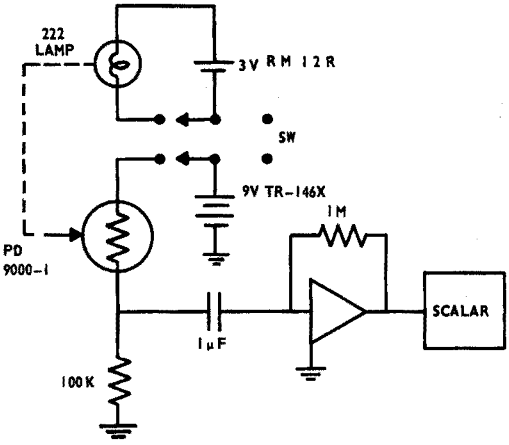

Fig. 2. Photo-diode timing circuit.

Fig. 2. In this manner, the rotational speed was obtained to 4 significant figures in the dimensions of cycles/sec directly.

Apparatus and chemicals

The electronic scanning potentiostat and cell assembly were described previously[1]. Phosphotungstate solutions were prepared from sodium tungstate and phosphoric acid as before. Solutions of the chloro complex were prepared from sodium tungstate (Allied Chemical) and concentrated 12 *N* hydrochloric acid (J. T. Baker Chemical).

Solution viscosities were measured with an Ubbelohde viscometer in a Sargent constant temperature water bath at 27°.

RESULTS AND DISCUSSION

Phosphotungstic heteropolyacids may exist in acid solution in a variety of structures. Predominantly the 12-PTA is formed in weak acid, with the 3-PTA formed in strong acid[2]. The crystalline structures of 12-PTA were examined by KEGGIN[8] and BRADLEY AND ILLINGWORTH[9]. It was ascertained that the $(PW_{12}O_{40})^{3-}$ anion was formed from a central PO_4 tetrahedron, surrounded by 12 slightly distorted WO_6 octahedra, linked together by shared oxygen atoms. KEGGIN[8] examined the 5-hydrate packing giving a cubic unit whereas BRADLEY AND ILLINGWORTH[9] examined the 29-hydrate packing, containing $(H_3 \cdot 29H_2O)^{3+}$ cations forming 2 interpenetrating diamond lattices. Further, the latter workers were able to show that the cubic lattice of the 29-hydrate maintained a face length of 23.28 Å for the unit cell. The $(PW_{12}O_{40})^{3-}$ anion may be fitted into a polyhedron bounded by 6 cube faces and 8 octahedral faces, with an ion diameter of 11.64 Å. This dimension of the unsolvated ion may be used to evaluate the diffusivities of the anion obtained experimentally.

For a diffusion-controlled reaction to a rotating disc electrode, LEVICH[10] has shown that the thickness of the diffusion layer (δ) is

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \tag{2}$$

where D is the diffusion coefficient of the reacting species and ν is the kinematic viscosity of the solution. ω is the angular velocity of the disc (radians/sec). The current density (i/A) of a diffusion-controlled reaction, when all electrochemical species striking the surface react is

$$i/A = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \cdot C_0 \cdot n \cdot F \tag{3}$$

where C_0 is the concentration of the electroactive species in the bulk of the solution (M cm^{-3}) and the electrode surface concentration of the species is zero. GREGORY AND RIDDIFORD[11] indicated that the equations presented by LEVICH predicted results which were higher than those obtained experimentally and were due to an approximation made by LEVICH, such that a closer situation was

$$\frac{i}{A} = \left\{1.61 \left(\frac{D}{\nu}\right)^{1/3} \left(\frac{\nu}{\omega}\right)^{1/2} \left[1 + 0.35 \left(\frac{D}{\nu}\right)^{0.36}\right]\right\}^{-1} D C_0 n F \tag{4}$$

This equation was shown to hold for situations where the flow at the surface of the disc is laminar up to Reynolds numbers of the order 10^4 to 10^5. The Reynolds number is $N_{Re} = \omega r^2/\nu$ when r is the radius of the disc. The lower limit of eqn. (4) occurs at about $N_{Re} = 10$ when the thickness of the diffusion layer becomes great enough for convective diffusion to be appreciable.

Experimental results obtained with the rotating disc apparatus are shown in Fig. 3. Results were obtained for reduction at a platinum disc (A, B, C, D, E) with (A, C, D, E) and without (B) carbon monoxide and at a copper electrode amalgamated with mercury (C). The influence of carbon monoxide in suppressing hydrogen evolution at the platinum electrode is clearly seen (B, C). At the electrode potential maintained (+0.15 V *vs.* H_2/H^+ 1 N), only adsorbed hydrogen is formed at the electrode surface and is not affected by the solution hydrodynamics; therefore, parallelism was obtained for the diffusion data obtained with (C) and without carbon monoxide (B). Diffusion controlled current densities in Fig. 3 are obtained for 2 phosphotungstate heteropolyacids. On preparing solutions by weighing sodium tungstate, dissolving in water and adding phosphoric acid, a polymer is formed, provided that the solution is not warmed. On heating to 85° for 2 h the 12-PTA is formed. Diffusion current densities for the former are shown in curve (D) and the latter in curve (A). The increase in current densities at constant ω is 5 times. Current–voltage curves obtained

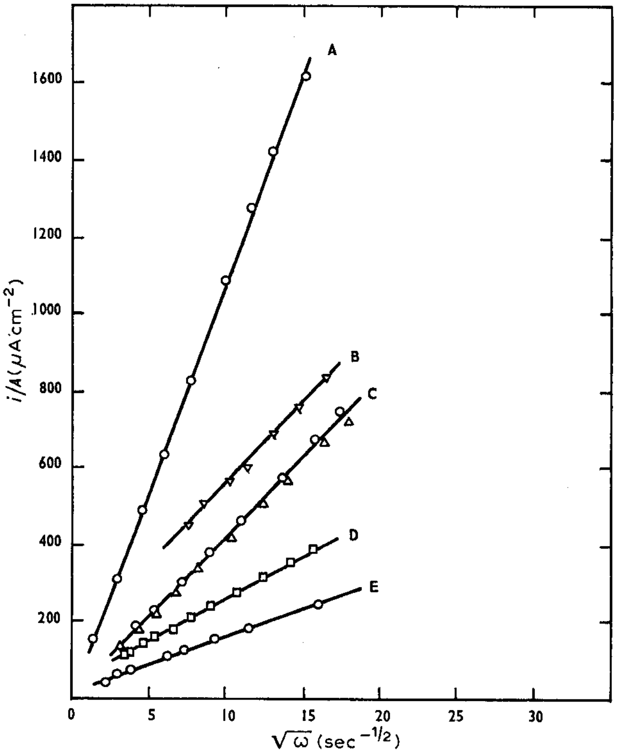

Fig. 3. Diffusion limited reduction of phosphotungstic acid at + 0.15 V *vs.* H_2/H^+ 1 N in 1 M H_3PO_4. (A) 0.050 M WO_4^{2-}; (B) 0.020 M WO_4^{2-}; (C) 0.020 M WO_4^{2-}; (D) 0.050 M WO_4^{2-}; (E) 0.010 M WO_4^{2-}. (○) Pt/CO—12-PTA; (△) Cu/Hg/CO—12-PTA; (□) Pt/CO—polymer; (▽) Pt/N_2—12-PTA.

for the 2 situations show no potential shift, only an increased magnitude for the current density.

Calculating diffusion coefficients from the results in Fig. 3, using eqn. (4) and assuming that all of the tungsten atoms in the polyacids were reduced from $W^{6+} \rightarrow W^{5+}$, gave anomalously low diffusion coefficients. Calculations were then carried out assuming that only *one* of the tungsten atoms in the heteropolyacid was reduced giving $D_{12\text{-PTA}} = 2.48 \cdot 10^{-6}$ and $D_{\text{polymer}} = 2.68 \cdot 10^{-7}$ cm^2/sec. The diffusion coefficients calculated above are based on the premise that not more than 1 tungsten atom in 12 on each agglomerate is reduced; indeed, any combination greater than one of the tungsten atoms reduced on the heteropolyacid would produce progressively lower diffusion coefficients. Although these results represent the *upper* diffusion limits, it is feasible that perhaps 5% of the molecules may approach the electrode in such a configuration that 2 tungsten atoms are within the electron transfer zone.

From the polarographic[2] reduction of the 12-PTA in sulphuric acid, wherein 2 tungsten atoms on the heteropoly anion were reduced and the cyclic voltammetry together with the diffusion data of 12-PTA in phosphoric acid whereby 1 tungsten atom is reduced, it appears that the electrons in the tungsten shell about the central phosphorus are completely delocalized. In particular, with the cyclic voltammetric results[1] in phosphoric acid at a stationary electrode, the reoxidation peak is nearly the same height as the reduction peak, so that if a specific tungsten atom is reduced to the W^{5+} state and the complex diffuses from the surface, then the probability of the same tungsten atom arriving in an identical configuration to be quantitatively reoxidized is very small.

There is no evidence from both the cyclic voltammetry[1] and this work that more than one tungsten atom in the heteropoly anion is reduced, although an extension from these results in excess phosphoric acid to the sulphuric acid electrolyte used by KENNEDY is not readily made, particularly owing to the large differences reported in reduction potentials for $W^{6+} \rightarrow W^{5+}$, with the resultant changes in the structure of the double layer.

The Stokes–Einstein equation relates the diffusion coefficient of a sphere to the radius of said sphere in a continuum. Two situations are possible[12]: either there is no tendency of the surrounding fluid to stick at the surface of the diffusing entity, then

$$D\mu/KT = 1/4\pi R' \qquad (5)$$

or there is no slip at the surface of the diffusion entity, then

$$D\mu/KT = 1/6\pi R' \qquad (6)$$

where K is the Boltzmann constant, T the temperature, μ the solution viscosity and R' the radius of the sphere. Assuming that the diffusing anion approximates to a sphere with a strongly bound hydration sheath at the anion surface, then the situation for eqn. (6) may be used. It is noted at this stage, however, that eqn. (5) has been suggested[20] to be more applicable for strongly solvated ions, with the consideration that there is no attraction between the solvated water molecules and the bulk of the solution. In this condition the solvated ion is regarded as a "hole" or "bubble" within the electrolyte.

Using the Stokes–Einstein equation and diffusion results obtained with the rotating disc, then hydrated ionic radii for the phosphotungstate anions are $R'_{12\text{-PTA}} = 6.99$ Å and $R'_{\text{polymer}} = 64$ Å. Assuming[13] that the volume of a water molecule is 30 Å^3 and occupies a surface area of approximately 21 Å^2, then the calculated volumes of water molecules as fractions of the total hydrated ion volumes may be obtained.

In the case of hydrated alkali metal ions[13], the volume of the metal ion is negligible compared to the volume of the hydration sheath. With the phosphotungstate ions, however, this is not the case and the volume of the unsolvated ion is 826 Å^3. Considering these factors, therefore, it is concluded that the 12-PTA exists as a monomer with 20 solvated water molecules and that polymers or agglomerates are initially formed not greater than tetramers, as this situation fits the data most closely. In addition, the effect of the structure of the phosphoric acid[14–17] should not be overlooked as this can have some effect upon the diffusion characteristics of these heteropoly anions. At present, this structural effect cannot be evaluated.

Using dropping mercury electrodes, diffusion coefficients may be obtained from diffusion limited currents at constant potential by means of the Ilkovic equation[18]

$$i_d = 607\, n\, D^{1/2} C_0\, m^{2/3}\, t^{1/6} \cdot 10^3 \tag{7}$$

where i_d is the diffusion current (μA), n the overall reaction electron transfer, m the mercury flow rate (mg/sec) and t the drop time (sec). For instantaneous currents at the expanding mercury surface and taking into account the curvature of the surface, the constant in eqn. (7) becomes 708[19]. Diffusion coefficients were calculated from the literature using eqn. (7) and are shown in Table I for comparison with the rotating disc results obtained here.

In Table I it is seen that for the chloro- and phosphotungsten compounds, very low diffusion coefficients result. The values obtained by REZNIK AND KOVALENKO[4]

TABLE I

DIFFUSION COEFFICIENTS OF TUNGSTEN HETEROPOLYACIDS

Electrolyte		*D(cm²/sec)*	*Technique*	*Reference*
1 *M* H_3PO_4	12-PTA	$2.48 \cdot 10^{-6}$	Rotating disc	This work (1 in 12)
	Polymer	$2.68 \cdot 10^{-7}$	Rotating disc	(1 in 12)
1 *N* H_2SO_4	12-PTA	$1.14 \cdot 10^{-6}$	DME	[2] (2 in 12)
	12-PTA	$4.05 \cdot 10^{-6}$ $4.58 \cdot 10^{-6}$	DME	[2] (1 in 12)
12 *N* HCl		$4.7 \cdot 10^{-6}$	DME	[3]
10 *N* HCl		$5.4 \cdot 10^{-6}$	DME	[3]
8 *N* HCl		$5.9 \cdot 10^{-6}$	DME	[3]
		$7 \cdot 10^{-7}$	DME	[4] (time function)
		$6 \cdot 10^{-6}$	DME	This work
4.6 *N* HCl + 0.1 *M* tart.		$5.8 \cdot 10^{-6}$	DME	[5]
1 *N* H_2SO_4 + 0.2 *M* oxalate		$3.3 \cdot 10^{-6}$	DME	[6]

are so much lower than expected that they must be in error. As these authors used a microcoulometric technique and deduced a mean n value of 3.22 for the $W^{6+} \rightarrow W^{3+}$ reaction, then the equations proposed to evaluate the diffusion data do not apply.

CONCLUSIONS

By means of controlled hydrodynamics at an electrode surface, diffusion coefficients have been obtained for the reversible $W^{6+} \rightleftarrows W^{5+}$ reaction in phosphoric acid. From the low diffusion values obtained it appears that only one tungsten atom of the phosphotungstate anion (12-PTA) in phosphoric acid is reduced and that the ion is solvated with 20 water molecules.

Diffusion data have been compared for tungsten compounds with different ligands and in other electrolytes.

SUMMARY

Controlled hydrodynamics at rotating platinum and amalgamated copper electrodes were used to measure diffusion coefficients for 12-phosphotungstic and polyphosphotungstic acids in 1 M phosphoric acid. $D_{12\text{-PTA}} = 2.48 \cdot 10^{-6}$; $D_{\text{polymer}} = 2.68 \cdot 10^{-7}$ cm²/sec, assuming only 1 tungsten atom in 12 is reduced at each diffusing entity. The phosphotungstic acids in phosphoric acid probably exist as polymers on initial formation, not greater than tetramers, rearranging to give monomers from calculations based on one reduced tungsten atom to each complex ion. Diffusion parameters of the phosphotungstic acids are compared with diffusion results of tungsten compounds from the literature obtained with dropping mercury electrodes. In all instances, low diffusion values are obtained indicating large diffusing entities.

RÉSUMÉ

L'auteur a effectué des mesures de coefficients de diffusion des acides phosphotungstiques (APT), à l'aide d'électrodes de platine rotatives et de cuivre amalgamé. $D_{12\text{-APT}} = 2.48 \cdot 10^{-6}$; $D_{\text{polymère}} = 2.68 \cdot 10^{-7}$ cm²/sec, un seul atome de tungstène est réduit par agglomérat. Les paramètres de diffusion des acides phosphotungstiques correspondent aux résultats de diffusion de composés de tungstène, obtenus avec électrodes à gouttes de mercure.

ZUSAMMENFASSUNG

Die Diffusionskoeffizienten von 12-Wolframphosphorsäure und Wolframpolyphosphorsäure in 1 M Phosphorsäure wurden mit rotierenden Platin- und amalgamierten Kupferelektroden gemessen. Die Grössen $D_{12} = 2.48 \cdot 10^{-6}$ und $D_{\text{polymere}} = 2.68 \cdot 10^{-7}$ cm²/sec lassen vermuten, dass in jedem Agglomerat nur Wolframatome reduziert werden. Die Diffusionsparameter der Phosphorwolframsäuren werden mit den Diffusionsergebnissen von Wolframverbindungen aus der Literatur verglichen, die mittels tropfender Quecksilberelektroden erhalten wurden. In allen Beispielen werden niedrige Diffusionswerte erhalten, die grosse diffundierende Teilchen anzeigen.

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ANION-EXCHANGE CHROMATOGRAPHY OF ORGANIC ACIDS IN MAGNESIUM ACETATE MEDIUM

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In earlier papers[1-3] it has been shown that anion-exchange chromatography in media containing a cation which can form complexes with organic acids is a valuable complement to other chromatographic methods used in the separations of organic acids. Copper(II) acetate can be used to advantage in some systems, but because it is an oxidant it cannot be used when certain acids, *e.g.* uronic acids, are involved. Complications of this type do not occur with zinc acetate and this eluant has been employed in several separations of interest in carbohydrate chemistry.

The aim of this work was to study the application of magnesium acetate as an eluant in the separations of various organic acids including oxalic acid. Because of the low solubility of zinc oxalate, eluants containing zinc ions cannot be used to advantage.

EXPERIMENTAL

The separations were carried out with the acetate form of a strongly basic anion-exchange resin (Dowex 1-X8) in two jacketed columns. If not otherwise mentioned, the temperature was kept at 60°. The acids to be separated were added in solution as their sodium salts. The standard technique with a plunger pump for feeding the eluant onto the column was employed[4]. The eluants were prepared from magnesium acetate (or for comparison sodium acetate) and acetic acid was added to obtain the desired pH. The eluant concentrations are given in molarities with respect to magnesium and sodium.

The eluate from one of the columns (6 × 850 mm) filled with a resin of particle size 40–55 μ was collected in a time-actuated fraction collector and analyzed by chromic acid oxidation using a Technicon AutoAnalyzer. The chromic acid consumption of the eluate fractions was determined automatically and the concentration of organic acid was calculated from calibration runs with standard solutions. The working conditions were the same as used previously[5] except for an increased sulfuric acid concentration (72% H_2SO_4). To obtain the same acidity in the final reaction with diphenylcarbazide, dilute sodium hydroxide was used instead of water in the final dilution.

The other column with bed dimensions 6 × 1350 mm was filled with a resin of particle size 26–32 μ. The eluate was analyzed automatically by chromic acid oxidation with a determination of the green Cr(III) complexes formed. The monitor consisted of a peristaltic pump, reaction coils of teflon, a multichannel photometer

(LKB-Produkter, Stockholm) and a recorder. Details of this analyzing system were reported previously[6].

RESULTS AND DISCUSSION

The peak elution volumes were determined from experiments with single acids and further checked in experiments with simple mixtures. From these determinations the volume distribution coefficients (D_v) were calculated as usual[4]. The results given in Table I were determined on the smaller column using 0.2 *M* magnesium acetate as eluant. To obtain information about the influence of complex formation between the acids to be separated and the magnesium ions, some determinations were made with 0.4 *M* sodium acetate solution also.

TABLE I

D_v VALUES OF SOME ORGANIC ACIDS DETERMINED IN 0.2 *M* MAGNESIUM ACETATE AND 0.4 *M* SODIUM ACETATE AT VARYING pH

Acid	*pH 3.9*		*pH 4.8* *MgAc₂*	*pH 7.0*	
	MgAc₂	*NaAc*		*MgAc₂*	*NaAc*
Oxalic	2.09	>20	2.29	2.36	>25
Tartronic	5.07		5.42	5.50	
Malic	6.39	6.84	7.78	7.84	20.5
Glucaric	7.26		10.7	11.9	
Galactaric	7.72	7.29	11.0	12.6	17.0
Tartaric			18.3	19.2	

Independent of the pH, oxalic acid appeared first in runs with magnesium acetate whereas this acid was held very strongly when eluted with sodium acetate at the corresponding pH values. The elution behavior of oxalic acid indicates that the formation of non-adsorbable complexes has a predominant influence within the whole pH-interval. Galactaric acid, on the other hand, appeared somewhat later in magnesiun acetate media than in sodium acetate at pH 3.9 indicating that the formation of non-adsorbable complexes is negligible at this pH. The small difference in D_v values is explained by differences in the activity coefficients. At pH 7 the complex formation between magnesium ions and galactaric acid has an appreciable influence. Malic acid which appeared between oxalic and galactaric acids takes an intermediate position also as far as the formation of non-adsorbable complexes is concerned.

From the Table it can be seen that, with the exception of the 2 saccharic acids included in the Table, the distribution coefficients differed greatly which means that the acids could be separated quite easily independently of the pH. It can be seen that tartaric acid appeared much later than the other acids and it is convenient therefore to speed up its elution by increasing the eluant concentration after the other acids have been eluted. The results from a run in which stepwise elution was employed is reproduced in Fig. 1. Maleic acid, which was held very strongly in 0.2 *M* magnesium acetate (peak elution volume >1000 ml) and is therefore not included in the Table, appeared very late even in 1 *M* magnesium acetate at this pH and was easily separated from the other acids. Whereas the distribution coefficients of all other acids decreased with decreasing pH because of a transformation of divalent anions into monovalent anions, maleic acid showed the opposite elution behavior. A probable explanation is that interacting forces between the double bond and the resin have a greater influence on the distribution coefficients in a more acidic medium. It is worth mentioning that on elution with 0.5 *M* magnesium acetate at pH 7, tartaric and maleic acids could not be separated from each other.

