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THE FACTORS AFFECTING THE REFLECTANCE SPECTRA OF SOME DYES ADSORBED ON ALUMINA

Various factors affecting the diffuse reflectance spectra of eosin B, rhodamine B, fuchsin, and *o*-nitrophenol adsorbed on chromatographic alumina under various conditions were studied to explore the potential analytical application of reflectance spectroscopy to dyestuffs separated by thin-layer chromatography. Regeneration temperature, pH and grade of adsorbent, and humidity were found to influence the spectra but the technique may be utilized for the photometric analysis of food dyes adsorbed on alumina; straight lines passing through the origin were obtained when the Kubelka–Munk function was plotted against a suitable concentration range of dye. For reproducible results, it is essential to employ the same grade of adsorbent and to prepare samples under uniform conditions of humidity.

R. W. FREI AND H. ZEITLIN,
Anal. Chim. Acta, 32 (1965) 32–39.

THE SOLUBILITIES AND ANION-EXCHANGE BEHAVIOR OF RARE EARTH ELEMENTS IN POTASSIUM CARBONATE SOLUTIONS

The solubilities of rare earth elements (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) in potassium carbonate solution, and the distribution coefficients of the rare earth ions between the carbonate solution and Dowex 1 resin were measured. The values obtained show a variation that depends on the concentration of potassium carbonate and atomic number. There is a clearly different tendency in these values between La–Ho and Er–Lu.

T. TAKETATSU,
Anal. Chim. Acta, 32 (1965) 40–45.

ANION-EXCHANGE SEPARATION OF IRON, COBALT AND NICKEL

From a 90% acetone–10% 6 *M* hydrochloric acid medium, cobalt and nickel are strongly adsorbed on the anion-exchange resin Dowex 1-X8; iron is not adsorbed and can thus be separated from cobalt and nickel. Cobalt and nickel are then separated by elution with 70% acetone–30% 2 *M* hydrochloric acid; nickel is eluted before cobalt. The method can be applied to the determination of nickel and cobalt in materials with high iron content such as steels; complexometric titrations are used for the final step.

I. HAZAN AND J. KORKISCH,
Anal. Chim. Acta, 32 (1965) 46–51.

DETERMINATION OF LANTHANUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

N-Benzoyl-N-phenylhydroxylamine is proposed for the gravimetric determination of lanthanum at pH 6.4–7.2. The precipitate can be weighed directly or ignited to the oxide. By suitable pH adjustment, many metals can be separated from lanthanum, which can then be determined in the filtrates. Interferences of Ni, Cu, Zn and Fe(II) are masked with cyanide. About 99.5% of cerium can be separated from lanthanum by precipitating cerium(IV) at pH 4.8–5.2.

B. Das and S. C. Shome,
Anal. Chim. Acta, 32 (1965) 52–56.

SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH CHROME AZUROL S

A comprehensive investigation of the spectrophotometric determination of aluminium with chrome azurol S is described. No heating is required for colour formation, and the method is considerably more reproducible and selective than either the eriochrome cyanine R or aluminon methods. In the presence of suitable masking agents, only Be^{2+}, Zr^{4+}, and F^- cause serious interference. A molar absorptivity of 21,500 at 567.5 mμ was found for the aluminium–chrome azurol S lake, with a relative standard deviation of ± 0.4 % at the 20 μg Al level. Beer's law is obeyed from 0 to 1.2 μg Al/ml.

P. Pakalns,
Anal. Chim. Acta, 32 (1965) 57–63.

PHOSPHORIMETRIC DETERMINATION OF PROCAINE, PHENOBARBITAL, COCAINE, AND CHLORPROMAZINE IN BLOOD SERUM, AND COCAINE AND ATROPINE IN URINE

A new sensitive and rapid method is proposed for the determination of procaine, cocaine, phenobarbital and chlorpromazine in blood serum, and cocaine and atropine in urine. The drug is extracted from the biological fluid using chloroform or ether, the solvent is evaporated and the resulting residue is dissolved in EPA; the EPA solution is measured phosphorimetrically. Recoveries of 100 ± 6% and relative standard deviations of 2–5% are obtained for most drugs.

J. D. Winefordner and M. Tin,
Anal. Chim. Acta, 32 (1965) 64–72.

POLAROGRAPHY OF INTERMEDIATES IN THE FIXATION OF NITROGEN BY *p*-QUINONE–AQUEOUS AMMONIA SYSTEMS

Air oxidation of aqueous *p*-quinone, as a model humic acid precursor, develops precipitates of different character in the presence and absence of ammonia. Polarographic analyses of the *p*-quinone–ammonia systems at different ammonia concentrations, pH levels, and reaction times reveal two reducible intermediates in the reaction leading to fixation of nitrogen. The intermediates give half-wave potentials, at pH 8.3, of -0.25 and -0.55 V *vs.* S.C.E. The waves are interpreted as resulting from the reduction of mono- and disubstituted aminoquinones. A mechanism and structure are proposed for the nitrogen-containing polymerization product.

M. R. Lindbeck and J. L. Young,
Anal. Chim. Acta, 32 (1965) 73–80.

THERMOGRAVIMETRIC INVESTIGATION OF THE COMPLEXES OF 6-CHLORO-2-METHOXY-9-THIOLACRIDINE

The thermolysis curves of thiolacridine and of thioacridine complexes with Cu(II), Hg(II), Ag(I), Au(III), Pt(IV) and Pd(II) are described. The orange form of thiolacridine is the monohydrate and the red form is anhydrous. The complexes are quite thermally stable, with the platinum thioacridine chloride being the least stable.

M. W. Goheen, K. E. Daugherty and R. J. Robinson,
Anal. Chim. Acta, 32 (1965) 81–85.

THE DETERMINATION OF CAESIUM-137 IN RAIN-WATER

(Short Communication, in German)

J. Beneš,
Anal. Chim. Acta, 32 (1965) 85–88.

ANALYTICAL APPLICATIONS OF THE REACTION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID. PART VII. DETERMINATION OF BISMUTH, ZINC AND MANGANESE

(Short Communication)

L. Erdey, H. Khalifa and G. Svehla,
Anal. Chim. Acta, 32 (1965) 88–90.

AN ANION-EXCHANGE METHOD FOR THE DETERMINATION OF RARE EARTHS, THORIUM AND URANIUM IN MONAZITE

(Short Communication)

B. L. Jangida, N. Krishnamachari, M. S. Varde and V. Venkatasubramanian,
Anal. Chim. Acta, 32 (1965) 91–94.

STEAM DISTILLATION FOR THE ISOLATION OF MILLIGRAM AMOUNTS OF BENZOIC ACID AND BENZOPHENONE FROM DEGRADATIVE OXIDATIONS

(Short Communication)

R. D. Kimbrough, Jr.,
Anal. Chim. Acta, 32 (1965) 95–96.

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DECOMPOSABILITY IN HYDROFLUORIC ACID OF THE MAIN AND SOME MINOR AND TRACE MINERALS OF SILICATE ROCKS

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(Received May 23rd, 1964)

SCHEELE, the discoverer of hydrofluoric acid, reported[1] that silica and glass were decomposed by this reagent. BERZELIUS* is usually credited with having introduced a mixture of hydrofluoric and sulfuric acid as decomposing agent for rocks. After the attack fluoride had to be removed by evaporation. However, this operation also removed silicon and consequently this constituent had to be determined on a separate sample.

HILLEBRAND[2] experienced difficulties in removing completely fluoride by evaporation (the presence of fluoride results in incomplete precipitation of the constituents of the mixed oxide group) and advised against the use of hydrofluoric acid as the decomposing agent for the main portion. HILLEBRAND recommended fluxes for the attack of the main portion, and in his authoritative scheme of analysis, which in a more or less modified form is still universally applied, the use of hydrofluoric acid as decomposing agent is restricted to the sample weighed out for the determination of iron(II).

There are, however, reasons for suggesting the reintroduction of hydrofluoric acid as the main decomposing agent for silicate rocks, *viz.*:

(*a*) The main objection of HILLEBRAND[2] to using the acid has long been invalidated by the results of other authors**.

(*b*) It has been demonstrated[3] that silica (and presumably also other silicon-containing materials, *e.g.* rocks) can be decomposed by an excess of hydrofluoric acid without any loss of silicon through evaporation, and that the silicon brought into solution as fluorosilicic acid can be determined spectrophotometrically as the yellow α,12-molybdosilicic acid.

On the basis of the results of the latter investigation a new scheme[4] of silicate rock analysis has been worked out. This scheme utilizes hydrofluoric acid as the only

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* The present authors were unable to find the paper in which Berzelius introduced hydrofluoric acid as a decomposing agent for rocks.

** It is interesting to note that as early as 1915 SELCH[5] demonstrated that a double evaporation with sulfuric acid resulted in complete expulsion of fluoride. This result was confirmed by LANGMYHR AND GRAFF[6]. The latter authors carried out the evaporations in vessels of polytetrafluoroethylene (teflon) and pointed out that, in order to expel the last traces of fluoride, it is necessary to evaporate twice — not only to dense fumes, but to complete dryness and at a final heating temperature of 280 ± 10°.

decomposing agent. A main feature of this scheme is that the conventional gravimetric method for silicon has been replaced by a photometric method without systematic error and with a precision better than that obtained by the classical scheme.

In connection with the development of a scheme based on decomposition by hydrofluoric acid, it was of interest to know whether this agent decomposed quantitatively the minerals normally met with in silicate rocks. A survey of the literature showed that no systematic studies have been made to elucidate the experimental conditions by which the largest possible number of minerals — and especially those of interest in the analysis of silicate rocks — could be decomposed quantitatively and rapidly.

The present paper describes a study of the decomposability in hydrofluoric acid of a selection of 28 minerals, the majority of which were main minerals of silicate rocks. Some of the factors relating to the use of hydrofluoric acid as decomposing agent were also investigated.

EXPERIMENTAL

Equipment

Decomposition experiments at temperatures up to about 100° were made in plastic beakers (capacity about 100 ml) covered with watch glasses of plastic material. Experiments at temperatures up to about 250° were carried out in a teflon-lined aluminium bomb of a type similar to that previously described by RILEY AND WILLIAMS[7] and ITO[8].

Temperatures were measured with an ordinary mercury thermometer. When dipped into hydrofluoric acid, the tip of the thermometer was protected with a piece of plastic tube closed at one end.

The beakers were heated on a water bath of standard construction. The bomb was heated on a hot plate.

Reagents

The aluminium trichloride hexahydrate was of purum quality; all other chemicals were of reagent-grade quality. The strengths of the acids used were: hydrofluoric acid 38–40%, perchloric acid 60%, sulfuric acid 95–97% and hydrochloric acid 37%.

Procedures

Selection of minerals. Although about 2500 different minerals are known, the number that composes more than 99% of igneous and metamorphic rocks is very small. In a survey of the distribution of minerals in igneous rocks, BARTH[9] lists 13 main and main groups of minerals. On the basis of this list 28 minerals (Table I) were selected for the present investigation. As can be seen from Table I all the main minerals of silicate rocks are represented, as well as a number normally present only in minor or trace amounts. Some of the rare minerals were included because they are known to be resistant to attack by hydrofluoric acid.

The purity of the samples varied considerably and was assumed to range from about 96% to about 99.9%, the purest specimens being those of quartz and the felspars.

Preparation of the samples. A suitable amount of the mineral to be tested was first crushed in a steel mortar and then pulverized in an agate mortar to pass a 100-mesh sieve. Before the experiments the samples were dried for 1 h at 105–110°.

Decomposability of the minerals in a mixture of concentrated hydrofluoric and perchloric acids. 200 ± 1 mg of the sample were weighed out (all weighings were made to the nearest 0.1 mg), transferred to a plastic beaker and moistened with 5–6 drops of distilled water. A mixture of 10 ml of concentrated hydrofluoric acid and 10 ml of concentrated perchloric acid was added, and the beaker was covered and kept in the boiling water bath for the times specified in Table I. Every 5 min the contents of the beaker were mixed by swirling. The temperature of the attacking solution was maintained at 95 ± 2°. The beaker was finally cooled in tap water and the contents were transferred to a 600-ml glass beaker containing 350 ml of 25% aluminium trichloride hexahydrate solution. Another portion of 50 ml of the same solution was used for washing the plastic beaker. The treatment with aluminium solution served the double purpose of dissolving precipitated fluorides and making the excess of hydrofluoric

TABLE I

DECOMPOSABILITY OF 200-mg SAMPLES OF SELECTED MINERALS IN 20 ml OF A 1 : 1 MIXTURE OF CONCENTRATED HYDROFLUORIC AND PERCHLORIC ACIDS

(For experimental details see text)

Mineral	*Amounts (mg) of mineral decomposed at 95° after*			*Amounts (mg) decomposed in the bomb*
	20 min	*40 min*	*60 min*	
Quartz	145	200	—	—
Sodium felspar	200	—	—	—
Potassium felspar	200	—	—	—
Plagioclase	200	—	—	—
Nepheline	200	—	—	—
Muscovite	200	—	—	—
Biotite	200	—	—	—
Talc	200	—	—	—
Enstatite	183	200	—	—
Antophyllite	172	200	—	—
Hornblende	200	—	—	—
Beryl	45	—	58	200
Cordierite	200	—	—	—
Wollastonite	200	—	—	—
Olivine	200	—	—	—
Kyanite	60	—	64	200
Topaz	22	—	24	70
Staurolite	120	—	124	200
Andradite	158	200	—	—
Epidote	178	200	—	—
Magnetite	141	200	—	—
Aragonite	200	—	—	—
Magnesite	200	—	—	—
Apatite	200	—	—	—
Fluorite	200	—	—	—
Pyrite	30	—	44	200
Chalcopyrite	29	—	32	200
Pyrrhotite	66	—	104	200

acid harmless. The solution in the glass beaker was heated for 30 min on the boiling water bath. During this period the solution was stirred occasionally. The solution was filtered through a glass filter crucible (porosity 20–30 μm) previously dried to constant weight at 105–110°. After washing with distilled water the crucible was redried to constant weight at the same temperature.

In the first series of experiments the samples were attacked for 20 min. Minerals which were completely decomposed by this treatment were not submitted to further experiments. From the first series 6 minerals — of which less than 200 mg, but more than 140 mg had been decomposed — were retested by weighing out a new sample and using an attacking period of 40 min. As seen from Table I, this prolonged treatment resulted in complete decomposition. Likewise, minerals — of which less than 140 mg had been decomposed in the first series — were attacked for a period of 60 min. As apparent from Table I, this treatment did not result in complete decomposition ot the 7 minerals in question. These samples were then attacked by the bomb technique using the following procedure. The bomb was preheated on the hot plate to about 90° and was removed from the plate; 200 ± 1 mg of mineral were transferred to it and moistened with 6–8 drops of distilled water and a mixture (preheated to about 90°) of 10 ml of concentrated hydrofluoric acid and 10 ml of concentrated perchloric acid was added.

The bomb was closed and heated for 60 min at 250 ± 10°; during the heating period the bomb was shielded and the temperature was controlled carefully. After cooling, the procedure was the same as in the previous experiments. The results are tabulated in Table I.

A study of some of the factors relating to the use of hydrofluoric acid as decomposing agent. In Tables II–V are reported the experimental results from a study of the effects of some variables on the decomposability of the minerals quartz, staurolite and epidote. With the exception of the factor under investigation, the experimental conditions were as described above for the series heated on the water bath. In all experiments the heating time was 20 min.

RESULTS AND DISCUSSION

The present investigation confirmed that hydrofluoric acid is a powerful decomposing agent for minerals. All main, as well as a number of minor and trace minerals of silicate rocks were decomposed easily at the temperature of the boiling water bath. Of the 28 minerals tested, 21 were successfully attacked in this way. The remaining minerals were only partially decomposed on the water bath, but — with the exception of topaz — these resistant minerals could all be brought into solution by applying the bomb technique*.

As to the effect of varying some experimental factors, some of the results were in accordance with what one would expect, *e.g.* the effect of the time of heating and of the temperature of the attacking solution. On the other hand, stirring did not seem to have any significant effect upon the rate of decomposition.

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* The present list of decomposable minerals may be extended by including those successfully attacked by Ito[8], *viz.*: tourmaline, axinite, kornerupine, chrysoberyl, garnet, ilmenite, chromite, tantalite, columbite, baddeleyite, rutile, corundum and zircon.

TABLE II

EFFECT OF TEMPERATURE

Mineral	*Amounts (mg) decomposed at*		
	20°	*60°*	*95°*
Quartz	42	90	145
Staurolite	50	120	120
Epidote	20	31	178

TABLE III

EFFECT OF STIRRING

Mineral	*Amounts (mg) decomposed*	
	With stirring[a]	*Without stirring*
Quartz	149	145
Staurolite	118	120
Epidote	160	178

[a] About 200 revolutions per min.

TABLE IV

EFFECT OF PARTICLE SIZE

Mineral	*Amounts (mg) decomposed when ground to pass*			
	70 mesh	*100 mesh*	*200 mesh*	*240 mesh*
Quartz	104	145	163	175
Staurolite	100	120	116	108
Epidote	105	178	200	200

TABLE V

EFFECT OF THE PRESENCE OF A SECOND CONCENTRATED MINERAL ACID

Mineral	*Amounts (mg) decomposed in*			
	10 ml HF	*10 ml HF + 10 ml* $HClO_4$	*10 ml HF + 10 ml HCl*	*10 ml HF + 10 ml* H_2SO_4
Quartz	165	145	135	147
Staurolite	119	120	117	124
Epidote	171	178	147	168

For quartz and epidote the effect of diminishing the particle size was as expected. However, for staurolite the amounts decomposed decreased when the sample was ground to pass 200- and 240-mesh sieves. A possible explanation for this result was that the prolonged pulverization led to the formation of lumps which were less easily moistened and attacked. Instead of trying to increase the rate of decomposition by grinding to a finer state of subdivision, it may be better to apply a higher temperature and/or to increase the time of attack. In general, grinding to below 100 mesh should be avoided because of the chemical changes that may take place, *e.g.* oxidation of iron(II), loss of gases, etc.

Some preliminary experiments indicated that it was advantageous to moisten the sample with water before the addition of the attacking solution.

As mentioned above, a decomposing mixture of hydrofluoric and sulfuric acid is universally employed in the analysis of rocks. However, in the literature no reasons are to be found for the presence of a second mineral acid during the decomposition. Nevertheless, the results shown in Table V demonstrate that hydrofluoric acid was more effective when used alone than in mixture with other mineral acids.

In the present main series of experiments — the results of which are given in Table I — a mixture of hydrofluoric and perchloric acid was used. However, the data of Table V indicate that in the main series of experiments better results could have been obtained by using only hydrofluoric acid. This conclusion is supported by the results of ITO[8], who reported that zircon was successfully decomposed by hydrofluoric acid, while a mixture of this acid and sulfuric acid (1:1) failed to do so. While ITO found pyrite to be undecomposable in the latter mixture, the mineral was successfully attacked by hydrofluoric acid alone in the present investigation.

During the main series of experiments it was observed that the dissolution of the minerals in practically all cases led to the formation of precipitates of slightly soluble fluorides or complex fluorides*. The addition of comparatively large volumes of concentrated acid, *e.g.* up to 30 ml of hydrochloric acid, failed to bring the precipitates into solution. The only way to get them into solution was to add a strong complexing agent for fluoride, *e.g.* an aluminium salt.

The authors are indebted to the Geological Museum of the University of Oslo for the selection of mineral samples.

SUMMARY

The decomposability in hydrofluoric acid of a selection of 28 main and some minor and trace minerals of silicate rocks was investigated. 21 minerals were decomposed successfully by heating on the water bath; the remainder — with the exception of topaz — were found to be decomposable at the higher temperatures of a teflon-lined bomb. The results indicate that hydrofluoric acid alone is more effective as decomposing agent than a mixture containing another mineral acid.

RÉSUMÉ

Les auteurs ont examiné le comportement dans l'acide fluorhydrique de 28 roches silicatées. 21 de ces mineraux ont pu être décomposés par chauffage au bain-marie; les autres, à l'exception de la topaze, ont été décomposés aux températures les plus élevées d'une bombe revêtue de téflon. Les résultats montrent que l'acide fluorhy-

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* In experiments with iron(II)-containing minerals it was observed that the precipitates held iron(II). Consequently, in the analysis of iron(II) according to the conventional scheme it is imperative that the precipitated fluorides are brought into solution before or during the addition of the oxidizing titrant.

drique seul est plus efficace comme agent de décomposition qu'un mélange renfermant un autre acide minéral.

ZUSAMMENFASSUNG

Die Zersetzbarkeit in Flusssäure von einer Auswahl von 28 Haupt-, einigen Neben- und Spurenmineralien in Silikatgesteinen wurde untersucht. 21 Mineralien wurden beim Erhitzen auf dem Wasserbad völlig zersetzt. Der Rückstand wurde ausser beim Topas bei höheren Temperaturen in einer mit Teflon ausgekleideten Bombe zersetzt. Die Ergebnisse zeigen, dass Flusssäure allein als zersetzendes Reagenz wirksamer ist als eine Mischung, die eine andere Mineralsäure enthält.

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THE SIMULTANEOUS DETERMINATION OF RHENIUM AND OSMIUM IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

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Rhenium and osmium are elements of very low cosmic and terrestrial abundance. The distribution of the two elements in natural sources can be studied only with very sensitive analytical methods; of the techniques readily available neutron activation analysis was chosen for this work, since it combines the advantages of extreme sensitivity with adequate precision and comparative freedom from contamination problems. Neutron activation analysis has previously been applied to the determination of rhenium in meteorites[1,2], igneous rocks[3], and minerals[4], and the distribution of osmium in cosmic and terrestrial sources has also been investigated by this technique[2,5].

Nuclear data

The nuclear data relevant to the determination of rhenium and osmium have been summarized by KOCH[6]. Rhenium analyses in the present work were based on the nuclide ^{186}Re ($t\frac{1}{2} = 89$ h) which has a sufficiently long half-life to survive the transit time from the reactor site, and that required for chemical processing. The half-life of ^{188}Re ($t\frac{1}{2} = 16.7$ h) is too short for convenience, and analyses based on this nuclide are subject to interference from a second order reaction on tungsten[3].

Osmium was determined by the nuclide ^{191}Os in all cases, and in some cases also by the nuclide ^{185}Os.

Irradiation

Samples and standards were generally irradiated in the HIFAR reactor at the Australian Atomic Energy Research Establishment at Lucas Heights in a predominantly thermal flux of $9 \cdot 10^{12}$ n/cm^2/sec for a period of one week. For samples with rhenium contents greater than 0.1 p.p.m., lower neutron doses were employed.

Outline of radiochemical procedure

In preliminary experiments standards were prepared by spiking *Specpure* silicon dioxide with rhenium and osmium, sealed in silica ampoules and irradiated. On opening the ampoules it was found that the active osmium was subject to serious losses by volatilization; in one experiment, for example, 30% of the osmium activity was lost by allowing the standard to remain open to the air for about 30 min, though, there was no loss of rhenium activity. A procedure was therefore developed, by which 100 ± 1.8% of the active osmium was retained until complete exchange with the carrier was established, by fusion with sodium hydroxide and sodium peroxide. In the case of the samples, loss of osmium at room temperature is not so likely to be serious; BATE AND HUIZENGA[5] consider that the rate of diffusion of osmium within the mineral grains is probably extremely slow. In view of this it was considered safe to weigh the sample before adding the carrier and equilibrating by an alkaline fusion.

The alkaline solution, produced by the dissolution of the cooled sodium hydroxide–sodium peroxide melt in water, contains rhenium and osmium in solution in their highest oxidation states, and the insoluble hydroxides can be removed by centrifuging. The preliminary separation of rhenium and osmium from each other was achieved by HERR *et al.*[2] by distillation; a similar method was used by BATE AND HUIZENGA[5]. In the present work the distillation step was replaced by an anion-exchange procedure, which is easier and safer to operate and requires simpler apparatus which can be readily decontaminated or replaced.

Rhenium(VII) has been shown to be strongly absorbed on strong base anion-exchange resins from hydrochloric acid solution[7,8] especially at low acid concentrations; HUFFMAN *et al.*[8] also studied the anion-exchange behaviour of rhenium in nitric acid media. In the present work the adsorption of rhenium on to an anion-exchange column from 1 N hydrochloric acid and subsequent elution with 2.3 N nitric acid was found convenient, and good recoveries were obtained.

There are few data on the anion-exchange behaviour of osmium; osmium(III) is strongly adsorbed on Dowex 1 from all concentrations of hydrochloric acid[7]. In the present work it was found that in chloride solution the anion-exchange behaviour of osmium depended on the number of chloride ions in the anionic complex: the complexes containing little chloride were eluted, at least in part, by 0.8 N nitric acid, the hexachloroosmate not at all. Further experiments showed that under suitable conditions (see p. 12) virtually quantitative elution of osmium could be achieved with 0.8 N nitric acid provided that the flow-rate was reduced to 0.25–0.5 ml/min, and not more than 5 mg of osmium carrier was used. No significant amount of rhenium was eluted in this lower concentration of nitric acid.

Rhenium was further purified by extraction into isoamyl alcohol from 2 N sulphuric acid, containing hydrazine to reduce any technetium present[9]; it was then back-extracted into 5 N sodium hydroxide[3,9] and finally precipitated as tetraphenylarsonium perrhenate[3].

Osmium, after the anion-exchange step, was precipitated as the hydrous dioxide, and further purified by extraction as osmium tetroxide into chloroform[10]. Osmium was removed from the organic phase by extraction into hydrochloric acid solution containing thiourea; in the aqueous phase the red osmium(III)–thiourea complex was formed. The addition of potassium chromithiocyanate precipitated $Os(NH_2 \cdot CS \cdot NH_2)_6Cr(SCN)_6$ which has been shown[11] to be a suitable compound for gravimetric determination of osmium.

EXPERIMENTAL

Preparation of anion-exchange columns

Prepare the columns by slurrying 1 g of De-acidite FF (SRA 71, 100–200 mesh, 7–9% cross-linked) into a glass tube, 6 mm internal diameter, drawn down to about 2 mm internal diameter at the lower end, the resin being retained by a small plug of cotton wool. Wash the column with 30 ml of demineralized water followed by 30 ml of 1 *N* hydrochloric acid.

Preparation of the carrier solution

Take about 2.5 g of *Specpure* $(NH_4)_2OsCl_6$ and 3.5 g of Specpure $KReO_4$ and dry to constant weight at 150°. (The osmium salt used in the present work consistently lost 2.6% of its original weight on heating; this was thought to be due to a slight excess of ammonium chloride, as the hexachloroosmate before heating was found to contain only 97.6 ± 0.8% of the theoretical amount of osmium. The loss of weight by the rhenium compound on heating was only 0.06%.) Make up to 500 ml in 3 *N* hydrochloric acid. This solution will contain about 2 mg Os/ml and 4 mg Re/ml.

Preparation of potassium chromihexathiocyanate

Dissolve 150 g of potassium thiocyanate in 85 ml of demineralized water, and 125 g of potassium chromium sulphate in 500 ml of demineralized water, warming slightly to assist solution. Cool the solutions and mix together in a 1-l beaker. Warm on a hot plate at low heat, until the temperature reaches 80°. Maintain at this temperature for 2 h, then allow to cool to room temperature. Add 200 ml of A.R. ethanol to precipitate the sulphate from solution. Filter the solution and evaporate to dryness on a water bath. When dry, grind to a powder and store in a glass-stoppered bottle.

Make a 40% solution of the reagent in water, and filter before use.

Preliminary treatment of samples

Weigh 0.1–0.2 g of the ground rock sample, or a smaller amount of mineral or iron meteorite, into a clean dry silica ampoule, and seal the tube.

Irradiate together with standards in a suitable thermal neutron flux for an appropriate period, generally one week. After irradiation allow to stand for about 24 h in order to allow the shorter-lived induced activities to decay.

Open the sample ampoule, transfer the sample to a clean weighed zirconium crucible and reweigh. Add 2 ml of the carrier solution containing about 2 mg Os/ml and 4 mg Re/ml, and add 1 ml of A.R. ethanol to ensure reduction of any osmium(VIII) dissolved from the sample by the 3 *N* hydrochloric acid carrier solution. Allow to stand for 10 min, then make alkaline by the addition of 2–3 pellets (about 0.25 g) of A.R. sodium hydroxide. (This procedure avoids loss by volatilization of osmium before equilibration of sample and carrier.) Dry under a heat lamp, taking care to avoid losses by spitting. When the sample is completely dry, add 2 g of sodium hydroxide and heat carefully over a gas flame until fusion takes place; cool. Add 2 g of A.R. sodium peroxide and heat gently until the peroxide melts. Increase the temperature to a dull red heat, swirling gently to aid mixing of sample and carriers, and sustain this temperature until all the sample is completely dissolved; usually 5 min suffices. After cooling, wash the outside of the crucible with demineralized water and transfer to a 250-ml beaker. Add 40–50 ml of demineralized water to the crucible, and cover the beaker with a watch glass until the reaction is finished. Wash the cover glass with water, allowing the washings to run into the beaker. Remove the crucible from the beaker with platinum-tipped tongs, and wash the outside of the crucible into the beaker. Rinse the crucible with 3 ml of concentrated (12 *N*) hydrochloric acid, warming to assist dissolution of any residue. Add 10 ml of demineralized water to the crucible and transfer the solution to the beaker. Centrifuge the solution in 30-ml batches in a glass tube, and transfer the supernatant liquid to a 250-ml beaker. Wash the precipitate in 10 ml of demineralized water, centrifuge, and add the washings to the contents of the beaker. Discard the precipitate. Add 2 ml of ethanol to the solution and warm on a hot plate to 40–50° for 3–5 min until the colour from the Os carrier changes from yellow through a pale purple to almost colourless. Remove from the hot plate. Pour into the solution 20 ml of 12 *N* hydrochloric acid (the acidification must be done quickly otherwise hydrolysis of the Os carrier takes place near the neutrality point) and stir vigorously for a few sec to remove carbon dioxide. Cool the solution quickly by standing the beaker in cold water. The osmium should give a pale yellow colour to the solution at this stage. Filter the solution through a Whatman No. 541 paper to remove any silica and then pass the filtrate under gravity through the prepared anion-exchange column. Osmium forms a narrow reddish brown band at the top of the resin. Wash the column with 30 ml of 1 *N* hydrochloric acid. Elute the osmium fraction with 30 ml of 0.8 *N* nitric acid at a flow-rate of 20–30 ml/h. Collect in a beaker containing 1.2 g of sodium hydroxide. When the elution is complete, add 1 ml of ethanol to the contents of the beaker and cover with a watch glass. Elute rhenium from the column with 30 ml of 2.3 *N* nitric acid at the same flow-rate as used for the osmium elution.

Procedure for rhenium

Evaporate the 2.3 *N* nitric acid rhenium solution to near dryness under a heat lamp, being careful not to allow the solution to go completely dry, when the rhenium will form a dark blue-green coating on the bottom of the beaker. If this does accidentally occur, dissolve the residue in about 1 ml of warm 2.3 *N* nitric acid and evaporate again. Dissolve the colourless residue in 10 ml of 2 *N* sulphuric acid containing 0.4% hydrazine sulphate, and transfer to a separating funnel. Rinse the beaker with a further 5 ml of the acidic hydrazine solution into the funnel. (Some silica may be found in the rhenium fraction; this can be removed by filtration.) Extract by agitating with 10 ml and then 5 ml of isoamyl alcohol. Combine the organic extracts in a centrifuge tube, wash by stirring with 3 ml of the acidic hydrazine solution, and centrifuge. Discard the aqueous washings. Add 10 ml of 5 *N* sodium hydroxide solution and back-extract by stirring for 10 min; centrifuge and transfer the alkaline solution to a centrifuge tube. Make the solution acid by the addition of 12 *N* hydrochloric acid, add 1 ml of 5 mg/ml Fe^{3+} carrier and mix well. Precipitate hydrated iron oxide by addition of dilute ammonia. Cool and centrifuge. Transfer the supernatant liquid to a centrifuge tube. Wash the precipitate with 5 ml of demineralized water, centrifuge and add the washings to the main solution. Add dropwise 1 ml of 0.05 *M* tetraphenylarsonium chloride solution, while stirring the solution. Allow to stand for 15 min, then centrifuge and discard the supernate. Wash the precipitate three times with 5-ml portions of ice-cold water, centrifuging each time and discarding the washings. Slurry the precipitate with about 0.5 ml of demineralized water on to a weighed aluminium counting tray. Dry at 60° in an oven, then dry to constant weight at 110°. The chemical yield, which is usually 20–50%, is determined from the weight of the precipitate recovered; the gravimetric factor for tetraphenylarsonium perrhenate is 0.2939.

Procedure for osmium

Neutralize the osmium fraction with 2 *N* sulphuric acid and sodium carbonate and warm on a hot plate for about 10 min to ensure complete precipitation of hydrated osmium dioxide. The supernate should be colourless; if it is not, neutralize more exactly. Cool, centrifuge and discard the supernate. Wash with 5 ml of water, centrifuge and discard the washings. To the black precipitate, add 1 ml of 82% phosphoric acid, 6 ml of 2 *N* sulphuric acid and sufficient 0.25 *M* potassium permanganate to oxidize it completely, and stir until solution is complete. Add a slight excess of solid iron(II) ammonium sulphate to discharge the permanganate colour, stirring to dissolve. Cool in ice water for a few min, then add 5 ml of ice-cold concentrated (16 *N*) nitric acid. Extract by agitating in a separating funnel with 10 ml and then 5 ml of chloroform. Combine the extracts in a centrifuge tube, and centrifuge to remove any aqueous phase entrained in the organic layer. Pour into a clean tube, add 10 ml of 1 *N* hydrochloric acid containing 1% of thiourea, and stir vigorously for 10 min. Centrifuge and transfer the aqueous phase to a centrifuge cone. Repeat the extraction with further 5-ml portions of the acidic thiourea solution, until no more of the red thiourea–osmium complex is formed. Combine the aqueous extracts, centrifuge and remove any chloroform with a transfer pipet. Add 1 ml of 40% potassium chromithiocyanate solution and stir until precipitation is complete. If precipitation is slow to start, scratching the tube with a glass rod will accelerate the reaction. Centrifuge and discard the supernate. Wash three times with 5 ml of demineralized water, centrifuging and discarding the washings each time. Slurry the precipitate in about 0.5 ml of demineralized water on to a weighed aluminium counting tray. Dry at 60° in an oven, then take to constant weight at a temperature of 105°. Chemical yield is determined from the weight of the precipitate and is generally between 30 and 60%. The gravimetric factor for $Os(NH_2\text{–}CS \cdot NH_2)_6Cr(SCN)_6$ is 0.1816.

Preliminary treatment of standards

Prepare a standard solution in 3 *N* hydrochloric acid containing about 50 µg of Os per ml and 10 µg of Re per ml. Weigh 20–30 mg of *Specpure* silica into a dry silica ampoule. Carefully add about 50–60 mg of the standard solution, reweigh and centrifuge. Dry overnight in an oven at 80° and seal before irradiation.

After irradiation it is advisable to leave the standards unopened until the processing of the samples is well advanced, in order to avoid any possibility of cross-contamination. Pipet 10 ml of carrier solution into a zirconium crucible, and add 1 ml of ethanol. Tap the silica down into the bottom of the ampoule, then carefully crack open the tube and quickly transfer the contents quantitatively into the carrier solution, rinsing the ampoule several times with demineralized water. Make alkaline by the addition of sodium hydroxide and take to dryness under a heat lamp. Add 2 g of sodium hydroxide and fuse carefully over a gas flame. Cool, add 2 g of A.R. sodium peroxide and fuse for about 5 min. After cooling, dissolve the fusion cake by the procedure described for the treatment of samples. Centrifuge the hydrated silica precipitate and store the supernate in a polythene bottle. Take suitable aliquots and treat in the same manner as the centrifuged alkaline solution of the sample melt.

Counting of samples and standards

Determine the β-activity of the samples and standards using an end-window G.M. counter; collect at least 10^4 counts in order to obtain good counting statistics.

Calculations

(*a*) *Rhenium.* Correct the β-count rate of the ^{186}Re sources for dead-time losses and for the background count rate. Divide the ^{186}Re activity by the fractional recovery and correct for decay, extrapolating all activities to a fixed reference time (half-life of ^{186}Re = 88.9 h). No self-absorption correction is necessary.
Then

$$\text{mass of Re in sample} = \frac{\text{mass of Re in standard} \cdot \text{corrected } ^{186}\text{Re activity in sample}}{\text{corrected } ^{186}\text{Re activity in standard}}$$

The determination assumes a normal ^{187}Re/^{185}Re ratio in all samples and standards.

(*b*) *Osmium.* Correct the β-count rate of ^{191}Os for dead-time losses and for the background contribution to the count rate. Apply a correction for self-absorption loss from an empirically determined graph of percentage counting efficiency, referred to an arbitrary source weight, against source weight.

Divide the corrected activity by the fractional yield and correct the resulting count rate for decay (half-life of ^{191}Os = 16 days).
Then

$$\text{mass of Os in sample} = \frac{\text{mass of Os in standard} \cdot \text{corrected } ^{191}\text{Os activity in sample}}{\text{corrected } ^{191}\text{Os activity in standard}}$$

The validity of the determination depends upon a normal isotopic composition of osmium in the sample. The method is completely insensitive to enrichment of ^{187}Os by the decay of ^{187}Re during the course of geological time.

RESULTS AND DISCUSSION

The results for the standard granite G-1, the standard diabase W-1, and also for *Specpure* SiO_2 are listed in Table I.

The average values for rhenium in the two rocks are in good agreement with those of MORRIS AND FIFIELD[3], especially considering the low abundances involved, and the apparent inhomogeneity of at least G-1 with respect to this element. The results obtained in the present work for the *Specpure* SiO_2 are approximately 4 times those obtained by MORRIS AND FIFIELD on a different batch of this material.

It is difficult to compare our osmium results with those of BATE AND HUIZENGA[5] as the latter report only a single value for each rock, and give no indication of the errors involved in the counting data. Taking the two sets of results at their face value, our figures appear to be smaller by a factor of two. However, if the error found by BATE AND HUIZENGA was of the same order as that in our determinations (standard deviation of 20–50%), then the agreement becomes reasonably close.

TABLE I

RHENIUM AND OSMIUM CONTENT OF G-1, W-1 AND "SPECPURE" SiO_2

	Re (10^{-9} g/g)		*Os (10^{-9} g/g)*		*Reference*
Standard Granite G-1	(5.2–8.4) 6.7		—		[3]
Westerly, Rhode	—		2.0		[5]
Island, U.S.A.	7.89 ±0.09	5.6	0.65 ±0.39		Present work
	3.34 ±0.04		≤ 0.48		
Standard Diabase W-1	(5.6–8.4) 7.1		—		[3]
Centerville	—		4.6		[5]
Virginia, U.S.A.	4.41 ±0.07	4.2	2.26 ±0.55	2.6	Present work
	4.05 ±0.04		2.85 ±0.43		
"Specpure" SiO_2 batch no. unknown	100	110	—		[3]
	120				
"Specpure" SiO_2 batch no. 23453	416 ±4	426	82 ±12	463	Present work
	435 ±4		843 ±16		

TABLE II

COMPARATIVE ABUNDANCES OF RHENIUM IN MOLYBDENITES

Molybdenite	*Rhenium (p.p.m.)*				
	Neutron activation analysis			*Isotope dilution*	
	Present work		HIRT *et al.* [12]	RILEY[13]	
Yetholme, N.S.W., Australia	63 ±1	64[a]	71.4 ±3.6	65.0	65.5
	65 ±1			66.0	
Mapoka River, Sierra Leone	31.9 ±0.3	32.5	33.5 ±0.6[b]	31.9	32.2
	33.1 ±0.3			32.6	

[a] One hour irradiation in a flux of about 10^{11} n/cm^2/sec.
[b] Three times the standard error.

TABLE III

OSMIUM ABUNDANCES IN CHONDRITES BASED ON ^{185}Os AND ^{191}Os ACTIVITIES

Meteorite	*^{185}Os (10^{-9} g/g)*		*^{191}Os (10^{-9} g/g)*	
Mokoia, carbonaceous olivine–pigeonite chondrite	736 ±9	726	721 ±8	691
	715 ±10		660 ±7	
Karoonda, olivine–pigeonite chondrite	803 ±9	841	808 ±8	845
	878 ±9		881 ±9	
Mocs, hypersthene chondrite	774 ±4	550	788 ±8	568
	325 ±3		348 ±4	
Hvittis, enstatite chondrite	809 ±12		797 ±9	

The analytical method described in the present work has been applied to the determination of the rhenium and (non-radiogenic) osmium abundances in a large number of sulphide minerals, two of which were molybdenites analysed by other workers for rhenium by neutron activation[12] and stable isotope dilution[13]. The results of the rhenium analyses are tabulated for comparison in Table II.

In order to establish the validity of the self-absorption correction made to the β-count rate in the osmium analyses, independent determinations were made based on ^{185}Os, determining the activity by γ-ray spectrometry with the ^{185}Os 0.646 MeV photopeak[5]. This γ-energy is sufficiently high to be unaffected by self-absorption in the small amount of solid in the source. A comparison of the two methods of osmium determination is made in Table III. It can be seen that the agreement between the two independent counting methods is generally very good.

Possible interferences

Morris and Fifield[3] made a study of possible interferences in the neutron activation determination of rhenium in igneous rocks. The only likely source of error in the method described here is the production of ^{186}Re by a second-order reaction on ^{184}W; however, as 50 p.p.m. of tungsten will in two weeks produce ^{186}Re activity equivalent to only $3.4 \cdot 10^{-6}$ p.p.m. of rhenium, this effect is likely to be insignificant except in the case of minerals containing large amounts of tungsten.

Osmium radionuclides may be produced by fast neutron reactions on iridium and platinum, but if irradiations are made in a predominantly thermal flux, the low cross-section of the reactions coupled with the low abundances of the elements in rocks make this an unlikely source of error.

The effect of neutron self-shielding in the samples is not considered significant because of the small sample size used and the low cross-section of the major matrix materials. The very small amounts of rhenium and osmium in the comparator standards combined with their moderate cross-sections for thermal neutrons reduce the probability of self-shielding in this energy region to a negligible level; however, there is the possibility of self-shielding for neutrons in the epithermal energy range as a consequence of resonance capture. In the irradiation facility used in the present work, the ratio of total epithermal neutron density to total thermal neutron density[14] was $4.0 \cdot 10^{-4}$. From this it can be calculated[15] that resonance capture by ^{185}Re produces only 0.5% of the total ^{186}Re activity, and by ^{190}Os less than 4% of the ^{191}Os activity. It can be seen that self-shielding for resonance energy neutrons would have to be very serious to cause a significant error in the osmium determinations and would cause no serious error in the rhenium measurements.

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SUMMARY

A neutron activation method is described for the determination of rhenium and osmium in rocks. Radiochemical separations, by carrier techniques, are carried out using anion-exchange and solvent extraction procedures. The results obtained for two molybdenites and the standard rocks G-1 and W-1 are compared with other published values.

RÉSUMÉ

On décrit une méthode par activation au moyen de neutrons pour le dosage du rhénium et de l'osmium dans les roches. Des séparations radiochimiques sont effectuées au moyen d'échangeur d'anions et par extraction dans un solvant. Les résultats obtenus pour deux molybdénites et pour les roches étalon G-1 et W-1 sont comparés avec d'autres valeurs déjà publiées.

ZUSAMMENFASSUNG

Die Bestimmung von Rhenium und Osmium in Gesteinen mit der Neutronenaktivierungsanalyse wird beschrieben. Es werden radiochemische Trennungen unter Zuhilfenahme der Trägertechnik und Anwendung von Ionenaustauschern und Flüssigextraktionen ausgeführt. Die Ergebnisse von 2 Molybdäniten und den Standardgesteinen G-1 und W-1 werden mit anderen veröffentlichten Werten verglichen.

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THE SIMULTANEOUS DETERMINATION OF RUTHENIUM AND IRIDIUM IN OSMIUM SPONGE BY NEUTRON ACTIVATION ANALYSIS

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The direct detection and determination of trace impurities in highly purified platinum metals, without previous concentration, offers many difficulties[1-3]. The direct spectrographic determination of impurities in platinum, rhodium and iridium has recently been described[4,5], but the method does not always provide sufficient sensitivity for ruthenium and particularly for iridium. Owing to these limitations of conventional methods of analysis, neutron activation procedures have been developed for the determination of trace amounts of ruthenium in platinum[6] and of iridium in platinum, palladium and rhodium[7-10]. No method has been described for the determination of impurities in an osmium matrix.

In the present work, the determination of ruthenium and iridium in osmium by neutron activation is described. The method involves a few simple chemical separations, in which no carriers are required, the separations being quantitative and sufficiently selective.

Nuclear data

Irradiation of osmium and ruthenium with thermal neutrons gives rise to a series of radionuclides, namely: ^{185}Os (93.6 d); ^{190m}Os (10 min); ^{191m}Os (14 h); ^{191}Os (16 d); ^{193}Os (31 h); ^{97}Ru (2.88 d); ^{103}Ru (39.8 d); ^{103m}Rh (57 m); ^{105}Ru (4.5 h); ^{105}Rh (37 h), as already summarized in a previous paper[11].

The neutral element iridium consists of two isotopes, ^{191}Ir and ^{193}Ir. Irradiation with thermal neutrons gives rise to the radionuclides ^{192}Ir and ^{194}Ir, as shown[12,13] in Table I. Taking into account the isotopic abundances of the naturally occurring isotopes, the activation cross-sections and the half-lives, it is obvious that the only radionuclides that need be considered a few days after the end of the irradiation are the following: ^{191}Os (16 d) and ^{185}Os (93.6 d), ^{103}Ru (39.8 d) and ^{192}Ir (74.4 d).

The gamma-spectra of these radioisotopes using a 3″ × 3″ NaI(Tl) detector, are represented in Fig. 1. It is obvious that, depending on the composition of the sample, long-lived radionuclides of other elements, such as gold, platinum, silver, etc. can be expected. Especially ^{198}Au (2.69 d; 411 KeV) was often identified shortly after the end of an irradiation.

TABLE I

Naturally occurring isotope	*Isotopic abundances (%)*	*Radionuclide formed by (n, γ) reaction*		
			$\sigma_{act.}$ *(barn)*	$T_{\frac{1}{2}}$
^{191}Ir	38.5	^{192m}Ir ^{192}Ir	260 ± 100 700 ± 200	1.45 min 74.4 d
^{193}Ir	61.5	^{194}Ir	130 ± 30	19 h

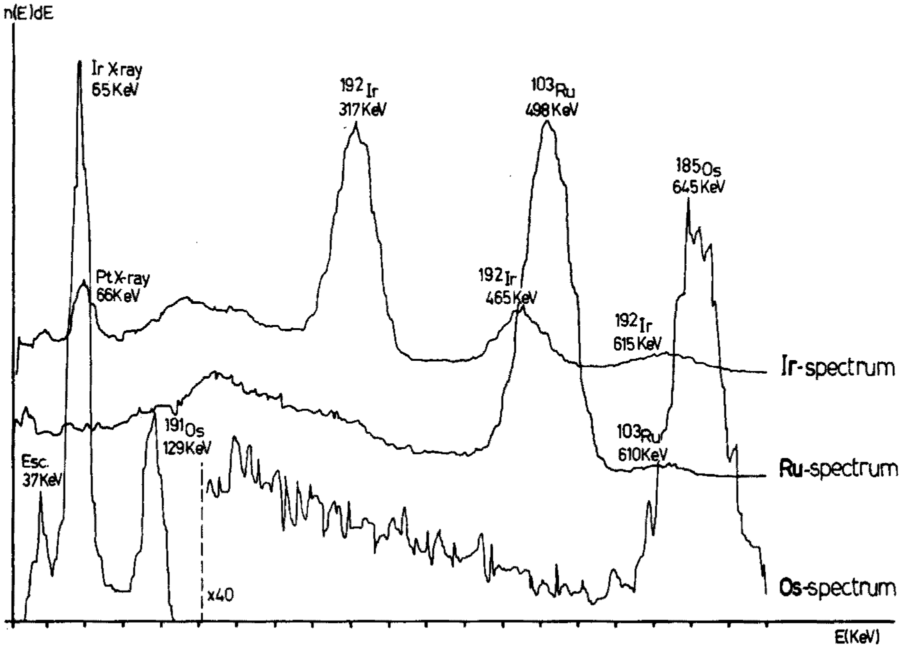


Fig. 1. γ-Ray spectra of irradiated osmium, ruthenium and iridium (3 weeks after the end of irradiation).

Sensitivity

If one accepts as the detection limit of an element, an induced activity, counted with a multichannel analyser, corresponding to a count rate of 10% of the background activity in a given energy region (photopeak), down to 0.1 μg of ruthenium (10 p.p.m. in 10-mg sample) can be determined in the case of ^{103}Ru. With an addition method of analysis (see below), a good quantitative estimate of the original ruthenium content is possible by graphical extrapolation or calculation.

The sensitivity for iridium is much higher: determination down to 0.1 ng

	Radioactive daughter		
Radiation (KeV)		$T_{\frac{1}{2}}$	*Radiation (KeV)*
γ(I.T.): 58 E.C.	^{192}Ir	74.4 d	See further
β^-: 100 to 673 γ : 136 to 1157 esp. 316, 468, 612	—	—	—
β^-: 430 to 2236 γ : 295 to 2000	—	—	—

(10 p.p.b. in 10-mg sample) is easily possible in the case of ^{192}Ir. However, for iridium contents below 0.5 p.p.m. the results must be corrected for second-order interference of the osmium matrix:

$$^{190}\mathrm{Os}(n,\gamma)^{191}\mathrm{Os} \xrightarrow{\beta^-} {}^{191}\mathrm{Ir}(n,\gamma)^{192}\mathrm{Ir}$$

These sensitivities were obtained for a neutron flux of *ca.* $4 \cdot 10^{11}$ and an irradiation period of one week, the measurements being carried out *ca.* 3 weeks after the end of the irradiation.

The separation of osmium, ruthenium and iridium by distillation

After irradiation for seven days at a flux of $4 \cdot 10^{11}$ n/cm^2/sec the bulk of the activity in a 10-mg osmium sample is due to ^{191}Os (and ^{185}Os): approximately $2 \cdot 10^7$ counts/min as measured with a 3″ × 3″ NaI(TI) detector, geometry 20–30%, three weeks after the end of the irradiation. Depending on the purity of the sponge under investigation, the ^{103}Ru activity varied from 20 to 200 counts/min whereas for ^{192}Ir, $6 \cdot 10^3$ to $4 \cdot 10^4$ counts/min were present. It is obvious that in these conditions a chemical separation is required.

At first attempts were made to separate osmium by distillation from a sulfuric acid–hydrogen peroxide solution[14,15,16]. This procedure allows a selective volatilization of approximately 99.8% of the osmium, the other elements remaining in the residue (Tables II–IV). Water was then evaporated, nitric and perchloric acid added and a distillation carried out[11] at approximately 200° for 1 h. Under these conditions ruthenium is quantitatively volatilized[17,18] as well as the remaining osmium. It was expected that all the other platinum metals would remain in the residue.

This procedure offers, however, two difficulties. It was not possible to distil more than *ca.* 99.9% of the osmium activity from the sulfuric acid–hydrogen peroxide solution, even after repeated distillation with freshly added hydrogen peroxide. Consequently the remaining osmium activity (±0.1%) which distilled with ruthenium in the following step, was still approximately a thousand times higher than the ruthenium activity to be determined. Thus the Compton continuum of the 646 (and 879) KeV peak of ^{185}Os strongly interfered with the 498 KeV photopeak of ^{103}Ru. Besides, contrary to established procedures[19–22] it was found that small amounts of iridium were volatilized from boiling perchloric acid (Table V).

The osmium and iridium contamination of the "ruthenium distillate" was so high, that no ruthenium could be detected in the investigated osmium sponges. It was

TABLE II

BEHAVIOUR OF Os IN H_2SO_4–H_2O_2(SEE TEXT)

% residue after 1st distillation	*% residue after $KMnO_4$ treatment and 2nd distillation*
0.25	0.28
0.10	0.11
% residue after NaOH treatment and 2nd distillation	0.0002[a] 0.0001[a]
0.06	
0.05	
0.17	

[a] No HCl present. In all other cases 10 ml 6 *N* HCl was present.

TABLE III

BEHAVIOUR OF Ru IN H_2SO_4–H_2O_2 AND IN H_2SO_4–$NaBrO_3$

% Dist. from H_2SO_4–H_2O_2		*% Dist. from $NaBrO_3$*	*% Residue*
1st distillation	*After $KMnO_4$ treatment and 2nd distillation*		
0.02	0.13	98.90	0.95
0.03	0.89	98.58	0.50
0.03	0.03	99.79	0.15

TABLE IV

BEHAVIOUR OF Ir IN H_2SO_4–H_2O_2 AND IN H_2SO_4–$NaBrO_3$

% Dist. from H_2SO_4–H_2O_2	*% Dist. from H_2SO_4–$NaBrO_3$*
0.0008	0.005
0.007	0.004
0.017	0.004
0.007 + 0.003[a]	0.002

[a] After $KMnO_4$ treatment and 2nd distillation.

TABLE V

BEHAVIOUR OF Ir IN H_2SO_4–$HClO_4$

% Dist. from H_2SO_4–HNO_3–$HClO_4$	*% Residue*
5.78	97.97
9.10	91.40
7.92	91.08
4.24	95.76

therefore necessary to remove at least 99.999% of the osmium activity. Furthermore, another oxidizing agent had to be chosen, from which ruthenium could be quantitatively distilled, leaving iridium quantitatively in the residue.

After selective volatilization of osmium for 99.8–99.9% from sulfuric acid–hydrogen peroxide solution, an attempt was made to remove the last traces of osmium as follows: the solution was successively made alkaline with sodium hydroxide pellets and then again acidified with an excess of sulfuric acid, followed by another distillation from sulfuric acid–hydrogen peroxide. No substantial reduction of the remaining osmium activity was obtained. The quantitative removal of osmium could be improved by adding a slight excess of finely powdered potassium permanganate after the distillation, to decompose the hydrogen peroxide, after which another distillation from sulfuric acid–hydrogen peroxide was carried out. Some typical results are given in Table II. It can be seen that an overall decontamination factor for osmium of 10^5 to 10^6 could be obtained, provided that a treatment with potassium permanganate was inserted and that hydrochloric acid was absent.

Neither ruthenium nor iridium distilled under these conditions as could be shown by tracer studies (Table III and IV).

Ruthenium could be quantitatively (*ca.* 99%) recovered by subsequent distillation from sulfuric acid–sodium bromate solution (Table III). The distillate was absolutely free from iridium, but was sometimes contaminated by small amounts of osmium (10^{-3}–10^{-4} %). In any case, sodium bromate is to be preferred as oxidizing agent to perchloric acid. The precipitation of MnO_2 in this step did not prevent ruthenium from distilling quantitatively.

Iridium remained quantitatively (>99.99%) in the residue (Table IV). (The quantitative distillation of microgram amounts of iridium from perchloric acid will be described in detail elsewhere[23].)

Activation analysis of ruthenium and iridium in osmium sponge

The proposed procedure was applied to 10-mg samples of osmium sponge. For the development, an addition method of analysis was used, as this technique gives a good estimate of the overall precision. The usual procedure can of course be applied, *i.e.* activity standard/activity in sample = weight standard/weight in sample. However, when very low activities, in the neighbourhood of the detection limit, are to be counted the addition method gives a more reliable estimate of the content by extrapolation (*cf.* ruthenium in spectrographically pure osmium). This technique yields the best results, when amounts up to 3–7 times the original content are added to the sample.

The addition method of analysis can be performed in several ways:

(*1*) samples are weighed and sealed in silica tubes and standards are prepared by soaking standard solutions into the sponge and evaporating to dryness. It is however very difficult to transfer sponge and standards quantitatively to the nickel crucible;

(*2*) according to WICHERS, SCHLECHT AND GORDON[24] it is possible to dissolve the samples in hydrochloric acid plus an oxidising agent at higher temperatures in a pressure tube. This can be done before the irradiation so that the latter occurs in homogeneous solution. However, in the described radiochemical separation procedure, hydrochloric acid must be absent. The method can be applied, if iridium only must be determined;

(3) the added amounts of ruthenium and iridium are spotted on filter paper; this is very convenient, because it is easily destroyed in the sodium peroxide melt.

Very dilute standard solutions of ruthenium chloride in 0.5 N hydrochloric acid are not stable, when stored in glass bottles. The concentration of the solutions decreases as a function of time (down to 70–80% of the original strength after 480 days). The standard solutions of iridium chloride are stable, even at the 0.01 μg Ir/100 μl level.

Neutron shielding effects in 10-mg osmium samples can be considered as negligible. According to ZWEIFEL[25], self-shielding of thermal neutrons in solid samples can be computed with reasonable accuracy. A sample of powder is treated in terms of an equivalent sphere:

$$f = 1 - 3/4\, n\sigma r$$

where f = "attenuation factor" = average flux within sample divided by flux if sample were absent;

n = atom density (atoms/cm^3);

σ = thermal total absorption cross-section (cm^2) $\simeq 15 \cdot 10^{-24}$ cm^2;

r = radius (cm).

The approximate density of the osmium powder is a maximum of 6 g/cm^3 (actually it is less when 10 mg are wrapped in a piece of mylar foil). Given that $f = 0.9$, the weight of osmium required to produce a reduction in thermal neutron-induced specific activity of 10%, is a minimum of *ca.* 150 mg. Actually no systematic deviation of the iridium content was observed for 10-mg and 60-mg osmium samples (*cf.* Table VIII, sample 9, 10, 11).

For iridium standards, the problem of neutron shielding due to the large absorption cross-section of this element ($\sigma_{abs} \simeq 430$ b for thermal neutrons) and the high resonance peaks in the total cross-section curve at relatively low neutron energies ($\simeq$ 5,000 to 6,000 b for neutron energies of 0.65 eV) may occur[14]. However, neutron shielding in the standards was found to be negligible if iridium amounts of 0.01 μg are irradiated, spotted on Whatman paper no. 1, although the specific activity seemed to decrease by a few per cent, if the weight was increased ten-fold (Fig. 2).

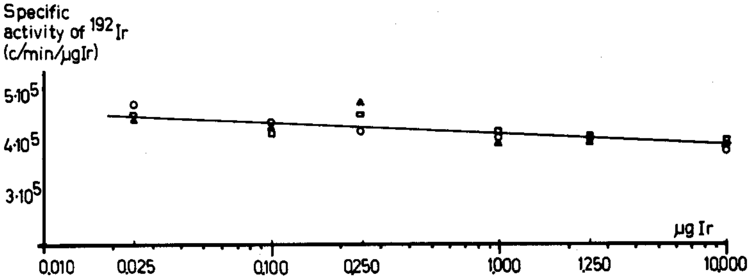


Fig. 2. ▲ Specific activity of ^{192}Ir as a function of weight of iridium (100 μl spotted on Whatman paper no. 1); ☐ id., in the presence of 10 mg of ruthenium sponge; ○ id., in the presence of 10 mg of osmium sponge.