Among the acids given in the Table glucaric and galactaric acids could only be partially separated from each other on the smaller column. A study on the longer column filled with smaller resin particles showed that both acids appeared in the same

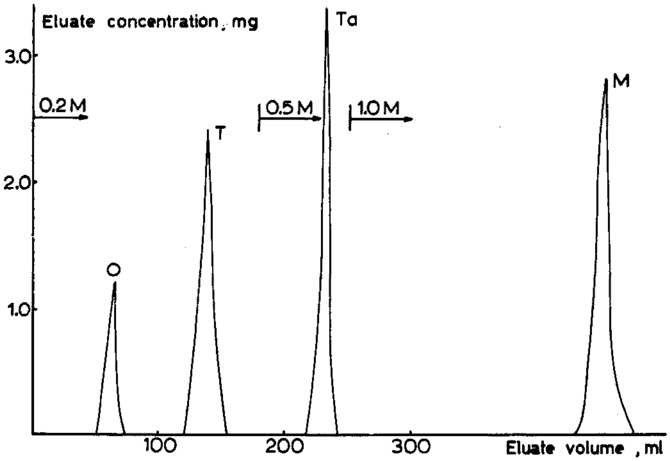

Fig. 1. Separation of oxalic acid (O), tartronic acid (T), tartaric acid (Ta) and maleic acid (M) by stepwise elution with magnesium acetate solution at pH 4.8. The concentration of oxalic acid is given in mg/ml and the other concentrations in mg/10 ml. Flow rate: 0.90 ml/min.

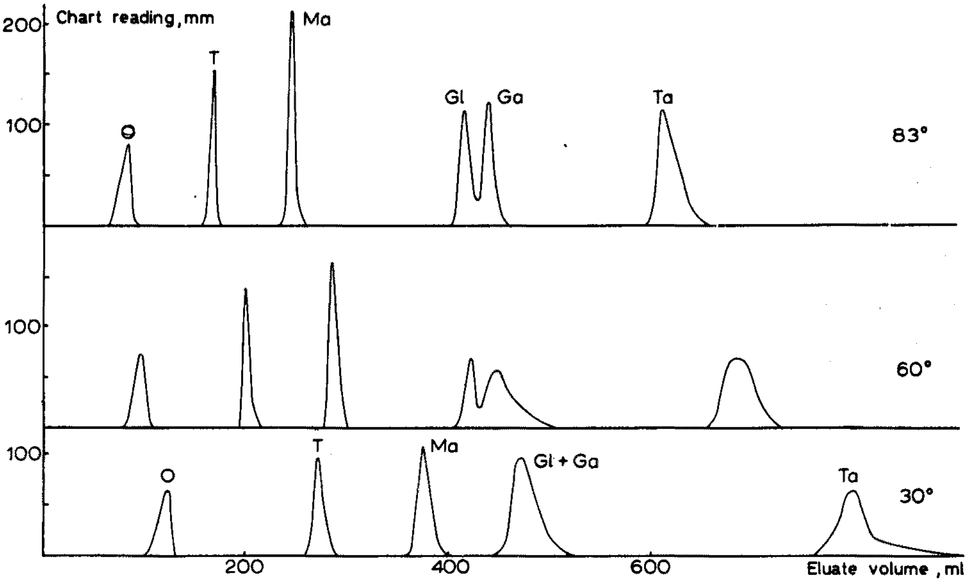

Fig. 2. Influence of the temperature upon the elution of 10 mg oxalic (O), 1.5 mg tartronic (T), 1.5 mg malic (Ma), 1.1 mg glucaric (Gl), 1.1 mg galactaric (Ga) and 5 mg tartaric (Ta) acid. Eluant: 0.2 *M* magnesium acetate at pH 7.0. Flow rate: 0.97 ml/min.

elution band when the column was run at 30°. At 60° a partial separation was achieved, whereas at 83° the separation was good enough to permit an evaluation of the chromatogram for quantitative purposes. Results obtained with a mixture of the 6 acids included in the Table are given in Fig. 2. The eluate concentration was recorded automatically and the monitor run during the night without attention. It can be seen that with all acids the peak elution volumes and band widths were lowered at an increased temperature. The reproducibility was the same as reported previously, which means that the method is well suited to quantitative analyses.

Earlier investigations have shown that lactic and glucuronic acids appeared in the same elution band when sodium acetate was used as eluant whereas the acids were well separated in 0.05 *M* zinc acetate (pH 4.6). In this medium lactic acid appeared at about half the eluate volume compared with that required for glucuronic acid[3]. This is explained by the formation of non-adsorbable zinc lactate complexes. With magnesium acetate at the same pH and concentration lactic acid appeared only slightly before glucuronic acid. In 0.05 *M* magnesium acetate at pH 3.3 a complete separation was achieved but the difference between the peak elution volumes was only about 15%. The peak elution volumes were almost the same as those observed in a parallel run with 0.1 *M* sodium acetate of the same pH which indicates that the formation of non-adsorbable complexes is negligible. The improved separation at the lower pH is explained by the fact that lactic acid is a weaker acid than glucuronic acid. From these results it can be seen that magnesium acetate, although it is a very efficient eluant in separations of many dibasic acids, is less efficient than zinc acetate when certain other acids are involved.

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SUMMARY

Magnesium acetate solution is a useful eluant in the separations of dibasic organic acids by anion-exchange chromatography. The following acids were separated: oxalic, tartronic, malic, glucaric, galactaric, tartaric and maleic acids. The eluate was analyzed automatically using chromic acid oxidation.

RÉSUMÉ

On propose l'acétate de magnésium comme éluant lors de la séparation d'acides organiques dibasiques, par chromatographie (échangeur d'anions). On a pu séparer ainsi les acides oxalique, tartronique, malique, gluconique, galactique, tartrique et maléique. L'éluat est analysé automatiquement par oxydation à l'acide chromique.

ZUSAMMENFASSUNG

Magnesiumacetatlösung ist ein nützliches Eluierungsmittel bei der Trennung von dibasischen organischen Säuren mit Hilfe der Anionenaustauschchromatographie. Die folgenden Säuren wurden getrennt: Oxal-, Tartron-, Malon-, Glukar-, Milch-, Wein- und Maleinsäure. Das Eluat wurde automatisch analysiert unter Verwendung der Chromsäure-oxydation.

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SEPARATION OF RHENIUM(VII) FROM MOLYBDENUM(VI) AND MANY OTHER ELEMENTS BY ANION EXCHANGE

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Most methods so far reported for the anion-exchange separation of rhenium(VII) from other metal ions are based on the retention of rhenium on strongly basic anion-exchange resins from dilute hydrochloric acid solutions in absence[1] or presence of thiocyanate ion as complexing agent[2-5], or from nitric-[6-8], perchloric[9-13] and phosphoric acid media[14,15]. Furthermore a good separation of perrhenate from molybdate is obtainable in sodium hydroxide media[16-18]. Common to all these methods is the fact that under the conditions selected by the various authors rhenium can only be separated from a relatively small number of elements so that these procedures are of a rather low selectivity.

Previous investigations[19] showed that in mixed aqueous–organic solvent systems very often the selectivity of separations of elements is considerably higher than in pure aqueous solutions. Therefore several such mixtures were investigated in the present work and a rather selective method for the separation of rhenium from molybdenum and many other elements was developed.

EXPERIMENTAL

Reagents and solutions

Ion-exchange resin. The strongly basic anion-exchange resin Dowex 1-X8 (100–200 mesh; nitrate form) was used for the column experiments.

Standard solutions. Stock solutions of rhenium(VII), molybdenum(VI) and various other elements were prepared by dissolution of reagent-grade salts of these metal ions in 6 M nitric or hydrochloric acid.

Solvents. The following organic solvents of reagent-grade purity were used: methanol, ethanol, *n*-propanol, *n*-butanol, isobutanol, methylglycol, ethylglycol, acetone, acetic acid and tetrahydrofuran.

Wash solution. 90% (v/v) methanol + 10% 6 M nitric acid.

Apparatus

Resin columns of 0.5 cm diameter each containing 1 g of the resin were used to determine the elution characteristics and for the separation experiments.

Separation of rhenium from molybdenum

Pretreatment of resin bed. The resin was soaked in a few milliliters of the wash solution and transferred to the ion-exchange column, and the resin bed was washed with 20 to 30 ml of this solution.

Sorption, washing and elution. Through the pretreated resin bed, 2 ml of a solution 90% in methanol and 10% in 6 *M* nitric acid containing rhenium(VII) and molybdenum(VI) was passed at a flow rate of 1 ml/4 min. During this operation molybdenum(VI) passes partly into the effluent while rhenium is strongly adsorbed on the top of the column. After passage of this solution the resin was washed with the wash solution until the effluent contained all of the molybdenum originally present in the sorption solution. For this purpose 20–25 ml of this wash solution had to be passed if molybdenum was present in amounts up to 5 mg. Then the adsorbed rhenium was eluted completely with 15 ml of a mixture consisting of 70% tetrahydrofuran and 30% 9 *M* hydrochloric acid (v/v).

Determination of rhenium in the eluate. For the direct spectrophotometric determination of rhenium in the eluate obtained above the thiocyanate method described by SANDELL[20] was modified. To 1 ml of the eluate containing 25–50 μg of rhenium, 1 ml of 6 *M* hydrochloric acid, 1 ml of tin(II) chloride solution (prepared as described by SANDELL[20]) and 2 ml of a 20% thiocyanate solution (prepared as described by SANDELL[20]) were added and the solution was diluted to 10 ml with tetrahydrofuran. After 20–30 min the absorbance of this solution was measured in a 1-cm cell at 440 mμ using a Beckman B spectrophotometer and a reagent blank solution as the reference. To determine the rhenium concentration of the measuring solution its absorbance was compared with a calibration curve which was set up in the same manner. Beer's law is obeyed up to more than 50 μg of rhenium/10 ml of measuring solution.

Determination of elution characteristics

The elution characteristics of rhenium, molybdenum and other elements were determined using the column method, *i.e.* the elution curves were recorded on 1-g columns of the resin. Under these conditions the retention volume (volume corresponding to the elution peak of the element in question) in milliliters is roughly equal to the distribution coefficient of the element. At the same time the breakthrough and elution volumes were determined. For these studies 1-mg amounts of rhenium, molybdenum and of the other elements dissolved in 2 ml of nitric or hydrochloric acid–organic solvent mixtures were used. The flow rate corresponded to 1 ml/4 min. The breakthrough, retention and elution volumes were detected by using sensitive colour reactions for the elements concerned.

RESULTS AND DISCUSSION

From Table I, which shows the elution characteristics of rhenium and molybdenum when 90% organic solvent–10% 6 *M* hydrochloric acid mixtures are used as eluants, it can be seen that for the quantitative chromatographic separation of these two elements the most suitable medium is that which contains methanol as the organic component. Under these conditions the molybdenum is eluted completely far ahead of the rhenium, *i.e.* its elution volume is much smaller than the breakthrough volume of rhenium. In all the other media a serious overlapping of the elution curves was observed. However, despite its favourable separation properties, this methanol–hydro-

TABLE I

ELUTION CHARACTERISTICS OF MOLYBDENUM(VI) AND RHENIUM(VII) ON 1-g COLUMNS OF DOWEX 1-X8 WITH 90% ORGANIC SOLVENT–10% 6 *M* HYDROCHLORIC ACID MIXTURES AS ELUANTS

Organic solvent	*Mo(VI)*			*Re(VII)*		
	BTV[a] *(ml)*	*VEP*[a] *(ml)*	*EV*[a] *(ml)*	*BTV (ml)*	*VEP (ml)*	*EV (ml)*
Methanol	17	28	45	100	125	150
Ethanol	27	30	50	46	52	75
n-Propanol	32	40	60	35	46	70
Isopropanol	>200	Not determined		21	33	65
n-Butanol	28	40	75	24	35	65
Isobutanol	46	57	80	23	30	54
Methylglycol	4	8	36	19	27	46
Ethylglycol	3	7	40	15	25	50
Acetone	2	4	14	3	5	15
Acetic acid	100	150	210	32	47	64
Tetrahydrofuran	5	5	15	2	5	15

[a] BTV = Breakthrough volume.
VEP = Volume of elution peak (retention volume) $\simeq$ distribution coefficient.
EV = Elution volume.

chloric acid system was not used for further studies because under these conditions many foreign ions, *e.g.* iron(III), cobalt and practically all those metal ions which form anionic chloride complexes, are coadsorbed with the rhenium and thus render the method rather inselective. For this reason the elution characteristics of rhenium and molybdenum were also recorded in media containing 10% 6 *M* nitric acid and 90% organic solvents. From these mixtures only a very small number of foreign ions would be expected to be coadsorbed with the rhenium. From the experimental data of these experiments, which are recorded in Table II, it can be seen that as in the hydrochloric acid systems, the most favourable conditions of separating rhenium from molybdenum exist in a medium containing 90% of methanol and 10% of 6 *M* nitric acid.

TABLE II

ELUTION CHARACTERISTICS OF MOLYBDENUM(VI) AND RHENIUM(VII) ON 1-g COLUMNS OF DOWEX 1-X8 WITH 90% ORGANIC SOLVENT–10% 6 *M* NITRIC ACID MIXTURES AS ELUANTS

Organic solvent	*Mo(VI)*			*Re(VII)*		
	BTV (ml)	*VEP (ml)*	*EV (ml)*	*BTV (ml)*	*VEP (ml)*	*EV (ml)*
Methanol	2	3·5	20	35	44	60
Ethanol	3	15	60	23	27	37
n-Propanol	2	12	40	20	27	40
Isopropanol	3	60	160	27	36	47
n-Butanol	4	10	26	18	28	42
Isobutanol	3	9	54	98	120	210
Methylglycol	6	10	33	23	33	48
Ethylglycol	2	5	60	13	25	40
Acetone	43	200	350	16	29	40
Acetic acid	>300	Not determined		48	120	210
Tetrahydrofuran	3	6	19	7	13	27

For this reason this medium was selected for all further investigations as well as for the separation of varying amounts of rhenium and molybdenum when present in μg and mg quantities.

By employing the working procedure described above, the results listed in Table III were obtained. These show that good separation of the two elements can be achieved in a concentration range which varies by more than one order of magnitude.

TABLE III

SEPARATION OF VARYING AMOUNTS OF RHENIUM AND MOLYBDENUM ON 1-g COLUMNS OF DOWEX 1-X8

Re taken (μg)	*Mo present (mg)*	*Re recovered (μg)*	*Error (%)*
100	0.1	99	−1.0
100	1.0	102	+2.0
100	2.5	100	0.0
100	5.0	100	0.0
1000	1.0	1015	+1.5
1000	2.5	1009	+0.9
1000	5.0	998	−0.2

TABLE IV

ELUTION CHARACTERISTICS OF METAL IONS ON 1-g COLUMNS OF DOWEX 1-X8

Metal ion	*BTV (ml)*	*VEP (ml)*	*EV (ml)*
Re(VII)	35	44	60
Mo(VI)	2	3.5	20
Mg(II)	2	6	15
Ca(II)	2	4	15
Fe(III)	2	2.5	10
V(V)	2	3.5	10
Co(II)	2	3	9
Ni(II)	2	3.5	9
Cu(II)	2	3	9
Cr(III)	2	3	10
Hg(II)	14	18	25
As(III)	2	5	9
Mn(II)	2	4	10
UO_2(II)	7	16	30
Zr(IV)	2	4	9
Pb(II)	>80	Not determined	Not determined
Bi(III)			
Ce(III)			
Th(IV)			
Au(III)			

Investigations concerning the adsorption behaviour of other metal ions from 90% methanol–10% 6 *M* nitric acid mixtures gave the results shown in Table IV. It can be seen that only lead, bismuth, cerium, thorium and gold (all of which form strong anionic nitrate complexes) will be coadsorbed with the rhenium, *i.e.* their breakthrough volumes are higher than that of rhenium. All the other metal ions investigated have elution volumes similar to that of molybdenum so that these elements will pass completely into the effluent before rhenium starts to be eluted. During the subsequent elution of rhenium with the tetrahydrofuran–hydrochloric acid mixture, these coadsorbed metal ions are partly (lead and gold) or completely eluted together with the rhenium but do not interfere with the spectrophotometric determination of rhenium even if present in milligram amounts.

In conclusion it should be pointed out that this separation method of rhenium from molybdenum and the other elements can, because of its rather high selectivity, be employed to solve many problems encountered in the analytical chemistry of rhenium especially when very complex mixtures are involved.

SUMMARY

A method is described for the selective separation of μg and mg amounts of rhenium(VII) from molybdenum(VI) and many other metal ions by means of the strongly basic anion-exchange resin Dowex 1-X8. The separation is based on the preferential elution of molybdenum by a 90% (v/v) methanol–10% 6 *M* nitric acid mixture; rhenium and a few other elements are retained while molybdenum and most other metal ions including Fe(III), Ca, Mg, Mn, U, Cu, V, etc., are practically unadsorbed. After elution of the adsorbed rhenium with 70% (v/v) tetrahydrofuran–30% 9 *M* hydrochloric acid, the rhenium is determined spectrophotometrically by a modified thiocyanate method.

RÉSUMÉ

Une méthode est décrite pour la séparation sélective du rhénium(VII) d'avec le molybdène(VI) et de nombreux autres ions métalliques, au moyen de la résine Dowex 1-X8 fortement basique (échangeur d'anions). La séparation est basée sur l'élution préférentielle du molybdène à l'aide d'un mélange méthanol–acide nitrique 6 *M* (90%: 10%, v/v). Le rhénium et quelques autres éléments sont retenus, tandis que le molybdène et la plupart des autres métaux (Fe(III), Ca, Mg, Mn, U, Cu, V, etc.) sont pratiquement non-adsorbés. Le rhénium, élué avec tétrahydrofurane–acide chlorhydrique 9 *M* 70% : 30% (v/v), est dosé spectrophotométriquement sous forme de thiocyanate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur selektiven Abtrennung von μg- und mg-Mengen Rhenium(VII) von Molybdän(VI) und vielen anderen Metallionen mittels des stark basischen Anionenaustauschers Dowex 1-X8. Die Trennung beruht auf der bevorzugten Elution des Molybdäns mit einer Mischung von 90 Vol.% Methanol und 10 Vol.% 6 *M* Salpetersäure. Rhenium und wenige andere Elemente werden zurückgehalten, während Molybdän und die meisten anderen Metallionen einschliesslich Fe(III), Ca, Mg, Mn, U, Cu, V usw. praktisch nicht absorbiert werden. Nach der Elution des absorbierten Rheniums mit einer Mischung aus 70 Vol.% Tetrahydrofuran und 30 Vol.% 9 *M* Salzsäure wird das Rhenium spektrophotometrisch mit einer modifizierten Thiocyanatmethode bestimmt.

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HALBQUANTITATIVE AUTORADIOGRAPHISCHE BESTIMMUNG VON ^{14}C-AKTIVITÄTEN IM PICO- BIS NANOCURIE-BEREICH MIT HILFE DER RINGOFENMETHODE

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Wie bereits früher gezeigt wurde[1,2], lassen sich radioaktive Substanzen mit Hilfe der Ringofenmethode sehr empfindlich und ohne ein spezielles Expositionsgerät halbquantitativ durch Autoradiographie bestimmen. Bei diesem als "Sandwich"-Technik bezeichneten Verfahren (zur Exposition wird jedes Filter mit Probering zwischen *zwei* Filme gepresst) befanden sich die Röntgenfilme in Taschen aus schwarzer Supronyl-Folie (Hersteller: Kalle & Co. AG., Wiesbaden), welche ein Flächengewicht von *ca.* 6.6 mg/cm^2 besitzt.

Wir fanden, dass man auch den schwachen β-Strahler ^{14}C mit angenähert der gleichen Empfindlichkeit wie die bisher untersuchten Isotopen nachweisen und bestimmen kann, wenn man die genannten Kunststofftaschen, welche den grössten Teil der weichen 0.155 MeV-Strahlung (Halbwertsdicke $\approx$ 2.6 mg/cm^2) absorbieren, weglässt. Eine zusätzliche Empfindlichkeitssteigerung erzielten wir durch die Verwendung neuen Filmmaterials: Als sehr geeignet für die ^{14}C-Autoradiographie erwiesen sich die Filmsorten "Royal Blue" (Kodak) und Structurix D 10 *ohne* Schutzschicht (Agfa-Gevaert AG.; vgl. [3]), welche gegenüber dem bisher benutzten ADOX-DONEO-Röntgenfilm (Dr. C. Schleusner GmbH, Frankfurt/Main) etwa um den Faktor 2 bzw. 3 empfindlicher sind.

METHODEN

Lösungen, Geräte und Filtermaterial

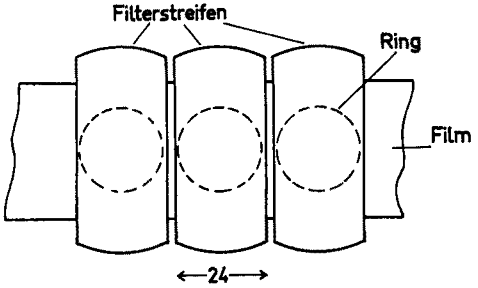
Aliquote Anteile einer wässrigen Lösung von D,L-Phenylalanin-1-^{14}C wurden unter Zusatz von inaktivem D,L-Phenylalanin als Träger auf verschiedene Volumina verdünnt. Es wurden 4 Probelösungen mit je 0.2 mg Träger pro ml und verschiedenen Aktivitätskonzentrationen a_p (in pC/μl) hergestellt. Eine Lösung mit $a_s = 92$ pC/μl diente als Standardlösung.