TABLE VI

DETERMINATION OF IRIDIUM IN COMMERCIAL OSMIUM BY AN ADDITION METHOD OF ANALYSIS IN DIFFERENT IRRADIATION CONDITIONS

Irradiation conditions	*Iridium content found (p.p.m.)*	*Number of samples*	*Remarks*
Os sponge in mylar wrapper + Ir standards on paper	21 ± 2	10	A priori, neutron shielding differences are not excluded, although unlikely
Os sponge in silica tube, + Ir solutions soaked into the metal powder and dried	21 ± 4.0[5]	5	Irradiation of almost identical samples
Os sponge in silica tube, Ir solutions soaked into metal powder, dried, and dissolved under pressure in 100 μl conc. HCl + a few drops HNO_3	19.0[5]	2	Irradiation of identical, homogeneous samples in solution

Actually no significant neutron-shielding differences were observed between samples and standard on paper, as can be seen from Table VI, as the results are in complete agreement with those obtained by irradiation in homogeneous solution, where no neutron-shielding differences between samples and standards were possible.

EXPERIMENTAL

Instrumental

Micro-distillation apparatus (pyrex glass). See previous paper[11].
Intertechnique 400-channel pulse-height analyzer S.A.-40.
Detector: Hilger and Watts 3″ × 3″ NaI(Tl) crystal and EMI multiplier phototube 9531A.
Tracerlab precision high-voltage supply R LI-7.

Tracer solutions

The tracer solutions of ^{103}Ru (1 mg/ml, approximately $2 \cdot 10^5$ counts/min) and of ^{191}Os (100 μg/ml, approximately $2 \cdot 10^5$ counts/min) were prepared as described earlier[11]. The tracer solution of ^{192}Ir (20 μg/ml, approximately $7 \cdot 10^5$ counts/min) was prepared in a similar way. However, after dissolution of the cold peroxide melt with water and acidification with hydrochloric acid, the resulting solution was first boiled for a few minutes to convert the colloidal iridium dioxide to the complex chloride (colour change from blue to yellow).

Standard solutions

Ruthenium and iridium stock solutions were prepared by fusion of the metal powder with sodium peroxide in a nickel crucible, as for the tracer solutions. Nickel contamination occurs, but does not interfere with the neutron activation analysis. The stock solutions contained 10 mg of the metal per 100 ml, and were 0.5–1 *N* in hydrochloric acid. Appropriate aliquots of the stock solutions were used to prepare more dilute solutions, which were also 0.5–1 *N* in hydrochloric acid. The dilute iridium solutions can be stored in glass bottles without loss of strength on standing. The concentration of the dilute ruthenium solutions, however, decreased when stored in glassware.

Radiochemical separations

Distillation of OsO_4. A known amount of ^{191}Os tracer solution (approximately 10^6 counts/min), corresponding to about 1 mg of the metal, is transferred to the distillation flask and 10 ml of water, 35 ml of sulfuric acid (1:2) and 25 ml of hydrogen peroxide (30%) are added. Five ml of sodium hydroxide (9 *N*) are placed in the two ice-chilled receivers, an air current is drawn through the apparatus, and the flask heated electrically at a temperature of 105 ± 5° for about 30 min. During the distillation, no addition of fresh hydrogen peroxide is required as the rate of decomposition of the latter in a sulfuric acid solution of osmium is very slow in the absence of hydrochloric acid. After cooling, the hydrogen peroxide is decomposed by addition of a slight excess of finely powdered potassium permanganate (pink colour). Fifteen ml of hydrogen peroxide (30%) and 10 ml of sulfuric acid (1:2) are added. The excess permanganate is reduced to manganese(II) and another distillation carried out at 105 ± 5° for about 30 min.

Distillation of RuO_4. After the removal of osmium, the absorption vessels are refilled with sodium hydroxide (9 *N*), the distillation flask is reassembled and 10 ml of a 20% sodium bromate solution are added dropwise, while an air current is drawn through the apparatus. Care must be taken to avoid a too vehement development of bromine, caused by the reaction of sodium bromate with the residual hydrogen peroxide. The temperature is raised to approximately 100° and the distillation continued for 1 h, under the continuous addition of 15–20 ml of 20% sodium bromate. In this step, the manganese(II) causes MnO_2 to precipitate.

Activation analysis

Samples of 10 mg of osmium powder are weighed, wrapped in mylar foil and placed in an aluminium container (saucers of 15 mm diameter and 2 mm height). To the same "saucer", two pieces of Whatman paper no. 1 (15–20 mg) are added, previously spotted with 100 μl of a ruthenium or iridium solution of known concentration (*e.g.* see Table VII). The samples are irradiated for 3–7 days at a neutron flux of $4 \cdot 10^{11}$ n/cm^2/sec. The complete contents of the container (*i.e.* mylar, osmium sponge and papers with Ru- and Ir-activities) are fused in a nickel crucible with approximately 1 g of sodium

TABLE VII

PREPARATION OF SAMPLES FOR THE DETERMINATION OF TRACES OF RUTHENIUM AND IRIDIUM IN SPECTROGRAPHICALLY PURE OSMIUM SPONGE

No. (10 mg Os)	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*[a]
Ru added (μg)	—	—	0.10	0.10	0.25	0.25	0.50	0.50	0.80	0.80	—
Ir added (μg)	0.050	0.040	0.040	0.025	0.025	0.020	0.016	0.010	—	—	—

[a] 60 mg Os.

peroxide. The cold melt is disintegrated with 10 ml of water, 35 ml of sulfuric acid (1:2) and 20 ml of hydrogen peroxide (30%). Double distillation is carried out, as described above. After the second distillation, gamma spectrometry of the residue shows a practically pure ^{192}Ir activity, as the ^{103}Ru and the remaining ^{191}Os (+ ^{185}Os) activities are negligible as compared with the former. Ruthenium is then selectively distilled from a sulfuric acid–sodium bromate solution. The ruthenium distillates are transferred into selected 100-ml volumetric flasks. These are placed directly on a 3″ × 3″ crystal and counted during 30–60 min with the multichannel analyzer, the background being subtracted automatically. The background activity is stored with a volumetric flask, filled with water on the detector. A typical γ-spectrum is represented in Fig. 3. A few drops of hydrogen peroxide are added to the residue to dissolve the MnO_2 precipitate formed during the bromate distillation. The resulting solution is evaporated to obtain less than 100 ml. Next the iridium activities are directly counted for 5–10 min in 100-ml flasks. A typical γ-spectrum is shown in Fig. 4. It can easily be seen that the activity is due to ^{192}Ir exclusively.

RESULTS AND DISCUSSION

Ruthenium determination

As already mentioned above, the ruthenium distillate from sulfuric acid–sodium bromate, is free from ^{192}Ir, bur contains from 10^{-4} to 10^{-3} % of the original osmium activity. The γ-spectrum of typical distillate is represented in Fig. 3. From this Fig. it appears that the Compton continuum of the 646 KeV peak (region 2) from ^{185}Os interferes with the quantitative determination of ^{103}Ru by means of its photopeak at 498 KeV (region 1). This contamination must be taken into account, particularly when very low ruthenium activities are to be determined. The corrected ruthenium activity is given by

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

where A_1 = the activity measured in energy region 1 (498 KeV);
A_2 = the activity measured in energy region 2 (646 KeV);
$k_{\mathrm{Os}} = A_{2_{\mathrm{Os}}}/A_{1_{\mathrm{Os}}} \simeq 3.8$ (determined with ^{191}Os + ^{185}Os standard, which was irradiated simultaneously);
$k_{\mathrm{Ru}} = A_{2_{\mathrm{Ru}}}/A_{1_{\mathrm{Ru}}} \simeq 0.05$ (determined with ^{103}Ru standard).

The net ruthenium activity $A_{1_{\mathrm{Ru}}}$ (y) is plotted against the added amounts of ruthenium (x); the slope of the straight line and its intercept with the ordinate allow the calculation of the original ruthenium content in the investigated osmium sponge (*cf.* Fig. 5). The calculations are carried out as described by GUEST[26]. The reproducibility of the determination can be improved by taking the osmium activity (first two distillates) as an internal standard; however, this is seldom necessary.

Commercial osmium. Added amounts: up to 200 p.p.m. (= 2 μg) Ru (10 samples).
Irradiation time: 3 days at $4 \cdot 10^{11}$ n/cm^2/sec.
Counting time: 30 min/distillate. (Sum of channels under 498 KeV peak.)
Original content found: 106 ± 9 p.p.m. Ru.

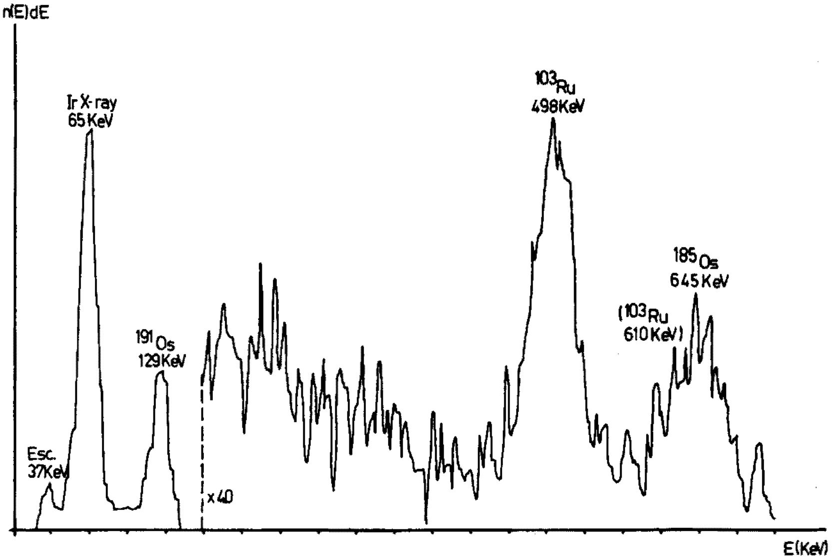


Fig. 3. γ-Ray spectrum of a typical ruthenium distillate (with osmium contamination).

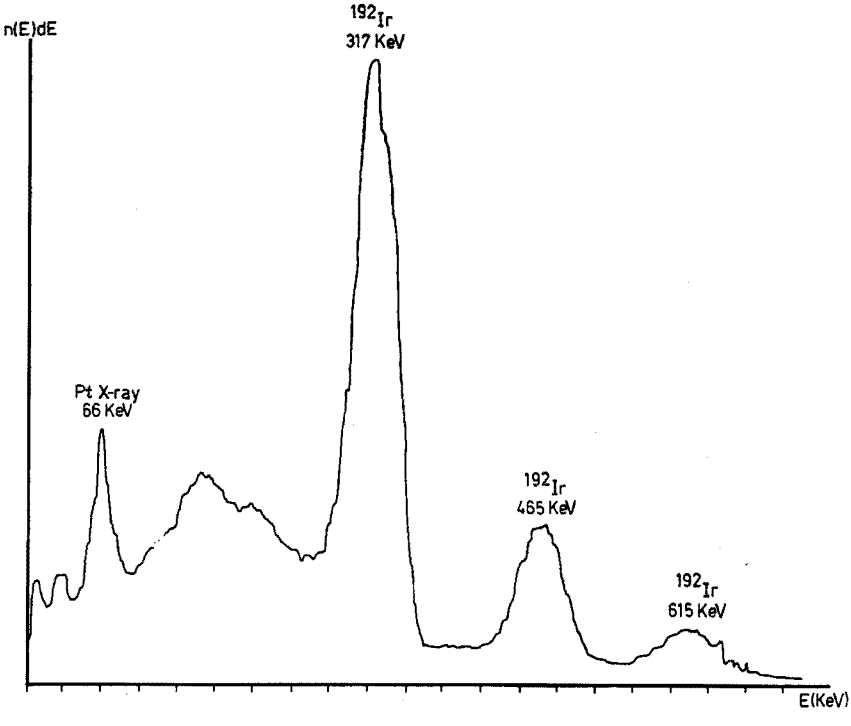


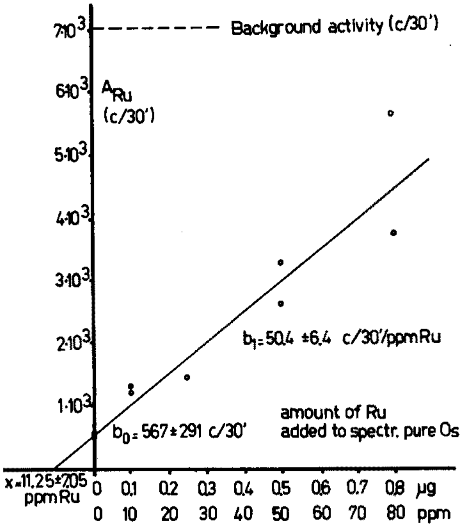
Fig. 4. γ-Ray spectrum of a typical iridium residue (2 weeks after the end of irradiation).

Spectrographically pure osmium. Added amounts: up to 80 p.p.m. (0.80 μg) Ru (see Table VII) (11 samples).
Irradiation time: 7 days at $4 \cdot 10^{11}$ n/cm²/sec.
Counting time: 30 min/distillate. (Sum of channels under 498 KeV peak.)
Original content found: 11 ± 7 p.p.m. Ru; see Fig. 5.

Note: in the latter analysis, the net activity $A_{1_{Ru}}$ in the samples 1 and 2 (see Table VII) was about 10% of the background activity in the same energy region, as indicated in Fig. 3.

Iridium determinations

As stated above, after distillation of Os and Ru the activity in the residue is due to ^{192}Ir (Fig. 4) because of its very high activation cross-section compared with other trace impurities. Moreover, some other important constituents, such as ^{24}Na and ^{198}Au have decayed, when the measurements are made two or three weeks after the end of the irradiation.



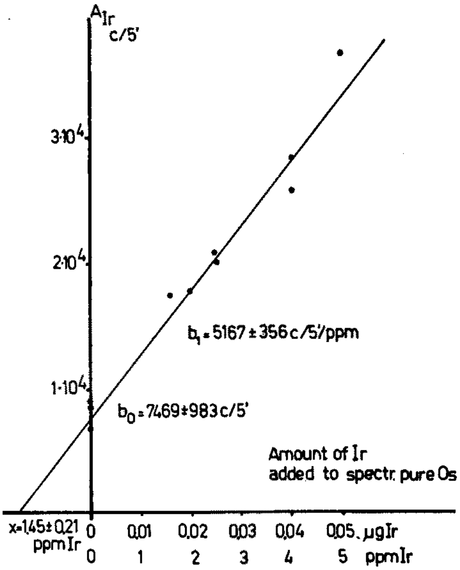


Fig. 5. Determination of ruthenium in "spectrographically pure" osmium.

Fig. 6. Determination of iridium in "spectrographically pure" osmium.

Normally, the ^{192}Ir activity can be determined from the 317-KeV photopeak without further chemical separations. Calculations are again made as described by GUEST. The determination of iridium in spectrographically pure osmium is treated in full detail.

Commercial osmium. Added amounts: up to 40 p.p.m. (= 40 μg) Ir (10 samples).
Irradiation time: 3 days at $4 \cdot 10^{11}$ n/cm²/sec.

Counting time: 5 min/sample. (Sum of channels under 317 KeV peak.)
Original content found: 21.3 ± 2.0 p.p.m. Ir.

Spectrographically pure osmium. Added amounts: up to 5 p.p.m. (= 0.05 μg) Ir (see Table VI) (11 samples).
Irradiation time: 7 days at $4 \cdot 10^{11}$ n/cm²/sec.
Counting time: 5 min/sample. (Sum of channels under 317 KeV peak.)
Original content found: 1.45 ± 0.21 p.p.m. Ir; see Fig. 6.
As an example, the complete calculations are given (see Table VIII).

TABLE VIII

CALCULATIONS FOR THE DETERMINATION OF IRIDIUM IN SPECTROGRAPHICALLY PURE OSMIUM

No. of sample	*y (act./5′) = sum of channels under 317 KeV peak*	*x (p.p.m. added)*	*xy*	x^2	y^2
1	36,516	5.0	182,580	25.00	1,333,418,256
2	28,176	4.0	112,704	16.00	793,886,976
3	25,472	4.0	101,888	16.00	648,822,784
4	20,759	2.5	51,897	6.25	430,936,081
5	17,635	2.5	44,087	6.25	310,993,225
6	17,179	2.0	34,358	4.00	295,118,041
7	16,742	1.6	26,787	2.56	280,294,564
8	19,911[a]	1.0	Disc.	Disc.	Disc.
9	8,830	—	—	—	77,968,900
10	6,629	—	—	—	43,143,641
11	8,351[b]	—	—	—	69,722,500

[a] Sample no. 8 discarded.
[b] 60-mg sample 50,101 counts/5 min or 8,351 counts/5 min/10 mg.

(a) Summations

$n = 10$ $\Sigma xy = 554{,}302$ $\Sigma y^2 = 4{,}285{,}104{,}968$
$\Sigma y = 186{,}288$ $\Sigma x = 21.60$ $\Sigma x^2 = 76.06$

(b) Coefficients b_0 and b_1 $[u_1(x) = b_0 + b_1 x]$

$D = n\Sigma x^2 - (\Sigma x)^2 = 294.04$
$b_1 = (n\Sigma xy - \Sigma x \Sigma y)/D = 5{,}167$
$b_0 = (-\Sigma x \Sigma xy + \Sigma x^2 \Sigma y)/D = 7{,}469$
check: $nb_0 + b_1 \Sigma x = 186{,}288 = \Sigma y$

(c) Calculated content

$x = b_0/b_1 = 1.45$ p.p.m.

(d) Standard deviations

$\Sigma y^2 = 4{,}285{,}104{,}968$
$-(\Sigma y)^2/n = -3{,}470{,}321{,}894$
$-(b_1 D)^2/nD = -784{,}918{,}384$
$s^2 = \Sigma v^2/(n-2) = 3{,}733{,}086$

$s^2(b_1) = s^2 n/D = 126{,}958$ hence $s\,(b_1) = 356$
and $s\,(b_1)\% = 6.9\%$

$s^2(b_0) = s^2 \Sigma x^2/D = 965{,}640$ hence $s\,(b_0) = 983$
and $s\,(b_0)\% = 13.2\%$

$s(x) = s(b_0/b_1) \simeq x\,[s^2(b_0)/b_0^2 + s^2(b_1)/b_1^2]^{1/2} = 0.21$
and $s(x)\% = 14.5\%$

Original iridium content = 1.45 ± 0.21 p.p.m.

TABLE IX

IRIDIUM CONTENT IN AN OSMIUM SAMPLE AS A FUNCTION OF IRRADIATION TIME

Irradiation time (h)	*Iridium content (p.p.m.)*
0 (extrapol.)	0.49
24	0.51
48	0.53
90	0.56
	Measured on ^{192}Ir

Osmium sponge prepared in the laboratory. A "classical" activation analysis was carried out with an osmium sponge prepared in the laboratory. Six samples of 10 mg were irradiated, together with iridium standards (0.01 μg Ir spotted on filter paper). Varying irradiation times, from 1 day to 4 days were chosen. Radiochemically pure iridium was obtained after direct distillation of osmium from sulfuric acid–sodium bromate. The iridium content of the osmium samples is given in Table IX.

This indicates that ^{192}Ir, formed by the second-order interference ^{190}Os (n,γ) ^{191}Os $\xrightarrow{\beta^-}$ ^{191}Ir(n,γ) ^{192}Ir is not negligible, due to the very high activation cross-section of ^{191}Ir.

More precise determinations, in highly purified osmium, which will be described elsewhere show that the apparent iridium content is 0.03 to 0.21 p.p.m. after irradiation periods of 3 to 10 days[23].

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SUMMARY

A radiochemical separation procedure for Os–Ru–Ir is decribed based upon selective distillation. In sulfuric acid–hydrogen peroxide 99.999–99.9999% of the osmium can be distilled if reoxidation of the osmium with permanganate is applied. From sulfuric acid–sodium bromate solution more than 99% of the ruthenium activity can be recovered. More than 99.995% of the iridium remains in the residue.

The method was applied to neutron activation analysis of 10-mg samples of osmium sponge and allows the determination of traces of ruthenium down to approximately 10 p.p.m. and of iridium down to 0.5 p.p.m. For lower iridium contents, second-order interference of the osmium must be taken into account, the error being approximately 0.05 p.p.m. after an irradiation period of 5 days at a flux of $4 \cdot 10^{11}$ n/sec/cm^2.

RÉSUMÉ

Une séparation radiochimique est décrite pour Os–Ru–Ir, basée sur une distillation sélective. Cette méthode a été appliquée à l'analyse d'échantillons d'osmium de 10 mg; par activation au moyen de neutrons. Elle permet le dosage de traces de ruthénium jusqu'à environ 10 p.p.m. et d'iridium jusqu'à 0.5 p.p.m. Pour des teneurs en iridium plus faibles, une interférence de second ordre de l'osmium doit être prise en considération, l'erreur étant approximativement 0.05 p.p.m. après une période d'irradiation de 5 jours à un flux de $4 \cdot 10^{11}$ n/sec/cm^2.

ZUSAMMENFASSUNG

Ein radiochemisches Trennungsverfahren für Os–Ru–Ir, das auf einer selektiven Destillation beruht, wirdt beschrieben. Aus einer Mischung aus Schwefelsäure und Wasserstoffperoxid können 99.999–99.9999% des Osmiums destilliert werden, wenn das Osmium mit Permanganat reoxidiert wird. Aus einer Schwefelsäure–Natriumbromatlösung können 99% der Ru-Aktivität zurückgewonnen werden. Mehr als 99.995% des Iridiums verbleibt im Rückstand. Die Methode wurde bei der Neutronenaktivierungsanalyse von Proben von 10 mg Os-Schwamm angewendet und erlaubte die Bestimmung von Ru-Spuren hinab bis zu etwa 10 p.p.m. und von Ir bis zu 0.5 p.p.m. Für niedriger Ir-Gehalte müssen Störungen durch Sekundärreaktionen des Os berücksichtigt werden. Der Fehler beträgt etwa 0.05 p.p.m. nach einer Bestrahlungszeit von 5 Tagen und einem Fluss von $4 \cdot 10^{11}$ n/sec/cm^2.

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THE FACTORS AFFECTING THE REFLECTANCE SPECTRA OF SOME DYES ADSORBED ON ALUMINA

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Early observations by WEITZ *et al.*[1,2] and DEBOER[3] on the color changes of various compounds upon adsorption on active surfaces have stimulated investigations into these phenomena with the aid of spectral reflectance, a tool particularly suitable for the measurement and examination of the diffuse reflectance spectra of species in the solid state. Recent studies[4-6] have endeavored to interpret similar observations made with various two-component solid systems on the basis of Lewis acid–base interactions and the polarization theory. In attempts to explore the analytical potential of spectral reflectance KORTÜM[7-11] has carried out a critical evaluation of the Kubelka–Munk function with respect to its use for photometric purposes. In a number of adsorbate–adsorbent systems the function was found to be proportional within limiting concentrations to the molar concentration of the adsorbate since straight lines passing through the origin were obtained when $F(R_\infty)$ (the Kubelka–Munk function) was plotted against molar concentration. He concluded that this relationship may be used for quantitative photometric analysis much in the same manner as the Beer–Lambert law. However, careful control of experimental conditions must be exercised in any analytical application since variables such as grain size, packing density, moisture, and pH can influence and modify spectra measured. The findings of KORTÜM have been confirmed by ZEITLIN and coworkers[12,13] in studies of the behavior of mononitrophenols adsorbed on alkali metal carbonates and alkaline earth oxides.

This communication has stemmed from the above and from a recent publication by FRODYMA, FREI AND WILLIAMS[14] who have pointed out the potential of spectral reflectance as applied to thin-layer chromatography. The present study was undertaken with the object of examining the effect of such variables as humidity, regeneration temperatures, and pH dependence on the reflectance spectra of a number of dyes adsorbed on grades of alumina commonly used in thin-layer chromatography, with the hope of gaining information concerning the experimental conditions necessary for reproducible and useful data. The dyes studied were eosin B, rhodamine B, and fuchsin. *o*-Nitrophenol was included since its behavior upon adsorption on various metal carbonates and oxides had been the subject of previous studies[12,13].

EXPERIMENTAL

Reagents

All reagents used were of analytical grade. The *o*-nitrophenol was recrystallized repeatedly until its melting point range indicated satisfactory purity. Weighed amounts of eosin B, fuchsin, and rhodamine B dyes were dissolved in absolute ethanol and the solutions were maintained in a moisture-free state by storage above anhydrous magnesium sulfate for use as stock solutions. Thin-layer chromatographic-grade alumina from "Merck" Darmstadt with a particle size of approximately 5 μ was employed as the adsorbent. Woelm alumina (basic and acid washed, activity grade 1) and the neutral Merck alumina were used in conjunction with *o*-nitrophenol in a study of pH dependence.

Apparatus

The diffuse reflectance spectra (350–750 mμ) were measured with an automatic recording DK-2 Beckman spectrophotometer equipped with the standard reflectance attachment. A magnesium oxide plate served as a reference standard. Photometric studies were carried out in a Beckman DU spectrophotometer equipped with a reflectance attachment at wavelength settings determined previously from the reflectance spectra. Transmittance spectra were recorded with the DK-2 spectrophotometer in 1-cm matched quartz cells. pH measurements were made with a Beckman pH meter, Model G. It was checked with certified standard buffer solutions.

Procedures

In order to evaluate the effect of moisture, samples were prepared in an "air-dry" state by grinding 3-g quantities of Merck alumina with 10 mg of *o*-nitrophenol in an agate mortar for about 1 min to attain uniform distribution of the two componets. The sample was "air-dried" by exposure to ambient temperature and humidity for approximately 1 h by which time an equilibrium condition of adsorption, color change, and humidity was attained. Other samples of the same adsorbent were preheated carefully at temperatures of 200°, 800° and 1100°, transferred quickly to a vacuum desiccator containing P_2O_5 evacuated to *ca.* 1 mm Hg, and allowed to cool to room temperature. The mixing and grinding of the adsorbate and the preheated adsorbent in the proportions given above were carried out in a dry box which had been dried by dynamic adsorption through activated silica gel for 12 h. The interaction was completed in 1 h. The solid system was packed into a special cell as described by BARNES *et al.*[15] in which the edge of the aluminum planchet was coated with silicone grease and the diffuse reflectance spectra measured. The pH effect on different grades of alumina with *o*-nitrophenol was studied by preparing samples as above in the "air-dry" state containing acid-washed, neutral, and basic alumina.

In the dye studies 1 ml of stock solutions of fuchsin, eosin B, and rhodamine B containing 0.3 mg of dye were treated with 3 g of adsorbent preheated at 200°, 800° and 1100°. The ethanol was removed completely *in vacuo* and the dry sample mixtures prepared for measurement as above. A sample system was also prepared in the "air-dry" state and measured. The recording time was about 1 min during which time little or no moisture was picked up by the sample.

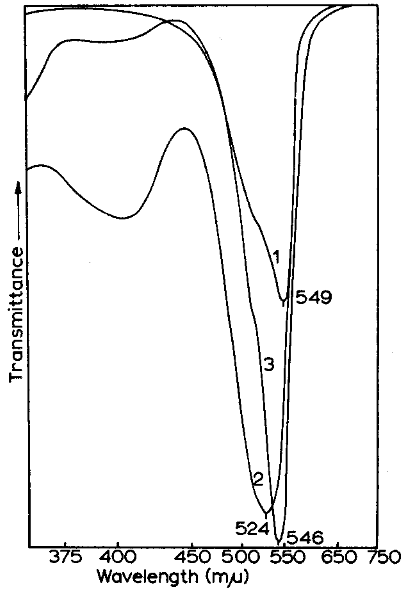
The photometric analysis of rhodamine B was carried out by preparing a dilution series of the dye adsorbed on alumina. Samples were prepared by mixing 1-ml samples of solution of varying and known concentrations of dye with the adsorbent following which the solvent was removed *in vacuo*. In this manner three series of samples were prepared, one in the "air-dry" state and two from adsorbents preheated to 200° and 1100°, each of which contained 6 concentrations of the dye. All measurements were carried out in duplicate. The reflectance of each sample was measured with the DU-Beckman spectrophotometer equipped with reflectance attachment at the wavelength of 562 mμ, a previously determined absorption maximum.

In order to measure the pH of different grades of alumina in conjunction with the pH dependence studies carried out above, slurries of neutral, acid-washed, and basic alumina were prepared from doubly distilled water and the pH determined.

RESULTS AND DISCUSSION

Figure 1 gives the transmittance spectra of ethanolic solutions of the 3 food dyes. Typical and reproducible reflectance spectra obtained by plotting reflectance *vs.* wavelength are compiled in Figs. 2–6. Graphs in which the Kubelka–Munk function is plotted against concentration of rhodamine B in mg/ml of ethanolic solution are furnished in Fig. 7.

As is customary in quantitative transmittance spectrophotometry the reflectance spectra were examined in order to determine the wavelength of maximum ab-



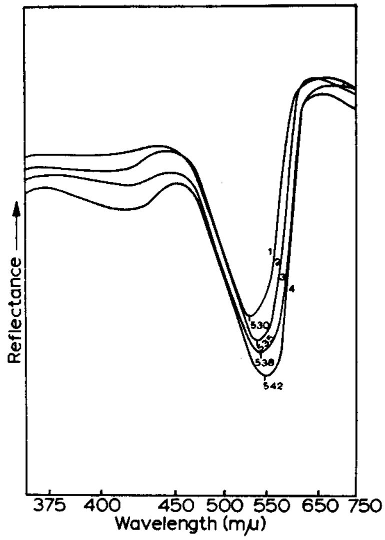
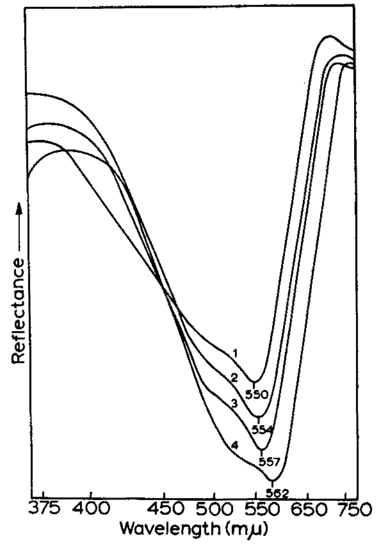


Fig. 1. Transmittance spectra of (1) fuchsin, (2) eosin B, (3) rhodamine B in ethanolic solution.

Fig. 2. Reflectance spectra of eosin B adsorbed on (1) alumina ("air-dry" state); (2) alumina (preheated to 200°); (3) γ-alumina (preheated to 800°); (4) α-alumina (preheated to 1100°).



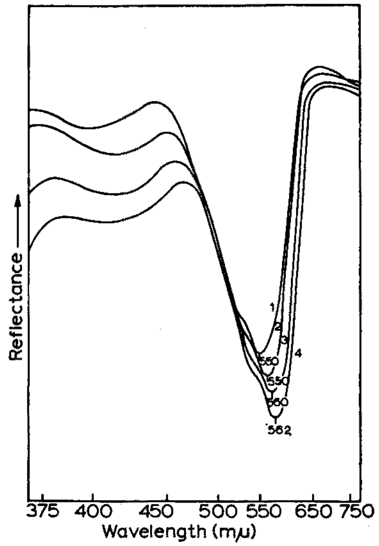
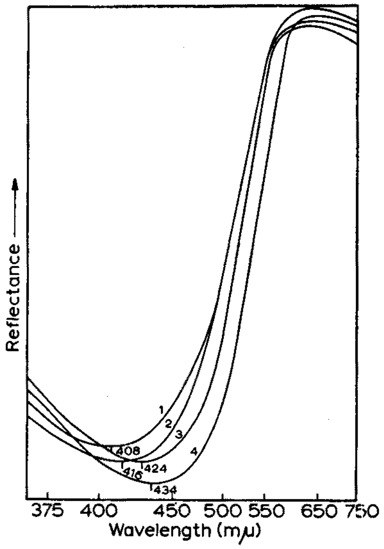


Fig. 3. Reflectance spectra of fuchsin adsorbed on (1) alumina ("air-dry" state); (2) alumina (preheated to 200°); (3) γ-alumina (preheated to 800°); (4) α-alumina (preheated to 1100°).

Fig. 4. Reflectance spectra of rhodamine B adsorbed on (1) alumina ("air-dry" state); (2) alumina (preheated to 200°); (3) γ-alumina (preheated to 800°); (4) α-alumina (preheated to 1100°).



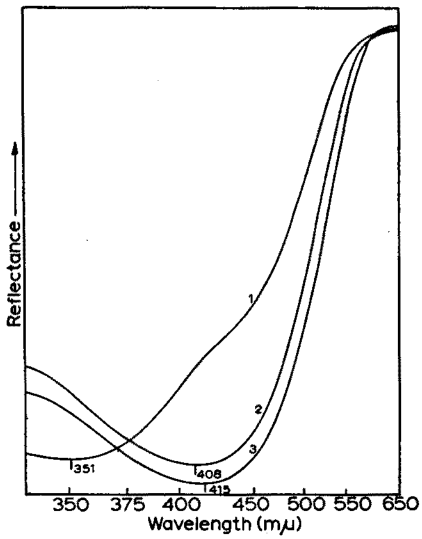


Fig. 5. Reflectance spectra of o-nitrophenol adsorbed on (1) alumina ("air-dry" state); (2) alumina (preheated to 200°); (3) γ-alumina (preheated to 800°); (4) α-alumina (preheated to 1100°).

Fig. 6. Reflectance spectra of o-nitrophenol adsorbed on (1) alumina (acidic); (2) alumina (neutral); (3) alumina (basic).

sorption since the sensitivity of the determination is greatest at this wavelength. A comparison of the visible transmittance spectra of the 3 food dyes (Fig. 1) and of *o*-nitrophenol with the corresponding reflectance spectra of the dyes adsorbed on alumina (Figs. 2–5) showed in all cases, in going from transmittance to reflectance, that the absorption maximum was retained in reflectance. The peaks in the latter

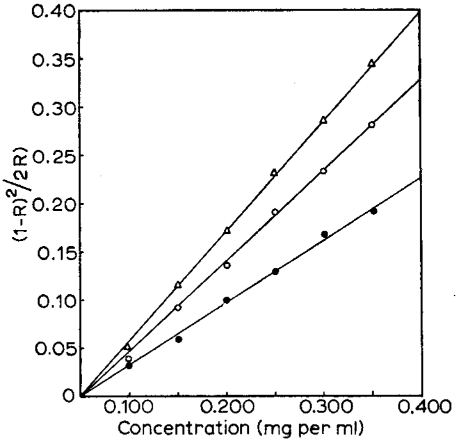


Fig. 7. Kubelka–Munk plots for a dilution series of rhodamine B adsorbed on ● alumina ("air-dry" state); ○ alumina (preheated to 200°); △ alumina (preheated to 1100°).

were broader and displaced bathochromically, a phenomenon which has been observed by several workers for a variety of systems[16–18]. For the 4 model compounds under study, the peaks in the reflectance spectra appear to be sufficiently well defined for photometric purposes. A key factor in this particular application is the elucidation of the influence of moisture, pretreatment, and pH on the reflectance absorption maximum.

The spectral data show clearly the effect of the pretreatment of the adsorbent on the reflectance spectra. This treatment which included heating of separate samples of alumina at 200°, 800° and 1100° prior to cooling and mixing with the adsorbate and the preparation of an "air-dry" system in which the adsorbate–adsorbent mixture was equilibrated with atmospheric moisture at room temperature yielded reflectance spectra in which there were definite displacements of the absorption maximum. The spectra (Figs. 2–5) show for all systems a bathochromic shift in the following order: Al_2O_3 (1100°) > Al_2O_3 (800°) > Al_2O_3 (200°) > Al_2O_3 ("air-dry"). The results, which are reproducible, are in accord with the findings of SCHWAB AND SCHNECK[6] for a series of adsorbed dyes. A similar trend was recently observed by ZEITLIN, FREI AND MCCARTER[13] for *o*-nitrophenol adsorbed on alkaline earth oxides.

The displacements are explainable in terms of Lewis acid–base interaction between adsorbate and adsorbent, the extent of the shift being governed by the amount of water coadsorbed with the adsorbate. This interpretation, originally suggested by KORTÜM[4,11,19] for a different system is one whereby moisture, which in turn is directly dependent on the preheating treatment of the adsorbent, assumes a dominant role. In essence, an equilibrium condition which is moisture-dependent exists between unadsorbed and adsorbed species relative to the active adsorbent. The competition for active adsorbent sites between molecules of each of the 4 model compounds studied and water is in favor of the latter. The heat treatment at 200° accorded the adsorbent prior to mixing with the adsorbate, results in the partial elimination of the adsorbed water. The organic adsorbate, with the concentration of the otherwise favored water molecules decreased, is more effectively and directly exposed to the polarizing action of the adsorbent. The resulting reflectance spectrum contains an absorption peak which has been shifted to the longer wavelengths compared to that of the "air-dry" system containing a higher concentration of water molecules. At 800° additional dehydration of the alumina, probably in the γ-form, occurs with enhancement of the bathochromic shift. This is particularly noticeable for *o*-nitrophenol (Fig. 5). The strongest effect in the same direction is observed after the alumina is subjected to a pretreatment temperature of 1100°. It is noteworthy that at this temperature there is a transition from the γ- to the α-modification of alumina. The reversibility of the above phenomena can be demonstrated by permitting the dry systems to be exposed to atmospheric humidity and measuring the reflectance spectra over a period of 24 h. Hypsochromic shifts of the absorption maxima occur gradually but cease when they are identical with those in the "air-dry" mixtures.

Since commercial grades of chromatographic alumina are prepared according to various specifications, pH dependence tests were performed on 3 commonly used grades to ascertain whether changes would result in the reflectance spectrum of a given species. pH determinations carried out on aqueous slurries of acid washed, neutral, and basic alumina yielded values of 4.2, 7.6 and 10.0 respectively. The reflectance spectra (Fig. 6) of *o*-nitrophenol adsorbed on the 3 grades of alumina and measured under similar conditions show the marked effect of the type of alumina used, particularly acid-washed, on the spectrum of the adsorbed species. Of interest is the bathochromic shift of the absorption peak with increasing pH of the adsorbent.

In order to examine the potential analytical application of spectral reflectance for dyes separated on alumina thin-layer chromatographic plates and to examine the effect of moisture by a different approach, 3 series of samples of rhodamine B were prepared (see experimental section). Calibration curves were constructed for the "air-dry" system and two samples in which the adsorbent had been preheated to 200° and 1100° by plotting the Kubelka–Munk function, valid for diffuse reflectance and infinite layer thickness, against mg of dye per ml of solution over a suitable concentration range. Straight line calibration plots (Fig. 7) passing through the origin were obtained in each case for the concentration range employed. The plots can be utilized, analogously to the Beer–Lambert law, to determine the concentration of an adsorbed dye species. However, in order to emphasize the effect of moisture the reflectance measurements for all 3 curves were taken at the absorption peak wavelength (562 mμ) of the dye–alumina system in which the absorbent had been preheated to 1100°. The slope of the calibration curve is observed to decrease with increasing humidity. These observations are in close agreement with those reported by KORTÜM AND VOGEL[9] for malachite green spotted on paper chromatograms. The changes in slope are undoubtedly related to the displacements of the absorption maxima (Fig. 4). An additional factor which may affect the slope is the varying intensity of rhodamine B with change in moisture. Spectra in Fig. 4 show an increase in color intensity with decrease in moisture for a constant concentration of dye (0.3 mg of dye per 3 g of "air-dry" adsorbent). Similar observations were made with the other dyes (Figs. 2, 3, 5). The interpretation given above for the bathochromic shifts of the absorption maximum can be invoked to explain the relation between color intensity and humidity and is in harmony with previous findings by KORTÜM and coworkers[4,19].

In conclusion, based on the above model studies, it appears that spectral reflectance may be employed successfully for the quantitative analysis of dyes adsorbed on alumina by the technique of thin-layer chromatography. It is essential, however, for reproducible results to use the same grade of adsorbent and to prepare samples for measurement under uniform conditions of regulated humidity such as those present in a desiccator over calcium chloride or in an air-conditioned room in order to control effectively the important moisture factor.

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SUMMARY

Various factors affecting the diffuse reflectance spectra of eosin B, rhodamine B, fuchsin, and *o*-nitrophenol adsorbed on chromatographic alumina under various conditions were studied to explore the potential analytical application of reflectance spectroscopy to dyestuffs separated by thin-layer chromatography. Regeneration temperature, pH and grade of adsorbent, and humidity were found to influence the spectra but the technique may be utilized for the photometric analysis of food dyes adsorbed on alumina; straight lines passing through the origin were obtained when the Kubelka–Munk function was plotted against a suitable concentration range of dye. For reproducible results, it is essential to employ the same grade of adsorbent and to prepare samples under uniform conditions of humidity.

RÉSUMÉ

Les auteurs ont examiné les divers facteurs pouvant affecter les spectres de réflexion de l'éosine B, de la rhodamine B, de la fuchsine et de l'*o*-nitrophénol, adsorbés sur alumine, afin d'explorer les possibilités d'applications analytiques de ce procédé à des colorants séparés par chromatographie sur couches minces. Cette technique peut être utilisée pour l'analyse photométrique de colorants alimentaires adsorbés sur alumine.

ZUSAMMENFASSUNG

Verschiedene Faktoren die die diffusen Reflektionsspektren von Eosin B, Rhodamin B, Fuchsin und *o*-Nitrophenol adsorbiert an Aluminumoxyd beeinflussen konnten, wurden studiert, zur Prüfung der analytischen Anwendungsmöglichkeit des Reflektionsspektroskopie für die quantitative Bestimmung von auf Dünnschichtchromatogrammen getrennten Farbstoffen. Regenerationstemperaturen, pH-Werte, sowie Luft-

feuchtigkeit konnten für Veränderungen der Spektren verantwortlich gemacht werden. Die Methode kann unter Anwendung der Kubelka–Munk Theorie für die Analyse von Farbstoffen in geeigneten Konzentrationsbereichen verwendet werden, vorausgesetzt, dass Qualität, Regenerationstemperatur und Feuchtigkeitsgehalt des Adsorbens konstant gehalten werden.

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THE SOLUBILITIES AND ANION-EXCHANGE BEHAVIOR OF RARE EARTH ELEMENTS IN POTASSIUM CARBONATE SOLUTIONS

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The dissolution and anion-exchange behavior of several rare earth elements (La, Ce, Pr, Nd, Sm, Gd, Er and Y) in potassium carbonate solution were reported previously[1,2]. However, it was impossible definitely to determine the order of the solubilities and adsorbabilities of these elements, as well as the position of yttrium in the series because of lack of data for the heavy rare earth elements.

In this paper, the relation between the solubilities of the rare earth elements (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) and the concentration of potassium carbonate is first described. Then, the distribution coefficients of rare earth ions between an anion-exchange resin and a potassium carbonate solution more concentrated than the minimum needed for dissolution are reported. Finally, the state of the dissolution and the anion-exchange behavior of the rare earth elements are discussed.

EXPERIMENTAL

Reagents

Standard solutions of rare earth ions. These were prepared by dissolving the oxides (purity $> 99.9\%$) in dilute hydrochloric acid. The concentrations were determined microtitrimetrically with EDTA at pH 5 in presence of xylenol orange as indicator[3].

Standard solution of potassium carbonate. This was prepared by dissolving an extra pure grade of reagent in water; the concentration was checked with standard hydrochloric acid.

The anion-exchange resin Dowex 1-X8 (carbonate form), 50–100 mesh, was used.

All other chemicals used were analytical-reagent grade.

Procedures

Solubility measurements. Ten ml of a standard 0.02 *M* solution of the rare earth ion was transferred to a glass-stoppered conical flask, and the solution was evaporated to dryness on a water bath to remove excess of hydrochloric acid. Then 5 ml of a series of potassium carbonate solutions of various concentrations was added to the residue. The flask was left to stand overnight and then vigorously shaken by a mechanical shaker for 4–5 h. The solution with the precipitate was transferred to a centrifuge tube and centrifuged for 10 min at 4000 rev./min. The solution was then completely separated from the precipitate. An aliquot (2 ml) of the supernate was used for the determination of rare earth ions by titration with 0.01 *M* EDTA as described above and the solubility was calculated. The experiment was carried out at 20°.

Measurement of the distribution coefficients. An aliquot (2 ml) of a standard 0.01 *M* solution of a rare earth ion was transferred to a conical flask and evaporated as described above. Then 20 ml of a series of the potassium carbonate solutions was added to the residue. After the precipitate had been completely dissolved by shaking, 1 g of air-dried resin was added to the solution. The solution was shaken mechanically for 3–4 h, and then the resin was rapidly separated by filtration on a sintered glass filter. An aliquot (15 ml) of the filtrate was used to determine the rare earth ions, as described above. The distribution coefficients (K_d) of the rare earth ions could then be calculated. This experiment was carried out at room temperature, which was about 20°.

RESULTS AND DISCUSSION

When an excess of a potassium carbonate solution was added to a rare earth chloride, a precipitate of the basic carbonate was formed: the precipitate was then dissolved partially or completely by shaking. In these experiments, the amounts of the elements taken (see Table I) were very similar, *i.e.*, about 0.2 mmole for the measurement of solubility and about 0.02 mmole for that of distribution coefficient. Since cerium is oxidized to cerium(IV) in potassium carbonate solution and promethium cannot be obtained in a macro scale, these elements were not studied.

A logarithmic diagram of the solubilities of the rare earth ions against the

TABLE I

QUANTITIES OF RARE EARTH IONS USED

Ions(III)	*Taken for measurements of solubilities (mmole/5 ml of K_2CO_3)*	*Taken for measurements of adsorbabilities (mmole/20 ml of K_2CO_3)*
La	0.2005	—
Pr	0.2023	—
Nd	0.1990	0.01990
Sm	0.2045	0.02045
Eu	0.2070	0.02070
Gd	0.2030	0.02030
Tb	0.2065	0.02065
Dy	0.2000	0.02085
Ho	0.2025	0.02025
Er	0.2020	0.02020
Tm	0.2015	0.02015
Yb	0.2005	0.02005
Lu	0.2105	0.02105
Y	0.2100	0.02100

concentration of potassium carbonate is given in Fig. 1. It can be seen that when more than one-half of the total amount of rare earth ion present is dissolved, the solubilities of the rare earth carbonates increase with an increase in the concentration of the carbonate and also as the atomic number increases. Moreover, the solubility of the yttrium salt lies between those of holmium and erbium. On the other hand, when less than one-half of the total amount of rare earth ion is dissolved, the slope of the curve log S *vs.* log [CO_3^{2-}] for the heavy elements, *i.e.* Y, Er, Tm, Yb and Lu, obviously differs from that in other elements. It may thus be concluded that the order of the solubilities of the rare earth elements, especially the heavy elements, depends on the concentration of potassium carbonate, and that yttrium is more similar to erbium than holmium. The inflexions which appear in the Nd–Lu curves are interesting but their cause cannot be decided from the present data.

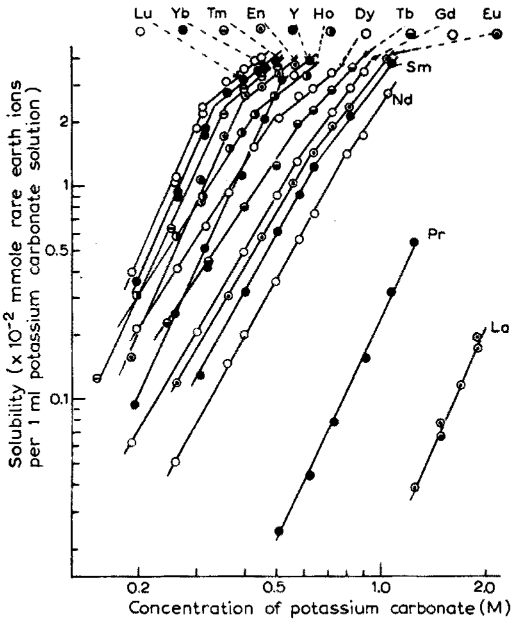

Fig. 1

The amounts of rare earth carbonates that could be dissolved completely were used to study the anion-exchange behavior as described above. Since the solubilities of lanthanum and praseodymium were small and a convenient concentration for the procedure could not be obtained, neither element was studied. The distribution coefficient K_d is given by: $K_d = [M_r]/[M_s]$ where M_r and M_s represent the amounts of rare earth ion in 1 g of the resin and 1 ml of the solution respectively. Logarithmic plots of the distribution coefficients of the rare earth ions against various concentrations of potassium carbonate are shown in Figs. 2 and 3. It can be seen that the adsorbabilities of the rare earth elements decrease as the concentration of potassium

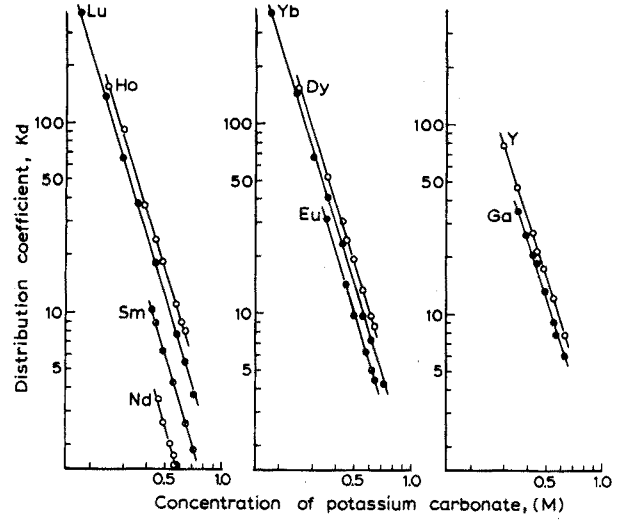

Fig. 2

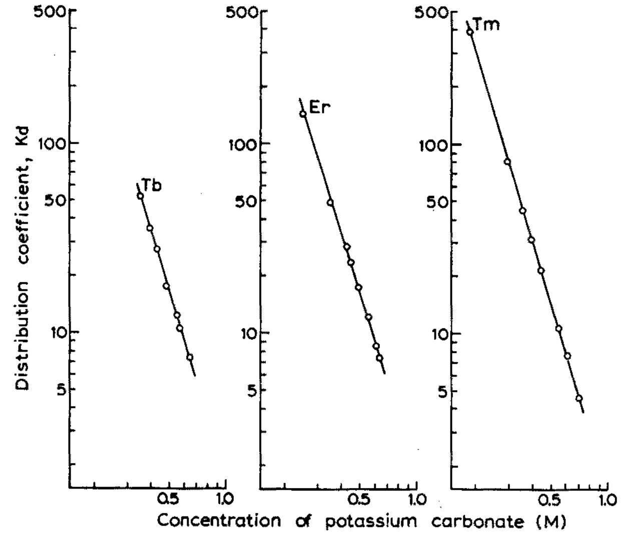

Fig. 3

carbonate increases. Since the slope of the curve log K_d *vs.* log $[CO_3^{2-}]$ is linear and the lines are parallel to one another with a negative slope, it is concluded, according to a method developed by KRAUS AND NELSON[4] for determining the composition of metal complex species using an anion-exchange resin, that the rare earth ions dissolved in a carbonate solution have an identical negative charge. However, the K_d values of the rare earth elements increase with increasing atomic number from Nd to Dy or Ho, whereas the values decrease with increasing atomic number from Er to Lu. This behavior is more distinctly represented in Fig. 4, which shows the relation between the adsorbabilities of rare earth elements in 0.5 M potassium carbonate solution and crystal radii given by ZACHARIESEN[5]. The position of yttrium again lies between erbium and holmium. It is interesting that the maximum in the K_d values corresponds with the maximum in the magnetic susceptibility of the rare earth element. The adsorbability on an anion-exchange resin is related to the formation constant (K_1) of an anionic complex ion and to the equilibrium constant (K_2) between this ion and the resin; if the K_1 value of the carbonate complex ion is more effective for the adsorbability than the K_2 value, then the K_1 value of the dysprosium or holmium carbonate complex may be given the highest value among the rare earth carbonate complexes.

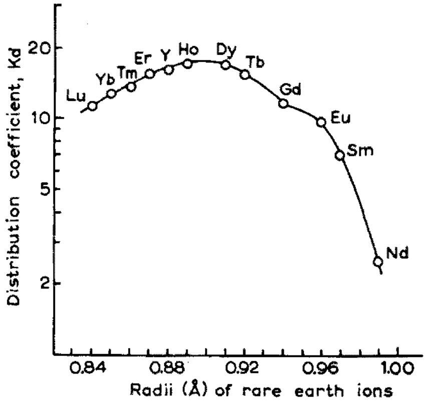

Fig. 4

The present data are insufficient to explain the behavior of the decrease of adsorbability in the heavy rare earth elements as well as the discontinuity at gadolinium shown in Fig. 4; however, the magnetic susceptibility, a steric effect resulting from lanthanide contraction, and the donor site of carbonate ion, may be involved.

SUMMARY

The solubilities of rare earth elements (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) in potassium carbonate solution, and the distribution coefficients of the rare earth ions between the carbonate solution and Dowex 1 resin were measured. The values obtained show a variation that depends on the concentration of potassium carbonate and atomic number. There is a clearly different tendency in these values between La–Ho and Er–Lu.

RÉSUMÉ

On a examiné les solubilités des éléments des terres rares dans une solution de carbonate de potassium et leurs coefficients de partage sur résine Dowex 1. Les valeurs obtenues montrent des variations dépendant de la concentration en carbonate de potassium et du nombre atomique, spécialement entre La–Ho et Er–Lu.

ZUSAMMENFASSUNG

Die Löslichkeiten folgender Elemente der Seltenen Erden La, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu und des Yttriums in Kaliumcarbonatlösung und ihre Verteilungskoeffizienten zwischen der Carbonatlösung und dem Austauscher Dowex-1 wurden gemessen. Die erhaltenen Werte zeigen Unterschiede, die von der Konzentration des Kaliumcarbonats und der Atomnummer abhängen. Besonders die Werte zwischen La–Ho und Er–Lu zeigen eine klare unterschiedliche Tendenz.

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ANION-EXCHANGE SEPARATION OF IRON, COBALT AND NICKEL

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Earlier investigations[1] concerning the anion-exhange separation of iron, cobalt and nickel in pure aqueous hydrochloric acid solutions have shown that cobalt is the most strongly adsorbed and nickel the least strongly adsorbed of these elements. To separate iron from nickel and cobalt chromatographic elution with varying concentrations of hydrochloric acid must be used, the elements passing into the effluent in the order: nickel, iron and cobalt. This method was found to be highly efficient and can be employed in most cases. If, however, small amounts especially of nickel must be separated from large quantities of iron, as would happen with ferrous alloys or other materials of high iron content, the resin column dimensions would have to be increased considerably in order to adsorb all the iron. In such a case small amounts of cobalt are liable to be replaced in the column by iron ions even during the sorption step, so that some or all of the cobalt might be lost. Ether extraction of iron(III) chloride before passage through the ion exchanger would avoid these adverse effects, but this would introduce another possible source of error which might assume importance in accurate analyses for the nickel and cobalt content of ferrous alloys. We have therefore investigated a large number of hydrochloric acid—organic solvent mixtures in order to find a medium in which cobalt and nickel but not iron (even if present in very large amounts) can be adsorbed on an anion-exchange resin. Since acetone forms a rather strong complex with iron(III), it proved a highly suitable solvent for this purpose.

A remarkable feature of the separation procedure described below is that nickel is adsorbed rather strongly when the acetone medium is used. This is in contrast to its behaviour in pure aqueous hydrochloric acid media, where no adsorption of nickel on strongly basic anion-exchange resins was observed even when concentrated hydrochloric acid was employed[1].

EXPERIMENTAL

Reagents and solutions

Ion-exchange resin. The strongly basic anion-exchange resin Dowex 1-X8 (100–200 mesh, chloride form) was used.

Standard solutions. Stock solutions of iron, cobalt, nickel, and other elements were prepared by dissolving the reagent-grade chlorides of these metal ions in 6 *M* hydrochloric acid. These solutions usually contained 5 mg of metal ion/ml.

Solvent. Acetone of reagent-grade purity.

Wash solutions: (a) 90% (v/v) acetone + 10% 6 *M* hydrochloric acid; (b) 70% (v/v) acetone + 30% 2 *M* hydrochloric acid.

Apparatus

Resin columns of 75 cm length and 1.0 cm in diameter were used.

Determination of the elements

For the determination of iron, cobalt, and nickel as well as of the other investigated elements, titrimetric methods were employed using 0.01 or 0.001 *M* solutions of EDTA (disodium salt) in presence of suitable indicators such as sulfosalicylic acid (for iron), xylenol orange (for cobalt) and murexide, or when manganese was present pyrocatechol violet[2] (for nickel).

Working procedure

Pretreatment of resin bed. The resin suspended in wash solution (a) was transferred to the ion-exchange column and washed with approximately 100 ml of wash solution (a).

Sorption, washing and elution. Dilute 2 ml of 6 *M* hydrochloric acid containing iron, nickel and cobalt to 20 ml with acetone. Pass this solution through the resin column at a flow-rate of 0.3 to 0.4 ml/min. Afterwards wash the resin with wash solution (a) until iron is quantitatively removed from the resin (negative thiocyanate test) (see Fig. 1). Then pass wash solution (b) through the column, effecting the separation of nickel from cobalt. If mg-quantities of nickel and cobalt were originally present in the sorption solution, their green and blue bands respectively can be observed visually on the resin column. After complete elution of nickel, which is the case when 130 ml of wash solution (b) have passed, cobalt appears in the effluent after an eluate fraction of 80 ml (see Fig. 1). Alternatively, cobalt can be eluted with 1 *M* hydrochloric acid; this is advantageous when speed is essential but has the disadvantage that air bubbles are formed in the resin bed and prolong the subsequent regeneration of the resin with wash solution (a) if a second column operation in the same column has to be performed.

Evaporate the respective fractions containing nickel and cobalt to dryness on a water bath and determine the elements as described above.

Analysis of steel samples

Heat 0.5–1.0 g of the sample with concentrated hydrochloric acid and a few ml of 30% hydrogen peroxide until most of the sample has dissolved. Filter off the residue and digest with hydrofluoric acid to remove silica and to dissolve oxides such as titanium oxide. Evaporate the solution to dryness on a water bath, take up the residue in concentrated hydrochloric acid, warm and add excess of boric acid to remove the fluoride ions. Then evaporate the solution to dryness (water bath) twice with a few ml of concentrated hydrochloric acid. Finally, take up the residue in hydrochloric acid and combine the solution with the original filtrate. Filter this solution to remove the insoluble portion of boric acid and evaporate to dryness on a water bath. Then dissolve the residue in 6 *M* hydrochloric acid while transferring to a 10-ml measuring flask. Fill to the mark with 6 *M* hydrochloric acid and dilute an aliquot of 2 ml to 20 ml with acetone. Then pass the mixture through the ion-exchange column as described above.

RESULTS AND DISCUSSION

Based on the results of measurements of distribution coefficients[3] of iron, cobalt, nickel and other metal ions (see Table I) in various mixtures of acetone with hydrochloric acid the most suitable conditions were selected for the quantitative separation of the sum of cobalt and nickel from large quantities of iron.

Table I shows that a medium consisting of 90% acetone and 10% 6 *M* hydrochloric acid could be used effectively. To separate cobalt from the co-adsorbed nickel, a mixture of 70% acetone and 30% 2 *M* hydrochloric acid seemed to be most promising. When this medium was used for the separation, nickel was accompanied into the eluate by manganese and aluminium as well as chromium(III) which was found to behave similarly. On the other hand cobalt was eluted together with copper if present.