Zum Auftragen verschiedener Volumina von Probe- und Standardlösung auf die Rundfilter (Macherey, Nagel & Co. MN 2260) wurde eine in μl geeichte Kapillarbürette (Benedetti-Pichler-Bürette; vgl. [2,4]) verwendet. Hierdurch gehen nicht mehr *Tropfenzahlen* sondern *unganzzahlige* μl in die Berechnungen ein.

Die Ringe wurden mit 0.05 *N* Salzsäure auf einem Ringofen der Fa. ROFA, Wien, gewaschen.

Arbeitsweise

Aus 9 verschiedenen Volumina der Standardlösung werden 9 Standardringe und aus 5 verschiedenen Volumina jeder Probelösung 5 Proberinge mit der bereits angegebenen Aktivitätsabstufung[1,2] angefertigt. Zur Exposition werden die zu 24 mm breiten Streifen zurechtgeschnittenen Filter mit den Proberingen (vgl. Fig. 1) auf Röntgenfilme R_u von 5.5×3.4 cm gelegt und zusammen mit diesen durch Blattfedern auf eine ebene Bodenplatte aus Bakelit gepresst (Fig. 2). Man deckt die Filter mit Röntgenfilmen R_o der Grösse 3.6×3.4 cm ab und beschwert jedes "Sandwich" in gleicher Weise mit Bakelit ($3.6 \times 3.4 \times 1$ cm) und Bandeisen ($3.6 \times 3.4 \times 0.8$ cm) (Fig. 2). Die 9 Filter mit den Standardringen legt man entsprechend Fig. 1 auf einer Bakelit-Bodenplatte auf Filmstreifen von 3.6×24 cm, deckt sie mit einem gleich grossen Filmstreifen ab und beschwert das Ganze ebenfalls mit Bakelit ($3.6 \times 24 \times 1$ cm) und Bandeisen ($3.6 \times 24 \times 0.8$ cm). Da man mit unverpacktem Filmmaterial arbeitet, darf man nur die schwächste mögliche Dunkelkammerbeleuchtung benutzen. Dies ist besonders wichtig für den Kodak-Film.



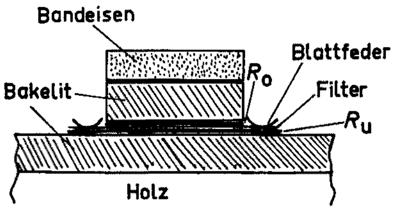


Fig. 1. Exposition der Standardskala.

Fig. 2. Exposition der Probefilme.

Die Exposition erfolgt zur Vermeidung von "Fading"-Effekten in einer Tiefkühltruhe ($\approx -20°$)[1,5]. Die Expositionszeit t_s für die Standardskala beträgt etwa 20 Stunden. Die erforderliche Expositionszeit t_p für die Probeautoradiogramme, die ja so bemessen sein muss, dass wenigstens 3 der 5 Probeschwärzungen in den Bereich der Standardskala fallen[6], lässt sich schon während der laufenden Exposition festlegen, indem man nach einem bestimmten, bereits angegebenen Schema[1,2] nur die oberen Filme R_o von den Proberingen entwickelt und die erzielten Schwärzungen grob abschätzt.

Nach beendeter Exposition werden die Probefilme R_u gemeinsam mit dem Standardfilm entwickelt. (Entwickler: Ilford ID-19, auf das Doppelte verdünnt; Entwicklungszeit bei 20° 5 min.) Die Auswertung erfolgt in der üblichen Weise[1,2] nach

$$\frac{a_p}{a_s} = \frac{\sum z_s \cdot t_s}{\sum z_p \cdot t_p} \quad \text{bzw.} \quad a_p = \frac{\sum z_s \cdot t_s}{\sum z_p \cdot t_p} \cdot a_s$$

$\sum z_s$ ($\sum z_p$) = Summe der μl-Zahlen derjenigen Standardringe (Proberinge), deren Autoradiogramme zur Berechnung herangezogen werden.

Es ist ohne weiteres möglich, mehrere Proben gleichzeitig mit einer einzigen

Standardskala zu exponieren. Die latenten Autoradiogramme der stärkeren Proben und die latente Standardskala können nämlich ohne merkliches "Fading" bis zum Entwickeln so lange in der Tiefkühltruhe aufbewahrt werden, bis die Exposition der schwächsten Probe beendet ist.

Die ^{14}C-Autoradiogramme zeigen extrem scharfe Abbildungen der Ringe, wie sie bei Isotopen mit hohen β-Energien nicht erreicht werden können.

ERGEBNISSE UND DISKUSSION

Nach dem geschilderten Verfahren wurden die Aktivitätskonzentrationen a_p von 4 Phenylalanin-1-^{14}C-Lösungen halbquantitativ bestimmt, und zwar durch Autoradiographie auf "Royal Blue"-Filmen und auf Structurix D 10-Filmen *ohne* Schutzschicht. Die Auswertung der Autoradiogramme durch verschiedene Personen (A, B, C) ergab beispielsweise die in Tabelle I (Kodak "Royal Blue") aufgeführten Ergebnisse.

TABELLE I

AUTORADIOGRAPHIE AUF "ROYAL BLUE" (KODAK)

Person	t_s *(h)*	t_p *(h)*	a_s *(pC/µl)*	a_p *(pC/µl)*	
				Sollwert	*Gefunden*
A	19.83	2.08	92	460	515
	19.83	20.0	92	92	93
	19.83	50.75	92	18.4	20.0
	19.83	121.92	92	9.2	9.4
B	19.83	2.08	92	460	445
	19.83	20.0	92	92	90
	19.83	50.75	92	18.4	18.9
	19.83	121.92	92	9.2	8.8
C	19.83	2.08	92	460	435
	19.83	20.0	92	92	84
	19.83	50.75	92	18.4	19.8
	19.83	121.92	92	9.2	9.0

Ähnliche Ergebnisse erhielten wir auch mit dem Structurix D 10-Film.

Wenn man bedenkt, wie gering die verwendeten ^{14}C-Aktivitäten sind—der stärkste Probering enthielt 9.22 nC (20.05 µl einer Lösung mit 460 pC/µl), der schwächste jedoch nur 11 pC (1.2 µl einer Lösung mit 9.2 pC/µl)—und mit welch einfachen experimentellen Mitteln sie bestimmt werden, dann können die Resultate durchaus als zufriedenstellend bezeichnet werden.

Besonders wichtig für die Reproduzierbarkeit des Verfahrens sind wegen der geringen Reichweite der ^{14}C-β-Strahlung der gleichmässige Auflagedruck bei Proberingen und Standardringen sowie die Verteilung der ^{14}C-markierten Substanz (im Ring) über den Querschnitt des Filterpapiers. Die verwendeten Rundfilter (MN 2260) besitzen ein relativ hohes Flächengewicht von *ca.* 9 mg/cm^2. Trotzdem werden die Filme R_o und R_u von jedem "Sandwich" ausreichend geschwärzt, und zwar beide annähernd im gleichen Ausmasse. Dies spricht—wenigstens bei den hier verwendeten Trägerkonzentrationen—für eine ziemlich gleichmässige Verteilung der markierten

Substanz über den Querschnitt des Filters. Für den empfindlichen autoradiographischen Nachweis tritiummarkierter Verbindungen ist das benutzte Filtermaterial zu dick. Hier kann nur derjenige Bruchteil der gesamten im Ring vorhandenen Substanzmenge photochemisch wirksam werden, der sich unmittelbar an der Oberfläche des Papiers befindet. Unter Umständen lässt sich diese Schwierigkeit dadurch umgehen, dass man, wie OTTENDORFER[7] vorgeschlagen hat, auf dünnen Schichten arbeitet.

Wir danken der Kodak AG., Stuttgart und der Agfa-Gevaert AG., Leverkusen für die Überlassung des Filmmaterials.

ZUSAMMENFASSUNG

Es wird die Anwendung der Ringofenmethode auf die halbquantitative autoradiographische Bestimmung von ^{14}C-markierten Verbindungen beschrieben. Im Aktivitätsbereich 460 pC/μl bis 9.2 pC/μl (Expositionszeiten von 2 Stunden bis 122 Stunden) wurden mit den Röntgenfilmen "Royal Blue" (Kodak) und Structurix D 10 *ohne* Schutzschicht (Agfa-Gevaert) befriedigende Ergebnisse erhalten.

SUMMARY

The use of the ring-oven method for the semiquantitative autoradiographic determination of ^{14}C-labelled compounds is described. Satisfactory results can be obtained in the activity range 9.2–460 pC/μl (exposure times of 122–2 h) with special commercial films.

RÉSUMÉ

On décrit une méthode à l'aide du four circulaire pour le dosage semiquantitatif autoradiographique des composés marqués ^{14}C. On obtient des résultats satisfaisants pour des activités de 9.2 à 460 pC/μl (temps d'exposition 122–2 h) avec un film commercial spécial.

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MICRODETERMINATION OF COPPER USING DITHIOOXAMIDE CRAYONS AND THE RING-OVEN TECHNIQUE

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The increasing interest in the problem of community and occupational air pollution has emphasized the need for sensitive, reliable and simple methods for the detection and determination of various pollutants. The present work has been carried out with the view of developing a rapid method for the microdetermination of copper in air pollution investigations.

The combination of the ring-oven technique and the spectrophotometric procedure for the determination of copper with dithiooxamide[1] seemed particularly attractive. In the procedure which was evolved, a novel way of applying the reagent is proposed whereby an alcoholic solution of the reagent is replaced by a crayon in which the dithiooxamide is incorporated in a solid supporting medium. This form of reagent proved to be just as satisfactory as the solution form and provided reproducible and reliable results. The reagent crayons have the advantage of superior stability and convenience.

EXPERIMENTAL

Reagents and stock solutions

Dithiooxamide crayon. A mixture of 3.5 g of monoglyceryl stearate and 1.5 g of paraffin wax in a test tube is placed in a water bath maintained at 90°. Next, 0.025 g of dithiooxamide (Eastman), previously dissolved in 4 drops of dimethylsulfoxide (Baker), is added. After homogenizing the mixture, the melt is drawn into a paper straw and allowed to cool. In reagent use, the crayon is prepared for application by simply peeling off the paper as required and rubbing the exposed reagent against the ring or spot to be tested for copper.

Malonic acid solution. A 5% solution of malonic acid was treated by dropwise addition of 20% sodium hydroxide until a pH of 4.0 was obtained.

Standard stock copper solution. A solution containing 1.00 mg of copper per ml was prepared by dissolving 0.100 g of pure copper in nitric acid, the excess acid being eliminated by evaporating the solution to dryness, and making up to 100 ml with distilled water. This solution was diluted as necessary for preparing standard working solutions.

Distilled water. All water used was twice distilled, the second distillation being carried out in an all-glass apparatus.

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Apparatus

Weisz ring-oven with accessories (National Appliance Company).

Surface thermometer (Pacific Transducer Corporation, Model 311 F).

J. H. Munktells filter paper No. 00, 5.5 mm diameter, or Whatman No. 41. The filter paper used should always be checked to be sure it does not contain traces of copper.

Recommended procedure

Place a filter paper, the center of which has been previously marked with a pencil dot, on a ring-oven maintained at 90–95°. Add a 10-μl portion of malonic acid, followed by the appropriate volume of the standard or unknown copper solution. Care should always be taken to avoid any diffusion of solutions beyond 1 mm from the heating block. Add 10 μl of malonic acid followed by 6 10-μl portions of 0.05 *N* hydrochloric acid. After the transfer to the ring zone has been completed and the paper is almost dry, remove it from the ring-oven and allow to dry in a stream of cool air (overdrying should be avoided). Rub the ring zone with the dithiooxamide crayon and expose to water vapor (70–80°) for a few seconds so as to melt the wax and so provide for intimate contact of the reagent with the sample.

Next dip the filter paper in chloroform for 5 min, dry in a stream of cool air and dip again in distilled water for 3 min. Then press between 2 filter papers and dry in a stream of cool air. The color intensity of the rings is stable for at least a month.

Analysis of an unknown

A standard scale is prepared following the above procedure, by making rings with 5-, 10-, 20-, 30- and 40-μl portions of a solution containing 0.01 μg of copper per μl. Three rings made from different numbers of microliter portions of the sample solution are sufficient for each unknown. The concentration of the unknown solution is given by the ratio of the sum of microliter portions of the ring made from the unknown solution with reference to the standard scale[2].

For sampling, the usual methods of dust collection are applicable such as the use of dust tapes, electrostatic precipitation, membrane filters, etc. When the copper particulates are soluble in water or dilute nitric acid no previous treatment is needed, and the tests can be run directly on dust tapes or on extracts obtained by conventional methods. For insoluble particulates the usual methods of collection can be used, but the solubilization will depend on the nature of the particulates.

Where sequential tape samplers are used an instrument having an orifice of less than 22 mm should be selected so that the total sample can be centered on the ring-oven without the spot extending to the ring area. Once the sample spot is properly positioned the copper can be dissolved by cautious treatment with dilute nitric acid and the dissolved salts washed to the ring zone and the copper estimated as described above. Because only one ring is obtained for the sample unknown, the statistical evaluation is not applied and the accuracy of the determination will be less than that reported in Table I.

RESULTS AND DISCUSSIONS

Munktells No. 00 filter paper was selected because of its purity and good diffusion properties. Whatman No. 41 is also suitable and tests can be run directly using Whatman dust tapes.

The mixture of monoglyceryl stearate and paraffin wax provided the necessary hardness for the reagent crayon. Dimethylsulfoxide was used to ensure the solubility and homogeneity of dithiooxamide in the body of the crayon.

Malonic acid was chosen as a masking agent because of its capacity to prevent other ions from reacting with dithiooxamide while not affecting the copper reaction. The pH of malonic acid solution was adjusted to 4 in order to maintain the sensitivity of the copper reaction and yet permit the masking of other cations that might otherwise interfere.

It was found that melting the wax in the vapors of a water bath kept at 70–80° gave the best results. Overheating increases the reactivity of the reagent and consequently enhances the possibility of interferences.

To prevent the reaction between interfering ions and excess of reagent, the latter was removed by bathing the filter paper in chloroform. Various solvents were tried but chloroform seemed to give the most satisfactory results. The final dip (water bath) removes colored ions which might otherwise interfere.

Interferences

The effect of interfering ions was investigated by preparing 2 rings for each ion. The first ring contained 10 μg of the potential interfering ion and the second, 0.1 μg of copper in the presence of 10 μg of the interfering ion. The ion was established as non-interfering when the first ring was identical to the blank and the second matched with the 0.1-μg copper ring of the standard scale.

The possible interfering effects of the following ions were investigated.

Group I. Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+ and Au^{3+}.

Group II. Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg_2^{2+} and Hg^{2+}.

Group III. BO_2^-, Al^{3+}, Ga^{3+}, Ce^{3+} and Tl^+.

Group IV. CO_3^{2-}, Ac^-, $HC_2O_4^-$, $Tart^{2-}$, SiO_3^{2-}, Ti^{4+}, GeO_3^{2-}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Pb^{2+} and Th^{4+}.

Group V. NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}, VO^{2+}, VO_3^-, $HAsO_3^{2-}$, $HAsO_4^{2-}$, Sb^{3+}, Sb^{5+} and Bi^{3+}.

Group VI. S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, TeO_4^{2-}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-} and UO_2^{2+}.

Group VII. F^-, Cl^-, ClO_3^-, ClO_4^-, Mn^{2+}, MnO_4^-, ReO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^-, NCS^- and $[Fe(CN)_6]^{4-}$.

Group VIII. Fe^{3+}, Co^{2+}, Ni^{2+}, Ru^{3+}, Rh^{3+}, Pd^{2+} and Pt^{4+}.

Ten-microgram amounts of Ni^{2+}, SeO_3^{2-} and SeO_4^{2-} interfered by reacting with dithiooxamide. When the concentration of these ions was decreased to 5 μg, no interference was observed.

Interferences were observed, however, from Hg_2^{2+}, Hg^{2+}, Au^{3+}, Ag^+, Pt^{4+}, Pd^{2+}, Rh^{3+}, $HC_2O_4^-$, IO_3^-, $S_2O_3^{2-}$, and $[Fe(CN)_6]^{4-}$. These are of no practical significance in air pollution studies.

Quantitative estimation

The accuracy and reproducibility of the method for the microdetermination of copper were ascertained by the procedure of WEISZ[2]. A standard scale and 3 rings using suitable portions of unknown were prepared as given in the recommended procedure. The rings were matched and the unknown concentration was established from the ratio of the sum of microliter portions of 3 rings matching rings of the standard scale to the sum of microliter portions of matching rings prepared from the unknown solution. Results are shown in Table I.

TABLE I

DETERMINATION OF COPPER

Taken	*Found*[a]
0.200	0.197±0.013[b]
0.300	0.296±0.015

[a] Based on averaging 5 values calculated from 3 rings, each by the method of WEISZ[2].
[b] Calculated at 90% confidence level.

The limit of detection for copper by the recommended procedure is 0.04 μg. The range 0.1 to 0.5 μg is, however, recommended for optimum accuracy for quantitative determinations.

This investigation was supported in whole by Public Health Service Research Grant AP 00117 from the Division of Air Pollution, Bureau of State Services.

SUMMARY

A method for the microdetermination of copper in air pollution investigations, using a dithiooxamide crayon and the ring-oven technique is presented. The limit of detection for the method is 0.04 μg, and the quantitative determination is applicable in the range of 0.05 to 0.5 μg of copper. The method is free from interferences that might be of significance in the study of air samples.

RÉSUMÉ

Une méthode est proposée pour le microdosage du cuivre, à l'aide de dithioxamide et de la technique du four circulaire, lors de recherches sur la pollution de l'air. La limite de détection est de 0.04 μg. Il est possible de doser ainsi de 0.05 à 0.5 μg de cuivre. Ce procédé est exempt d'interférences; ce qui est important pour l'examen d'échantillons d'air.

ZUSAMMENFASSUNG

Es wird eine Methode angegeben zur Mikrobestimmung von Kupfer in Luftverunreinigungen unter Verwendung von Dithiooxamid und der Ringofentechnik.

Die Nachweisgrenze dieser Methode beträgt 0.04 µg; die quantitative Bestimmung ist im Bereich von 0.05–0.5 µg Cu anwendbar. Die Methode ist frei von Störungen, welche bei der Untersuchung von Luftproben von Bedeutung sein könnten.

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SIMULTANEOUS DETERMINATION OF TRACE CONCENTRATIONS OF SATURATED AND α,β-UNSATURATED CARBONYL COMPOUNDS IN ORGANIC SYSTEMS

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Few of the numerous methods for determining carbonyl compounds as 2,4-dinitrophenylhydrazones are applicable for low concentrations. Almost without exception these procedures neglect and/or disregard the possible presence of α,β-unsaturated carbonyl compounds in the systems studied.

LAPPIN AND CLARK[1] showed that a strongly alkaline alcoholic solution of 2,4-dinitrophenylhydrazone produced an intense wine-red color due to the possible formation of a resonating quinoidal ion. They extended this to a quantitative method for carbonyl in ketosteroids and observed that extraction of excess 2,4-dinitrophenylhydrazine was unnecessary as long as a reagent reference blank was used. JONES *et al.*[2,3] studied the absorption characteristics and other physicochemical relationships of several classes and types of carbonyl and dicarbonyl 2,4-dinitrophenylhydrazones in neutral chloroform and ethanolic sodium hydroxide solutions. In every case they observed a significantly larger molar absorptivity and bathochromic shift to a longer wavelength for maximum absorption of α,β-unsaturated carbonyl compounds compared to similar saturated carbonyl compounds. This was associated with conjugation, resonance and configurational structures of the 2,4-dinitrophenylhydrazones, as well as aromatic substitution and substituent substitution on the aromatic nucleus. LOHMAN[4] extracted 2,4-dinitrophenylhydrazones from an acid solution into hexane and observed a significant difference between saturated and α,β-unsaturated carbonyl-2,4-dinitrophenylhydrazone molar absorptivity.

MARTIN, SCHEPARTZ AND DAUBERT[5] and KAWAHARA AND DUTTON[6] isolated reversion compounds from soybean oil and identified one of them as 2-heptenal. They separated it as the 2,4-dinitrophenylhydrazone on a chromatographic column containing absorbent talc and Supercel, recrystallized and identified it by well-known techniques. Later[7], reversion compounds were tested for the presence of α,β-unsaturation using a modified colorimetric *m*-phenylenediamine dihydrochloride procedure[8]. The method is unsuitable for mixed carbonyl systems.

HENICK, BENCA AND MITCHELL[9] described a method for the simultaneous determination of saturated and α,β-unsaturated carbonyl compounds. The procedure is based on the formation of 2,4-dinitrophenylhydrazones in benzene solution, trichloroacetic acid catalyst, and the spectrophotometric determination in alkaline solutions. The mixed types of carbonyls are determined from absorbances at 430 and 460 nm. Work in this laboratory shows trichloroacetic acid to be a poor catalyst but acceptable under carefully controlled conditions.