TABLE I

DISTRIBUTION COEFFICIENTS IN ACETONE–HYDROCHLORIC ACID MEDIA

Mixture	*Elements*					
	Fe	*Ni*	*Co*	*Cu*	*Mn*	*Al*
90% acetone + 10% 6 *M* HCl	<1	40	170	70	230	38
80% acetone + 20% 3 *M* HCl	<1	14	87	45	60	25
70% acetone + 30% 2 *M* HCl	<1	2	20	23	3	8

TABLE II

SEPARATION OF IRON, COBALT AND NICKEL IN ACETONE–HYDROCHLORIC ACID MEDIUM

Amounts taken (mg)			*Amounts recovered (mg)*		
Iron	*Cobalt*	*Nickel*	*Iron*	*Cobalt*	*Nickel*
500	1.0	1.0	500.2	0.99	1.01
500	2.5	2.5	500.7	2.5	2.52
500	5.0	5.0	498.6	4.97	5.01
500	5.0	10.0	500.0	5.03	9.97
500	10.0	5.0	500.9	10.06	5.0
500	20.0	20.0	501.2	20.1	20.0
500	50.0	50.0	500.8	49.8	50.1
500	75.0	75.0	498.7	74.9	75.4
500	100.0	100.0	497.9	100.0	99.9
500	1.0	100.0	500.0	0.99	100.3
500	100.0	1.0	501.3	100.4	1.02
100	100.0	100.0	100.0	99.8	99.7

Separation experiments with test solutions carried out by the above working procedure showed that these selected eluants were very effective for the separation. The results recorded in Table II show that in all cases a quantitative separation of nickel and cobalt from each other and large amounts of iron could be accomplished without any loss or cross-contamination of the iron, nickel and cobalt fractions.

To illustrate the effectiveness of this separation method more clearly, a typical chromatogram is shown in Fig. 1; it can be seen that no overlapping of the elution curves would occur even under the most critical conditions, *e.g.* if still larger amounts of iron than those used in this experiment were present.

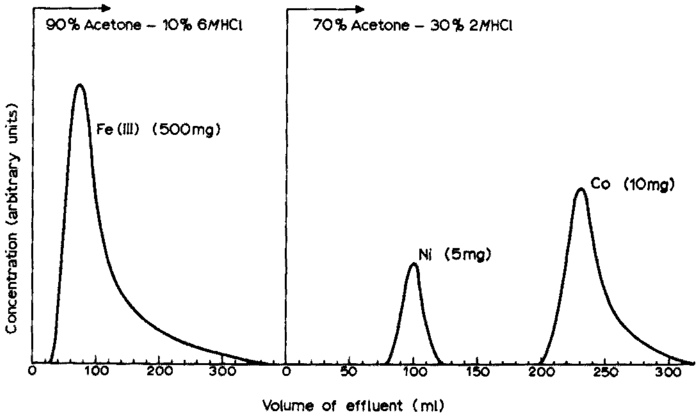

Fig. 1.

The same medium which is used for the elution of iron (wash solution (a)) can also be employed very effectively to separate large amounts of iron from aluminium, the latter element being retained by the resin like nickel, whereas iron appears in the effluent. In pure aqueous hydrochloric acid systems the reverse occurs, *i.e.* iron is strongly adsorbed and aluminium passes into the effluent[1].

Based on all these results the working procedure described in the experimental part was developed and applied to the analysis of 5 steel samples to which in parallel experiments known amounts of nickel and cobalt were added in order to check the applicability of the method to steel analysis. From the results of these investigations (Table III) it can be seen that in all cases a quantitative recovery of the added amounts of nickel and cobalt was achieved.

In conclusion, it is worth mentioning that this method would not only be applicable to the analysis of ferrous alloys but could also be adapted for the analysis of cobalt and nickel in meteorites, soils, ashes of biological materials, crude oils, marine sediments and other natural substances.

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TABLE III

ANALYSIS OF STEEL SAMPLES

Amount of Ni and Co present in steel sample		*Amount of Ni and Co added to steel sample*		*Recovered amount of Ni and Co*	
Ni(mg)	*Co(mg)*	*Ni(mg)*	*Co(mg)*	*Ni(mg)*	*Co(mg)*
8.2	0.5	5	5	13.3	5.54
		10	10	18.2	10.48
		20	20	28.4	20.62
0.0	0.0	5	5	4.97	5.0
		10	10	9.98	9.89
		20	20	20.0	20.1
0.0	0.0	5	5	5.04	5.02
		10	10	9.97	10.04
		20	20	19.92	20.2
0.15	0.0	5	5	5.2	5.0
		10	10	10.08	10.01
		20	20	20.17	20.04
43.0	0.5	5	5	48.2	5.48
		10	10	52.7	10.53
		20	20	63.0	20.6

SUMMARY

From 90% acetone–10% 6 M hydrochloric acid medium, cobalt and nickel are strongly adsorbed on the anion-exchange resin Dowex 1-X8; iron is not adsorbed and can thus be separated from cobalt and nickel. Cobalt and nickel are then separated by elution with 70% acetone–30% 2 M hydrochloric acid; nickel is eluted before cobalt. The method can be applied to the determination of nickel and cobalt in materials with high iron content such as steels; compleximetric titrations are used for the final step.

RÉSUMÉ

Le cobalt et le nickel sont fortement adsorbés sur résine Dowex 1-X8 (échangeur d'anions) en milieu acétone/acide chlorhydrique 6 M (90/10). Ils peuvent être ensuite séparés par élution avec un mélange acétone/acide chlorhydrique 2 M (70/30), le nickel étant élué avant le cobalt. Cette méthode peut s'appliquer au dosage du nickel et du cobalt dans des produits riches en fer, tels que des aciers, le fer n'étant pas adsorbé. On termine par titrages compleximétriques.

ZUSAMMENFASSUNG

Zur Bestimmung von Nickel und Kobalt in Materialien mit hohem Eisengehalt werden Kobalt und Nickel im Gegensatz zum Eisen vom Anionenaustauscher Dowex 1-X8 aus einem Medium von 90% Aceton und 10% 6 N Salzsäure stark absorbiert.

Durch Elution mit einer Lösung aus 70% Aceton und 30% 2 *N* Salzsäure wird Nickel vor dem Kobalt eluiert. Beide Elemente werden komplexometrisch bestimmt.

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DETERMINATION OF LANTHANUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

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For the determination of lanthanum and rare earths gravimetric methods are most widely employed. The rare-earth metals can be precipitated from simple solutions as their oxalates, hydroxides, oxinates, cupferrates, etc., and the precipitates obtained are ignited to the oxides. Organic reagents such as arsenazo, stilbazo, etc., have also been recommended for the precipitation of these metals but these methods are not of wide applicability.

N-Benzoyl-N-phenylhydroxylamine (N-BPHA) has been widely investigated by SHOME[1] and others[2] in the field of gravimetry, spectrophotometry, solvent extraction and compleximetric titrations. In the present paper, N-BPHA is suggested for the determination of lanthanum and its separation from other metals.

The rare-earth metals in the trivalent state form precipitates with N-BPHA, which are almost white in colour. In the case of lanthanum the precipitate is slightly soluble in water above 60°; it is soluble in chloroform, ethanol, ether and benzene, sparingly soluble in acetone, acetic acid and ethyl acetate, and freely soluble in mineral acids. The lanthanum complex corresponds to the formula $La(C_{13}H_{10}O_2N)_3$ and decomposes at 135–136°; the lanthanum content in the precipitate was established by igniting a known weight of the complex and weighing as La_2O_3 (La found, 17.90%; theoretical, 17.94%. N found, 5.46%; theoretical, 5.42%). Lanthanum can thus be determined by direct weighing of the precipitate formed with N-BPHA.

EXPERIMENTAL

Chemicals

Metal solutions. A standard solution of lanthanum was prepared from La_2O_3 (E. Merck) and hydrochloric acid (A.R.). Lanthanum nitrate solution was also prepared. Separate standard solutions of ferric alum, uranyl nitrate, thorium nitrate, aluminium sulphate, ceric ammonium nitrate, etc. were also prepared.

Reagent solution. A solution of N-BPHA in 95% ethanol was used; for 0.2 g of reagent, 8–10 ml of alcohol was taken.

Determination of lanthanum

Dilute a known amount of standard lanthanum solution with distilled water to 200 ml, heat to 50–55° and add the alcoholic reagent solution slowly with stirring.

Increase the pH of the solution to 6.7 (checked by indicator paper) by dropwise addition of dilute ammonia. Thoroughly stir the precipitate formed at intervals and when it appears to have settled, filter through a sintered glass crucible (No. 4). Wash the precipitate with distilled water, dry at 110–115° for 1 h, cool and weigh. Typical results are shown in Table I.

TABLE I

DETERMINATION OF LANTHANUM WITH N-BPHA
(pH = 6.4 to 7.0)

La taken (mg)	*Weight of precipitate (mg)*	*La found (mg)*	*Error (mg)*
25.92	143.9	25.91	−0.01
20.74	116.2	20.75	+0.01
12.96	72.0	12.91	−0.05
12.96	72.5	13.00	+0.04
7.78	41.9	7.70	−0.08
5.19	27.3	4.90	−0.29

Study of optimum conditions for precipitation of lanthanum

It was found that approximately 2–2.25 times the theoretical quantity of reagent was necessary for the complete precipitation of lanthanum from 200 ml of solution. The reagent may be precipitated if excessive quantities are used.

In examining the effect of pH on the precipitation, 1 *M* ammonia solution was added to adjust the pH of solutions containing the same amounts of lanthanum and N-BPHA to different values. It was found that precipitation of lanthanum commenced at pH 5.4 and was quantitative at pH 6.4–7.2. (The pH values of the filtrates were determined with a Cambridge pH meter.) Below this range the precipitate did not coagulate readily and above pH 7.2 both the reagent and the precipitate tended to decompose.

Temperature had a marked effect on the precipitation and determination of lanthanum; for quantitative precipitation, the optimum temperature was about 50°. The digestion of the precipitate should not be prolonged, otherwise the precipitate may change to a thermally unstable state.

POSSIBLE SEPARATIONS

Separation of iron, aluminium, thorium and uranium from lanthanum

Iron(III) and aluminium were separated from lanthanum by precipitating the metals completely with N-BPHA at pH 3.5 and 4.0–4.5 respectively. The precipitate of iron or aluminium was filtered and washed with an aqueous 0.1% solution of the reagent at pH 4.0–4.5. Lanthanum was subsequently determined in the filtrate by raising the pH to 6.7 as described above.

For the separation of thorium, the pH of the solution was adjusted to 4.5–5.0 with 10% ammonium acetate before the reagent was added. The thorium precipitate formed was digested on a water bath at 60–70°, filtered and washed with a hot aqueous 0.1% solution of the reagent at pH 5.0 and was rejected.

Although uranium was not precipitated with N-BPHA at pH 6.5–7.0, it was largely coprecipitated with lanthanum and hydrated uranium oxides were also slowly precipitated. For the separation of uranium, the solution was adjusted to pH 5.0–5.2 with a dilute ammonia solution and kept on a water bath below 50° with occasional stirring until it became colourless and the red crystals of the uranium–N-BPHA complex had separated[3]. The uranium precipitate was filtered and washed, and the combined filtrate was reserved for the determination of lanthanum. The results are shown in Table II.

TABLE II

SEPARATION OF LANTHANUM FROM Fe, Al, Th, U, Sc, Ce

La taken (mg)	*Foreign ion*	*Amount added (mg)*	*La found (mg)*	*Error (mg)*	*La taken (mg)*	*Foreign ion*	*Amount added (mg)*	*La found (mg)*	*Error (mg)*
12.96	Fe^{3+}	9.0	12.96	0.00	5.20	UO$_2^{2+}$	14.25	5.04	−0.16
12.96	Fe^{3+}	31.5	12.98	+0.02	12.96	UO$_2^{2+}$	4.75	12.92	−0.04
5.20	Al^{3+}	16.8	4.90	−0.30	12.96	Sc^{3+}	9.5	12.91	−0.05
12.96	Al^{3+}	16.8	12.93	−0.03	*12.96*	*Sc^{3+}*	*28.5*	12.98	+0.02
5.20	Th^{4+}	11.6	4.94	−0.26	12.96	Ce^{4+}	6.1	13.01	+0.05
12.96	Th^{4+}	11.6	12.90	−0.06	12.96	Ce^{4+}	24.4	13.20	+0.24

Separation of lanthanum from scandium and cerium

Scandium was completely precipitated at pH 4.8–5.4 with N-BPHA; ammonium acetate was used to adjust the pH of the solution. The precipitate was filtered and washed, and the lanthanum was determined in the filtrate.

Cerium was determined previously[4] by precipitation with N-BPHA after reduction of cerium(IV) to cerium(III) with hydroxylamine; the precipitates had to be ignited before weighing. It was also pointed out that cerium(IV) formed precipitates with N-BPHA at lower pH values but these precipitates were hydrous in nature and difficult to filter. In the present work it was found that 99–99.5% of the cerium(IV) could be precipitated with N-BPHA from a nitrate solution at pH 4.8–5.2; the incompleteness of precipitation was due to the partial reduction of cerium(IV) to cerium(III) by the reagent. By this method about 99% of cerium could be removed from a cerium–lanthanum mixture. Cerium(IV) was precipitated at room temperature and the precipitate was kept for about 2 h on a water bath below 50° with occasional stirring. The more or less granular precipitate thus formed was filtered and washed several times with a cold aqueous 0.1% solution of the reagent at pH 5.0. The lanthanum precipitate obtained from the filtrate assumed a faint buff colour on drying because of slight contamination with cerium. The precipitate on ignition to the oxide contained 0.5 to 1% of cerium.

The presence of acetate, other complexing ions and large amounts of chloride interfered with the separation of cerium; the results are shown in Table II.

Separation from other metals and interferences

Nickel, copper or zinc interfered unless they were previously masked with potassium cyanide. Small amounts of iron were masked with cyanide after reduction of iron(III) with sodium sulphite. Gallium[5], indium[5] and manganese[6] could be separated by prior precipitation of the metals at pH 2.0, 4.5 and 4.8 respectively; lanthanum was then determined in the filtrate after increasing the pH.

Zirconium[7] and hafnium[8] can be precipitated with the reagent from 0.5 N sulphuric acid or hydrochloric acid; titanium[9], molybdenum[10] and tungsten[11] from 0.02 N sulphuric or hydrochloric acid, vanadium[11] at pH 2.5, and niobium or tantalum[12] from 10% sulphuric acid media. Accordingly, it is simple to precipitate these ions and then determine lanthanum in the filtrate as described above.

Lanthanum was incompletely precipitated with N-BPHA in presence of tartrate or carbonate. There was no precipitation in the presence of citrate or EDTA. Phosphates and fluorides interfered seriously in the determination.

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SUMMARY

N-Benzoyl-N-phenylhydroxylamine is proposed for the gravimetric determination of lanthanum at pH 6.4–7.2. The precipitates can be weighed directly or ignited to the oxide. By suitable pH adjustment, many metals can be separated from lanthanum, which can then be determined in the filtrates. Interferences of Ni, Cu, Zn and Fe(II) are masked with cyanide. About 99.5% of cerium can be separated from lanthanum by precipitating cerium(IV) at pH 4.8–5.2.

RÉSUMÉ

La N-benzoyl-N-phénylhydroxylamine est proposée pour le dosage gravimétrique du lanthane au pH 6.4–7.2. Le précipité peut être pesé directement ou calciné sous forme d'oxyde. Plusieurs métaux peuvent être séparés du lanthane par précipitation à un pH déterminé; ils peuvent ensuite être dosés dans le filtrat. Nickel, cuivre, zinc et fer(II) gênent; ils sont masqués par les cyanures. Il est possible de séparer environ 99.5% de cérium d'avec le lanthane, par précipitation du cérium(IV) au pH 4.8–5.2.

ZUSAMMENFASSUNG

N-Benzoyl-N-phenylhydroxylamin wird für die gravimetrische Bestimmung des Lanthans beim pH-Wert 6.4 bis 7.2 vorgeschlagen. Der Niederschlag kann direkt gewogen oder zum Oxid verglüht werden. Durch passende pH-Wert-Einstellung können viele Metalle vom Lanthan getrennt und im Filtrat bestimmt werden. Störungen durch Ni, Cu, Zn und Fe(II) werden mit Cyanid maskiert. Etwa 99.5% des Cers können vom Lanthan durch Fällung des Cer(IV) beim pH-Wert 4.8 bis 5.2 getrennt werden.

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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH CHROME AZUROL S

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Methods commonly used for the spectrophotometric determination of aluminium have been summarized by SANDELL[1]. The most important reagents are aluminon, eriochrome cyanine R and 8-hydroxyquinoline. The aluminon method is based on the formation of a coloured lake with aluminium and has the disadvantage that heating is required, and that experimental variables must be carefully controlled to ensure reproducible results. The 8-hydroxyquinoline method is often too lengthy for routine use. Eriochrome cyanine R is more than three times as sensitive as aluminon, but can be used only under very rigid experimental conditions.

KASHKOVSKAIA AND MUSTAFIN[2] used chrome azurol S (C.I. No. 723, also known as solochrome brilliant blue B, and polytrop blue R, or sodium salt of 3″-sulfo-2″,6″-dichloro-3,3′-dimethyl-4-hydroxy fuchson-5,5′-dicarboxylic acid) to determine aluminium in steels and aluminium bronzes. They measured the absorbance of the aluminium–chrome azurol S lake at 530 mμ, where Beer's law is not obeyed. By choosing a wavelength of 567.5 mμ for absorbance measurements, the aluminium–chrome azurol S complex was found to obey Beer's law from 0 to 1.2 μg Al/ml. Chrome azurol S reacts with aluminium at room temperatures, thereby eliminating the heating needed with some other lake-forming reagents. The present investigation shows that chrome azurol S is a fairly sensitive reagent for the determination of aluminium, and is superior to aluminon and eriochrome cyanine R for the direct spectrophotometric determination of aluminium in mixtures of diverse ions.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 1-cm glass cuvettes was used in all experimental work.

Chrome azurol S solution, 0.165%. Dissolve 0.165 g of chrome azurol S (Geigy (A/sia),Pty.Ltd.) in water and dilute to 100 ml.

Acetate buffer solution, pH 4.60. Dissolve 238 g of sodium acetate trihydrate in 500 ml of water, add 102 ml of glacial acetic acid, and dilute to 1 l with water. When 5 ml of buffer solution was diluted to 25 ml the pH was 4.6.

Standard aluminium solution, 10 μg/ml. Dissolve 0.0200 g of pure aluminium foil in 20 ml of 2 *M* hydrochloric acid by heating gently, and dilute with water to 2 l in a volumetric flask.

Recommended procedure

Transfer an aliquot of the slightly acid sample solution (1–35 μg Al) to a 25-ml volumetric flask. On a separate aliquot determine the amount of 10% sodium hydroxide required to neutralise the free acid to methyl orange indicator. Add 1.0 ml of 1% ascorbic acid and 5.00 ml of acetate buffer solution. Add the predetermined amount of 10% sodium hydroxide. Dilute to about 20 ml with water. Add 1.0 ml of 2% sodium thiosulphate solution, 2.00 ml of 0.165% chrome azurol S and dilute to volume. Measure the absorbance within 10 min against a blank at 567.5 mμ in 1-cm cells.

If more than 2 mg of copper, 4 mg of iron, or molybdenum, thorium, titanium, tungsten and vanadium is present, special precautions must be taken (see *Study of interferences*).

DISCUSSION

Sensitivity and stability of the method

The aluminium–chrome azurol S lake when measured against the blank, has maximum absorbance at 545 mμ (Fig. 1). However at this wavelength the absorbance–wavelength curve does not pass through the origin. It was found that when a wavelength of 567.5 mμ was used, a curve was obtained which did pass through the origin.

At 567.5 mμ the molar absorptivity of the lake is $21.6 \cdot 10^3$ (20°), corresponding to 0.00125 μg Al/cm^2 on the Sandell scale. Beer's law is obeyed to at least 1.2 μg Al/ml, but at 1.6 μg Al/ml there is a 2% deviation. The absorptivity varies considerably with change in pH, concentration of chrome azurol S, and buffer. When only

Fig. 1

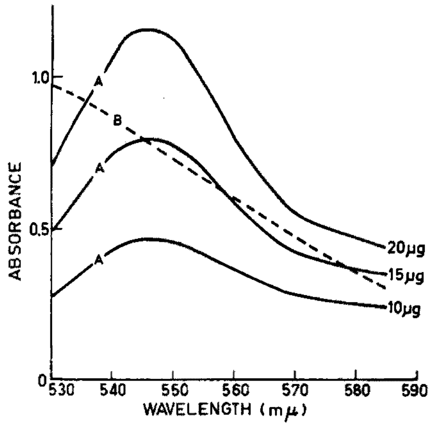

Fig. 2

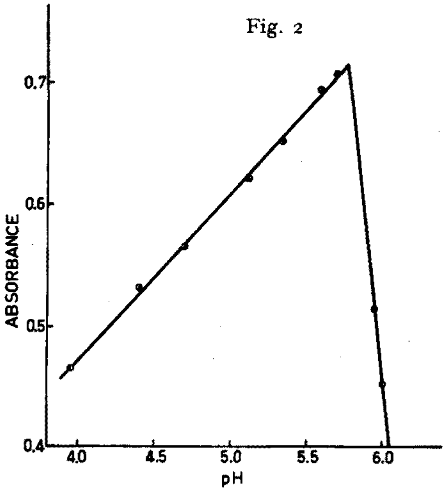

Fig. 1. Absorbance–wavelength curves. Final volume 25 ml, 1-cm cuvettes. (A) Al^{3+} *versus* blank, (B) blank *versus* water.

Fig. 2. Absorbance–pH curve. 10 μg Al, 0.05 ml buffer, 2 ml 0.165% chrome azurol S, final volume 25 ml, at 560 mμ, 1-cm cuvettes.

0.05 ml of buffer solution is used, the molar absorptivity increases to $38.4 \cdot 10^3$ (0.0007 μg Al/cm^2 on the Sandell scale).

At the specified pH of 4.6 the aluminium–chrome azurol S lake is formed instantly. The absorbance decreases slowly on standing (2% pei hour), but is somewhat less stable when interfering ions are present.

The stability of the lake was tested in the temperature range 15° to 35° and found to be stable. The absorbance decreases by 1% for each 1° rise in temperature, when measured against the blank.

Effect of varying reagent concentrations

A decrease in the concentration of the buffer solution increases the absorbance of the lake. A change from 5 ml to 2 ml of buffer solution increases the absorbance by 20%, and a change from 1 ml to 2 ml of the reagent increases the absorbance by 55%. However it was impracticable to raise the dye concentration above 0.014%because of the high blank absorbance (0.510 at 0.014% dye).

Choice of pH

The absorbance of the aluminium–chrome azurol S lake increases gradually with increasing pH and reaches a maximum at pH 5.8, after which the absorbance drops very sharply (Fig. 2).

KASHKOVSKAIA AND MUSTAFIN[2] used an ammonium acetate buffer solution of pH 5.12. The pH value of 4.6, which is in the middle of the sodium acetate–acetic acid buffer range, was selected in the present work to minimise any pH changes caused either by free acid or free alkali. Additions were made to solutions containing 2 ml and 5 ml of buffer solution, and from the results obtained (Table I), it was decided to use 5 ml of buffer solution. In addition, the interference of iron(III) was much larger at pH 5.1 than at pH 4.6.

TABLE I

RECOVERY OF Al AND CHANGES OF pH AFTER ADDITION OF FREE ACID AND FREE ALKALI

Added	*5 ml buffer*		*2 ml buffer*	
	Al found (µg)	*pH*	*Al found (µg)*	*pH*
Nil	20.0	4.60	20.0	4.63
0.1 ml 10 *M* HCl	21.0	4.49	22.3	4.35
0.1 ml 10 *M* NaOH	19.5	4.69	18.3	4.90

Interference by diverse ions

Many elements form strong colours with chrome azurol S, for example, Be^{2+}, Cu^{2+}, Fe^{3+}, Th^{4+}, Ti^{4+}, and Zr^{4+}. Many interferences can be minimised by using various masking agents (Table II).

The interference of iron(III) can be masked by ascorbic acid. One ml of 1% ascorbic acid is sufficient to mask 4 mg of ferric ion. To determine aluminium in solutions which contain more than 4 mg of iron, proportionately more ascorbic acid

TABLE II

STUDY OF INTERFERENCES IN THE DETERMINATION OF Al WITH CHROME AZUROL S

Foreign ion added	*Amount taken (mg)*	*Aluminium taken (µg)*	*Aluminium found (µg)*	*Relative error (%)*
Be^{2+}	0.025	20.0	32.7	64
Bi^{3+}	1.0	20.0	20.0	0
Ca^{2+}	2.0	20.0	19.8	− 1
Cd^{2+}	2.0	20.0	20.2	1
Co^{2+}	2.0	20.0	20.0	0
Cr^{3+}	0.5	20.0	19.3	− 4
Cr^{3+}	1.0	20.0	18.9	− 6
Cu^{2+}	2.0	20.0	19.8	− 1
Cu^{2+}	2.0	20.0	20.0	0[a]
Cu^{2+}	10.0	20.0	19.8	− 1[a]
Fe^{3+}	2.0	20.0	19.8	− 1
Fe^{3+}	4.0	20.0	20.0	0
Fe^{3+}	5.0	20.0	18.9	− 6[b]
Fe^{3+}	10.0	20.0	18.8	− 6[b]
Fe^{3+}	10.0	10.0	9.4	− 6[b]
Mg^{2+}	2.0	20.0	19.6	− 2
Mn^{2+}	2.0	20.0	20.0	0
Mo(VI)	0.5	20.0	20.3	2[c]
Mo(VI)	0.5	10.0	10.3	3[c]
Mo(VI)	1.0	20.0	19.7	− 2[c]
Mo(VI)	1.0	10.0	9.7	− 3[c]
Ni^{2+}	2.0	20.0	19.7	− 2
Pb^{2+}	2.0	20.0	20.0	0
Sb^{3+}	2.0	20.0	20.0	0
Sn^{4+}	0.5	20.0	18.2	− 9
Th^{4+}	0.5	20.0	22.2	11
Th^{4+}	0.5	10.0	12.2	22
Th^{4+}	1.0	20.0	24.4	22
Th^{4+}	1.0	10.0	14.4	44
Ti^{4+}	0.1	20.0	20.3	2[d]
U(VI)	2.0	20.0	19.6	− 2
V(V)	1.0	20.0	20.6	3[e]
V(V)	0.2	20.0	36.0	80
W(VI)	2.0	20.0	19.8	− 1[f]
Zn^{2+}	2.0	20.0	19.8	− 1
Zr^{4+}	0.2	20.0	24.1	21
F^-	0.019	20.0	11.2	−42
F^-	0.038	20.0	6.1	−70
F^-	0.095	20.0	2.0	−90
PO_4^{3-}	0.5	20.0	19.8	− 1
PO_4^{3-}	1.0	20.0	19.6	− 2
PO_4^{3-}	2.0	20.0	19.0	− 5

[a] Buffer added before ascorbic acid; 5 ml of 2% $Na_2S_2O_3$.

[b] 2.5 ml of 1% ascorbic acid added.

[c] 0.5 mg PO_4^{3-} added to weakly acid solution.

[d] 0.5 mg PO_4^{3-} added.

[e] Without ascorbic acid.

[f] 4 mg Ca^{2+} added.

should be added, and it is necessary to prepare standard aluminium solutions which contain an amount of iron equivalent to that in the sample aliquot.

Copper can be complexed satisfactorily with sodium thiosulphate. One ml of 2% sodium thiosulphate is sufficient to complex 2 mg of copper(II), and proportionately more of the sodium thiosulphate solution should be used for larger amounts of copper. In slightly acid solutions ascorbic acid has a tendency to reduce Cu^{2+} to Cu^{+} forming a precipitate. The maximum amount of copper(II) which can be tolerated in the recommended procedure is 2 mg. It was found that at pH 4.6 copper(II) is not reduced by ascorbic acid, and by changing the order of addition — buffer solution followed by ascorbic acid — it was possible to determine aluminium in solutions containing larger amounts of copper.

Molybdate ion interferes seriously, but the interference can be overcome by complexing with phosphate ion. The following procedure should be used: to the slightly acidic solution (pH 1.5) add 0.5 mg of phosphate ion and let it stand for 5 min. Add 1.0 ml of 1% ascorbic acid, shake, and immediately add 5.00 ml of buffer solution. Continue as in the recommended procedure.

Thorium interferes to a large extent, and the interference is proportional to the amount of thorium present. Titanium forms a strongly coloured complex with chrome azurol S. The interference in the microgram range can be masked by the addition of 0.5 mg phosphate ion. Tungstate reduces the aluminium absorbance, but the addition of calcium makes the interference negligible. Vanadium(V) interferes slightly, but vanadium(IV), which is formed by reduction with ascorbic acid, interferes seriously.

The interference of various neutral salts was studied at the 20 μg of aluminium level, by measuring the absorbance against the standard blank (Table III).

TABLE III

RECOVERY OF Al (μg) AFTER SALT ADDITION TO 20 μg OF Al

Gram equivalent salt added	*NaCl*	*Na_2SO_4*	*$NaNO_3$*	*$NaClO_4$*	*NH_4Cl*
0.001	20.0	19.8	20.0	20.0	20.0
0.0025	19.9	19.4	19.9	20.1	19.9
0.005	19.8	18.6	19.8	20.2	19.8

Reproducibility of the method

Ten replicate determinations were made at the 20 μg of aluminium level using the recommended procedure; the relative standard deviation was ± 0.4%.

COMPARISON BETWEEN CHROME AZUROL S, ERIOCHROME CYANINE R, AND ALUMINON

The procedures used for the determination of aluminium with eriochrome cyanine R and aluminon have been described previously[3,4]. A comparison of interferences in the 3 methods is given in Table IV. The results show that the eriochrome

TABLE IV

COMPARISON OF INTERFERENCES USING ALL THREE REAGENTS

Foreign ion added	*Weight ratio (ion : Al)*	*Relative error (%)*		
		Chrome azurol S (20 μg/25 ml)	*Eriochrome cyanine R (10 μg/50 ml)*	*Aluminon (20 μg/50 ml)*
Ca^{2+}	100	−1	0	+2[a]
Co^{2+}	100	0	>+100	>+100
Cr^{3+}	50	−6	−80	>+100
Cu^{2+}	100	−1	+8	+25
Fe^{3+}	100	−1	+11	+5
Mg^{2+}	100	−2	+5	−4
Mn^{2+}	100	0	+7	−6
Ni^{2+}	100	−2	+14	−10
Th^{4+}	50	+22	+11	[b]
U(VI)	100	−2	0	+2
Zn^{2+}	100	−1	+4	−6
PO_4^{3-}	50	−2	−76	−3

[a] Reference 4.
[b] Hazy.

TABLE V

COMPARISON OF EFFECT OF FREE ACID AND FREE ALKALI ON CHROME AZUROL S AND ERIOCHROME CYANINE R METHODS

Added	*Chrome azurol S*		*Eriochrome cyanine R*	
	μg	*pH*	*μg*	*pH*
Nil	20.0	4.6	10.0	6.0
1 ml of 1 *M* HCl	21.0	4.5	13.0	5.7
1 ml of 1 *M* NaOH	19.5	4.7	6.0	6.7

cyanine R and aluminon methods are subject to large errors by many foreign ions, in particular chromium and cobalt, which must be completely removed. Even small amounts of phosphate interfere seriously in the eriochrome cyanine R method.

Small amounts of free acid or free alkali produce negligible errors in the chrome azurol S method, but very large errors with eriochrome cyanine R (Table V) which requires precise pH adjustment. For this reason, the eriochrome cyanine R procedures recommended for the determination of aluminium in magnesium alloys[5], zinc metal[6], and iron ores[3], all use strictly controlled amounts of acid for dissolution and specified sample aliquot sizes.

On the basis of selectivity, simplicity, and rapidity, chrome azurol S appears to be the most suitable reagent yet proposed for the routine spectrophotometric determination of aluminium, even though it is less sensitive than eriochrome cyanine R. As an example of the versatility of the chrome azurol S spectrophotometric method, aluminium was determined directly in a permanent magnet alloy (B.C.S. sample 233, Co–23.7%, Ni–11.2%, Al–6.98%, Cu–5.1%, Ti–0.8%, Mn–0.2%, Si–0.6%, Fe–51.2%). The result found was 7.04 ± 0.03% Al, which compares favourably with the certificate value of 6.98% Al. Both the eriochrome cyanine R and aluminon methods failed when applied directly to this alloy, because of the interference of cobalt.

SUMMARY

A comprehensive investigation of the spectrophotometric determination of aluminium with chrome azurol S is described. No heating is required for colour formation, and the method is considerably more reproducible and selective than either the eriochrome cyanine R or aluminon methods. In the presence of suitable masking agents, only Be^{2+}, Zr^{4+}, and F^- cause serious interference. A molar absorptivity of 21,500 at 567.5 mμ was found for the aluminium–chrome azurol S lake, with a relative standard deviation of ± 0.4% at the 20 μg Al level. Beer's law is obeyed from 0 to 1.2 μg Al/ml.

RÉSUMÉ

L'auteur décrit une méthode de dosage de l'aluminium au moyen de chrome azurol S. Ce procédé ne nécessite pas de chauffage; sa reproductibilité et sa sélectivité sont meilleures que celles des méthodes à l'ériochrome cyanine R ou à l'aluminon. En présence de réactifs de masquage appropriés, seuls Be^{2+}, Zr^{4+} et F^- gênent sérieusement. La loi de Beer s'applique de 0 à 1.2 μg Al/ml.

ZUSAMMENFASSUNG

Eine ausführliche Untersuchung der spektralphotometrischen Bestimmung des Aluminiums mit Chromazurol S wird beschrieben. Für die benötigte Farbbildung ist kein Erwärmen erforderlich. Die Methode besitzt eine bessere Reproduzierbarkeit und ist selektiver als die Eriochromcyanin R- oder Aluminon-Methode. In Gegenwart von brauchbaren maskierenden Reagentien verursachen nur Be^{2+}, Zr^{4+} und F^- ernsthafte Störungen. Die molare Extinktion für den Aluminium–Chromazurol S-Lack betrug 21500 bei 557.5 mμ, die relative Standardabweichung 0.4% bei 20 μg Aluminium. Das Beersche Gesetz wird von 0–1.2 μg Al/ml befolgt.

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PHOSPHORIMETRIC DETERMINATION OF PROCAINE, PHENOBARBITAL, COCAINE, AND CHLORPROMAZINE IN BLOOD SERUM, AND COCAINE AND ATROPINE IN URINE

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Phosphorimetry was first applied to the analysis of drugs in biological fluids by WINEFORDNER AND LATZ[1] who determined aspirin in blood serum and plasma. They compared phosphorimetry to fluorimetry as well as other spectrophotometric methods and indicated that the most significant advantages lie in its extreme sensitivity and selectivity. WINEFORDNER AND TIN[2] have studied the phosphorescence emission and excitation spectra, the phosphorescence decay times, the analytical curves and the limits of detection of a number of drugs in ethanol. Because of the above results and because of the low phosphorescence background of a chloroform or ether extract of blood at any pH and urine at a pH greater[1,3] than 5, the determination of low concentrations of several drugs not normally present in blood serum and urine was examined as described below. The results indicate that phosphorimetry is not only extremely sensitive and nearly free from interference, but is also quite rapid and accurate.

The accurate, rapid analysis of drugs over a wide concentration range in biological fluids is extremely important in medical research. Some of the areas of application include the study of drug administration, the dosage of the drug to be used, the toxicological limitations of various drugs, the exact fate of drugs within the body, the efficiency and activity of drugs and the rate of elimination of drugs from the body. The analytical method most commonly used for the determination of drugs in biological fluids usually involves a time-consuming separation of the drug from a large amount of the biological fluid and a spectrophotometric measurement of the resulting solution. Both the separation step and the measurement step involve the use of several chemical reagents, which generally results in contamination of the sample and therefore seriously limits the accuracy and the sensitivity of the method.

Procaine undergoes rapid hydrolysis to *p*-aminobenzoic acid in biological fluids[4]. KISCH AND STRAUSS[5] used a micro-method to determine the total amount of procaine and *p*-aminobenzoic acid in blood. They obtained the best results with procaine concentrations between 0.02 and 0.04 mg/ml of blood and obtained recoveries between 97 and 106% for a procaine concentration of 0.030 mg/ml. Using their technique, a skilled worker could only perform 12 determinations a day.

The characterization of the metabolic products of cocaine has never been carried out, although it is known that the complete elimination of cocaine is a slow process[4]. WOODS *et al.*[6] have described a spectrophotometric determination of cocaine, mescaline and several other amines in biological materials; their extraction procedure is specific for mescaline and cocaine. The method used is, however, involved, reliable only to ±15%, and of little value for concentrations below 2–3 μg/ml of blood.

Atropine is readily absorbed from the intestinal tract in a short time and is one of the more difficult alkaloids to determine. TØNNESEN[7] used an extraction technique combined with a biological technique (PULEWKA's mouse eye test) for analysis of atropine and allied alkaloids in urine. The method was fairly slow, complicated and quite insensitive to small amounts of atropine.

Phenobarbital undergoes slow metabolism to *p*-hydroxyphenobarbital, either in the free or conjugated states[8,9]. It undergoes almost no change in the blood, and normally 80 to 100% is excreted in urine[9]. Several spectrophotometric methods[10] have been used to determine phenobarbital in blood and urine. In these studies, the presence of *p*-hydroxyphenobarbital was ignored. BUTLER[11], for example, was able to determine 3–35 μg of phenobarbital per ml of blood.

Chlorpromazine undergoes rapid metabolism to the sulfoxide derivative in the blood, and only small percentages of it have been found in either the blood or urine[9]. SALZMAN AND BRODIE[4] have determined chlorpromazine at high concentration levels in plasma by a spectrophotometric method. They could determine 10–100 μg of chlorpromazine in 1–4 ml of plasma or urine with fair precision.

In most of the drugs discussed above, either no accurate analytical method is available or the methods used are insufficiently sensitive and/or time-consuming and/or subject to interferences. In the proposed method, procaine, chlorpromazine, cocaine and phenobarbital in blood, and cocaine and atropine in urine are extracted into spectrograde chloroform or ether; the ether or chloroform is evaporated, and the residue is dissolved in EPA[1] and analyzed phosphorimetrically. The analysis for each drug requires less than 20 min and recoveries of drugs added *in vitro* are usually between 94% and 106%.

EXPERIMENTAL

Equipment

All phosphorimetric measurements were obtained with an Aminco spectrofluorimeter with phosphoroscope attachment (American Instrument Co., Inc.). A rotary evaporator (rotary vacuum type, Rinco, Fisher Scientific Co.) was used to evaporate the solvent used for extraction.

Reagents and chemicals

The chloroform and ether used in the extraction procedure were spectrograde solvents. The EPA was fluorimetric grade (Hartman Leddon Co.). The ethanol was especially purified as previously described[2]. All drugs were of U.S.P. quality, and all other chemicals were of reagent-grade quality. Stock solutions containing 3.00 mg of procaine, 0.0300 mg of cocaine, 10.0 mg of phenobarbital, 0.100 mg of chlorpromazine hydrochloride or 4.00 mg of atropine per ml of ethanol were prepared. By successive dilutions, ethanolic solutions containing less of each drug were also prepared. Ethanol was used as the solvent for preparation of standard drug solutions to be added to the blood or urine because it has a very low phosphorescence background[2] and the solubility of most drugs in it is high.

Introduction of drugs into blood and urine

In this work, all drugs were added to the biological fluid *in vitro*. The main purpose of these studies was to show that the sensitive method of phosphorimetry can be used to give rapid, accurate and selective results for low concentrations of several drugs extracted from blood and urine. Therefore, the drugs were added to the blood after removal from the body and deproteinization, and to the urine after excretion. In this way the extraction could be performed rapidly without fear of significant hydrolysis. The drugs were added to known volumes, *e.g.* 1 ml of blood, and urine by accurately pipetting small volumes, *e.g.* 100 µl, of the appropriate drug.

Extraction procedures

For procaine in blood. (Because of the small volumes of sample used for phosphorimetric measurements, the volumes in the following procedure could be decreased by ten-fold or even more.) Add 10 ml of 50% trichloroacetic acid to 10.0 ml of blood serum in a 50-ml centrifuge tube. After centrifuging for 3 min, decant the clear, supernatant fluid into a phosphorimetrically clean[1,3] 25-ml volumetric flask and dilute to 25 ml with distilled water. Neutralize a 2.5-ml aliquot of this solution to phenolphthalein by adding dropwise a half-saturated solution of sodium hydroxide[5]. Note the volume used for neutralization and add to a phosphorimetrically clean 20-ml vial with plastic cap. To the vial, add a second 2.5-ml aliquot of the above serum solution. Then add 0.2 ml of a 25% sodium carbonate solution and 10.0 ml of chloroform to the vial, and shake vigorously for 2 min (preferably with a mechanical shaker). Carefully remove the chloroform with a 10-ml hypodermic syringe, taking care not to remove any of the aqueous layer. Transfer the chloroform into a 50-ml distilling flask with standard-taper joint, and repeat the extraction procedure using a second 10.0 ml of chloroform. Combine the chloroform extracts, and evaporate the chloroform rapidly using a vacuum evaporator. Dissolve the residue in exactly 10.0 ml of EPA, and the resulting solution is ready for phosphorimetric measurement. A sample of blood serum, known to be free from drugs, is extracted with chloroform, the chloroform is evaporated and the residue is dissolved in EPA as described above; the resulting EPA solution is then the blank for the procaine determination.

For cocaine in blood and urine. The reagents and general procedure described by WOODS *et al.*[6] were used for the extraction of cocaine from blood and urine. Therefore, only the essential steps of the procedure will be given here. Add 1 ml of blood serum or urine to 3 ml of a borate buffer (for serum) or 0.4 ml of a phosphate buffer (for urine) and 10.0 ml of chloroform in a 20-ml phosphorimetrically clean vial with cap. Remove as much of the aqueous layer as possible and then remove 5.0 ml of the chloroform extract with a pipet. Transfer the 5 ml of chloroform to a 50-ml flask with standard-taper joint, and evaporate the chloroform with a vacuum evaporator. Dissolve the residue in 5.0 ml of EPA which will be used for the phosphorimetric measurement of cocaine. A sample of blood or urine, known to be free from drugs, is extracted with chloroform, the chloroform is evaporated and the residue is dissolved in EPA as described above; this solution is then the blank for the cocaine determination.

For phenobarbital in blood. Pipet 1 ml of blood serum into a phosphorimetrically clean 20-ml vial with cap. Add exactly 0.2 ml of concentrated HCl and 10.0 ml of chloroform and shake for 2 min. Then remove 5.0 ml of the chloroform carefully with a pipet and transfer to a 50-ml flask with standard-taper joint. Evaporate this solution rapidly with a vacuum evaporator. Dissolve the residue in 5.0 ml of EPA; this solution is then used for phosphorimetric measurement. A 1-ml sample of blood, known to contain no drugs, is extracted with chloroform, the chloroform is evaporated and the residue is dissolved in EPA as described above; this solution is the blank for the phenobarbital determination.

For chlorpromazine hydrochloride in blood. Use exactly the same procedure as for phenobarbital except that 20.0 ml of chloroform is required and 10.0 ml of extract is evaporated. A blank is prepared in the same manner as for phenobarbital with the above exceptions.

For atropine in urine. Essentially the procedure described by TØNNESEN[7] is used; therefore, only the essential steps of the procedure will be given. Transfer a 5.0-ml aliquot of urine to a phosphorimetrically clean 20-ml vial with cap and adjust to pH *ca.* 10 by addition of 0.2 ml of 25% (w/v) sodium carbonate solution. Then add 10.0 ml of ether saturated with water, and shake vigorously for 2 min. Using a pipet, remove 5.0 ml of the ether extract and transfer to a 50-ml flask with standard-taper joint. Rapidly evaporate the ether with a vacuum evaporator, and dissolve the resulting residue in 5.0 ml of EPA. Use this solution for the phosphorimetric measurement. Extract a 5.0-ml sample of urine, known to be free from drugs, with ether, evaporate the ether and dissolve the residue in EPA as described above; this solution is the blank for the atropine determination.

Phosphorimetric measurement

Before any drug measurements, calibrate the instrument. To do so, pipet 0.5–1.0 ml of a standard toluene solution (0.2 ml of toluene per 100 ml of phosphorimetrically pure ethanol[2]; this solution is stored at 0° to prevent any losses) into an Aminco phosphorimetric sample tube. Position the tube in the Aminco Dewar flask containing liquid nitrogen, and adjust the excitation and emission monochromators to 270 mμ and 385 mμ respectively. Set the meter multiplier knob to 0.3, and adjust the fine sensitivity control until the photometer meter reads 43. For this measurement, set the phosphoroscope (shutter) speed to approximately one-third of maximum, and use the slit program of a—3 mm, b—4 mm, c—4 mm, d—3 mm, and e—3 mm. In all other respects, operate the spectrophosphorimeter as specified by the manufacturer.

By the above procedure, analytical curves for each of the drugs in EPA solvent were found to be reproducible over a period of 4 months within the reading error of the meter (±1 division — full-scale is 100 divisions). The calibration procedure, therefore, eliminated the necessity of re-running analytical curves on a daily basis due to small instrumental changes, *e.g.*, small variations in the sensitivity of the detector, in source intensity and in transmittance or reflectance of optical components within the monochromator.

For a determination, pipet 0.5–1.0 ml of the EPA solution containing the drug into the Aminco sample tube, and position the tube in the Dewar flask containing liquid nitrogen. Adjust the phosphoroscope speed and the slit program to the values used for the calibration, and then operate the instrument according to the manufacturer's directions. Adjust the excitation and emission monochromators to wavelengths giving maximum response. The excitation wavelength settings for procaine, cocaine, phenobarbital, atropine and chlorpromazine hydrochloride are 310 mμ, 240 mμ, 240 mμ, 240 mμ and 320 mμ, respectively, and the emission wavelength settings for the same drugs are 430 mμ, 400 mμ, 380 mμ, 380 mμ, and 490 mμ, respectively. The peak wavelengths for excitation and emission of procaine, cocaine, phenobarbital and atropine were previously given[2].

After the sample tube has equilibrated (about 1 min is sufficient), adjust the meter multiplier of the photomultiplier photometer to give a meter reading of 30% or greater. This is done to avoid significant meter reading errors. Then multiply the meter reading by the meter multiplier setting to give a phosphorescence intensity reading corresponding to sample plus blank. Measure the blank EPA solution for the drug by the same procedure as for the EPA solution of the drug, and also multiply this meter reading by the meter multiplier setting to give a phosphorescence intensity reading corresponding to just the blank. Subtract the blank reading from the sample plus blank reading to give a phosphorescence intensity reading characteristic of the drug only. The amount of drug being measured in μg per ml of blood or urine (in the case of atropine—per 5 ml of urine) can then be found by reading the absolute value from the concentration axis of the appropriate analytical (working) curve corresponding to the phosphorescence intensity (meter reading) of the drug. The analytical curves are therefore plots of phosphorescence intensity (or meter reading) *vs.* concentration of the drug in EPA in μg of drug per 10 ml of EPA.

All analytical curves were prepared by measuring a series of standard EPA solutions of each drug using the emission and excitation wavelength settings and phosphoroscope speed discussed above. Of course, before the phosphorimetric measurement of these solutions, the instrument was calibrated using the standard toluene solution. Each point of each analytical curve was corrected for the phosphorescence background of the solvent (trace impurities in EPA) and normal pick-up of impurities from the atmosphere[1,3].

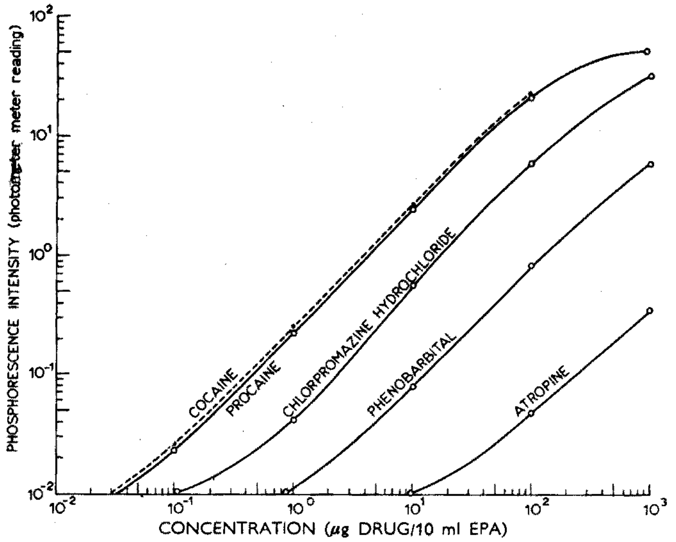

Fig. 1. Analytical curves of drugs in EPA. A, cocaine; B, procaine; C, chlorpromazine hydrochloride; D, phenobarbital; E, atropine.

RESULTS AND DISCUSSION

Analytical curves for procaine, cocaine, phenobarbital, atropine and chlorpromazine in EPA solvent are given in Fig. 1. Typical recovery and reproducibility results for each of the drugs in blood or urine are given in Table I. In most cases the recovery and reproducibility are excellent and considerably better than those of most of the methods normally used.

The reproducibility of the determination depends largely on the readability (±1 division) of the photomultiplier photometer meter, on the random fluctuation due to the bubbling of liquid nitrogen (±2.5 divisions) and on the pick-up of phosphorimetric impurities on glassware and apparatus. The accuracy of measurement depends primarily on the non-random pick-up of phosphorimetric impurities, on the portion of the analytical curve used for analyses and on the readability of the meter if only several analyses are carried out. The percentage error due to the readability of the meter can also be made relatively small by always adjusting the meter multiplier so that no meter reading of less than 30% of full-scale ever results.

In previous studies[1] and in the present work, it was shown that all blood serum or urine samples, free from drugs, extracted at a given pH resulted in nearly the same phosphorescence background reading. This was true as long as all glassware was phosphorimetrically clean[1,3] and all background measurements were carried

TABLE I

ACCURACY AND REPRODUCIBILITY OF RECOVERING DRUGS FROM BLOOD AND URINE

Biological fluid	*Volume of fluid extracted (ml)*	*Drug*	*Amount of drug added (μg)*	*Amount of drug recovered (μg)*	*% Recovery*	*Relative standard deviation*[a]
Blood	10	Procaine	0.30	0.25	83	5.2
			3.0	2.8	93	4.3
			30.0	29.5	98	2.8
			300.0	300	100	2.5
			3.0[b]	2.7	90	5.5
			30.0[b]	28.0	93	4.5
Blood	1	Cocaine	0.030	0.033	110	10.0
			0.30	0.29	97	2.8
			3.0	3.0	100	2.0
Urine	1	Cocaine	0.030	0.031	103	10.0
			0.30	0.29	97	2.5
			3.00	2.92	97	2.1
Blood	1	Phenobarbital	1.0	1.5	150	50.0
			10.0	9.4	94	3.2
			100.0	97	97	3.0
			1000	950	95	2.0
Urine	5	Atropine	40	36	90	3.5
			400	384	96	2.5
Blood	1	Chlorpromazine hydrochloride	0.10	0.11	110	4.2
			1.0	0.94	94	2.8
			10.0	9.5	95	4.2

[a] Relative standard deviation for five replicate determinations for each amount of each drug.
[b] Blood (10 ml) contains 0.3 mg of *p*-aminobenzoic acid as well as procaine.

out using the extraction solvent and EPA solvent from the same bottles. In all cases, the phosphorescence background for blood and urine was less than 70% of full-scale on the most sensitive meter multiplier setting (0.001). Therefore, it was possible to determine only one blank at the beginning of a series of determinations. However, in order to recognize contamination problems, it was best to re-run a blank after every 5 to 10 determinations. Even so, the average length of time required for the extraction and measurement of any of the drugs studied here was less than 30 min per analysis.

Because only 0.5 ml of EPA is required for phosphorimetric measurement, it should be possible to utilize micro-techniques to decrease the amount of biological fluid required for analysis by at least ten-fold.

The presence of metabolic products of each of the drugs was also considered. The only metabolite of procaine which will phosphoresce, is *p*-aminobenzoic acid. The addition of small amounts of *p*-aminobenzoic acid to procaine resulted in no significant change in the procaine analysis (see Table I). In fact, because of the small distribution coefficient of *p*-aminobenzoic acid between chloroform and water at pH *ca.* 10, no phosphorescence of *p*-aminobenzoic acid could be detected upon chloroform extraction. The metabolites of cocaine, phenobarbital, atropine and chlorpromazine were not studied experimentally for the reasons given below. The metabolic products of cocaine have not been completely characterized[9]. However, if hydrolysis is the major metabolic pathway, then methanol, benzoic acid and ergonine are produced and of these only benzoic acid will phosphoresce. At the pH used for extraction (pH 7–10), benzoic acid, like *p*-aminobenzoic acid, is not extracted by chloroform, and so no interference due to the metabolic products should result. The only metabolite of phenobarbital which phosphoresces is *p*-hydroxyphenobarbital which is normally not present in blood[8]. Therefore, no metabolite interferences should result in the phosphorimetric determination of phenobarbital in blood. The metabolic products of atropine are tropine and tropic acid, and of these only tropic acid should phosphoresce. Again, as with procaine or cocaine, the acid is not appreciably extracted into ether from an aqueous solution at pH 10. The metabolite of chlorpromazine is the sulfoxide derivative which undoubtedly will phosphoresce. This derivative will, however, probably not be present in significant concentration in the blood[9], and little interference should result. If the sulfoxide were important in blood, chlorpromazine would then have to be separated chromatographically or by a suitable extraction technique[4]. Of course, in the present work, only the single drug in the presence of the normal constituents in blood and urine was determined. Because of the large number of other drugs and substances which might also be simultaneously present, it was impossible to study the influence of other materials in a general manner. However, if other drugs, metabolites or materials, which are also extracted under the experimental conditions described, also phosphoresced, then it would be necessary to make a judicious choice of excitation and emission wavelengths and phosphoroscope speed. If a spectral separation of the phosphorescence of the required drug from the interferences were not possible, a physical separation of the interferences would be needed.

The method presented here should be of value for medical and biological research. The phosphorimetric measurement requires fewer steps and chemical reagents, which often result in appreciable contamination and loss in sensitivity and selectivity, than most other instrumental methods. In phosphorimetry, the species required and not a reaction product of that species is measured. Finally, the general background phosphorescence is extremely low, which results in high sensitivity and selectivity of analysis. It would seem that the extraction technique combined with phosphorimetric measurement would be useful for pharmacological studies, especially those involving the rate of disappearance of a drug or the rate of appearance of a certain metabolite in a given biological fluid or material.

This research was carried out as part of a study on the phosphorimetric analysis of drugs in blood and urine, supported by a grant from the U.S. Public Health Service (GM 11373-01). The authors would also like to thank Professor P. A. FOOTE, Dean of the College of Pharmacy, for the donation of small amounts of several of the drugs used.

SUMMARY

A new sensitive and rapid method is proposed for the determination of procaine, cocaine, phenobarbital and chlorpromazine in blood serum, and cocaine and atropine in urine. The drug is extracted from the biological fluid using chloroform or ether, the solvent is evaporated and the resulting residue is dissolved in EPA; the EPA solution is measured phosphorimetrically. Recoveries of 100 ± 6% and relative standard deviations of 2–5% are obtained for most drugs.

RÉSUMÉ

On propose une nouvelle méthode sensible et rapide pour le dosage de procaïne, de cocaïne, de phénobarbital et de chloropromazine dans le sérum sanguin, ainsi que pour le dosage de la cocaïne et de l'atropine dans l'urine. On procède par extraction de la drogue dans un solvant organique et dosage par phosphorimétrie.

ZUSAMMENFASSUNG

Es wird eine neue empfindliche und schnelle Methode zur Bestimmung von Procain, Cocain, Phenobarbital und Chlorpromazin in Blutserum und Cocain und Atropin in Urin vorgeschlagen. Die Stoffe werden aus der biologischen Flüssigkeit mit Chloroform oder Äther extrahiert, das Lösungsmittel wird verdampft, der Rückstand in EPA gelöst und die EPA-Lösung phosphorimetrisch gemessen. Es wurden 100 ± 6% wiedergefunden; die relative Standardabweichung betrug 2–5%.

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POLAROGRAPHY OF INTERMEDIATES IN THE FIXATION OF NITROGEN BY *p*-QUINONE–AQUEOUS AMMONIA SYSTEMS*

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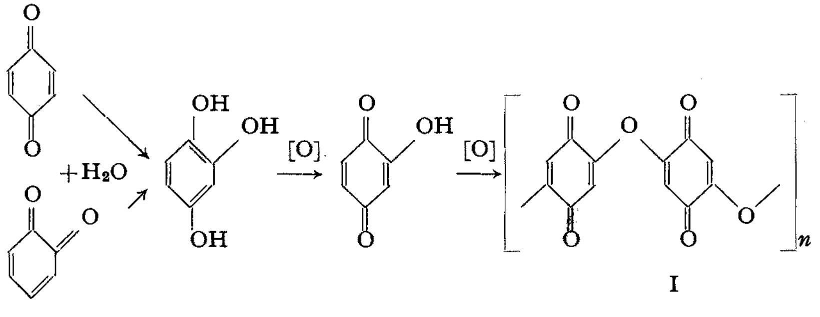
Soil organic materials are responsible for considerable chemical fixation of nitrogen during both the natural formation of humus and the retention of applied aqueous and anhydrous ammonia. The fixation mechanism is not understood in either case, being complicated by the diverse composition of humus material. The rapidly increasing practice of direct application of ammonia as a fertilizer requires better definition of the nitrogen-containing compounds formed during the relatively drastic conditions arising from the concentrated ammonia atmosphere. Recent reports have shown that significant quantities of polyphenolic units are present in soil humic materials[1]. This supports the generally accepted belief that quinones, formed by oxidation of polyphenols, are prominent reactants in the nitrogen fixation process.

Because of the complexity of natural soil organic materials, several studies have employed "model" compounds and synthetic "humic-like materials" in efforts to clarify the reaction involved. FLAIG[2] oxidized catechol and hydroquinone in the presence of ammonia and proposed the following mechanism for the formation of the polymerization product. He reported a nitrogen content of 12.29% for the product formed at pH 10.



I

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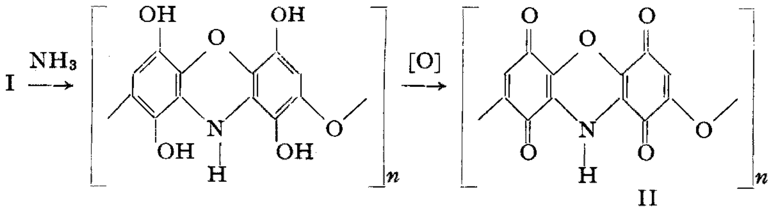
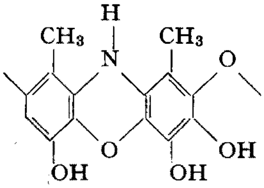


II

Murphy and Moore[3] oxidized 4-methylcatechol in the presence of ammonia and obtained a product containing a low nitrogen content of 2.9%. On the basis of methylation, hydrogenation, chlorination, and periodate oxidation they proposed the following partial structure.



Erdtman[4] disagreed with Flaig's proposed mechanism and concluded that the formation of the polymerization product from *p*-quinone in weak alkali solution by way of the hydroxyquinone intermediate is improbable.