Previously described work[10] presents an extension of the LAPPIN AND CLARK procedure which includes a general solvent system and solubilization of the inorganic chloride formed by the addition of alcoholic alkali. The present work describes an extension of the work whereby saturated and α,β-unsaturated carbonyl compounds are determined simultaneously at 480 and 426 nm as the alkaline hydrazones.

The absorbance decrease with time for α,β-unsaturated carbonyl compounds is slow and quite similar to that for aliphatic saturated ketones. The shift in absorbance maximum for α,β-unsaturated compounds is significant and from 430 to 450 nm for the pure compounds. The systems for which this method has been used include alcohols, ethers, esters, petroleum distillates, kerosene, organic acids, hydrocarbons, cyclic ethers, simple aromatics and mixtures of these.

EXPERIMENTAL

Apparatus and reagents

Absorbance measurements were made with a Beckman DB spectrophotometer using 1-cm matched silica cells and a suitable recorder.

Carbonyl-free Formula 30 alcohol (95% ethanol, 5% methanol). 2,4-Dinitrophenylhydrazine (2 g) and 5 ml of concentrated hydrochloric acid were added to 5 l of alcohol and the mixture refluxed for 1 h. The alcohol was distilled from an all-glass distillation column.

n-Hexane (95 mole % minimum) purified as described for Formula 30 alcohol except it was refluxed a minimum of 12 h.

2,4-Dinitrophenylhydrazine (Eastman Kodak No. 284 or Matheson, Coleman and Bell No. 2385). Saturated solution in carbonyl-free Formula 30 alcohol.

2-Ethyl-2-hexenal (K and K Laboratories, Jamaica, N.Y.). Purified to 99.3% by GLC fractionation using Wilkens Instrument Co. "Autoprep" equipped with a 3/8" × 7' Carbowax GLC column.

Solution I. 3:7 carbonyl-free *n*-hexane–Formula 30 alcohol.

Preparation of calibration curves

Prepare separate appropriate standard solutions of *n*-heptaldehyde and 2-ethyl-2-hexenal. *n*-Heptaldehyde standards should contain 0.40–2.00 μg carbonyl (as C=O) per ml, and the 2-ethyl-2-hexenal standards should contain 0.20–1.00 μg carbonyl per ml in solution I. Pipette a 5-ml aliquot of each standard solution into separate 25-ml graduated mixing cylinders. Add 0.1 ml of concentrated hydrochloric acid and 2 ml of saturated 2,4-dinitrophenylhydrazine solution to each mixing cylinder. Prepare a reference blank in the same manner using a 5-ml aliquot of solution I but no sample. Heat at $55 \pm 1°$ for 30 min in a water bath. Cool to room temperature and dilute to volume with a solution containing 59 g of potassium hydroxide and 180 ml of water, diluted to 1 l with carbonyl-free Formula 30 alcohol. Mix well and read the absorbance of each solution against the reagent reference using 1-cm matched cells on an appropriate double beam spectrophotometer at 480 and 426 nm between 8 and 15 min after diluting to volume. Plot absorbance *vs.* concentration at 480 and 426 nm for both *n*-heptaldehyde and 2-ethyl-2-hexenal (Fig. 1). The two 2-ethyl-2-hexenal curves are used only for calculating calibration factors. The *n*-heptaldehyde curves are used for calibration factors and are the working curves.

Recommended procedure

Weigh an appropriate size sample into a graduated 25-ml mixing cylinder. Add 5 ml of solution I, 2 ml of saturated 2,4-dinitrophenylhydrazine solution and 0.1 ml of concentrated hydrochloric acid to each flask. Prepare a reagent reference exactly the same way but without sample. Proceed as outlined in *Preparation of calibration curves* obtaining the absorbances at 480 and 426 nm. Obtain apparent μg C=O/ml at 480 and 426 nm from the 2 *n*-heptaldehyde calibration curves.

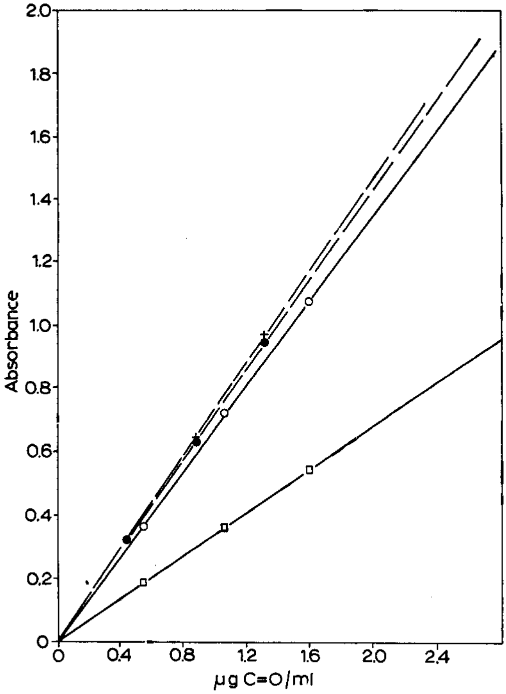

Fig. 1. Calibration curves for standard saturated and α,β-unsaturated carbonyl compounds. □, ○, *n*-heptaldehyde; ●, +, 2-ethyl-2-hexenal at 480 and 426 nm, respectively.

Calculations

All calculations are based on carbonyl concentrations as C=O (28 g/mole) using only the *n*-heptaldehyde standard curves (Fig. 1). Calibration factors calculated from *n*-heptaldehyde and 2-ethyl-2-hexenal curves are used to relate relative molar response of saturated and α,β-unsaturated carbonyl as C=O at the 2 wavelengths and are shown below.

Calibration factors (Δ). Determine the molar absorptivity ε as C=O from the calibration curves for saturated and α,β-unsaturated carbonyls at 480 and 426 nm. Various saturated, α,β-unsaturated, mixed standard as well as recovery of added carbonyls have been analyzed. In every case, the calibration factors have remained consistent and constant. The absolute values will, however, vary from instrument to instrument.

Then

$$\Delta_{480} = \frac{\varepsilon_{480}\ \text{2-ethyl-2-hexenal as C=O}}{\varepsilon_{480}\ n\text{-heptaldehyde as C=O}} \tag{1}$$

$$\Delta_{426} = \frac{\varepsilon_{426}\ \text{2-ethyl-2-hexenal as C=O}}{\varepsilon_{426}\ n\text{-heptaldehyde as C=O}} \tag{2}$$

Calculation of data.

Δ_λ = Calibration factor constant at a given wavelength.

Γ = Apparent total carbonyl as C=O (28 g/mole) based on the standard *n*-heptaldehyde curve at 480 nm.

Θ = Apparent total carbonyl as C=O (28 g/mole) based on the standard *n*-heptaldehyde curve at 426 nm.

Ω = Actual concentration (as μg C=O/ml) of saturated carbonyl.

Ψ = Actual concentration (as μg C=O/ml) of α,β-unsaturated carbonyl.

Thus

$$\Gamma = \Omega + \Delta_{480}\,[\Psi] \tag{3}$$

$$\Theta = \Omega + \Delta_{426}\,[\Psi] \tag{4}$$

Subtracting eqn. (4) from eqn. (3)

$$\frac{\Gamma - \Theta}{\Delta_{480} - \Delta_{426}} = \Psi \tag{5}$$

$$\Gamma - \Delta_{480}\,[\Psi] = \Omega \tag{6}$$

and

$$\frac{[\Psi]\,[10^6]}{\text{g sample/ml dilution}} = \mu\text{g/g } \alpha,\beta\text{-unsaturated carbonyl as C=O} \tag{7}$$

$$\frac{[\Omega]\,[10^6]}{\text{g sample/ml dilution}} = \mu\text{g/g saturated carbonyl as C=O} \tag{8}$$

RESULTS AND DISCUSSION

Table I shows the recovery of known amounts of pure α,β-unsaturated carbonyl compounds by the proposed procedure. Different concentrations of each

TABLE I

RECOVERY OF α,β-UNSATURATED CARBONYL COMPOUNDS BY THE PROPOSED PROCEDURE

Sample	*No. of detns.*	*Microgram C=O*				*% Relative standard deviation*
		Added	*Recovered*			
			Range	*Avg.*	*%*	
2-Ethyl-2-hexenal	8	33.0	31.5–33.5	32.4	98.2	±2.6
	5	22.0	21.6–22.1	21.9	99.5	±0.7
	5	44.0	43.7–45.1	44.9	102.0	±1.8
	7	11.0	10.6–11.9	11.2	101.8	±4.1
2-Octyl-2-dodecenal	4	11.6	12.6–13.4	13.0	112.1	±2.9
	6	23.2	25.6–26.8	26.0	112.1	±1.1
	6	34.9	39.2–40.9	39.9	113.8	±3.0
Acetophenone	5	24.4	26.0–26.4	26.2	107.4	±0.6

carbonyl were determined to test the validity of the procedure for α,β-unsaturated carbonyl recovery. Results for 2-octyl-2-dodecanol are high but consistent for the 3 different concentrations. Attempts to purify 2-octyl-2-dodecenal by GLC fractionation resulted in degradation products. Acetophenone was used from the shelf without purification. Recovery of 2-ethyl-2-hexenal at 4 different concentrations is excellent and ranged from 98.2 to 102.0% with a percent relative standard deviation from 0.7 to 4.1.

Table II shows the results obtained by the simultaneous determination of various mixtures of pure *n*-heptanal and 2-ethyl-2-hexenal in solution I.

TABLE II

SIMULTANEOUS DETERMINATION[a] OF MIXTURES OF PURE *n*-HEPTALDEHYDE AND 2-ETHYL-2-HEXENAL

Sample	*μg C=O* n-*heptanal*			*μg C=O as 2-ethyl-2-hexenal*			*% Saturated*
	Added	*Recovered*	*%*	*Added*	*Recovered*	*%*	
1	32.0	31.7	99.1	0	0	0	100
2	40.5	41.1	101.5	11.0	11.0	100	79
3	26.8	25.2	94.0	11.0	11.0	100	71
4	13.4	13.9	103.7	11.0	11.0	100	55
5	13.4	13.6	101.5	33.0	32	97.0	29
6	5.4	6.2	114.8	22	21	95.4	20
7	0	0	0	28	28.2	100.7	0

[a] Each result is the average of 2 or more determinations.

Recovery of the known amounts of carbonyl ranges from 94 to 114.8% for all samples. These samples range from pure saturated to pure α,β-unsaturated carbonyl with the mixtures ranging from 20 to 79% *n*-heptaldehyde. The recovery of 2-ethyl-2-hexenal is generally somewhat more consistent than that of *n*-heptanal. This is the expected trend, since the difference in absorbance at 480 and 426 nm is due to the unsaturated carbonyl while the saturated carbonyl is calculated from the observed concentration at 480 nm using their difference. Any error in the difference of absorbance will be increased twofold in the calculation at 480 nm. This is specifically shown in Table II, sample 6, where the absorbance shows only 95.4% recovery of 2-ethyl-2-hexenal, while for *n*-heptanal the recovery is abnormally high. Recovery of 2-heptanal in sample 3 is quite low. The probable reason is a greater than desirable time elapsed before the absorbance was determined, resulting in decreased color for *n*-heptanal, but not for 2-ethyl-2-hexenal. α,β-Unsaturated alkaline hydrazones have much greater stability than saturated aldehydic alkaline hydrazones[10], due to greater electron delocalization.

Recovery of known amounts of α,β-unsaturated carbonyl compounds from simple solvent systems and simultaneous determination of them and saturated carbonyl 2-component mixtures is relatively easy. However, the adequacy of a procedure is more accurately described when added and recovered data are obtained from complex systems already containing a multitude of trace impurities including both types of carbonyl. Table III describes recovery of α,β-unsaturated molecules. In addition to the carbonyl impurity present, different concentrations of 2-ethyl-2-hexenal and/or 2-octyl-2-dodecenal were added and recovered from each one. In every case the

TABLE III

RECOVERY OF 2-ETHYL-2-HEXENAL AND 2-OCTYL-2-DODECENAL[a] FROM CRUDE ALCOHOLS

A, B, C are complex distillation residues having approximate composition of 50–70% alcohols, 20–25% hydrocarbons and olefins, 10–15% esters, acids, ethers and carbonyls all ranging from C_{20} to C_{40} as identified by GLC, silica gel, and alumina chromatography.

Sample	No. of replicate detns.	*Microgram C=O*				*Microgram C=O/g sample*						
		Added	*Recovered*			*Saturated*		*α,β-Unsaturated*		*Total*	*% Rel. std. dev.*	
			Range	*Avg.*	*% Rel. std. dev.*	*Range*	*Avg.*	*Range*	*Avg.*		*Sat.*	*α,β-Unsat.*
A	6	0	—	—	—	606–645	620	70–81	75	695	1.6	3.9
A + 2-ethyl-2-hexenal	5	11	9.4–10.8	10.2	3.0							
A + 2-octyl-2-dodecenal	4	33	31.9–33.5	32.4								
B	6	0	0	0	0	447–499	470	47–48	47	518	2.3	1.0
B + 2-ethyl-2-hexenal	4	22	21.6–22.1	21.9	0.7							
B + 2-octyl-2-dodecenal	4	23.2	26.8–28.5	27.7	3.1							
C	4	0	0	0	0	980–1054	1002	740–853	782	1812	2.0	3.6
C + 2-ethyl-2-hexenal	4	11	9.6–10.9	10.6	1.3							
C + 2-octyl-2-dodecenal	3	11.6	13.0–13.4	13.2	0.6							

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[a] Approximately 90% 2-octyl-2-dodecenal by GLC and infrared techniques.

recovery is excellent and compares extremely well with the results for the pure 2-component system (Table II). The percent relative standard deviation for both the mixtures and the carbonyl compounds added to and recovered from them is excellent, indicating that the amount of saturated and α,β-unsaturated carbonyl already present whether large or small had little or no effect on the recovery of added carbonyl by the described procedure.

The results obtained for a variety of samples analyzed in this laboratory are described in Table IV.

TABLE IV

TYPICAL SAMPLES

	μg C=O/g sample[a]		
	Saturated	*α,β-Unsaturated*	*Total*
Alcohols			
Hexanol	42	0	42
Octanol	73	0	73
Decanol	77	0	77
Dodecanol A	107	0	107
Dodecanol B	212	0	212
Tetradecanol	193	2	195
Eicosanol	1000	414	1414
Hydrocarbons			
Octene 1	17	6	23
Hexadecane	32	7	39
Tetracontane	443	227	670
Octane 1	2	0	2
Kerosene 1	7	3	10
Kerosene 2	6	2	8
Kerosene 3	5	0	5
Miscellaneous			
Complex mixture D	983	809	1792
Complex mixture E	1600	1722	3322
Complex mixture F	523	662	1185
Thermal coker gas Residue 4[b]	2260	597	2857
Thermal coker gas Residue 5[b]	1963	2620	4583
n-Heptanoic acid	104	10	114
Dotricontanoic acid	732	119	851
Hexadecyl-octadecanoate	387	61	448

[a] Each result is the average of 2 or more determinations.
[b] Composition similar to that described for A, B, C in Table III.

The samples cover a wide range of types, molecular weight and a very wide range of carbonyl concentration. Our earlier work demonstrated that common oxygenated compounds, such as esters, acids, ethers, paraffins, etc., interfered with the carbonyl determination neither at 480 nm nor at 426 nm. Kerosene samples 1 and 2 contained approximately 15% while kerosene number 3 contains less than 0.02% of aromatics which also show no interference. In addition to lack of interferences the wide range of applicability of the method is shown by the extremely low and high levels of carbonyl impurity in the kerosene and thermal coker gas samples. Investigation of selected acids, esters and thermal coker gas residue samples also showed no interference in the determination of carbonyl compounds.

Jones *et al.*[2,3] observed that the presence of aromatic and aromatic ring-substituted carbonyl compounds shifted the wavelength for maximum absorption to a higher value. They used only a solvent reference in measuring the absorbance of previously prepared pure 2,4-dinitrophenylhydrazones, and a large shift was not unexpected. Recent work[10] utilizing a reagent reference shows the same trend for α,β-unsaturated carbonyl but not for simple aromatic carbonyl compounds. All pure α,β-unsaturated compounds, except benzophenone, exhibited a characteristic shift from 430 to 450 nm for maximum absorption. Figure 1 shows the absorbance, each at 480 and 426 nm, of known concentrations of *n*-heptaldehyde and 2-ethyl-2-hexenal, used for calibration factors and working curves. The curves represent reactions at $55 \pm 1°$ with the absorbance determined at 10 min after formation of the alkaline 2,4-dinitrophenylhydrazone. The decrease in color intensity is linear with time but significant only for saturated aliphatic aldehydes (Fig. 3). Absorbance values determined later than 15 min after the formation of the hydrazone will be significantly in error for saturated aliphatic aldehydes but not ketones or α,β-unsaturated carbonyl compounds[10].

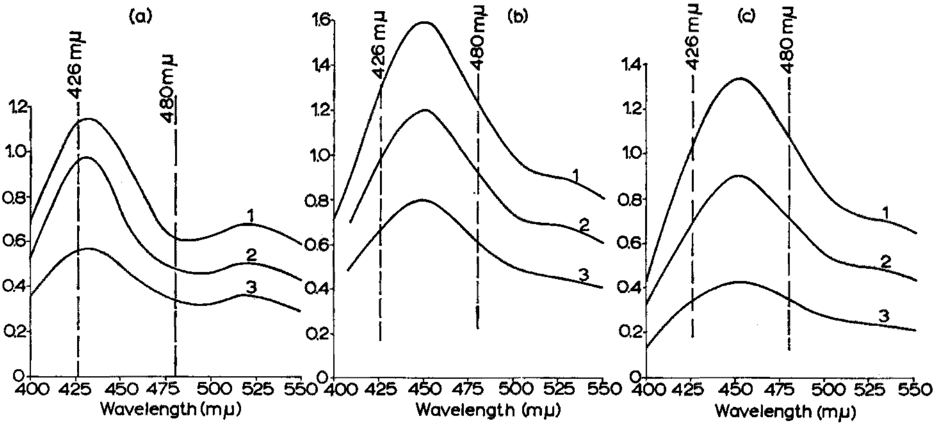

Fig. 2. Spectra of (a) 0.533, 1.066, 1.600; (b) 0.86, 1.29, 1.72; (c) 0.50, 1.0, 1.5 μg C=O/ml of standard *n*-heptaldehyde, 2-ethyl-2-hexenal, and 2-octyl-2-dodecenal respectively obtained 10 min after addition of alcoholic potassium hydroxide solution.

Figure 2 shows comparative absorption spectra at different concentrations for the 2,4-dinitrophenylhydrazones of saturated and α,β-unsaturated aldehydes. Linearity with changing sensitivity is observed between 400 and 500 nm. Parts a and b each represent heptaldehyde and 2-ethyl-2-hexenal, respectively, while part c represents 2-octyl-2-dodecenal. All spectra were obtained 10 min after the formation of the hydrazone; parts a and b were used to develop the standard linear curves shown in Fig. 1. Spectra in part a have the characteristic shape of typical α,β-unsaturated carbonyls having a minimum near 510 nm and primary and secondary maxima at 450 and near 525 nm. Although qualitatively the observed shape of a carbonyl-2,4-dinitrophenylhydrazone spectrum serves as a guide to the presence of

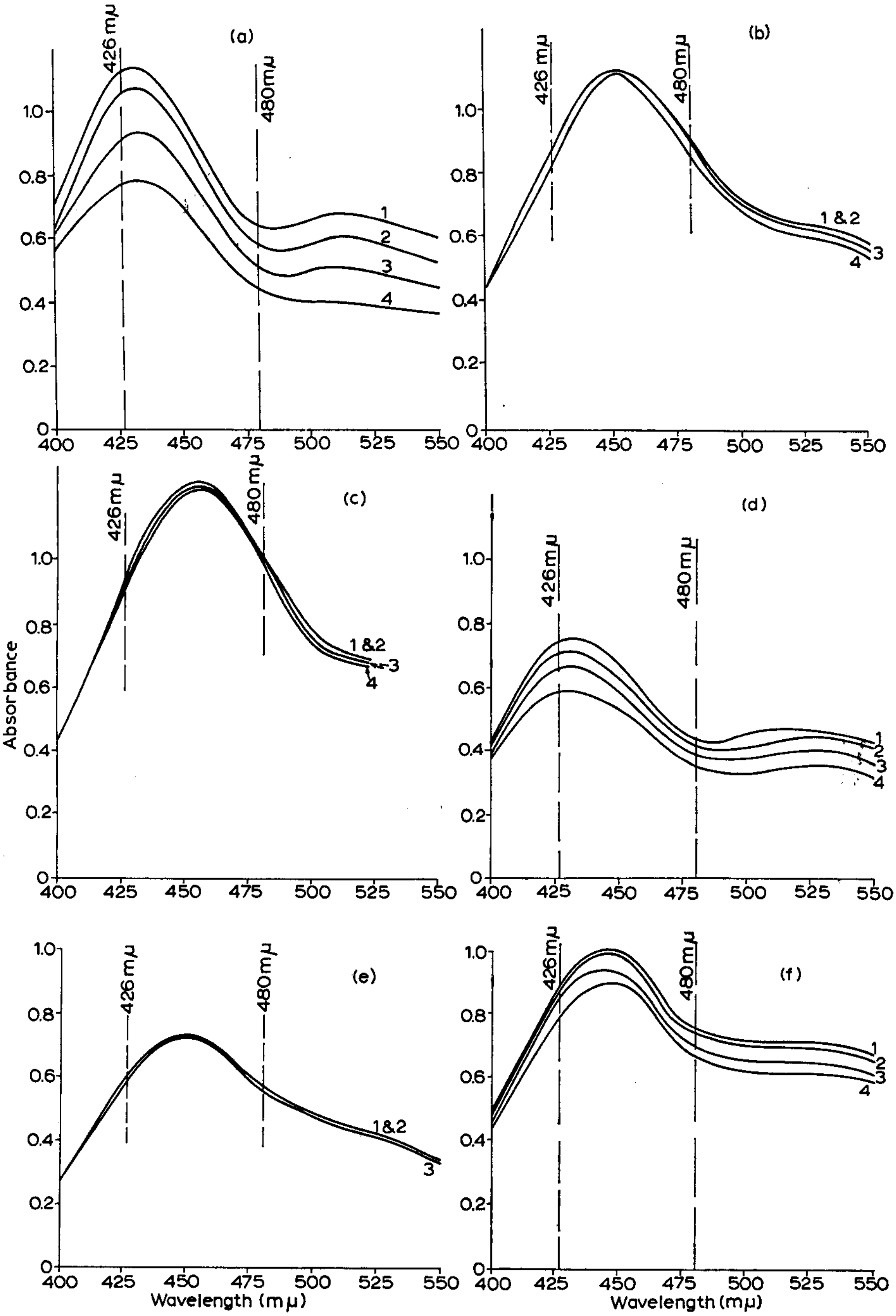

Fig. 3. Spectra obtained on (a) *n*-heptaldehyde, (b) 2-ethyl-2-hexenal, (c) 2-octyl-2-dodecenal, (d) octanol–decanol mixture, (e) hydrolyzed acrolein diethyl acetal, and (f) complex organic mixture. Curves 1, 2, 3 and 4 represent spectra obtained 10, 15, 60 and 120 min after addition of base.

saturated and α,β-unsaturated carbonyl compounds in a system, it is nearly as simple to differentiate and determine them quantitatively.