Although the quinone–ammonia systems have received some attention, there appears to be little agreement as to the mechanisms of reaction and the structures of the resulting products. The objective of this investigation was, by the use of polarographic techniques, to establish the intermediates involved in the formation of the nitrogen-containing polymerization products and thereby to provide a better understanding of the mechanism of fixation and allow some speculation as to the structure of the final product.

EXPERIMENTAL

Materials

Buffers were prepared as described by Britton and Robinson[5]. The phosphate buffers were prepared from 0.1 *M* Na_2HPO_4 by addition of 0.1 *M* NaH_2PO_4 to give the desired pH. The ammonia–ammonium chloride buffers were prepared by addition of 6 *N* ammonia to 0.5 *M* ammonium chloride to give the desired pH. All buffers were deaerated with purified nitrogen before addition of *p*-quinone. For the ammonia buffers it was first necessary to pass the nitrogen through a buffer solution with the same ammonia concentration in order to prevent change in pH.

The *p*-quinone was Eastman Kodak white label grade. All other reagents were of analytical reagent grade.

Apparatus

Polarograms were recorded with a Sargent Model XXI polarograph. All potentials were measured against a saturated calomel electrode (S.C.E.). Typical capillary characteristics at −0.50 V in 0.5 *N* NH_4Cl with 55 cm mercury were: $m = 1.96$ mg/sec, and $t = 4.05$ sec. All measurements were made at 25°. pH measurements were made with a Beckman Zeromatic pH Meter.

Procedure

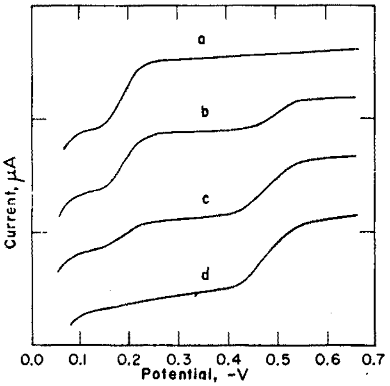
After polarographic analysis the bulk of the solution was aerated to oxidize the hydroquinone formed. After all the *p*-quinone had polymerized, which was determined polarographically, the product in the phosphate buffer was precipitated by acidifying the solution with hydrochloric acid. The ammonia solutions were allowed to stand for several days to permit the precipitate to form. All precipitates were washed by suspension and centrifugation until all traces of buffer ions were removed, and then dried at 105°.

RESULTS AND DISCUSSION

Reaction intermediates

When *p*-quinone is added to a phosphate buffer of pH 7.9, the yellow solution turns red. Polarographic analysis of the solution gives a comparatively small reduction wave with a half-wave potential of −0.29 V riding on the *p*-quinone wave. VINTERA[6] reported that this wave is given by the reduction of the red hydroxyquinonehydroquinone.

When *p*-quinone is added to an ammonia–ammonium chloride buffer of pH 8.3, to give m*M* *p*-quinone, the solution rapidly turns brown and two well-defined reduction waves are given with $E_{\frac{1}{2}}$ values of −0.25 and −0.55 V riding on the *p*-quinone wave, which has $E_{\frac{1}{2}} = -0.06$ V. Figures 1, 2 and 3 show the effect of ammonia concentration on the relative rate of formation of the two reduction waves. At lower



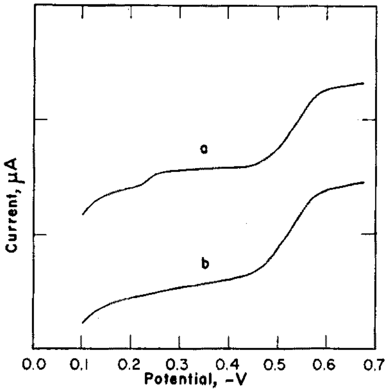


Fig. 1. Polarograms of the intermediates in the reaction of *p*-quinone and ammonia at pH 7.1, originally m*M* *p*-quinone in 0.002 *M* NH_3–0.5 *M* NH_4Cl: (a) 1 h, (b) 2 h, (c) 5 h, and (d) 8 h after addition of *p*-quinone. In Figs. 1–3, the intervals on the current ordinate represent 1 μA.

Fig. 2. Polarograms of the intermediates in the reaction of *p*-quinone and ammonia at pH 8.1, originally m*M* *p*-quinone in 0.02 *M* NH_3–0.5 *M* NH_4Cl: (a) 40 min, (b) 70 min after addition of *p*-quinone.

ammonia concentrations where only the first or both waves appear, the polarograms are riding on a preceding *p*-quinone wave (not shown) which subsides as the *p*-quinone concentration decreases. The final polarograms where only the second wave appears represent the time at which the *p*-quinone is completely reacted and the first wave disappears. The experimental results strongly suggest that the first wave is given by the reduction of the monosubstituted *p*-quinone (III), and the second wave is given by the reduction of the disubstituted *p*-quinone (IV).

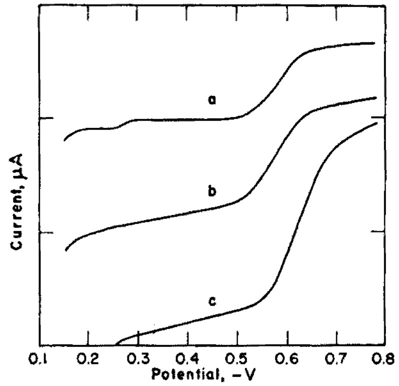
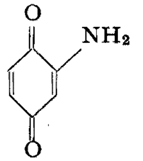
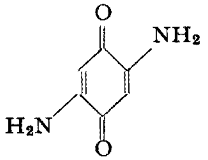


Fig. 3. Polarograms of the intermediates in the reaction of *p*-quinone and ammonia at pH 9.0, originally m*M* *p*-quinone in 0.1 *M* NH_3–0.5 *M* NH_4Cl (pH 9.9 and 0.6 *M* NH_3 for polarogram c): (a) 10 min, (b) 20 min, and (c) 10 min after addition of *p*-quinone.



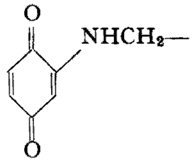
III

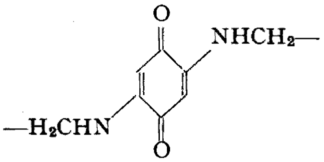


IV

The reaction giving III would be expected to proceed faster than the reaction giving IV, and this is shown in Fig. 1 where the ammonia concentration is low; IV increases at the expense of III until only IV remains. Where the ammonia concentration is high, the formation of IV is so rapid that III does not exist long enough to be detected (*e.g.*, wave c, Fig. 3). Regardless of the pH or ammonia concentration, the diffusion current of the second wave decreases over a period of several days, leaving a black precipitate.

Asserting that III and IV are reaction intermediates on the basis of experimental half-wave potentials is in close agreement with results found by other investigators. WIESNER[7] reported two polarographic reduction waves for the reaction products of *p*-quinone and various amino acids. In a phosphate buffer of pH 8.3 the $E_{\frac{1}{2}}$ values *vs.* S.C.E. are given as approximately −0.3 and −0.6 V. He reported that both waves are reversible and that the wave at −0.6 V slowly grows at the expense of the other. BERG AND KONIG[8] reported that in phosphate buffers the half-wave potential for the reduction of *p*-quinone is shifted 0.225 V more negative by monosubstitutions of the type V and 0.525 V by disubstitutions of the type VI.


V


VI

The $E_{\frac{1}{2}}$ values reported for the N-monosubstituted aminoquinones[7,8] are approximately 0.05 V more negative than the values for III and IV. This difference can be explained by the greater electron-repelling effect of N-monosubstitution. An example of this is illustrated by the effect of 2-substitution on the oxidation–reduction potentials of 1,4-naphthoquinone[9]. 2-Amino-substitution shifts the potential 0.210 V more negative, whereas 2-monomethylamine substitution shifts the potential 0.252 V more negative.

Figure 4 shows the pH dependency for both waves. The slopes are somewhat less than −0.059 V per pH unit. This may be caused by an imine equilibrium which will shift the reduction potentials more positive at the higher ammonia concentrations.

The reversibility of the second intermediate in the original ammonia buffer system is shown in Fig. 5. Controlled potential reduction at a large mercury cathode causes the brown color to disappear. Polarography of this solution reveals an oxidation wave with the same $E_{\frac{1}{2}}$ as the reduction wave. Upon air oxidation the reduction wave and color reappear.

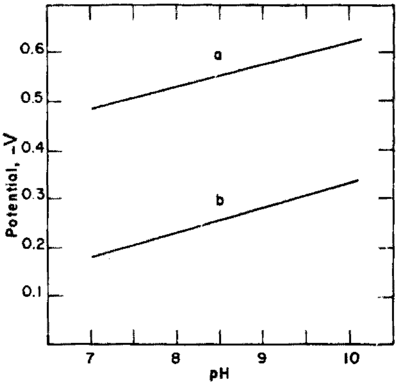


Fig. 4. pH dependency of the half-wave potentials for: (a) the second intermediate, (b) the first intermediate in the reaction of *p*-quinone and ammonia.

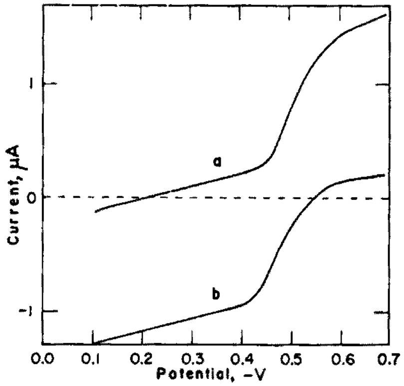


Fig. 5. Polarograms of the second intermediate in the reaction of *p*-quinone and ammonia at pH 8.1: (a) before controlled potential reduction and after air reoxidation, (b) after controlled potential reduction.

Polymerization products

The polymerization product formed by addition of *p*-quinone to 0.1 *N* sodium hydroxide or phosphate buffer of pH 9 is soluble but gives a brown precipitate when the solution is acidified with hydrochloric acid. Neither product gives a polarographic reduction wave when dissolved in Britton–Robinson buffers or 0.1 *N* sodium hydroxide.

The insoluble polymerization product formed in the ammonia–ammonium chloride buffer is a black powder when dry and does not melt below 300°. The product is soluble in Britton–Robinson buffers from pH 7 to 10 or in 0.1 *N* sodium hydroxide with diffusion currents that appear to be proportional to the product concentration. However, the diffusion currents in both media slowly decrease over a period of several weeks. No precipitation from the alkaline solutions was observed. Sixteen mg of the product dissolved in 16 ml of buffer pH 9.7 gave a $E_{\frac{1}{2}}$ value of -0.63 V with a diffusion current of 2.6 μA; 10.6 mg of the product dissolved in 25 ml of 0.1 *N* sodium hydroxide gave $E_{\frac{1}{2}} = -0.77$ V with a diffusion current of 1.1 μA. The pH dependency approximates -0.059 V per pH unit, although the wave does not show reversibility by controlled potential reduction. The wave may be given by small molecular weight condensation products such as VII, which could slowly undergo further polymerization in alkaline media. It is also possible that the wave is given by a substituted phenazine-type compound formed by side reactions. A reduction wave due to coprecipitated IV is unlikely because it would not exist in 0.1 *N* sodium hydroxide for any length of time.

Infrared absorption spectrophotometric analysis of both the non-nitrogen and nitrogen-containing polymerization products gives sharp bands at 3400 cm^{-1} and 1600 cm^{-1}, with the latter showing a band at 1500 cm^{-1}. However, the major part of both spectra is featureless, resembling absorption patterns of humic material from soils and coals.

Elemental analyses of the precipitates are shown in Table I. The low percentage of nitrogen in the precipitate prepared at pH 7.1 is probably due to competitive side-reactions which may predominate at low ammonia concentrations.

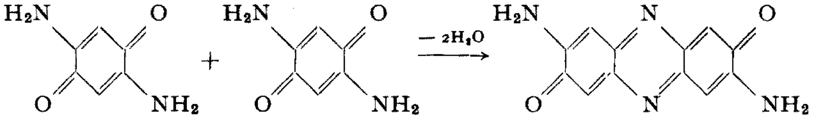
TABLE I

ELEMENTAL ANALYSES[a] OF THE POLYMERIZATION PRODUCTS PREPARED AT DIFFERENT AMMONIA CONCENTRATIONS AND pH VALUES

NH_3 (mole/l)	*pH*	*%C*	*%H*	*%O*	*%N*
0.002	7.1	59.09	3.73	34.88	2.30
0.02	8.1	58.42	2.78	29.46	9.34
0.1	9.0	58.72	3.30	29.20	8.78
0.6	9.9	—	—	—	11.37

[a] Analyses by Galbraith Laboratories, Knoxville, Tenn.

In view of the evidence that the polymerization product is formed from IV it is possible to propose a reaction giving VII which is capable of further polymerization. The hydrolyzable, terminal amino groups explain the ease of solubility in Britton–Robinson buffers.



VII

A polymer with a skeletal structure of VII contrasts with that of II which is commonly accepted but which remains to be corroborated. FLAIG reported that polymerization products of p-quinone previously formed in non-ammonia alkaline solutions will not later react in an ammonia solution to incorporate nitrogen. He concluded that the chemical fixation of nitrogen must take place during the polymerization. However, the formation of II from I does not show that ammonia must undergo fixation during polymerization. A better explanation of these observations follows from the formation of VII.

Conclusions

In view of the polarographic evidence for the existence of the mono- and disubstituted aminoquinones in p-quinone–aqueous ammonia systems, any mechanism proposed for the fixation of nitrogen under these conditions should take into consideration the amino intermediates. In solutions of high ammonia concentration, the major portion of the polymerization probably involves the 2,5-diaminoquinone rather than the previously postulated hydroxyquinone. The product formed is probably non-uniform and admixed with varying amounts of side-reaction products, depending on the ammonia concentration and pH.

The product or some major constituent of the product is reducible at the dropping mercury electrode and from electrochemical evidence is probably a highly conjugated nitrogen heterocyclic compound. Thus a reevaluation appears in order, with respect to accepted views about native soil humic materials having the same basic structure as products formed during the relatively drastic conditions accompanying a concentrated ammonia environment.

The study emphasizes the importance and the possibility of isolating and characterizing the compounds responsible for the fixation of nitrogen by quinones.

SUMMARY

Air oxidation of aqueous p-quinone, as a model humic acid precursor, develops precipitates of different character in the presence and absence of ammonia. Polarographic analyses of the p-quinone–ammonia systems at different ammonia concentrations, pH levels, and reaction times reveal two reducible intermediates in the reaction leading to fixation of nitrogen. The intermediates give half-wave potentials, at pH 8.3, of -0.25 and -0.55 V *vs.* S.C.E. The waves are interpreted as resulting from the reduction of mono- and disubstituted aminoquinones. A mechanism and structure are proposed for the nitrogen-containing polymerization product.

RÉSUMÉ

L'oxydation à l'air de la *p*-quinone, en solution aqueuse, donne divers précipités, en présence ou en l'absence d'ammoniaque. L'analyse polarographique révèle, pour le système *p*-quinone/ammoniaque, deux produits intermédiaires réductibles (à pH 8.3 : −0.25 et −0.55 V *vs.* ECS), dans la réaction conduisant à la fixation de l'azote. Ces deux vagues sont attribuées à la réduction d'aminoquinones mono- et disubstituées. Un mécanisme et une structure sont proposés pour le produit de polymérisation renfermant l'azote.

ZUSAMMENFASSUNG

Die Luftoxydation von wässrigem *p*-Chinon als Modell für Humussäure ergibt Niederschläge verschiedenen Charakters in Gegenwart und Abwesenheit von Ammoniak. Die polarographische Analyse des *p*-Chinon–Ammoniak-Systems bei verschiedenen Ammoniakkonzentrationen, pH-Werten und Reaktionszeiten zeigt zwei reduzierbare Zwischenprodukte bei der Reaktion, die zur Bindung von Stickstoff führt. Die Zwischenprodukte ergeben Halbstufenpotentiale beim pH-Wert 8.3 von −0.25 und −0.55 V. Die Stufen werden als das Ergebnis der Reduktion von mono- und disubstituierten Aminochinonen gedeutet. Ein Mechanismus und die Struktur für die Stickstoff enthaltenden Polymerisationsprodukte werden vorgeschlagen.

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THERMOGRAVIMETRIC INVESTIGATION OF THE COMPLEXES OF 6-CHLORO-2-METHOXY-9-THIOLACRIDINE

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(Received May 29th, 1964)

In 1940, DAS GUPTA[1] reported the synthesis of 6-chloro-2-methoxy-9-thiolacridine (termed "thiolacridine" in this paper). He also found that thiolacridine formed complexes with several transition metals[2]. Additional work on thiolacridine complexes has recently been reported by DAUGHERTY *et al.*[3]. In the present paper the compositions and stabilities of these complexes thermogravimetrically are reported. The complexes studied were the thioacridines of Cu(II), Hg(II), Ag(I), Au(III), Pt(IV) and Pd(II).

Previously DUVAL[4] reported thermolysis curves for the copper and mercury thioacridines. His thermolysis curves differed markedly from those we obtained for these compounds. DUVAL found that these complexes lost weight starting at room temperature while we found that they were stable up to the initial decomposition temperatures of somewhat above 200°. DUVAL used DAS GUPTA's method to synthesize thiolacridine and doubted the purity of the product which he was using as a precipitating agent. Reagent impurities occluded on the complexed precipitates could change the shape of the thermolysis curves. The thiolacridine used in the present investigation was synthesized by the method of KITANI[5] and was of excellent purity.

EXPERIMENTAL

Equipment

An ADAMEL recording thermobalance (Chevenard system) was used to obtain the thermolysis curves. The samples were heated in Coors porcelain crucibles, No. 00000.

Reagents

Thiolacridine was prepared[5] from 6,9-dichloro-2-methoxyacridine (Aldrich Chemical Co.). When thiolacridine was recrystallized from aqueous 2% sodium hydroxide solution, it appeared in the orange form. When it was recrystallized from 95% ethanol the red form was obtained.

Thiolacridine solution was prepared by dissolving 0.10 g in 100 ml of 95% ethanol mixed with 3.5 ml of aqueous 0.1 *N* sodium hydroxide solution. This solution was filtered and used the same day as prepared.

Thioacridines. Two ml of a 0.1 *M* copper(II) acetate solution was diluted with

100 ml of distilled water and the copper(II) was precipitated with thiolacridine solution. The solution was adjusted to pH 3 with hydrochloric acid, stirred and allowed to stand overnight. The precipitate was collected in a fritted glass filtering crucible and washed 3 times with 95% ethanol. The copper(II)–dithioacridine was then dried in a vacuum desiccator.

Other metal thioacridines were prepared in a similar manner: mercury(II) dithioacridine from 0.1 *M* mercury(II) acetate, silver(I) thioacridine from a 0.1 *M* silver nitrate solution, gold(III) trithioacridine from a 0.1 *M* gold(III) chloride ($AuCl_3 \cdot HCl \cdot 3H_2O$) solution, platinum(IV) trithioacridine chloride from a 0.1 *M* chloroplatinic acid solution, and palladium(II) dithioacridine from a 0.1 *M* palladium(II) chloride solution.

Analysis of the metal thioacridines

Metal ashing of the thioacridine complexes was done by heating in the thermobalance at about 950° until decomposition was complete. The platinum thioacridine chloride was analyzed for its chlorine content by the Pregl catalytic combustion method. The results of the determinations are listed in Table I.

TABLE I

ANALYSIS OF METAL THIOACRIDINES

Compound	*% Metal found*	*% Metal calculated*	*% Deviation*
Metal ashing			
$Cu(C_{14}H_9ONSCl)_2 \cdot 4H_2O$	22.8[a]	23.2[a]	−1.7
$Pd(C_{14}H_9ONSCl)_2$	16.0	16.2	−1.2
$Ag(C_{14}H_9ONSCl)$	28.6	28.2	+1.4
$Au(C_{14}H_9ONSCl)_3$	19.4	19.4	0.0
$Pt(C_{14}H_9ONSCl)_3Cl$	18.4	18.5	−0.5
Chloride			
$Pt(C_{14}H_9ONSCl)_3Cl$	13.47	13.44	+0.2

[a] % Cu_2S.

Thermolysis curves

The thermolysis curves were obtained by heating the compounds in No. 00000 porcelain crucibles at a rate of 300° per hour. All samples were run in nitrogen (dried by passing through solid calcium sulfate) flowing at a rate of 3 l/h. The weights of the samples are recorded on the Figs.

The thermolysis curves for the orange and red forms of thiolacridine (Fig. 1) were quite similar except that the orange form lost one mole of water between 70° and 135°. Both forms started to decompose fairly rapidly at 245°. From 360° the decomposition was slow and some residue remained even at 1050° which is the upper temperature limit of the thermobalance.

Copper(II) thioacridine tetrahydrate (Fig. 2A) was stable to 318°. At 318° the compound decomposed rapidly to 380° and then slowly to 1000° without reaching a stable plateau.

Mercury(II) thioacridine (Fig. 2B) was found to be stable to 220°. From 220° to 340° the decomposition proceeded rapidly and from 340° to 1000° the decomposition was slow with no stable regions.

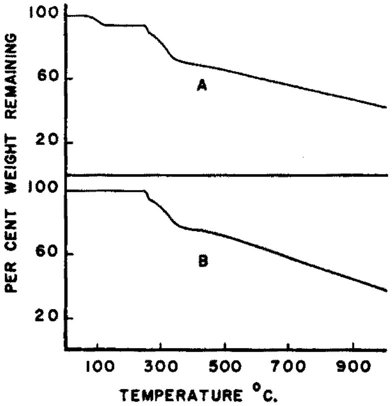
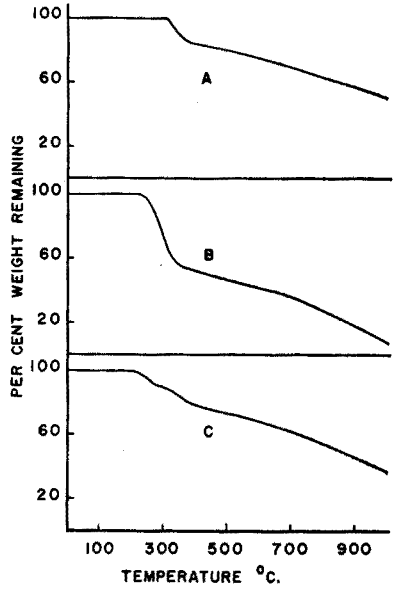


Fig. 1. Thermolysis curves of thiolacridine. (A) thiolacridine (orange form), 20.1 mg; (B) thiolacridine (red form), 25.5 mg.



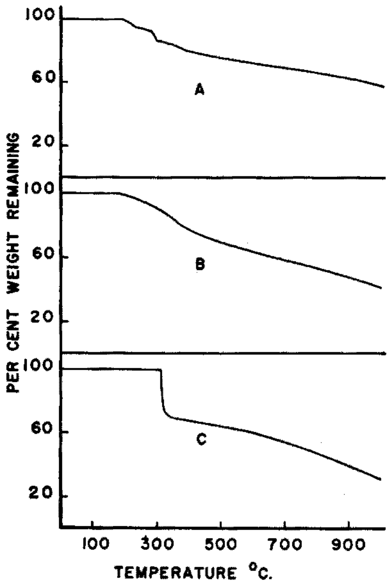


Fig. 2. Thermolysis curves of copper, mercury and silver thioacridine. (A) copper(II) thioacridine 23.0 mg; (B) mercury(II) thioacridine, 19.5 mg; (C) silver(I) thioacridine 23.1 mg.

Fig. 3. Thermolysis curves of gold, platinum and palladium thioacridine. (A) gold(III) thioacridine, 25.1 mg; (B) platinum(IV) thioacridine chloride, 27.1 mg; (C) palladium(II) thioacridine, 31.6 mg.

Silver(I) thioacridine (Fig. 2C) was stable to 208°. No stable regions were found after the initial decomposition occurred.

Gold(III) thioacridine (Fig. 3A) was stable to 190°. From 190° to 380° the decomposition rate was variable but fairly fast. From 380° the decomposition proceeded slowly to 1000°.

Platinum(IV) thioacridine chloride (Fig. 3B) slowly started to decompose at 170°, then more rapidly to 380°. From 380° the decomposition was slow with no stable regions to 1000°.

Palladium(II) thioacridine (Fig. 3C) was stable to 315°. There was a very rapid decomposition at 315° followed by a slow gradual decomposition to 1000°. When the thermolysis was run at 80° per hour, the rapid decomposition occurred at the same temperature as before and was identical.

DISCUSSION OF RESULTS

From the metal ashing, chloride analysis and thermolysis curves, the compositions of the compounds were determined. The orange form of thiolacridine contains one mole of water while the red form is anhydrous. Copper forms a complex with 2 thiolacridine molecules and contains 4 moles of water. The anhydrous mercury complex contains a 1:2 ratio of mercury to thiolacridine and silver forms a 1:1 anhydrous complex. The anhydrous gold complex contains a 1:3 ratio of gold to thiolacridine. Platinum forms an anhydrous complex containing platinum, chloride and thiolacridine in the ratio 1:1:3. The palladium complex contains a 1:2 ratio of palladium to thiolacridine.

SUMMARY

The thermolysis curves of thiolacridine and of thioacridine complexes with Cu(II), Hg(II), Ag(I), Au(III), Pt(IV) and Pd(II) are described. The orange form of thiolacridine is the monohydrate and the red form is anhydrous. The complexes are quite thermally stable, with the platinum thioacridine chloride being the least stable.

RÉSUMÉ

Les auteurs décrivent les courbes de thermolyse de complexes de la thiolacridine et de la thioacridine avec Cu(II), Hg(II), Ag(I), Au(III), Pt(IV) et Pd(II). La forme orange de la thiolacridine correspond au monohydrate; la forme rouge est anhydre. Ces complexes sont thermiquement stables.

ZUSAMMENFASSUNG

Es wurden die Thermolysekurven von Thiolacridin und der Thioacridinkomplexe met Cu(II), Hg(II), Ag(I), Au(III), Pt(IV) und Pd(II) beschrieben. Das Monohydrat des Thiolacridins ist orange, das wasserfreie rot gefärbt. Die Komplexe sind thermisch völlig stabil.

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Anal. Chim. Acta, 32 (1965) 81–85

SHORT COMMUNICATIONS

Cäsium-137 im Regenwasser

Zur Isolierung von Cäsium-137 aus flüssigen, radioaktiven Niederschlägen wurde eine Methode ausgearbeitet[1], die in der Konzentrierung des Cäsiums durch Kopräzipitation mit Berlinerblau und seiner Auflösung in einer gesättigten EDTA-Lösung mit dem pH-Wert 10 und in der darauffolgenden Extraktion des Cäsiums als Dipikrylaminat mit Nitrobenzol beruht. Mit der vorgeschlagenen Methode können auf einmal Wassermengen in der Grössenordnung von ein Liter verarbeitet werden. Bei ihrer Einführung in die Praxis zeigte sich aber, dass mit Rücksicht auf die Empfindlichkeit der Messgeräte bedeutend grössere Mengen flüssiger, radioaktiver Niederschläge verarbeitet werden müssen. Die Konzentrierung des Cäsiums durch Kopräzipitation mit Berlinerblau erwies sich in diesem Falle als sehr unvorteilhaft, denn es muss eine ganze Reihe von Ausfällungen vorgenommen werden, bevor die ganze Wassermenge verarbeitet ist.

Daher wurde für die Konzentrierung des Cäsiums aus beliebig grossen Mengen flüssiger, radioaktiver Niederschläge die Methode der Sorption der Radionuklide an Ionenaustauschern gewählt. Hierzu war es notwendig, die Optimalbedingungen für die Sorption des Cäsiums am Kationenaustauscher und für seine Elution festzustellen, eine geeignete Kontinuierlichkeit dieser Methode mit dem früher ausgearbeiteten Verfahren zu finden und die Angaben über gewisse Arbeitsstufen durch weitere notwendige Werte zu ergänzen.

Versuchsteil

Sämtliche, bei dieser Arbeit verwendeten Chemikalien hatten eine für Analysen notwendige Reinheit.

Verwendet wurde ein stark saurer Kationeneaustauscher tschechoslowakischer Produktion, Katex S, mit einer handelsüblichen Körnung 0.3–1.2 mm, im Wasserstoffzyklus. Für Cäsium war die ermittelte Kapazität des Kationenaustauschers 2.9 mval/g bei 58% relativer Feuchtigkeit. Der Wassergehalt in einem Gramm des Kationenaustauschers Katex S ist bei dieser Feuchtigkeit 0.361 ± 0.002 g.

Die Verfolgung der Cäsiumsorption und seiner Elution aus dem Kationenaustauscher wurde sowohl für unwägbare als auch wägbare Cäsiummengen vorgenommen, wobei übereinstimmende Ergebnisse gewonnen wurden.

Das Studium der Sorptionskinetik unter statischen Bedingungen führten wir so durch, dass wir zu der Cäsiumsalz enthaltenden Lösung unter intensivem Rühren mit einem Glaspropeller 1 Gramm des Katex S, der bei 58% relativer Feuchtigkeit aufbewahrt wurde, zugaben und nach bestimmten Zeitintervallen Proben der flüssigen Phase abnahmen.

Die Kollonenoperationen führten wir mit einer Ionenaustauschersäule mit einem Durchmesser von 1 cm und einer Länge von 12 cm durch. Das Harzbett enthielt hierbei 5.5 g lufttrockenen Katex S. Die Durchflussgeschwindigkeit bei der Sorption der Cäsiumionen betrug 10 ml/Stunde und bei der Elution 1 ml/Minute.

Alle weitere Operationen, einschliesslich der Vorbereitung der Proben, erfolgten wie in unserer früheren Arbeit[1]. Die Aktivität der zubereiteten Proben wurde mit einem Geiger-Müller'schen Fensterzählrohr gemessen. Bei den Berechnungen wurden sämtliche notwendigen Korrekturen berücksichtigt.