Spectra in Fig. 3, parts a, b and c, represent the color stability with respect to time for alkaline 2,4-dinitrophenylhydrazones of *n*-heptaldehyde, 2-ethyl-2-hexenal and 2-octyl-2-dodecenal in mono-component systems. The color stability of α,β-unsaturated carbonyl compounds is much greater than for saturated aliphatic aldehydes, comparing quite closely with the stability, but not the shape, of aliphatic ketones. It was previously reported[2,3] that aldehydes and ketones could be qualitatively identified by the disappearance of the secondary maximum near 525 nm for saturated aliphatic aldehydes as shown by curves 1, 2, 3 and 4 of part a. However, neither α,β-unsaturated, nor aliphatic ketone carbonyl compounds in general show the disappearance of the secondary maximum. Thus, the presence of low concentration of either type of carbonyl in the presence of saturated aliphatic aldehydes by visual observation would require additional information.

Parts d, e and f of Fig. 3, show spectra of typical saturated, α,β-unsaturated and mixtures of these carbonyl compounds. Part d represents an octanol–decanol mixture showing the typical saturated carbonyl spectrum with maximum absorption at 430 nm, the gradual disappearance of the secondary maximum near 525 nm, and the typical decrease in color stability with time. Part e represents hydrolyzed acrolein diethyl acetal with maximum absorption at 448 nm; the absorbances are typical of α,β-unsaturated carbonyl both in shape and extreme color stability. Acrolein, however, unlike 2-ethyl-2-hexenal, has little if any secondary maximum near 525 nm, and thus the presence or disappearance of any secondary maximum is poorly defined.

Part f represents complex mixture D (see Table IV) and is similar to complex mixtures described in earlier work[10] which suggested that the complexity of the system affected the absorption characteristics, but the reasons were not understood. Visually the spectral shape is due to the presence of both saturated and α,β-unsaturated carbonyl compounds in the mixture. For example, the spectra are not representative of either moiety but similar to parts of each. The primary maximum occurs at 440 nm, not 430 or 450, the color stability is between that observed for each pure

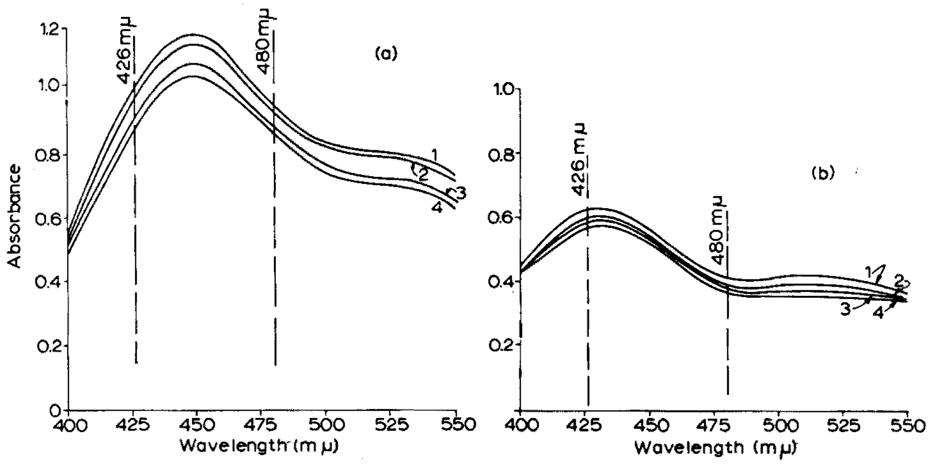

Fig. 4. Comparative spectra for co-planar and non-planar 2,4-dinitrophenylhydrazone of (a) acetophenone and (b) benzophenone.

type, the secondary maximum near 525 nm decreases only slightly with time, and a ratio of about 1:1 saturated to α,β-unsaturated carbonyl would be predicted. By actual analysis the carbonyl was nearly 55 and 45% saturated and α,β-unsaturated, respectively.

Figure 4 shows the absorption spectra for acetophenone and benzophenone. Both are α,β-unsaturated carbonyl compounds, but only acetophenone shows the characteristic spectral shape and enhanced molar absorptivity. Benzophenone spectra are anomalous and typical of saturated aliphatic ketones. It is known that non-planarity of the benzophenone molecule occurs with 2-halogen substitution on the aromatic rings, while for 4-halogen substitution the molecule is mostly co-planar. In the present work the molecule is the 2,4-dinitrophenylhydrazone of benzophenone and the aromatic rings can be co-planar only with the carbonyl group but non-planar with the 2,4-dinitrophenylhydrazone.

SUMMARY

A method for the simultaneous determination of trace concentrations of saturated and α,β-unsaturated carbonyl compounds in complex systems is presented. Carbonyl as the alkaline 2,4-dinitrophenylhydrazone is determined spectrophotometrically at 2 selected wavelengths of 480 and 426 nm. The apparent total carbonyl concentration is obtained from prepared calibration curves at the selected wavelengths based on known concentrations of *n*-heptaldehyde. From the observed relative response of known concentrations of *n*-heptaldehyde and 2-ethyl-2-hexenal, the true concentration for saturated and α,β-unsaturated carbonyl is obtained by a simple calculation. The method has been used extensively for alcohol systems ranging up to tetracontanol but is equally useful for hydrocarbons, aromatic oxygenates and hydrocarbons, petroleum distillates and kerosenes, organic acids and esters, and some ethers.

RÉSUMÉ

L'auteur propose une méthode pour le dosage simultané de traces de composés carbonyles non saturés α,β dans des systèmes complexes. Le carbonyle sous forme de dinitro-2,4-phénylhydrazone est dosé par spectrophotométrie aux deux longueurs d'onde 480 et 426 nm. Ce procédé est très utilisé pour les systèmes d'alcools; il est également applicable aux dosages d'hydrocarbures, de distillats de pétrole et de kérosènes, d'acides organiques et d'esters, de même que de quelques éthers.

ZUSAMMENFASSUNG

Es wird eine Methode angegeben zur gleichzeitigen Bestimmung von Spuren gesättigter und α,β-ungesättigter Carbonylverbindungen in komplexen organischen Systemen. Das Carbonyl wird als das alkalische 2,4-Dinitrophenylhydrazon spektralphotometrisch bei zwei ausgewählten Wellenlängen von 480 und 426 nm bestimmt. Die scheinbare gesamte Carbonylkonzentration wird aus Eichkurven erhalten, die für die ausgewählten Wellenlängen auf bekannten Konzentrationen von *n*-Heptaldehyd basieren. Die wahre Konzentration wird durch eine einfache Berechnung er-

halten. Die Methode wurde ausführlich bei alkoholischen Systemen verwendet, die bis hinauf zum Tetracontanol reichten. Sie ist ebenso brauchbar für Kohlenwasserstoffe, Petroleumdestillate und Leuchtöle, organische Säuren und Ester und einige Äther.

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SHORT COMMUNICATIONS

Spot test detection of sulfide in minerals

The study described below was designed to give comparative data on some old and new tests for the detection of sulfides in minerals, in order to find out if there are any differences in the behavior of different sulfide minerals. The following tests were examined.

Methods

(I) Iodine–azide test. This test is based on the catalytic action by sulfide on the reduction of iodine by sodium azide[1].

(II) Benzoin fusion test. Molten benzoin (m.p. 137°) reacts specifically with elemental sulfur to give hydrogen sulfide[1].

(III) Pyrolytic formation of $(CN)_2S$ *and* $(CNS)_2$.

Method A. Small amounts of the sample were mixed with excess of mercury(II) cyanide and heated to 130–180° in a glycerine bath in micro test tubes. For the detection of $(CN)_2S$ the tubes were covered with a piece of congo-red paper moistened with 5% hydrogen peroxide. A black spot shows the presence of $(CN)_2S$.

Method B. The mineral sulfide was heated at 130–180° with mercury(II) cyanide to form HgS and the respective metal cyanide. Mercury(II) sulfide reacts further with mercury(II) cyanide to form $(CNS)_2$ which can be readily reacted with hydrocyanic acid reagent[2].

(IV) Behavior toward aqueous mercury(II) cyanide. If sulfide minerals are suspended in a water solution of mercury(II) cyanide and heated, HCN is usually found. The latter can be detected by means of paper moistened with a solution containing 5 mg of tetrabase and 5 mg of copper methylacetoacetate in 4 ml of chloroform[3].

(V) Reaction with sodium formate[4]. If alkali formate is pyrolysed to about 250°, active hydrogen is formed and reacts with mineral sulfide to release hydrogen sulfide which can be detected with lead acetate paper.

(VI) Pyrolysis with oxalic acid. When solid oxalic acid is heated above its melting point with mineral sulfide, hydrogen sulfide is liberated and can be detected with lead acetate paper.

(VII) Pyrolysis with ammonium chloride. When ammonium chloride is heated to its sublimation temperature (335–340°) the vapor acts like anhydrous hydrogen chloride; thus, in the presence of metal sulfide, hydrogen sulfide is liberated, the metal chloride being formed. The liberated hydrogen sulfide is again detected with lead acetate paper.

(VIII) Pyrolysis with ammonium sulfate. If heated at about 280° ammonium sulfate is decomposed and acts like concentrated sulfuric acid which reacts with the mineral sulfides to form hydrogen sulfide; this liberated gas can again be detected with lead acetate paper.

(IX) Chromic acid oxidation test. It is well-known that metal sulfides can be

oxidized by strong oxidizing agents. Among the reagents tried, chromic acid dissolved in concentrated sulfuric or phosphoric acid may be used as oxidant; the disappearance of the orange color indicates the presence of oxidizable sulfides. The test can be carried out by heating 4 drops of 0.1% potassium chromate in concentrated sulfuric acid (with 2 drops of saturated ammonium bifluoride) or concentrated phosphoric acid with 2 mg of sulfide at 140–145° for 80 sec. A complete disappearance of the yellow color (+) and the partial removal of it (−) may be discerned (Table I).

Results and discussion

The sulfide minerals examined and the results obtained based on the reactions and procedures described in tests I to IX inclusive are listed in Table I.

TABLE I

SPOT DETECTION OF SULFIDES IN MINERALS

(I), Iodine–azide test; (II), benzoin fusion test; (IIIA), pyrolytic formation of $(CN)_2S$ and $(CNS)_2$ (detection with congo-red paper); (IIIB), idem (detection with HCN reagent); (IV), behavior toward aqueous mercury(II) cyanide; (V), reaction with sodium formate; (VI), pyrolysis with oxalic acid; (VII), pyrolysis with ammonium chloride; (VIII), pyrolysis with ammonium sulfate; (IX), chromic acid oxidation test.

Name	*Formula*	*I*	*II*	*IIIA*	*IIIB*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*
Molybdenite	MoS_2	−	−	−	+	+	+	−	−	−	+
Cinnabar	HgS	+	−	−	+	−	++	+	−	−	+
Marcasite	FeS_2	+	+	+	+	+	++	++	++	−	−
Pyrrhotite	FeS_2	+	+	+	+	+	++	++	++	+	+
Pyrite	FeS_2	+	−	−	+	+	++	++	++	+	+
Galena	PbS	+	−	−	+	+	++	++	++	−	+
Arsenopyrite	$FeAsS$	+	−	−	+	+	++	++	++	+	+
Calcopyrite	$CuFeS_2$	+	−	−	+	+	+	−	−	−	−
Chalcocite	Cu_2S	+	−	−	+	+	+	++	+	−	+
Cubanite	$CuFe_2S_3$	+	−	−	+	+	++	++	++	+	+
Covellite	CuS	+	−	−	+	−	+	++	++	−	+
Stibnite	Sb_2S_3	+	+	−	++	++	++	++	++	+	+
Tennantite	$Cu_6Sb_2S_6+m(Fe,Zn)_6\ Sb_2S_3$	+	−	−	+	+	++	++	++	−	+
Jamesonite	$2PbS.Sb_2S_3$	+	−	−	++	+	++	++	++	+	+
Greenockite	CdS	+	−	−	+	+	+	+	++	+	+
Orpiment	As_2S_3	+	+	−	+	+	+	+	++	++	+

These results show some interesting differences between the tests, which can be utilized for the characterization of sulfide minerals. For instance, molybdenite gives a negative response to the iodine–azide reaction in contrast to the other sulfides.

Cinnabar on heating with ammonium chloride in a small test tube sublimes along with the ammonium chloride; thus cinnabar can be detected by the formation of a black mirror on the wall. A large excess of ammonium chloride causes disappearance of the mirror, due probably to the formation of a complex compound.

The most outstanding phenomena observed in this study concern the behavior of marcasite, pyrrhotite and pyrite. The chemical composition of these minerals is the same, FeS_2, but these sulfides differ in their reactions with benzoin (test II). Pyrite gives a negative response whereas marcasite and pyrrhotite respond positively to the test. Likewise in test IIIA, marcasite and pyrrhotite split off $(CN)_2S$ whereas pyrite does not.

Galena gives a positive response to tests V, VI and VII but not to test VIII.

Since ammonium chloride and ammonium sulfate are both salts of a weak base with a strong acid, one would expect a similarity in their pyrolytic behavior towards the sulfide, but this is not always the case. A possible explanation is that the sulfuric acid formed at elevated temperature, as in the case of ammonium sulfate, being a powerful oxidizing agent, reacts with the hydrogen sulfide as follows:

$$H_2S + 3\ H_2SO_4 \rightarrow 4\ H_2SO_3$$

Thus no sulfide is released, but the sulfur dioxide vapor formed can be detected by bluing of congo paper moistened with dilute hydrogen peroxide.

Of special interest is the difference between arsenopyrite and orpiment; while the peroxide-moistened congo-red paper gives a negative response to both, the benzoin reaction gives a negative response to arsenopyrite and a positive response to orpiment. Precipitated arsenic trisulfide prepared in the laboratory also gives a positive response to the benzoin reaction. Possibly, under the experimental conditions, arsenic trisulfide behaves like a mixture of sulfur and arsenic pentasulfide:

$$2\ As_2S_3 \rightarrow As_2S_5 + S^\circ + 2\ As^\circ$$

Chalcocite, Cu_2S, and covellite, CuS, behave similarly in all the tests listed with the exception of test IV.

Conclusion

Numerous theoretical and practical studies of sulfide minerals have been made in recent years, particularly in regard to the use of sulfides for energy conversion. The methods described in this paper could probably be used not only for natural sulfides but also for sulfides produced synthetically for semi-conductor purposes.

The author would like to thank Prof. FRITZ FEIGL for his interest in this problem. This work was partly done in his laboratory in Rio de Janeiro, Brazil. The mineral samples were obtained from the Museum of the Ministerio das Minas e Energia, Brazil, whose help is also acknowledged.

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The determination of nitrogen in beryllium without distillation

Nitrogen is usually determined in beryllium[1] by application of a micro Kjeldahl method, ammonia being removed by steam distillation after addition of sodium hydroxide and determined either by micro-titration with acid or absorptiometrically with Nessler's reagent. The distillation step can be time-consuming when large numbers of samples are involved and the possibility of conversion of nitride nitrogen to ammonia by dissolution in acid followed by direct spectrophotometric determination has been investigated. Such a method results in a relatively large final volume of solution since precipitation of beryllium hydroxide has to be prevented by addition of a complexing agent, *e.g.* citrate, and a highly sensitive spectrophotometric method for ammonia is therefore required. The indophenol blue method which is now used extensively for the determination of ammonia was selected and the procedure adopted is in general based on the work of TETLOW AND WILSON[2].

Whilst this work was undertaken primarily for the analysis of zone-refined beryllium of high purity the method has also been applied to lower purity material for which interference by metallic impurities could lead to difficulties.

Development of spectrophotometric procedure

Effect of pH. Several workers[2-4] have studied the effects of varying the concentration of sodium hydroxide in the sodium phenate solution on the formation of indophenol blue. Since in this application considerable additional amounts of sodium hydroxide are required for neutralisation of the acidified beryllium citrate solution some further studies on the effect of pH were made. From the proposed mechanism for the formation of indophenol blue, involving initial reaction of ammonia with hypochlorite it seemed probable that variation of pH before the addition of hypochlorite would be most critical and this was investigated using a series of solutions containing 0.5 μg N per ml. The results (Table I) showed the optimum pH range before the addition of hypochlorite to be 11.2–12.0. In practice, the most satisfactory technique is to adjust the pH before the phenate addition, to a value such that the phenate solution increases the pH to fall within the optimum range. For solutions containing 100 mg of beryllium this pH is 11.0 ± 0.2 and for the reagent blank is 8.0 ± 0.5.

TABLE I

EFFECT OF pH ON COLOUR FORMATION

pH of solution before addition of NaOCl	*Absorbance (d = 20 mm)*		
	Reagent blank	*Sample*	*Net*
10.2	0.022	0.125	0.103
10.6	0.032	0.208	0.176
11.0	0.046	0.500	0.454
11.2	0.055	0.515	0.460
11.4	0.053	0.510	0.457
12.0	0.046	0.506	0.460

Rate of formation of indophenol blue. According to TETLOW AND WILSON[2], 60 ± 5 min was the optimum development time for highest precision. Repeating this work under the conditions described in this paper, showed that maximum absorbance was reached after 25 min and this was reduced by approximately 4% after 60 min. Absorbance was therefore measured after 30 ± 5 min.

Effect of impurities. Certain cations can seriously interfere in the indophenol blue method and EDTA has been successfully used to complex a large number of elements[2]. The effects of elements present as major impurities in beryllium, *viz.* Fe, Al, Cu, Cr, Mn, Ni and Mg, were investigated. Copper was shown to be the most serious interference, the presence of 100 μg reducing the absorbance due to 25 μg N by 75%; iron gave an increase of 6% and the remainder were without effect. Addition of citrate completely eliminated these interferences but EDTA was also added to minimise the effect of other possible interfering elements.

Reagents

Water (<2 μg NH_3/l). Distil from a 0.5 *M* sulphuric acid solution rejecting the first 100 ml of distillate. Store in a sealed glass bottle.

Sodium citrate solution, 50% (w/v) (<20 μg NH_3/l). Dissolve 100 g of A.R. sodium citrate in 400 ml of water, add 1 ml of 50% (w/v) sodium hydroxide solution and evaporate to 200 ml.

Sodium hydroxide solution 5 M. Dissolve 50 g of A.R. sodium hydroxide in 500 ml of water and evaporate the solution to 250 ml. Standardise by titration with standard hydrochloric acid.

Sodium phenate solution. Dissolve 62.5 g ± 0.1 g of phenol in 135 ± 1 ml of 5 *M* sodium hydroxide (or equivalent). Dilute to 500 ml with water, quickly transfer to a dark glass bottle and store in a refrigerator.

Sodium hypochlorite (1% w/v available chlorine). Determine the available chlorine content of a suitable concentrated sodium hypochlorite solution and dilute to 1 ± 0.05% with water. Store in a dark glass bottle in a refrigerator.

Nitrogen standard (250 μg N per ml). Dissolve 0.4774 g of dry A.R. ammonium chloride in water, add 3 ml of concentrated hydrochloric acid and dilute to 500 ml.

Working standard (50 μg N per ml). Dilute 10 ml of the above solution to 50 ml with water.

Procedure

Weigh accurately about 100 mg of beryllium into a 50-ml B24 conical flask and attach a reflux condenser. Slowly add 2 ml of 9 *M* sulphuric acid until reaction ceases. Wash down the walls of the condenser with the minimum of water and warm the solution until dissolution is complete. Cool, transfer to a 30-ml beaker, add 1 ml of 6% (w/v) EDTA and 12 ml of 50% (w/v) sodium citrate solution. Adjust the pH of the solution to about 6 with 50% (w/v) sodium hydroxide solution and then to 11.0 ± 0.2 with 5 *M* sodium hydroxide; transfer to a 50-ml volumetric flask. Add 0.3 ml of A.R. acetone followed by 10 ml of sodium phenate solution, then immediately add 5 ml of 1% (w/v) sodium hypochlorite solution and dilute to the mark with water. Allow the solution to stand for 30 ± 5 min and determine the absorbance at 630 nm. Carry out a reagent blank in the absence of beryllium, adjusting the pH to 8 ± 0.5 before addition of sodium phenate solution.

Calibration data

Rectilinear calibration plots were obtained in the range 0–50 μg N in 50 ml by the method described and absorbance was shown to be unaffected by the presence of 100 mg of beryllium. The sensitivity of the procedure was 0.002 μg/cm^2.

Recovery experiments

Known additions of nitrogen (as NH_4Cl) were made to 100-mg samples of electrolytically refined beryllium flake (<20 p.p.m. N) and recoveries estimated as shown in Table II.

Analysis of beryllium

Three samples were analysed: two of low-purity metal (99.5%) supplied by the New Brunswick Laboratory of U.S.A.E.C. which contained 600 p.p.m. Al, 100 p.p.m. Cr, 100 p.p.m. Cu, 1400 p.p.m. Fe, 300 p.p.m. Mg, 100 p.p.m. Mn, and 150 p.p.m. Ni, and one of electrolytically refined beryllium flake. Table III shows the results obtained with some comparative values using the distillation procedure.

TABLE II

RECOVERY OF NITROGEN FROM BERYLLIUM

Sample	*N added (μg)*	*N found (μg) (corrected for N in sample)*	*% Recovery*
1	10.0	10.8	108
2	20.0	20.8	104
3	20.0	20.0	100
4	30.0	29.0	97
5	30.0	28.9	96

TABLE III

ANALYSIS OF BERYLLIUM

Sample	*Nitrogen content (p.p.m.)*	
	Without distillation	*Distillation*
NBL. 224	226, 255	270
NBL. 225	270, 281	273
Pechiney S.R. flake	21, 38, 31, 20, 17, 15 Mean 24 p.p.m., σ=9 p.p.m.	24

The poor precision of results for Pechiney S.R. material was attributed to inhomogeneity and repeating the analysis on aliquots containing 100 mg of beryllium taken from a stock solution prepared from 1 g of sample indicated this to be the case. Results obtained were: p.p.m. nitrogen 21, 23, 23, 19, 25; mean 22 p.p.m., $\sigma = 2.3$ p.p.m.

Limit of detection

Analysis of a number of reagent blanks gave a mean value of 1.6 μg nitrogen with standard deviation (σ_B) 0.16 μg. Using the criterion defined by Roos[5] (limit of detection = $1.645\sqrt{2}\sigma_B$ for 95% confidence) gives a value of 0.37 μg nitrogen, *i.e.* 4 p.p.m. on 100 mg beryllium sample.

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The palladium(II) complex of picolinealdehyde 2-quinolylhydrazone

HEIT AND RYAN[1] have recently reported the reaction between palladium(II) sulfate and picolinealdehyde 2-quinolylhydrazone in acid solution. The present investigation reports the reaction between palladium(II) chloride and this reagent in basic solution. The structures of the palladium complexes were investigated and the colorimetric determination of palladium ion in palladium catalysts is reported.

Apparatus

A Cary Model 14 Recording Spectrophotometer equipped with 1.00-cm cells was used. The conductance measurements were made on the Industrial Instruments Inc. conductivity bridge, Model RC16B2. The conductance cell, specifically designed for low conductivities, was also manufactured by Industrial Instruments Inc.

Solutions

Picolinealdehyde 2-quinolylhydrazone (PAQH) was prepared[2] and a solution, $8 \cdot 10^{-3}$ *M*, was prepared in a minimum of 0.1 *N* hydrochloric acid.

A $1.034 \cdot 10^{-2}$ *M* palladium stock solution was prepared by dissolving palladium chloride in 10% hydrochloric acid and standardized by the dimethylglyoxime method[3].

A buffer solution, 0.5 *M* in trishydroxymethylaminomethane was prepared by dissolving 61 g of trishydroxymethylaminomethane in deionized water and adding concentrated hydrochloric acid until a pH of 8.0 was attained.

Procedure

Dissolve the sample containing palladium by appropriate means. To a 5-ml aliquot containing 0.6–13 p.p.m. of palladium(II) in a 125-ml separatory funnel add at least a two-fold excess of PAQH and 10 ml of pH 8.0 buffer and dilute to *ca.* 75 ml with deionized water. Extract the aqueous solution with three 5-ml portions of chloroform and pass the extracts through cotton to remove water. Dilute the solution to volume in a 50-ml volumetric flask with chloroform and measure the absorbance at a wavelength of 589 nm. From a previously prepared calibration curve, determine the amount of palladium in the unknown sample.

For the thiocyanate derivative, add 10 ml of potassium thiocyanate solution (10 mg/10 ml) after the addition of buffer. Carry out the extraction as described and measure the absorbance at 592 nm.

Discussion

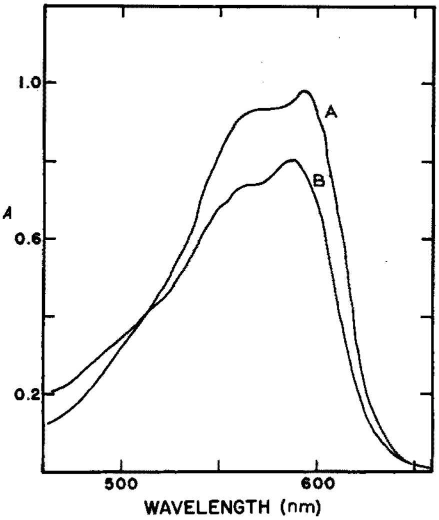
The spectrophotometric method for measuring palladium ion with PAQH is best carried out as an extraction procedure. The palladium complexes, which exist as precipitates in buffered aqueous solution, can be readily extracted from aqueous solution into chloroform.

The palladium complex of PAQH, in the chloro or thiocyanato form, is intense purple in color when extracted into chloroform. The absorption spectra of the 2 palladium complexes in chloroform are shown in Fig. 1. The chloro complex displays maximum absorbance at 589 nm and the thiocyanato complex at 592 nm.

The effect of pH on the palladium(II) complex was ascertained. Extraction and color formation are essentially constant over a pH range of 6.3 to 8.9. Full color development does not occur at higher and lower pH values.

A study of excess of reagent on the palladium system showed that a two-fold excess of reagent is required to obtain maximum and reproducible color formation.

All the preceding experiments were performed with chloride ion as the only anion in solution. It was found that when thiocyanate ion was also present in the solution, a bathochromic shift in the absorption maxima from 589 to 592 nm occurred for the extracted palladium complex.



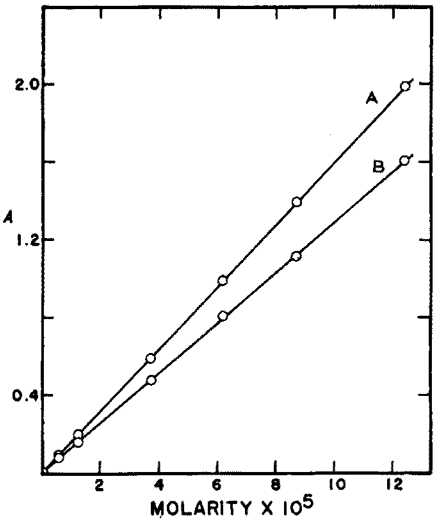


Fig. 1. Absorbance of palladium(II) picolinealdehyde 2-quinolylhydrazone complexes. Concentration of palladium = $6.204 \cdot 10^{-5}$ *M*. (A) Thiocyanato complex at 592 nm; (B) Chloro complex at 589 nm.

Fig. 2. Beer's law study of palladium systems. (A) Thiocyanato complex; (B) Chloro complex.

Under the appropriate conditions, the palladium complexes could be extracted from aqueous solution into benzene, carbon tetrachloride, chloroform, ethyl acetate, isoamyl alcohol and nitrobenzene. Chloroform was selected as the extractant because it is denser than water and can be obtained in pure form.

The efficiency of extraction of the palladium complexes from aqueous solution into chloroform was determined. The distribution coefficient, at pH 8.0, was found to be about 23 for the palladium(II)–chloro complex and about 500 for the palladium(II)–thiocyanato complex.

The palladium(II)–PAQH–chloro complex was found to obey Beer's law over a concentration range of $6.20 \cdot 10^{-6}$ to $124 \cdot 10^{-6}$ *M* palladium(II) ion. The palladium(II)–PAQH–thiocyanato complex obeyed Beer's law over the same range. The Beer's law plots are shown in Fig. 2. The best values for the molar absorptivities of the two complexes are 12,800 at 589 nm for the chloro and 15,800 at 592 nm for the thiocyanato complex.

PAQH acts as a nonselective reagent towards transition metal ions in basic solution. The other platinum metals, ruthenium(III), rhodium(III), osmium(III) and iridium(IV) all interfere due to the formation of the respective insoluble hydroxides. This makes a clean-cut extraction virtually impossible. It is possible, by means of the recommended procedure, to determine palladium(II) in the presence of 10-fold amounts of platinum(IV) in the chloro system and 20-fold amounts in the thiocyanato system. Of the other transition metal ions, Fe(II), Co(II), Ni(II), Cu(II), Au(III), Mn(II), Zn(II), V(V), Cr(III) and Al(III) interfere. Of the anions tested, thiosulfate, nitrate, phosphate, and fluoride, only thiosulfate ion shows any interference.

The solid palladium complex in the presence of chloride ion was prepared by dissolving 0.4518 g of PAQH in *ca.* 50 ml of hot ethanol. In a separate beaker, 0.3227 g of palladium chloride was dissolved in hot 10% hydrochloric acid. The two hot solutions were mixed and then allowed to cool to room temperature. The dark purple solid was filtered, washed with ethanol and water, and dried in a drying pistol at 80° for 15 h. Approximately 0.5 g of complex was obtained. (Calcd. for $C_{15}H_{12}N_4Cl_2Pd$: C, 42.33%; H, 2.84%; N, 13.17%. Found: C, 42.05%; H, 2.44%; N, 12.86%.)

In the presence of an excess of thiocyanate, the synthesis was accomplished by dissolving 0.2507 g of PAQH and 1.5953 g of potassium thiocyanate in 70 ml of hot 85% ethanol. In a separate beaker, 0.1768 g of palladium chloride was dissolved in hot 10% hydrochloric acid–ethanol. The two hot solutions were mixed and solid sodium hydroxide added until precipitation was essentially complete. The solution was cooled and filtered, and the precipitate washed with water and dried in a dry pistol for

TABLE I

CONDUCTANCE MEASUREMENTS OF THE SOLID PALLADIUM COMPLEXES

Complex	*Concentration (M)*	*Conductance (μΩ)*
—[a]	—	1.919
$Pd(PAQH)Cl_2$	$4.04 \cdot 10^{-4}$	1.656
$Pd(PAQH)(SCN)_2$	$7.43 \cdot 10^{-5}$	2.899
$Fe(TPTZ)_2(ClO_4)_2$	$8.30 \cdot 10^{-5}$	63.0

[a] Nitrobenzene.

10 h. Approximately 0.3 g of the complex was obtained. (Calcd. for $C_{17}H_{12}N_6S_2Pd \cdot H_2O$: C, 40.28%; H, 3.18%; N, 16.58%. Found: C, 39.34%; H, 3.18%; N, 16.54 %.)

The results of conductance measurements on the 2 solid palladium complexes are shown in Table I. These conductance values demonstrate that the complexes are nonionic in nitrobenzene, as compared to a reference 2:1 electrolyte. The increase in the conductance of the thiocyanate complex could be due in part to the molecule of water associated with the isolated solid. It is, therefore, concluded that the anions are associated with the coordination sphere.

TABLE II

ANALYSES OF PALLADIUM SAMPLES

Reagent	*Pd found (g/250 ml)*	
	Pd on carbon	*Pd on $CaCO_3$*
Picolinealdehyde 2-quinolylhydrazone (chloride system)	0.0035 (3)[a]	0.0093 (6)
Picolinealdehyde 2-quinolylhydrazone (thiocyanate system)	0.0034 (3)	0.0089 (6)
2-Pyridinealdoxime[4]	0.0037 (5)	0.0093 (5)
8-Aminoquinoline[5]	0.0035 (3)	0.0093 (3)

[a] Number of determinations averaged for result.

The spectra for the solid palladium complexes redissolved in chloroform are superimposable with those of the extracted species. The average molar absorptivities of the solids dissolved in chloroform are 12,500 for the chloro complex and 16,000 for the thiocyanato complex.

Results of the analyses of selected samples (Table II) demonstrate that the previously discussed method compares quite favorably with those currently found in the literature. Procedures for comparative analysis were undertaken as dictated by literature directions. In the absence of interfering ions the method for palladium(II) ion is accurate over the range of 0.6 to 13 p.p.m. palladium.

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Spectrophotometric determination of zirconium

DEHNE AND MELLON[1] have published the results of a study whose principal objective was to define the nature of the chemical reaction between zirconium(IV) and molybdenum(VI) in a sulfate medium between pH 1.0 and 2.0. The molar absorptivity of the resulting complex was $3.64 \cdot 10^3$. A large number of substances interfered in the color reaction. This study reports the results of an investigation designed to optimize the variables in this system and to achieve maximum sensitivity and selectivity with respect to zirconium.

Although LIBERTI *et al.*[2] have synthesized 12-molybdozirconic acid, the only study involving the determination of zirconium(IV) with a heteropoly compound was the molybdozirconophosphate system of VEITSMAN[3].

Reagents

Analytical reagents and twice-distilled water were used to prepare all solutions.

Apparatus

All absorbance measurements were made on a Cary Model 15 Recording Spectrophotometer using 1-cm quartz cells. A Beckman Zeromatic pH meter was used for all pH measurements.

Recommended procedure

To 150-ml beakers add 0–35 p.p.m. of zirconium(IV). To each beaker add 3 ml of 10% (w/v) sodium sulfate solution, 25 ml of water and 10 ml of 5% (w/v) ammonium heptamolybdate tetrahydrate solution. Using a pH meter, adjust the pH to 1.3 by dropwise addition of 1:4 sulfuric acid. Transfer the solutions to 100-ml volumetric flasks, and place in a water bath at 45° for 2 h. Add rapidly to the warm solutions 5 ml of 1:1 aqueous sulfuric acid, and 10 sec later, 3 ml of 0.55% (w/v) tin(II) chloride solution. Dilute to the mark and read the absorbance at 725 nm 10–60 min after addition of the reductant.

Results and discussion

Little need be said concerning the qualitative nature of the reactions leading to formation of the reducible zirconium heteropoly since this has been covered elsewhere[1].

The present procedure has extended the upper limit of the range of the zirco-

TABLE I

INTERFERING IONS

Ion	*Added (p.p.m.)*	*Permitted (p.p.m.)*	*Ion*	*Added (p.p.m.)*	*Permitted (p.p.m.)*
Al(III)	100	100	Hf(IV)	100	0
NH_4^+	100	100	I^-	100	100
BO_3^{3-}	100	100	NO_3^-	100	100
Br^-	100	100	ClO_4^-	100	100
Cl^-	100	100	SCN^-	100	100
Cu(II)	100	25	Th(IV)	100	100
Cr(III)	100	25	Zn(II)	100	100
CN^-	100	10			

nium determination to 35 p.p.m. and has increased the sensitivity by 25% ($\varepsilon_{725} = 4.75 \cdot 10^3$) so that 1 p.p.m. of zirconium can readily be measured. Analysis of zirconium(IV)-containing solutions at 5 different concentration levels gave excellent results with relative errors of *ca.* 1%.

Table I gives the results of a diverse ion study carried out on the present system. In addition to the ions given in the Table Ag(I), Pb(II), and Ba(II) form precipitates, and SiO_3^{2-}, AsO_4^{3-}, PO_4^{3-}, ClO_3^-, WO_4^{2-}, and F^- interfere seriously while Co(II), Ni(II), Mn(II), and Fe(II) can be tolerated in a 5-fold excess over the zirconium. These results represent a vast improvement over the previous technique.

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Liquid–liquid extraction by tri-iso-octylamine in methyl isobutyl ketone from aqueous hydrochloric acid

The use of high molecular weight amines (HMWA) as extractants was first reported by SMITH AND PAGE[1] and has since been greatly extended. MOORE[2] used 5% (w/v) tri-iso-octylamine in xylene and methyl isobutyl ketone for the extraction of uranium and plutonium and noted that zinc was also extracted. Various workers[3–5] have used this amine for the separation of zinc, trivalent actinides from lanthanides and neptunium from plutonium, americium, curium, uranium, thorium and fission products. Various procedures have been reported which involve precipitation, solvent extraction and/or ion-exchange, but the methods are either time-consuming or do not give carrier-free separations. In the development of methods for the determination of trace nutrients in soil and plants by destructive activation analysis, procedures were required which would give carrier-free, specific and rapid separations and as good a decontamination factor as any other procedure. The present paper deals with the behaviour of tri-iso-octylamine in methyl isobutyl ketone for the extraction of different elements and with the radiochemical separation of zinc from cobalt and mercury, and of tin from antimony.

Reagents and apparatus

Tri-iso-octylamine was used as a 5% (w/v) solution in methyl isobutyl ketone

(AnalaR grade). All aqueous solutions were prepared from reagent-grade chemicals and the radionuclides used (obtained from A.E.R.E., Harwell) were diluted with deionized water.

Counting was generally done with a well-type scintillation counter; γ-activities of ca. $2.5 \cdot 10^5$ cpm were normally taken. For β-emitters, a G.-M. counter was used; the organic phase and an aliquot of the aqueous phase were both dried and counted, measurements being repeated 4–5 times to minimize errors.

Procedures

Solutions containing the carrier-free tracer in 10 ml of aqueous phase adjusted to the appropriate normality in hydrochloric acid, were shaken with 10 ml of the amine solution for 3 min at room temperature. (Preliminary investigations revealed that in most cases equilibria were established in 2–3 min.) The amount of tracer remaining in the aqueous phase was then determined by counting as described above.

The results tabulated are the mean of triplicate runs. It should be noted that the presence of anions other than chloride may change the extraction characteristics for various elements.

Results and discussions

The extraction behaviour of the major fission products, *i.e.* Ce, Cs, Ru, Zr, Nb and Sr, was investigated in a series of experiments. Among the fission products ruthenium exhibited the maximum extraction; caesium was only *ca.* 0.02% extracted from 1 *N* hydrochloric acid, the percentage extraction decreasing to zero from 5 *N* acid. Strontium was not extracted at any of the acidities tested. The percentage extraction of cerium(IV) was *ca.* 0.01% over the whole 1–6 *N* hydrochloric acid range, while yttrium was extracted to the extent of 0.05–0.1%. Other results are shown in Table I, which also gives the data found for various transition elements.

TABLE I

EXTRACTION OF VARIOUS ELEMENTS WITH TRI-ISO-OCTYLAMINE IN METHYL ISOBUTYL KETONE FROM AQUEOUS PHASES OF VARYING ACIDITY

Element	*Percentage extraction from HCl (M)*						*Element*	*Percentage extraction from HCl (M)*					
	1.0	*2.0*	*3.0*	*4.0*	*5.0*	*6.0*		*1.0*	*2.0*	*3.0*	*4.0*	*5.0*	*6.0*
Mn	0.0	0.0	0.1	0.1	1.3	4.8	Ir	3.1	2.4	1.3	0.6	0.1	0.0
Fe	97.8	100.0	100.0	100.0	100.0	100.0	Cd	80.0	78.0	76.0	72.0	68.0	65.0
Co	0.0	0.4	5.8	8.8	32.0	55.0	In	100.0	100.0	99.1	98.5	98.1	99.0
Zn	97.6	96.0	99.0	98.7	100.0	100.0	Sn	90.0	90.0	91.2	91.4	96.0	100.0
Zr	0.0	0.0^5	0.3	0.5	0.5	0.8	Sb	0.6	15.8	55.3	100.0	100.0	100.0
Nb	0.2	0.4	2.5	4.1	16.8	82.7	Ba	0.1	0.2	0.5	2.1	2.1	2.2
Ru	72.0	73.9	76.0	70.5	67.1	63.2	Hg	64.0	65.0	67.0	88.0	89.5	100.0
Ag	100.0	100.0	100.0	100.0	91.3	66.3	Tl	26.0	31.2	35.1	43.0	43.9	44.2
Ta	6.0	5.2	5.9	5.0	5.0	2.8	Pb	77.0	76.0	76.0	77.0	75.0	77.3
W	8.6	7.8	11.1	17.2	43.1	58.0							

It can be seen that with solutions 1 *M* in hydrochloric acid, zinc can be separated from cobalt. The only other common member of the first transition series which is extracted is iron, the interference of which can be prevented by preliminary extraction with isopropyl ether.

The possibility of some other separations can also be seen, *e.g.* tungsten from iridium.

Several experiments were performed to ascertain the recovery of zinc, mercury, antimony and tin extracted by tri-iso-octylamine in methyl isobutyl ketone from aqueous hydrochloric acid. These elements could be stripped from the organic phase by mixing thoroughly for 3 min with an equal volume of deionized water or 0.05 *M* hydrochloric acid. The recoveries for Zn, Sb and Sn were 91.7, 11.8 and 70% respectively; mercury could not be back-extracted. Thus a separation of Zn from Co and Hg, and of Sn from Sb was possible.

Separation of zinc from cobalt and mercury. This separation was achieved at 1 *M* hydrochloric acid where the cobalt was not extracted. Zinc was recovered from the organic phase, and thus separated from mercury, by stripping with deionized water. A decontamination factor of 10^6 was obtained with a maximum yield of about 80–90%. The whole procedure took 10 min.

Separation of tin from antimony. From 1 *M* hydrochloric acid media, tin was extracted almost quantitatively from the aqueous phase while antimony exhibited only 0.6% extraction. Stripping experiments with deionized water showed 70% recovery of tin with an antimony contamination of 0.004%. Thus, in a single cycle a decontamination factor of $4 \cdot 10^5$ was obtained which may be improved by repeating the extraction.

Conclusion

Tri-iso-octylamine is an efficient extractant for Fe, Zn, Co, Ag, Ru, Nb, W, Cd, In, Sb, Hg, Tl, and Pb at various hydrochloric acid concentrations. The factors of economy, extractability and working efficiency can be balanced to obtain various useful separations. An advantage of this amine is its low cost and easy availability.

We are grateful to the Health Physics Division of the Atomic Energy Centre for preparing tracer solutions used in the present work.

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Fluorimetric determination of thorium with flavonol

Flavonol (3-hydroxyflavone) has been used for the fluorimetric determination of zirconium[1], tin[2], and tungsten[3]. It has been reported that thorium produces a blue fluorescence with flavonol in hydrochloric acid medium[1,4]. This paper concerns a study of the fluorescence of the thorium–flavonol system and its application to monazite materials.

Apparatus

Fluorescence intensity measurements were made with a Turner manual fluorimeter, Model 110. A Corning filter CS 7-51 was used as a primary filter and a combination of a Wratten CS 2A and a Corning CS 5-61 as a secondary filter.

Fluorescence spectra were obtained with a Beckman Model DU spectrophotometer equipped with a Beckman Model 73500 fluorescence attachment. Absorption spectra were obtained with a Beckman Model DB spectrophotometer.

Ion-exchange columns were made of 13-mm (O.D.) pyrex tubing attached to a capillary stopcock at one end; the other end was attached to a 15-cm length of 18-mm (O.D.) pyrex tubing which serves as a reservoir. The resins were supported on a glass wool plug.

Reagents

Standard thorium solution. A standard solution was prepared by dissolving 0.5963 g of thorium nitrate tetrahydrate (Fisher certified reagent) in 1 l of water. Gravimetric analysis by precipitation as thorium hydroxide with ammonia confirmed the concentration to be 250.2 μg/ml.

Flavonol solution. A 0.05% solution was prepared by dissolving 0.125 g of Eastman Kodak 3-hydroxyflavone, lot No. 6585, in 250 ml of 95% ethanol.

Metal salts. Solutions of metal salts were prepared by dissolving reagent-grade chloride or nitrate salts in water or oxides in hydrochloric or nitric acid. Solutions of silicon and titanium salts were prepared by fusion of oxides with sodium carbonate and subsequent treatment with dilute hydrochloric acid.

Anion-exchange resins. For milligram quantities of thorium, Dowex 1-X8, 100–200 mesh, in the nitrate form was used, while for quantities less than 200 μg, Dowex 1-X10, 200–400 mesh, was used. The resins were pretreated at room temperature by a number of alternating treatments with 1 *M*-hydrochloric acid, water, and 0.5 *M* sodium hydroxide. The resins were converted to the nitrate form by passing 5 *M* nitric acid through the column until no chloride could be detected in the effluent.

Test solutions. Solutions to be compared were prepared by introducing suitable aliquots of either standard thorium solution, the "unknown" solution (see Table I), or water (the blank) and 5 ml of 0.1 *M* hydrochloric acid, 45 ml of 0.1 *M* sodium chloride, 25 ml of 95% ethanol and 2 ml of 0.5% flavonol solution into a 100-ml volumetric flask and bringing to volume with water.

Analysis of monazite materials

Weigh a 50–900 mg sample (see Table I) into a platinum crucible. Wet the powder with water; add a few ml of hydrofluoric acid, and heat on a hot plate until all of the liquid has evaporated. Add 2 ml of concentrated sulfuric acid and heat gently to

TABLE I

EXPERIMENTAL CONDITIONS FOR THE ANALYSIS OF MONAZITE MINERALS

Th in mineral (%)	*Sample weight (mg)*	*Aliquot through column (ml)*	*Aliquot of effluent (ml)*	*Range of calibration curve (µg)*	*Filter (% transmittance)*
10	50–100	5	2–5	0–50	25
1	100–300	10	10	0–25	50
0.1	100–300	25	10	0–10	—
0.01	500–900	25	25	0–5	—

avoid spattering during the conversion of fluorides to sulfates. Cover the crucible and heat slowly to 350°; then maintain at this temperature for 3 h. (Add more sulfuric acid, if necessary, but the volume of sulfuric acid should not exceed 2 ml since sulfate must be removed in the next step by ion exchange and its concentration must be carefully controlled.) Cool, wash the crucible down with about 50 ml of water and heat to dissolve all the salts. Transfer the sample to a 100-ml volumetric flask and dilute to volume.

Pass the sample through an anion-exchange column to remove interferences (see Table II). For samples containing more than 1% thorium, fill the column with Dowex 1-X8, 100–200 mesh, in 6 *M* nitric acid to a height of 16 cm, while for samples with less than 1% thorium, use an 8-cm resin bed of Dowex 1-X10, 200–400 mesh. Pass aliquots of sample solution (see Table I) diluted with 6 *M* nitric acid to 30 ml; use a flow-rate of *ca.* 2 ml/min for the Dowex 1-X8 column, and the maximum rate that can be attained for the Dowex 1-X10 column. Wash the columns with 100 ml of 6 *M* nitric acid. Elute thorium with 2.5 *M* hydrochloric acid, collecting 100 ml of effluent in a volumetric flask. Place an aliquot of effluent (see Table I) into a 50-ml beaker

TABLE II

EFFECTS OF OTHER SUBSTANCES

Maximum quantities which do not produce an error in fluorescent intensity greater than 3%[a]					
Li	250 µg	Ce(IV)	300 µg	Al	50 µg
Ca	500 µg	Ce(III)	1 mg	W(VI)	0
Ba	25 mg	La	200 µg	Mo(VI)	20 µg
Sr	5 mg	Sm	300 µg	AsO$_2^-$	5 mg
Fe(III)	5 µg	Y	300 µg	CrO$_4^{2-}$	250 µg
Cr(III)	1 mg	Ru	50 µg	PO$_4^{3-}$	2 µg
Ti	25 µg	Ge	5 mg	SO$_4^{2-}$	5 µg
Si	150 µg	Bi	200 µg	F$^-$	2 µg
Zr	30 µg	Ag	250 µg		
Co(II)	5 mg	Pt	1 mg		
Non-interfering substances[b]					
Na	50 mg	Pr	500 µg	Hg	10 mg
K	20 mg	Nd	5 mg	U(VI)	5 mg
Be	10 mg	Cd	25 mg	Mn(II)	10 mg
Mg	20 mg	Yb	500 µg	Pb(II)	10 mg
Zn	5 mg	Gd	1 mg	NO$_3^-$	50 mg
Ni	10 mg				

[a] With 40 µg Th in 100 ml of test solution.

[b] Amounts indicated are the maximum amounts tested.

with 5 ml of nitric acid and 1.5 ml of perchloric acid, and evaporate to dryness. Cool to room temperature, add 5 ml of 0.1 *M* hydrochloric acid and heat to boiling. Then cool and transfer to a 100-ml volumetric flask. Wash the beaker with 45 ml of 0.1 *M* sodium chloride and then add 25 ml of ethanol and 2 ml of 0.05 % flavonol. Dilute to volume with water. Prepare a working standard thorium solution by treating aliquots of standard thorium solution as in the above procedure beginning with the evaporation with nitric and perchloric acid.

Results

Effect of solvent. Maximum fluorescence was obtained with 25 ml of 95 % ethanol in 100 ml of solution. Although the curve of fluorescence intensity *vs.* concentration of 95 % ethanol did not show a sharp peak, there was no plateau, and the concentration of ethanol should not vary by more than 1 % from the stated amount. Dimethylformamide was also tried but the fluorescence was not as intense as with ethanol.

Effect of pH. The curve of fluorescence intensity *vs.* pH also showed no plateau, hence the solutions whose fluorescence is to be compared must be at the same pH. A pH of 2.2 was maintained by using 5 ml of 0.1 *M* hydrochloric acid and 45 ml of 0.1 *M* sodium chloride.

Concentration of flavonol. With a given amount of thorium the fluorescence intensity increased with increasing flavonol concentration until a plateau was reached. Using 0.16 ml of standard thorium solution in 100 ml of solution, for example, the maximum fluorescence (*vs.* a blank of equal flavonol concentration) was reached with 1 ml of 0.05 % flavonol solution.

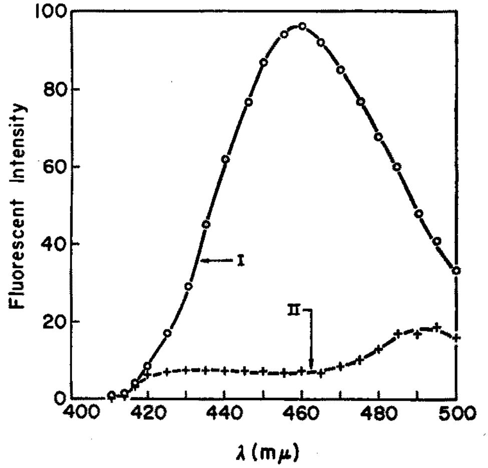

Fig. 1. Fluorescence spectra. (I) Flavonol with thorium. (II) Flavonol (solution prepared as described under *Test solutions*).

Fluorescence and absorption spectra. Solutions were prepared as described under *Test solutions* using 10 μg of thorium in 100 ml of solution. The fluorescence spectrum of the thorium–flavonol complex had a peak at 460 nm and that of flavonol had a weak peak at 490 nm (see Fig. 1). The Corning filter, CS 5-61, used in the secondary filter, transmits 66 % at 460 nm and 30 % at 490 nm. The Wratten CS-2A filter was used to eliminate stray exciting light (shorter than 415 nm). The absorption spectrum showed a broad band from 360 nm to 420 nm with a maximum at about 390 nm.

Effect of time. The fluorescence of test solutions in stoppered flasks was stable for almost 5 days, but in open cuvettes the fluorescence was stable for only 1 h and then began to decay. This decay was not accelerated by exposure to ultraviolet light.

Effect of temperature. The fluorescence intensity of the test solutions decreased 1.2% per degree rise in temperature. Because the proposed method makes use of a standard thorium solution for every determination, any possible temperature effect is compensated when all test solutions are at the same temperature.

Calibration curves. Curves of fluorescence intensity *vs.* thorium concentration were linear between the limits of 1 to 100 μg of thorium with 2 ml of 0.05 % flavonol in 100 ml of test solution.

Interferences. Many cations or anions that occur in thorium minerals or can appear during chemical analysis were tested with pure thorium solutions and are listed in Table II. The only ion that increased the fluorescence intensity was aluminum; all others quenched the fluorescence.

Analytical applications

The proposed method has good sensitivity even for concentrations of a few μg of thorium in 100 ml of solution. For example, 6 μg of thorium in 100 ml of solution had a sensitivity of 0.08 μg per meter reading with a standard deviation of 3.6%, *i.e.*, a 0.4-μg limit of detection at a 95% confidence level.

To apply this method to monazite materials, it was necessary to develop the procedure described which provides for easy dissolution of the sample and removal of interferences. The results are presented in Table III.

TABLE III

DETERMINATION OF THORIUM IN STANDARD MONAZITE SAMPLES

NBL analyzed samples	*Certificate value*[a] *Th (%)*	*Th found (%)*	*No. of analyses*
7-A	8.52	8.43 ± 0.34[b]	6
79	1.01 ± 0.01	0.97 ± 0.04	6
80	0.101 ± 0.003	0.098 ± 0.005	6
83	0.0102 ± 0.0002	0.0097 ± 0.0004	5

[a] Values are given at the 95% confidence level.

[b] Precision expressed as standard deviation.

Compared with the only other method for the fluorimetric determination of thorium[5], this method provides for the analysis to be done in acidic medium, is subject to less interference by other substances, provides a simple and rapid method for removing interferences, and has good accuracy.

The thorium samples were generously furnished by C. J. Rodden of the New Brunswick Laboratory of the Atomic Energy Commission.

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Ion-exchange separation and fluorimetric determination of tungsten in steels

A fluorimetric method for the quantitative determination of tungsten with flavonol has been described[1]. In that paper it was noted that almost all of the metals commonly occurring in steels interfere with the fluorescence of the tungstate–flavonol complex. It was, therefore, necessary to develop a method of isolating the tungsten from these metals before the fluorimetric procedure could be applied successfully. This paper describes an ion-exchange separation technique in which the cationic metals are taken up by the resin and the tungstate is washed through in alkaline solution. The effluent is then used for the fluorimetric analysis.

Apparatus

Fluorescence intensity measurements were made with a Turner manual fluorimeter as previously described[1].

The ion-exchange column was a 12-inch chromatographic tube (inner diameter 15 mm) equipped with an Ultramax valve and a filter disc (Scientific Glass unit, No. C 4225).

Reagents

The standard tungstate solution and the flavonol solution were prepared as previously described[1].

Stock buffer solution. This mixture contained 10.0 g of potassium hydrogen phthalate, 8.0 g of sodium chloride, and 12 ml of 2.5 N sodium cyanide per liter. All chemicals were reagent grade.

Diluting solution. The flavonol and stock buffer solutions were mixed shortly before use in a ratio of 5 to 85. This solution must be used within 4 h of mixing, otherwise the potassium hydrogen phthalate begins to precipitate.

Test solutions. Solutions to be compared for fluorescence intensity were prepared by introducing 10 ml of either the standard tungstate solution[1], the unknown solution, or water (the blank) into 100-ml volumetric flasks and bringing to volume with diluting solution.

Preparation of the resin and ion-exchange column

The resin used was Dowex 50W-X4, 50–100 mesh, which was converted to the sodium form and washed free of alkali-soluble impurities. After the resin was used in the subsequent procedure for iron(III) separations, it was regenerated by passing 3 *N* hydrochloric acid until the effluent no longer gave a positive thiocyanate test for iron(III). This recovered resin was again converted to the sodium form. The portion of the chromatographic tube below the filter disc must be filled with water to minimize drying of the resin during the subsequent application of suction. The resin was introduced in a water slurry to a height of about 17 cm. The column was then back-flushed with about 500 ml of water. Enough paper pulp was added to provide a mat about 1–2 mm thick on top of the resin. Once prepared as described, the column could be used for at least 3 samples.

Analysis of steel samples

Into a 250-ml Erlenmeyer flask weigh out enough sample to supply about 1.5 mg of tungsten. If the concentration range of the tungsten is not known, use about 100 mg. Cover the sample with 25 ml of hydrochloric acid. Heat below boiling until the volume is reduced to one-half. Add 25 ml of nitric acid and heat until the volume is reduced to about 2 ml. It is desirable to reduce the volume as much as possible without allowing any salts to crystallize. If there is any unreacted tungsten, as indicated by the presence of dark particles, add another 25 ml of nitric acid and repeat the evaporation. Immediately wash the flask with 10–15 ml of water. Add one drop of formaldehyde (A.R., 37%) and return the flask to the hot plate until it begins to boil. Remove and set aside until ready for the ion-exchange process.

Place the ion-exchange column so that the effluent can be collected in a 500-ml suction flask. Into the top of the tube insert a short-neck funnel mounted in a rubber stopper to provide a sealed system. Decant the sample solution into the funnel, when most of the tungsten precipitate will adhere to the walls of the flask. In heavier samples some of the yellow precipitate will go into the tube but this will be caught on the paper layer. Adjust the flow rate to about 3–4 ml/min. Rinse the flask with 10–15 ml portions of water and decant 3 washings successively into the funnel. When the last rinse has passed from the funnel close the valve.

Place 50 ml of 1 *N* sodium hydroxide in the sample flask. If the tungstic acid precipitate does not dissolve immediately, heat the flask. If heating is required, cool before continuing. Connect the suction flask to a vacuum system. Remove the funnel and add water to raise the level above the resin, to just below the stopper, and replace the funnel. Pour the sample solution into the funnel. Turn on the vacuum and open the valve to provide a flow rate which is as fast as can be controlled through the following steps while still keeping the liquid always above the resin; a rate of about 30–40 ml/min is satisfactory. Rinse the flask with 3 40–50 ml portions of water. Remove the funnel. Add water to the column as needed until about 450 ml of effluent have been collected.

Transfer the effluent to a 1-l volumetric flask. Add 2 drops of phenolphthalein to the sample and neutralize with hydrochloric acid until one drop of 1 *N* acid just turns the solution colorless. Allow the solution to come to room temperature before bringing to volume with water.

This solution is then used for fluorimetric comparison with a standard tungstate solution as indicated in the section above on *Test solutions*. If the tungstate concentration is too high and the fluorescence is beyond the range of linearity of the calibration curve[1], suitable dilutions of the unknown can be made and the fluorescence reread. If the fluorescence is too weak, a larger sample of the steel must be used.

Results

The analytical procedure described was tested on 7 steel samples of various tungsten concentrations. The results are presented in Table I. For purposes of discussion, the vanadium and molybdenum concentrations in these steels are also listed.

Since the ion-exchange process removed cations, it was necessary to test for the effect of any anions in the analysis. It was found that only chromate, vanadate and molybdate ions were present in the effluent in sufficient concentration to cause any interference with the fluorescence. Chromate interferes seriously with the fluorescence even at a chromium/tungsten weight ratio of 0.0001. This interference is completely removed by the addition of formaldehyde which reduces Cr(VI) to Cr(III). Vanadium and molybdenum suppress at metal/tungsten weight ratios of 0.025 and 0.1, respectively; sodium cyanide was found to be an effective but limited masking agent for vanadium and molybdenum. Other possible masking agents were tried but were not successful. In synthetic mixtures the tolerances of these elements in cyanide solution were raised to a metal/tungsten ratio of two. Sample 3 contains molybdenum in a Mo/W ratio greater than 4, indicating that the practical molybdenum tolerance is higher than that determined with synthetic mixtures. However, with another steel in which the Mo/W ratio was 5, suppression of the fluorescence was evident. This method is, therefore, limited to steels in which the V/W ratio does not exceed 2 and the Mo/W ratio does not exceed about 4.

TABLE I

ANALYSES OF STEEL SAMPLES

Steel no.	*Reported %W*	*Found %W*	*No. of samples*	*V%*	*Mo%*
1[a]	18.25	18.23 ± 0.26[c]	7	0.97	0.009
2[a]	6.29	6.29 ± 0.094	7	1.64	7.07
3[a]	2.00	2.00 ± 0.076	8	1.25	8.35
4[b]	1.20	1.20 ± 0.024	5	0.033	?
5[b]	0.81	0.808 ± 0.023	5	0.011	?
6[a]	0.517	0.523 ± 0.026	5	0.014	0.039
7[b]	0.43	0.444 ± 0.071	3	0.004	?

[a] National Bureau of Standards: Nos. 50a, 132, 134a, 155, respectively.
[b] Crucible Steel Co. of America: Nos. TS6, LAS81W, LAS43, respectively.
[c] Precision expressed as standard deviation.

Discussion

Since the preparation of a bulk quantity of resin can be done in a few hours the actual time per steel sample is only a few minutes. Similarly, the preparation of the ion-exchange column is quite short. Four columns, to accommodate up to 16 steel samples, can be prepared in lesss than 15 min. The back-flushing process requires about 20 min, but after the levelling bulb has been set in position the operation does not require any further attention. Including the time for these preparations, the total ion-exchange process is much faster than a tungstic acid filtration.

In the ion-exchange process described there are several points to be considered. It is desired to remove cations completely, especially iron, while permitting the tungstate to be eluted quantitatively. It was found that this could not be done with a column in the hydrogen form while the sodium form was effective. Yet, it is necessary that the sample solution be acidic to keep the iron(III) in solution. In order to minimize any hydrogen ion exchange with iron(III) it is necessary to minimize the acidity of the sample solution. Hence the evaporation to a minimum volume. One might minimize this acidity by adding base but the adjustment is delicate and it was found that the evaporation process was more satisfactory. When too much acid was left in the sample, the iron band did not stay at the top of the column.

The two-step elution process, with different flow rates, is necessary. In the slow step there is effective cation exchange. In the fast step it is desirable to minimize exchange and merely remove the alkaline tungstate solution.

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A simple sodium thermionic detector for organic halogen and phosphorus compounds

KARMEN AND GIUFFRIDA[1-4] have described several modifications of hydrogen flame ionization detectors (F.I.D.) which show an enhanced response to compounds containing halogens and/or phosphorus. These detectors are now commercially available and have been designated as Sodium Thermionic Detectors by at least one company*.

One F.I.D. has a probe treated with a sodium salt interposed between the burner and the collector electrode. This detector gives an enhanced response to halogen- and phosphorus-containing compounds as well as a normal response to organic compounds. The outputs of the 2 detectors are recorded simultaneously, and the halogen- and phosphorus-containing compounds are located by the relative peak heights of the 2 chromatograms.

This communication describes a similar, but simpler detector which can be easily constructed from inexpensive material found in most laboratories. A diagram of the apparatus is shown in Fig. 1. The burner is a length of 1/8″-tubing about 1″ long. The probe is made of a short length of 24-gauge Nichrome wire. The loop is 10 mm in diameter and is positioned 5–10 mm above the burner tip. It is held in position by wrapping the other end around the burner. The probe is treated by dipping it into

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* Packard Instrument Company, Inc., Downers Grove, Illinois.

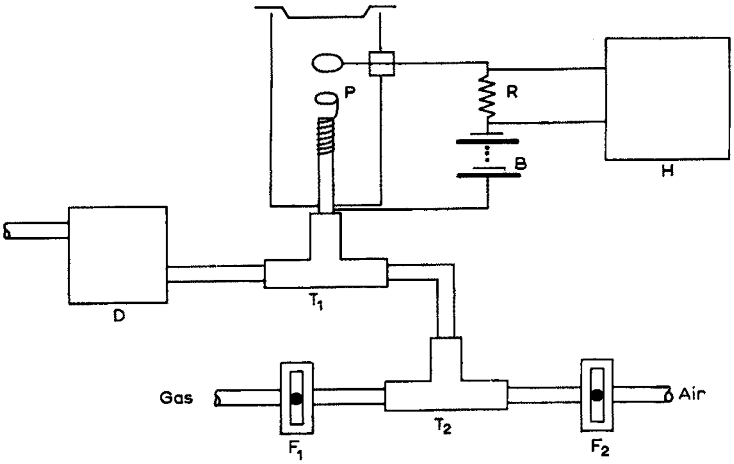

Fig. 1. Simple sodium thermionic detector. (B) $22\frac{1}{2}$-V battery; (D) thermal conductivity detector; (F_1, F_2) flowmeters; (H) Heath EUW-20A recorder; (P) sodium treated probe; (R) resistor 47 kΩ; (T_1, T_2) all tubing tees, $\frac{1}{8}$″.

a 1% sodium hydroxide solution and igniting in a Bunsen flame. The collector electrode is also a Nichrome loop approximately 12 mm in diameter and positioned about 10 mm above the probe. The burner chimney may be either glass or metal tubing. No shielding is required for the glass chimney.

The burner may be connected to the outlet of a thermal conductivity detector either inside or outside the chromatograph oven. If the connection is on the outside of the oven, the tubing leading to the burner and the burner tee should be wrapped with heating tape to prevent condensation of the sample. Ordinary laboratory gas which has been passed through concentrated sulfuric acid to remove impurities is a satisfactory fuel. The air may be from any convenient source.

The gas flow rates were 30 ml/min for fuel and 160 ml/min for air. However, these might require some adjustment depending upon the flow rate of the chromatograph carrier gas.

This detector responds only to compounds which contain halogen or phosphorus. Therefore, the 2-burner arrangement is not necessary. The sensitivity of this detector is comparable to a thermistor thermal conductivity detector. Therefore, it should be used only in cases where the halogen- or phosphorus-containing compounds constitute an appreciable fraction of the total sample. The response of the detector decreases with repeated use with halogenated compounds. Repeated experiments with the Karmen detector revealed a similar pattern of decreasing sensitivity with use. Quantitative data should, therefore, be obtained from the thermal-conductivity chromatogram. This detector should prove useful as a means of quickly identifying the presence of organophosphorus and halogen compounds and semiquantitatively determining their concentration.

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Anal. Chim. Acta, 37 (1967) 412–414

Alkyl-8-quinolinols

Although only the 2-methyl derivative has any significant difference in chelating properties from 8-quinolinol itself[1], all 6 monomethyl 8-quinolinols are known[2]. Of the polymethyl derivatives 6 of the 12 dimethyl compounds have been made[3], and one trimethyl[4] and one tetramethyl[5] derivative. There are extended series of both 5- and 6-alkyl-8-quinolinols[6,7] and a few ethyl derivatives, including 4-ethyl-8-quinolinol, a degradation product from an antibiotic[8].

In the course of making some new formyl-8-quinolinols we have prepared 5 new alkyl-8-quinolinols (Table I), including 2 new dimethyl, one trimethyl and one tetramethyl compound, by variations of the Doebner–Miller reaction of *o*-aminophenols with α,β-unsaturated aldehydes or ketones. The 2,5-dimethyl-8-quinolinol is not new[9], but there has been no previous report of its spectra and chelating properties.

TABLE I

SUBSTITUTED 8-QUINOLINOLS

Substituents	*M.p.(°)*	*Yield (%)*	*Formula*	*% Nitrogen*	
				Calcd.	*Found*
4,5-Dimethyl	154	25	$C_{11}H_{11}NO$	8.08	7.87
4,7-Dimethyl	73	20	$C_{11}H_{11}NO$	8.08	7.97
4-Ethyl-5-methyl	116	15	$C_{12}H_{13}NO$	7.53	7.47
2,3,5-Trimethyl	93	10	$C_{12}H_{13}NO$	7.50	7.70
2,3,4,5-Tetramethyl	126	15	$C_{13}H_{15}NO$	6.98	7.00

Only qualitative chelate testing was undertaken with these reagents, since all were expected to follow known patterns of behavior. The reagents containing 2-methyl substituents did not appear to chelate with aluminum, and the 2,5-dimethyl and 2,3,5-trimethyl did not precipitate iron and copper at pH 3, although they did at higher pH. Chelation with other common ions closely followed results with 8-quinolinol itself.

Ultraviolet spectra of the new compounds and of 2,5-dimethyl-8-quinolinol were determined in ethanol, acid and base (Table II). Maxima in both acid and base tended to fall at somewhat longer wavelengths than those of compounds with methyl groups in the pyridine ring only[2], and are fairly distinctive. The greatest departures from the average belong to 4,7-dimethyl-8-quinolinol, no doubt because one methyl group is close enough to the hydroxyl for interaction.

TABLE II

ULTRAVIOLET SPECTRA OF SUBSTITUTED 8-QUINOLINOLS

Substituents	*Maxima (nm) (log ε)*		
	EtOH	*0.1 N HCl*	*0.1 N NaOH*
2,5-Dimethyl	251(4.67) 322(3.68)	261(4.87) 315(3.44) 327(3.44) 372(3.39)	262(4.48) 343(3.52) 362s(3.45)
4,5-Dimethyl	246(4.74) 329(3.64)	256(4.85) 311(3.15) 370(3.50)	255(4.52) 344(3.71)
4,7-Dimethyl	246(4.88) 272(4.81) 330(3.42)	250(4.70) 308s(3.37) 320(3.45) 350(3.36)	257(4.54) 337(3.45) 365(3.49)
2,3,5-Trimethyl	252(4.68) 315(3.55)	263(4.82) 316(3.40) 327(3.49) 368(3.33)	263(4.72) 345(3.52) 363s(3.44)
2,3,4,5-Tetramethyl	254(4.46) 312 (3.50)	262(4.67) 313(3.29) 325(3.32) 360(3.32)	262(4.48) 344(3.64)
4-Ethyl-5-methyl	247(4.67) 330(3.56)	257(4.70) 310(3.04) 371(3.40)	257(4.47) 344(3.58) 362s(3.51)

NMR spectra were also obtained and τ values for the methyl group protons are listed in Table III. For comparison (and because they do not appear to have been published before) values for 2-, 4- and 5-monomethyl-8-quinolinols are also included. In the polymethyl compounds interactions of adjacent groups make it difficult to associate τ values with substituent positions; the 4,5-dimethyl and 4-ethyl-5-methyl compounds in particular have very low τ values.

TABLE III

NMR SPECTRA OF METHYL PROTONS IN 8-QUINOLINOLS

Substituents	τ	*Substituents*	τ
2-Methyl	7.32	4,7-Dimethyl	7.39 7.61
4-Methyl	7.34	2,3,5-Trimethyl	7.28 7.43 7.46
5-Methyl	7.44		
2,5-Dimethyl	7.33 7.49	2,3,4,5-Tetramethyl	7.27 7.28 7.38 7.64
4,5-Dimethyl	7.12 7.20		
4-Ethyl-5-methyl (ring methyl only)	7.22		

Experimental

Preparation of compounds. With the exception of 2,3,5-trimethyl-8-quinolinol, prepared by the standard Doebner–Miller reaction in hydrochloric acid, all compounds were made by the polyphosphoric acid modification as described below because of better yields. Methyl and ethyl vinyl ketones, 2,β-dimethylacrolein and 3-methyl-3-penten-2-one were the α,β-unsaturated compounds employed, and 2-hydroxy-5-methyl- and 2-hydroxy-3-methylanilines were the amines; all were commercially available except the last[10,11].

The appropriate *o*-aminophenol (0.25–1.25 mole) was added to 100 g of polyphosphoric acid heated to 90° and the mixture was stirred for 5 min before adding over a period of 5–10 min, a 50% excess of the α,β-unsaturated carbonyl compound. After 20 min of stirring at 110°, the mixture was cooled to 60° and about 400 ml of water added. Impurities were removed by steam distillation and the phosphate complex was then broken by addition of 20 ml of hydrochloric acid. The mixture was made alkaline with sodium hydroxide, reacidified with acetic acid and steam-distilled. Neutralization of the distillate precipitated the products. These were filtered, washed and recrystallized from 50% ethanol.

Qualitative tests. Chelation tests were performed at pH 3, 5 and 9 with the divalent ions of Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd and UO_2 and trivalent ions of Al, Fe, Cr and La. In compounds with a vacant 4-position, no precipitates of Cu or Fe at pH 3 were observed; these were the only ions precipitated at this pH by the other reagents. At pH 5 and 9 chelates comparable to those of oxine itself were generally obtained, with the exception of the 2-alkyl substituted reagents and aluminum.

Spectra. Ultraviolet spectra were recorded on a Cary Model 14 Spectrophotometer in 95% ethanol, 0.1 *N* HCl and 0.1 *N* NaOH.

NMR spectra were run in carbon tetrachloride solutions at several dilutions on a Varian HR 60 instrument, extrapolating results to infinite dilution.

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BOOK REVIEWS

W. T. Elwell and D. F. Wood, *Analysis of the New Metals–Titanium, Niobium, Tantalum, Tungsten and their Alloys*, Pergamon Press, Oxford, 1966, xii+275 pp., price 60 s.

This book is an extension of the authors' *The Analysis of Titanium, Zirconium and their Alloys*, published in 1961. It is essentially a new book in that it now includes methods for niobium, tantalum, tungsten and their alloys, as well as newer methods for the analysis of titanium and zirconium, although the greatest emphasis is still on the analysis of titanium, zirconium and hafnium metals and alloys.

The text is divided into sections, each dealing with the particular metal and its alloys. An introductory discussion to each section outlines the principles and limitations of the various available procedures which follow. In general, more than one procedure is described for each element to be determined. These procedures cover an extremely broad range of analytical techniques, from classical gravimetry to X-ray fluorescence spectrometry, and illustrate most admirably the versatility of the modern analytical chemist in a large industrial laboratory.

The authors have set themselves the task of providing a laboratory manual of tested and proved methods for the analysis of these new metals and alloys. Their experience in this field covers a period of many years of commercial development of these materials, and their recommendations are all the more authoritative as a result of the intensive research with which they have been concerned. The outcome of this is a text which amply reflects the best current practice in the analysis of these newer metals, and which must be accepted as a standard work in metallurgical analysis.

W. I. Stephen (Birmingham)

Anal. Chim. Acta, 37 (1967) 417

R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, Amsterdam, 1966, vi+137 pp., price 55 s.

This sixth monograph in Elsevier's collected Topics in Inorganic and General Chemistry provides an extremely useful source of information on the chemistry of the two less common elements, rhenium and technetium. The special properties of these elements and their compounds are giving rise to several new applications and significant amounts of these comparatively expensive chemicals are becoming commercially available. The publication of this monograph is timely because it brings together most of the available knowledge on the chemical behaviour of the two elements; this is the importance of the book to analytical chemists. Increasing technological uses for rhenium and technetium will require better methods for their determination, not only in pure forms, but in combination with other materials; the sparseness of available methods is only too apparent in Chapter 11 of the present monograph, where little over 3 pages is devoted to analytical considerations.

Essentially a research text, this book must be of considerable value to anyone embarking on the development of new analytical methods for rhenium and technetium.

W. I. STEPHEN (Birmingham)

Anal. Chim. Acta, 37 (1967) 417–418

WILLIAM F. PICKERING, *Fundamental Principles of Chemical Analysis*, Elsevier Publishing Co., Amsterdam, 1966, ix + 270 pp., price 60 s. or Dfl. 30,—.

It is an unfortunate fact that there are too few textbooks available which deal exclusively with the basic principles of chemical analysis. And those which are available are out-of-date, or are too advanced for the undergraduate, or do not cover some of the more modern techniques which are now included in many advanced teaching courses. In this new text, Dr. PICKERING has succeeded in overcoming all these shortcomings, for he deals admirably with all the fundamental requirements of a modern teaching course in analytical chemistry.

The book is divided into 12 chapters consisting of: Introduction; Phase Separations; Electrical Transformations; Ionic Equilibria; Energy Transitions; Physical Properties of Matter; Statistics, Sampling and Solution of Samples; Selective Chemical Reactions; Heterogeneous Equilibrium Reactions; Chromatographic Separations; Selection of Analytical Methods; Tutorial Problems. There is also an Appendix listing recent publications in analytical chemistry. Under these various headings the theory of electrochemical and optical methods are covered from every aspect as well as classical analysis, ion exchange, extraction and chromatography.

This is a very thoughtful, concise and well-written book; it can be recommended for all stages in the teaching of analytical chemistry.

R. BELCHER (Birmingham)

Anal. Chim. Acta, 37 (1967) 418

PUBLICATIONS RECEIVED

B. CAPON, M. J. PERKINS AND C. W. REES, *Organic Reaction Mechanisms, 1965*, Interscience Publishers – J. Wiley and Sons, Ltd., London, 1966, viii+352 pp., price 63 s.

This is the first of a series of annual surveys and covers the literature dated December 1964 through November 1965. Chapter heads: Classical and Non-classical Carbonium Ions; Nucleophilic Aliphatic Substitution; Electrophilic Aliphatic Substitution; Elimination Reactions; Addition Reactions; Nucleophilic Aromatic Substitution; Molecular Rearrangements; Radical Reactions; Carbenes and Nitrenes; Reactions of Aldehydes and Ketones and their Derivatives; Reactions of Acids and their Derivatives; Photochemistry; Oxidations and Reductions.

Anal. Chim. Acta, 37 (1967) 418

Progress in Nuclear Energy. Series IX. Analytical Chemistry, Vol. IV, Edited by C. E. CROUTHAMEL, Pergamon Press, Oxford, 1966, v+166 pp., price 70 s.

This book contains the following reviews: Solid State Charged Particle Detectors (N. J. HANSEN); Advances in Neutron Activation Analysis (V. P. GUINN); Slow Electron Interaction with Adsorbed Gases (D. LICHTMAN AND R. B. MCQUISTAN); Use of Neutron Generators in Activation Analysis (J. E. STRAIN).

Progress in Nuclear Energy. Series IX. Analytical Chemistry, Vol. VI, Edited by D. C. STEWART AND H. A. ELION, Pergamon Press, Oxford, 1966, v+260 pp., price 90 s.

This book contains the following reviews: Ion Exchange in Mixed and Nonaqueous Solvents (J. KORKISCH); Some Neutral Bifunctional Organiphosphorus Compounds as Solvent Extractants (J. W. O'LAUGHLIN); Anion Exchange in Nitrate Solutions (J. FARIS AND R. F. BUCHANAN); Analytical Chemistry of Neptunium (G. A. BURNEY, E. K. DUKES AND H. J. GROH); The Analytical Chemistry of Polonium (R. C. LANGE).

The Radiochemical Manual, 2nd Edn., Edited by B. J. WILSON, The Radiochemical Centre, Amersham, 1966, 327 pp., price 50 s.

Chapter heads: The general nature of isotopes; The basic nuclear and chemical processes; Synthesis of labelled compounds; Design and manufacture of radiation sources; The concept and determination of purity; Instability in radioactive chemicals; Behaviour of small masses and very dilute solutions; Radioactive chemicals as pharmaceuticals; The quantification of radioactive substances; The exact specification of materials; Radiological safety and waste disposal; Packaging and carriage of radioactive materials; Regulation of ownership and use; A guide to the literature on isotopes.

Tables of physical data for the commoner radioisotopes, radiation sources, synthetic routes to labelled compounds, decomposition rates of labelled compounds, measurement and safety are provided as appendices.

The Electron Microprobe, Edited by T. D. MCKINLEY, K. F. H. HEINRICH AND D. B. WITTRY, J. Wiley and Sons, Inc., New York, 1966, xvi+1035 pp., price 210 s.

This book contains the proceedings of the symposium sponsored by the Electrothermics and Metallurgy Division of the Electrochemical Society, held in Washington, D.C. during October, 1964.

ERRATA

J. D. Winefordner, W. W. McGee, J. M. Mansfield, M. L. Parsons and K. E. Zacha, Intensity of thermal radiation of metal spectra in flame emission spectrometry, *Anal. Chim. Acta*, 36 (1966) 25.

Eqns. 1 and 2, change 10^7 to 10^{-7}.
Fig. 1, the intensity at right hand side of left hand figure should be $(I_t)_\nu$.
Eqn. 18, replace $B(T)$ in denominator by g_n.
Eqn. 21, replace 2 in numerator by 4.

p. 32, right Eqn. 7, should read: $= \dfrac{2\,h\nu_0{}^3\pi e^2}{10^7\,mc^3} N_M f L \exp(-h\nu_0/kT)$.

Eqn. 29, should read: $A_T = \dfrac{\sqrt{\pi}\,\Delta\nu_D}{\sqrt{\ln 2}} \sqrt{\dfrac{k^0 La}{\sqrt{\pi}}}$

Left Eqn. 30, replace A_T by A_t,

Right Eqn. 30, should read: $\dfrac{2\,h\nu_0{}^2 \exp(-h\nu_0/kT)}{10^7 c^2} \sqrt{\dfrac{2\pi e^2 \Delta\nu_D N_M f L a}{mc\sqrt{\ln 2}}}$

Eqn. 36, one large bracket should come *after* $2\,h\nu_0{}^3/10^7c^2$ and one large bracket at the end of equation, i.e.,

$$I_{\nu_R} = \frac{2\,h\nu_0{}^3}{10^7c^2}\Big[[\ldots]\exp(\ldots) + [\ldots]\exp(\ldots)\exp(\ldots)\Big].$$

p. 38, line 16 from top, should read: ... and 5.0 and $NfL\sqrt{\ln 2}/\pi\Delta\nu_D = \ldots$

p. 38, line 2 of paragraph 2, should read: $(\nu_0, E_m, g_m \ldots)$

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ANNOUNCEMENT
concerning the
JOURNAL OF ELECTROANALYTICAL CHEMISTRY

The boundaries between what are regarded as electroanalytical chemistry, electrochemistry and colloid chemistry are becoming increasingly diffuse. This has been reflected in the pages of the journal, where many of the papers published are of interest to chemists who consider themselves as falling under any of these three broad divisions.

The linking phenomena are those associated with the electrical double layer, and it is felt that it would be both useful and appropriate to acknowledge these broader interests by extending the scope of the journal to include all phenomena in which the electrical double layer plays an essential role.

These extend from applications in analytical chemistry through the fundamentals of electrode reactions, which are already the staple part of the journal, to studies of the double layer around colloidal particles, the stability of dispersions and electrokinetic phenomena as well as other surface chemical problems such as monolayers and soap films.

Since this broadening of the scope does not involve any change in the basic interests of the journal, the title has been only slightly modified. From January 1967 it has become:

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Since the aim of a journal must be to publish papers rapidly, it has been decided that three volumes will be published in 1967. The delay in publication will thereby be reduced to a minimum level.

Dr. R. H. Ottewill of the University of Bristol has joined the board of Editors, and has special responsibility for the papers which fall within his field of interest.

Papers for publication should be sent to one of the following addresses:

Professor J. O'M. Bockris, John Harrison Laboratory of Chemistry, University of Pennsylvania,
Philadelphia 4, Pa. 19104, U.S.A.;

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(Until July, 1967: Gates and Crellin Laboratories of Chemistry, California Institute of
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A printed pamphlet "hints to authors" is available free of charge from the publishers, who will be glad to supply any further information to intending authors.

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