Ergebnisse und Diskussion

Die Sorption der Cäsiumionen aus dem Wasser kann sowohl unter statischen Bedingungen, *d.h.* bei intensivem Rühren des Kationenaustauschers in der Lösung, als auch unter dynamischen Bedingungen erfolgen, wobei wir das Wasser mit einer sehr geringen Durchflussgeschwindigkeit durch die Kationenaustauschersäule fliessen lassen. Die Untersuchung des Sorptionseffekts zeigte, dass in beiden Fällen die Sorption unter geeigneten Versuchsbedingungen praktisch 100% ist und dass mit Hilfe von Ionenaustauschern die Radionuklide aus grossen Mengen radioaktiver Niederschläge konzentriert werden können.

Die Sorption in der Kollone ist bei der Verarbeitung grosser Mengen der Lösungen sehr langwierig, erlaubt aber eine Trennung der Radionuklide in Gruppen. Sie eignet sich besonders zur Verfolgung des Gehalts an Cäsium-137 in den durchschnittlichen monatlichen Proben der flüssigen Niederschläge während des Sommers. Im Winterhalbjahr, oder wenn es notwendig ist, den Konzentrationsvorgang zu beschleunigen, ist dagegen das erste Verfahren vorteilhafter. In diesem Falle ist die Kinetik der Sorption des Cäsiums am Kationenaustauscher sehr stark durch die Intensität des Rührens und das Volumen der Lösung beeinflusst (Fig. 1). Bei grossen Mengen kann

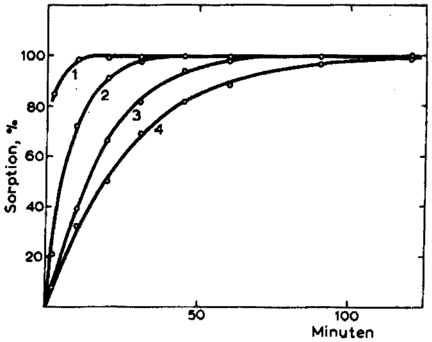

Fig. 1. Kinetik der Cäsiumsorption am Kationenaustauscher Katex S aus verschiedenen Wassermengen: 1, 150 ml; 2, 700 ml; 3, 1500 ml; 4, 3000 ml.

aber der Sorptionsverlauf beschleunigt werden, indem man die berechnete Kationenaustauschermenge in einige Dosen teilt, die dann nach und nach zugesetzt werden.

Zur Elution der sorbierten Radionuklide verwendeten wir Salzsäure. Wir stellten fest, dass eine Salzsäurekonzentration bis zu 6 *N* weder die Ausbeute der Cäsiumionenelution noch die Ausbeute der Kopräzipitation der Cäsiumionen durch das Berlinerblau beeinflusst. Sie wirkt aber auf den Verlauf der Elutionskurven und dadurch auch auf das Volumen der Lösung, die in der nächsten Phase verarbeitet werden muss (Fig. 2). Die Salzsäurekonzentration kann auch für die Trennung der Gruppen des aus den flüssigen, radioaktiven Niederschlägen gewonnenen Gemisches der Spaltprodukte verwendet werden. Wenn wir verdünnte Salzsäurelösungen (~ 1 *N*) verwenden, erscheinen in den ersten Fraktionen der Eluate die einwertigen Ionen der radioaktiven Isotope der alkalischen Metalle, während die mehrwertigen Ionen der anderen radioaktiven Isotope erst in den weiteren Fraktionen des Eluats zum Vorschein kommen. Bei Verwendung von Salzsäure mit einer Konzentration von 6 *N* tritt keine Trennung des Gemisches der Spaltprodukte ein.

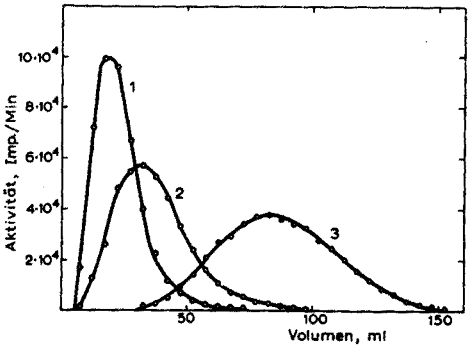

Fig. 2. Cäsiumelution mit Salzsäure: 1, 6 *N* HCl; 2, 3 *N* HCl; 3, 0.75 *N* HCl.

Unsere früheren Versuche[1] verweisen darauf, dass die Ausbeute der Kopräzipitation der Cäsiumionen mit Berlinerblau vom Volumen der Lösung, in dem wir die Fällung durchführten, abhängig ist. In der vorliegenden Arbeit war es notwendig, diesen Faktor zu untersuchen. Hierbei zeigte sich, dass die niedrigeren Ausbeuten der Kopräzipitation bei Verwendung einer grossen Menge durch die ungenügende Rührung der Lösung beim Ausfällen des Berlinerblaus verursacht werden kann. Unter optimalen Rührungsbedingungen durchgeführte Versuche führten nämlich zu Ausbeuten, die praktisch von dem Umfang der Ausgangslösung unabhängig waren, wenigstens bis zu 500 ml Lösungsmenge.

Die Salzsäurereste in dem durch Zentrifugieren getrennten Berlinerblau-Niederschlag sind die Ursache, dass seine Auflösung in der gesättigten EDTA-Lösung mit dem pH-Wert 10 nicht vollständig ist. Bei einer nachträglichen Änderung des pH mit Natriumhydroxyd oder bei der Verwendung einer EDTA-Lösung mit einem höheren pH wird Eisen(III)-hydroxyd ausgefällt, das bei der vorgeschlagenen Art der Isolierung die Ursache für ziemlich hohe Cäsiumverluste ist. Nach unseren Messungen können die Verluste bis 9% betragen. Der Niederschlag von Berlinerblau muss daher vor dem Auflösen im EDTA-Lösung durch Dekantierung mit destilliertem Wasser bis zu neutralen Reaktion der Lösung über dem Berlinerblau-Niederschlag gewaschen werden.

Durch die Verwendung eines stark sauren Kationenaustauschers können die Radionuklide aus einer beliebig grossen Menge des Regenwassers konzentriert werden. Aus der vorkonzentrierten Lösung wird das reine radioaktive Cäsium durch Koprsä zipitation mit Berlinerblau und durch Extraktion des Cäsiumdipikrylaminats mittel-Nitrobenzol aus der EDTA-Lösung gewonnen. Bei der Durchführung einer Serie von Analysen nach diesem Verfahren, wurde immer eine Cäsiumausbeute von mehr als 95% festgestellt.

Der Autor dankt Frau M. JÁCHIMOVÁ für die technische Hilfe.

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Anal. Chim. Acta, 32 (1965) 85–88

Analytical applications of the reaction of hexacyanoferrate(III) with ascorbic acid. Part VII. Determination of bismuth, zinc and manganese

Titrations with ascorbic acid solutions proceed quantitatively and possess distinct and highly accurate end-points. The numerous applications of such titrations have been recently reviewed[1]. Most recently, the titration of hexacyanoferrate(III) with ascorbic acid has been utilized for the indircet determination of silver[2]. Since hexacyanoferrate(III) and hexacyanoferrate(II) ions form precipitates with several other metals, the possibility of applying similar methods for the indirect determination of metals such as bismuth, zinc and manganese was examined.

Bismuth ions in nitric acid-containing medium formed a greyish-brown precipitate with hexacyanoferrate(III), which, contrary to the reddish-brown silver precipitate, was easily filtered without the addition of foreign electrolytes (*e.g.* ammonium nitrate). With zinc, however, the filtration of the light-brown hexacyanoferrate(III) precipitate on medium-pore filter paper was time-consuming, even when ammonium nitrate was present. In the case of manganese the dark brown hexacyanoferrate(III) precipitate was easily filtered either in the presence or absence of ammonium nitrate.

These determinations are based upon the exchange reactions which occur when sufficient hexacyanoferrate(II) solution is added to a given precipitate, or preferably to its solution in ammonium hydroxide. The exchange reactions with the bismuth, zinc and manganese precipitates may be represented as follows:

$$BiFe(CN)_6 + K_4Fe(CN)_6 \rightarrow KBiFe(CN)_6 + K_3Fe(CN)_6$$

$$Zn_3[Fe(CN)_6]_2 + 3\ K_4Fe(CN)_6 \rightarrow 3\ K_2ZnFe(CN)_6 + 2\ K_3Fe(CN)_6$$

$$Mn_3[Fe(CN)_6]_2 + 3\ K_4Fe(CN)_6 \rightarrow 3\ K_2MnFe(CN)_6 + 2\ K_3Fe(CN)_6$$

The hexacyanoferrate(III) ions thus released can be separated by simple filtration, and subsequently titrated with ascorbic acid, the amount of ascorbic acid being directly proportional to the amount of metal ion originally present in the sample solution.

Chemicals

0.05 M Bismuth nitrate solution. Dissolve 10.45 g of pure bismuth metal in hot 1:1 nitric acid solution and dilute to 1 l. Standardize against 0.05 *M* EDTA solution using pyrocatechol violet as indicator.

0.1 M Zinc nitrate solution. Prepare a stock solution (0.308 *M*) from the pure metal as described for bismuth, and standardize against 0.05 *M* EDTA solution using eriochrome black T (E.B.T.) indicator. From this solution prepare 0.1 *M* zinc solution by appropriate dilution.

0.2 M Manganese solution. Prepare a stock solution (0.50 *M*) from pure manganous carbonate and standardize against 0.05 *M* EDTA solution using E.B.I. indicator. Prepare a 0.2 *M* manganese solution by appropriate dilution.

0.1 N Ascorbid acid solution. Dissolve 8.9 g of ascorbid acid in glass-distilled water and dilute to 1 l. Standardize by titrating an aliquot of 0.1 *N* potassium hexacyanoferrate(III) containing 0.5 g of 2.6-dichlorophenolindophenol indicator mixture (1 part indicator to 500 parts of pure sodium chloride) and buffered with 1 g of potassium hydrogen carbonate to the disappearance of the blue color. Alternatively, standardize by titrating an aliquot of 0.1 *N* potassium hydrogen iodate containing 1–2 g of potassium iodide to the disappearance of the yellow color.

Procedures

Precipitation of metal hexacyanoferrate(III). The solution containing 104.5–522.5 mg Bi, 65.38–130.16 mg Zn or 109.88–438.52 mg Mn may contain some nitric acid. If required (Zn), add 1–2 g of ammonium nitrate and shake to dissolve. From a 100-ml buret add dropwise with constant stirring 10–30 ml of 5% potassium hexacyanoferrate(III) solution. Let the precipitate settle for 20–60 min. Pour the clear supernatant solution on a medium-pore filter paper containing a small bed of macerated filter paper, and wash the precipitate in the beaker 5 times with water (Bi and Mn) or with 1% ammonium nitrate solution (Zn), filtering by decantation each time. Finally transfer the precipitate to the filter paper and wash it once more.

Precipitation exchange reaction. Transfer the filter paper containing the precipitate to the original beaker. Add 20 ml of 2 *N* ammonium hydroxide and in the case of bismuth or zinc, break the filter paper up as much as possible with a glass rod. Direct a fine jet of a 5% potassium hexacyanoferrate(II) solution (10–20 ml) on to the precipitate until the exchange reaction is complete as indicated by the appearance of the yellowish white metal hexacyanoferrate(II) precipitate and disappearance of the last traces of the brown hexacyanoferrate(III) precipitate. Add 2 drops of phenolphthalein indicator and neutralize the solution cautiously with 1:1 nitric acid (for Bi and Zn but not for Mn). Add 1 g of potassium hydrogen carbonate, and after settling for 20–60 min, filter and wash the precipitate thoroughly, essentially as described for the first filtration.

Titration. In order to obtain reproducible and accurate results, transfer the filter paper containing the precipitate to the original beaker and break it up thoroughly with hot water (40 ml). Add 1 g of potassium hydrogen carbonate and 0.2 g of indicator mixture and keep aside.

TABLE I

Metal	*Number of parallel determinations*	*Metal taken (mg)*	*Metal found (mg) (Mean)*	*Difference*		*Standard deviation (mg)*	*Coefficient of variation (%)*
				(mg)	*(%)*		
Bi	6	104.50	104.30	−0.2	−0.2	±0.4	±0.4
	12	209.00	209.30	+0.6	+0.4	±1.0	±0.5
	6	313.50	314.70	+1.2	+0.4	±2.7	±0.9
Zn	6	32.69	32.89	+0.2	+0.8	±0.46	±1.4
	12	65.38	65.70	+0.32	+0.5	±0.46	±0.7
	6	98.07	98.46	+0.39	+0.4	±0.49	±0.5
	12	130.76	131.41	+0.65	+0.5	±0.78	±0.6
Mn	12	54.94	55.27	+0.33	+0.6	±0.44	±0.8
	6	109.88	110.43	+0.55	+0.5	±0.65	±0.6
	6	219.76	211.07	+1.31	+0.6	±1.10	±0.5

To the filtrate from the exchange reaction, add 1 g of potassium hydrogen carbonate and 0.5 g of indicator mixture. Titrate these two solutions separately with 0.1 *N* ascorbic acid to the disappearance of the blue color. Register the total consumption. 1 ml 0.1 *N* ascorbic acid is equivalent to 20.9 mg Bi, 98.01 mg Zn and 82.41 mg Mn as computed from the above reactions. Representative results of such determinations are summarized in Table I. The agreement between theoretical and experimental values is satisfactory.

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An anion-exchange method for the determination of rare earths, thorium and uranium in monazite

Applications of ion-exchange techniques for the separation of the three important constituents of monazite, *viz.* thorium, uranium and rare earths, are relatively few. The existence of complexes of thorium and uranium in chloride, nitrate or sulphate medium has been made use of for the anion-exchange separation of uranium[1] and thorium[2,3] from monazite. However, a clear-cut separation of the three individual constituents from one another in any of these media has not been reported. The sulphate medium appeared promising for effecting such a separation and was therefore investigated further.

Equilibrium studies

The distribution coefficients (K_d) of uranium and thorium on Dowex 2-X8 anion-exchange resin (sulphate form) in different concentrations of sulphuric acid were determined as described by KRAUS AND NELSON[4].

Uranium was found to be completely adsorbed on the resin at acidities below 10^{-2} M sulphuric acid (pH > 1.5). Thorium showed strong adsorption at acidities between 10^{-2} and 10^{-3} M sulphuric acid (pH 1.5 to 2.5). Figure 1 shows a plot of K_d values as a function of sulphuric acid concentration. It is seen that in 0.25 M sulphuric acid the adsorption of thorium is negligible, while that of uranium is still considerable. This was utilised to effect a separation between the two ions.

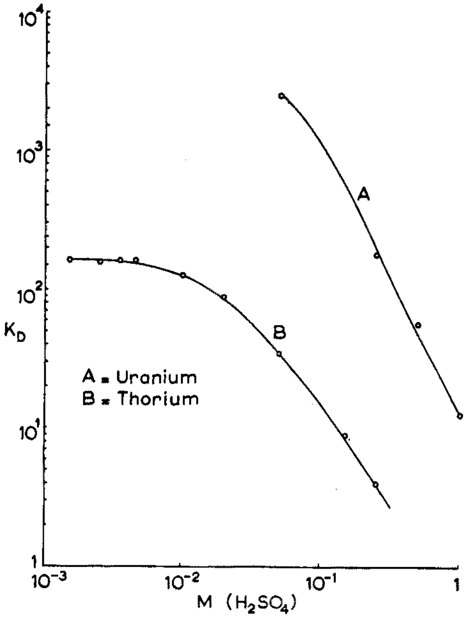

Fig. 1.

Column studies

The quantitative adsorption of uranium and thorium on Dowex 2-X8 resin (sulphate form) from sulphuric acid solutions of pH 2.5 was confirmed by dolumn studies. No break-through of either ion was detected even after the passage of a large volume of dilute sulphuric acid of pH 2.5 ± 0.1. The adsorbed thorium could be completely and preferentially eluted with 0.5 *N* sulphuric acid and uranium subsequently removed by 0.5 *N* nitric acid. Figure 2 shows the elution profile of these two ions.

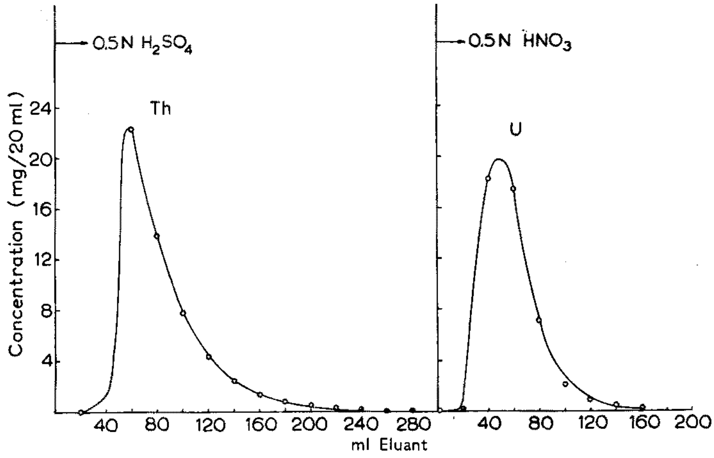

Fig. 2.

The following ions in sulphuric acid solution of pH 2.5 were found to pass out of the column quantitatively: Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}. Iron(III) was partly held on the column while Zr^{4+}, Ti^{4+} and Ce^{4+} hydrolysed and precipitated on the column under these conditions. Quantitative separations of thorium, uranium and cerium in synthetic mixtures were achieved.

Interference of phosphate

The phosphates of thorium and rare earths precipitate at low acidity such as that required for the anion-exchange adsorption of thorium. A prior separation of phosphate was therefore essential for the analysis of monazite.

Acid-treated alumina strongly adsorbs anions like fluoride, sulphate, phosphate, etc.[5,6]. It was observed that while the retention of phosphate was complete in nitric, perchloric and hydrochloric acid media of even very high concentrations, such was not the case with sulphuric acid medium probably because of the competition of sulphate ions for the adsorption sites on alumina. 2 *N* Nitric acid was found to be a convenient medium for effecting a separation of phosphate from the metal ions on an activated alumina column. Table I shows typical results for the recovery of cerium, thorium and uranium from synthetic mixtures containing phosphate.

TABLE I

SEPARATION ON ALUMINA COLUMN AND ION EXCHANGE

Phosphate added (mg)	*Cerium (CeO_2)*		*Thorium (ThO_2)*		*Uranium (U_3O_8)*	
	Added (mg)	*Recovered (mg)*	*Added (mg)*	*Recovered (mg)*	*Added (μg)*	*Recovered (μg)*
27.5	59.4	59.6	10.69	10.64	198	191
39.3	59.4	59.2	10.69	10.58	198	191
28.6	47.5	47.5	8.56	8.42	158	150
39.3	83.2	83.8	14.97	15.25	277	271

Procedure for analysis of monazite

Opening of mineral and removal of sulphate. Accurately weigh about 100 mg of the well-powdered mineral sample and dissolve by fuming with sulphuric acid and diluting with ice-cold water[7]. Remove sulphate by an ammonia precipitation and finally dissolve (along with the filter paper) in a mixture of 3.5 ml of concentrated nitric acid and 0.5 ml of concentrated hydrochloric acid. Warm the solution on a hot plate until the filter paper is converted to pulp. Dilute to about 25 ml.

Removal of phosphate. Pour a 12-ml slurry of alumina (Brockman treated chromatography grade) into a glass column 15 × 1.0 cm. Wash with water until the effluent is free from turbidity. Suck through the bed 10–20 ml of 2 N nitric acid.

Pass the sample solution (with the pulp) through the alumina column at a rate of 1–2 ml/min. Wash the column with 80 ml of 2 N nitric acid at the same rate. Collect the effluent and washings in a 250-ml beaker. Add about 2 ml of concentrated sulphuric acid and evaporate to a very low volume. Fume off most of the sulphuric acid over a sandbath. Dissolve the residue in 100 ml of water by boiling for a few minutes. Add a few drops of sulphurous acid to reduce any Ce^{4+} or Fe^{3+} present. Adjust the pH of the solution to 2.5 ± 0.1 with ammonia or sulphuric acid.

Ion-exchange separation. Pour a 40-ml slurry of Dowex 2-X8 resin (sulphate form) into a glass column 30 × 1.5 cm to give a bed length of about 20 cm. Wash with dilute sulphuric acid (pH 2.5) until the effluent shows a pH of 2.5.

Pass the sample solution through the column at a flow rate of 2–3 ml/min. Wash the bed with about 300 ml of the dilute sulphuric acid. In the combined effluent determine rare earths by precipitating them as oxalates[8a]. Pass about 300 ml of 0.5 N sulphuric acid at a rate of 1 ml per min and determine thorium colorimetrically[9]. Remove uranium from the column by passing about 300 ml of 0.5 N nitric acid at a rate of 2–3 ml/min and analyse this fraction for uranium colorimetrically[8b].

Results and discussion

Four monazite samples were analysed by this procedure. The results are given in Table II. The values obtained by the application of the present method compare favourably with those obtained by conventional methods[7,10]. The standard deviations (σ) calculated on the results of eleven analyses of sample No. 1 are as follows: for rare earths: 0.24; for thorium: 0.17; for uranium: 0.016.

TABLE II

COMPARISON OF MONAZITE ANALYSIS BY ION EXCHANGE AND CONVENTIONAL METHODS

Sample no.	*Rare earths (R_2O_3) (%)*		*Thorium (ThO_2) (%)*		*Uranium (U_3O_8) (%)*	
	Conventional	*Ion exchange*	*Conventional*	*Ion exchange*	*Conventional*	*Ion exchange*
1[a]	59.7	59.8	8.70	8.77	0.41	0.41
2[b]	59.6	60.3	8.43	8.46	0.41	0.43
3[b]	60.6	60.6	9.84	9.91	0.39	0.36
4[b]	60.3	60.5	9.55	9.50	0.37	0.38

[a] Mean of 11 results.
[b] Mean of 2 results.

The authors wish to thank Dr. V. T. ATHAVALE, Head of Analytical Division, AEET for his keen interest and helpful discussions.

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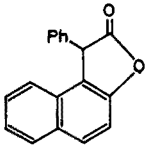
(Received April 12th, 1964)

Steam distillation for the isolation of milligram amounts of benzoic acid and benzophenone from degradative oxidations

The standard methods for the isolation of benzoic acid from the oxidation of aromatic side chains with chromic acid or permanganate are filtration of the benzoic acid from acidic solution or extraction of it with chloroform or ether. These methods give good yields of benzoic acid when only small amounts of the oxidizing agents are necessary. In cases which require ten or twenty moles of oxidizing agent per mole of benzoic acid produced (*e.g.* with compounds I[1] and II[2]) the isolation of small amounts of benzoic acid in good yield is more difficult.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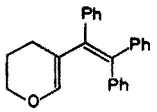
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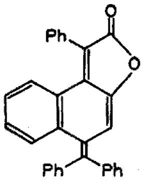
III*

Steam distillation has been used for the determination of milligram amounts of benzoic acid, obtained from the hydrolysis of N- or O-benzoyl compounds[3]. That benzoic acid is steam-distilled with acetic acid in C-methyl determinations on compounds containing phenyl groups when the oxidation time is short has also been reported[4]. In one case this benzoic acid was determined by ultraviolet analysis[5]. Steam distillation for the *isolation* of benzoic acid produced by chromic acid or permanganate oxidations does not appear to be mentioned in the literature.

Through the use of steam distillation, milligram quantities of benzoic acid can be isolated (in 70–80% yields from chromic acid and in 50–60% yields from permanganate oxidations) from reactions in which 10 or 20 moles of oxidizing agent are neces-

TABLE I

Compound	*Weight (mg)*	*Benzoic acid yield (mg)*	*Benzophenone yield (mg)*
Chromic acid oxidation			
Mandelic acid	200	120 (75%)	
I	200	65 (70%)	
II	100	29 (79%)	40 (74%)
III[a]	46	10 (77%)	11 (55%)
Permanganate oxidation			
Mandelic acid	200	80 (50%)	
II[b]	100	18 (49%)	15 (28%)

[a] The synthesis of this substance will be described later.
[b] The reflux was continued for 40 h.

---

[*] The synthesis of this substance will be described later.

sary per mole of benzoic acid produced. The results of several typical experiments are summarized in Table I.

A diphenylmethylene group in the compound oxidized gives benzophenone which is steam-distilled with the benzoic acid. These products are easily separated by extraction with bicarbonate. Benzophenone has been reported to decompose slightly during chromic acid oxidations[6]; however, no benzoic acid could be detected as a product of this decomposition. No benzoic acid was obtained from the chromic acid oxidation of compounds, such as naphthalene derivatives, which are oxidized via phthalic acid to carbon dioxide and water.

The only limitation to this method is the large amount of steam necessary to obtain a small amount of benzoic acid. Since the distillate contains only about 1 mg of benzoic acid per ml, the isolation of more than a few hundred milligrams is impractical.

Experimental

Chromic acid oxidation. The compound to be oxidized (50–500 mg) was added to a cooled solution of 2 g of sodium dichromate dihydrate in 6 ml of water and 4 ml of concentrated sulfuric acid. (If this was not twice the calculated amount of dichromate, more of the solution was used.) The mixture was heated gently until the reaction started and the flame was removed until the reaction subsided. Then the reaction mixture was refluxed for 15 min. Water (10 ml) was added and the mixture was steam-distilled until all the benzoic acid had been distilled. (About 1 mg of benzoic acid was distilled per ml of distillate.) Sodium bicarbonate (1 g) was added to the distillate and it was extracted twice with 15 ml of chloroform (or ether). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. The residue contained the benzophenone formed, m.p. 44–46°. The water layer from above was acidified with 4 ml of concentrated sulfuric acid and extracted twice with 15 ml of chloroform (or ether). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. The residue contained the benzoic acid formed, m.p. 118–120°.

Permanganate oxidation. The compound to be oxidized (50–500 mg) was added to a solution of 2 g of potassium permanganate and 0.5 g of sodium hydroxide in 25 ml of water. (If this was not twice the calculated amount of permanganate, more of the solution was used.) This mixture was refluxed for 3 h. Concentrated sulfuric acid (4 ml) was added dropwise with swirling and then saturated sodium bisulfite solution was added until a clear solution was obtained. This solution was steam-distilled and the distillate was processed as described above.

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(Received June 1st, 1964)

BOOK REVIEWS

J. PAUL CALI, *Trace Analysis of Semiconductor Materials*, Pergamon Press, Oxford–London–New York–Paris, 1964, ix + 282 pp., price 70 s.

The provision of materials on a commercial basis, in which impurities do not exceed the part per million level, and even ower levels, is becoming increasingly "fashionable", and in the semiconductor industry the restricted weight of sample often adds considerably to analysts' problems. Analysis is recognised as an important factor in the rapidly developing technology of semiconductors, and it is not surprising that the emphasis of this book is on physical methods of analysis. For example, recommended techniques involve neutron activation, emission spectroscopy and spark-source mass spectrometry. Three chapters, occupying about two-thirds of the book, deal with these subjects; thereafter the final chapter is devoted to *Absorption, Flurescence and Polarographic Methods*.

In all sections of the book a useful background is given to the basic principles involved. This is a useful approach to anyone analysing semiconductor materials, or materials of a similar nature, for the first time. A criticism, however, is the somewhat lengthy discourse under *Absorption Spectrophotometry* and, to a lesser extent, under *Emission Spectroscopy*, where it would have been reasonable to assume a basic knowledge of some of the underlying principles associated with the types of instrument used, in view of their extensive application in most analytical laboratories.

The analysis of semiconductor materials covers a very wide, highly specialised field, hence the main object of the book is to advise rather than instruct the analyst how to set about his task. For this reason the book is sensibly devoid of detailed operational instructions but contains a wealth of practical information, adequately condensed in appropriate chapters. The book, which comprises contributions by specialists, is well-presented. Anyone faced with the problem of analysing semiconductors or inorganic materials generally where the emphasis is on the determination of impurities at very low levels, will find it by present-day monetary standards, a good investment.

W. T. ELWELL (Birmingham)

Anal. Chim. Acta, 32 (1965) 97

ROSS W. MOSHIER, *Analytical Chemistry of Niobium and Tantalum*, International Series of Monographs on Analytical Chemistry, Vol. 16, Pergamon Press, Oxford, 1964, v + 278 pp., price 90 s.

Concurrently with new and important technological applications of niobium and tantalum in recent years, considerable progress has been made in the analytical chemistry of these closely related metals. This publication fills an outstanding need in analytical chemistry because it presents under a single cover, up-to-date information on this important topic.

A brief historical account of the two metals, with details of processes used for recovering them from their ores is followed by chapters on the chemical and physical properties of the metals and their compounds; chapter IV deals exclusively with compounds of analytical interest. In Chapter V, identification tests are given. In the following twelve chapters every aspect of analytical chemistry relevant to the determination of the two metals appears to have been covered; these include recommended procedures based on solvent extraction, ion-exchange chromatography, polarography, X-ray fluorescence and neutron activation. Chapter XVIII deals with the determination of impurities associated with niobium and tantalum; most methods are adequately discussed, although some warrant considerable expansion, particularly the vacuum-fusion procedure for the determination of oxygen.

The book is well written and suitably edited, and the author is to be congratulated for presenting the information logically and in such a stimulating manner.

D. F. Wood (Birmingham)

Anal. Chim. Acta, 32 (1965) 97–98

B. Breyer and H. H. Bauer, *Alternating Current Polarography and Tensammetry*, Wiley–Interscience, New York, 1963, xix + 287 pp., price 90 s.

This book is Volume 13 of the series of monographs published by Wiley–Interscience under the general title "Chemical Analysis". It surveys the field of analytical and electrochemical studies in which alternating current (sine-wave or square-wave) is applied to a dropping mercury electrode in a suitable electrolyte solution, covering the literature up to and including 1960. Of the work that has been done in this field, about half has had an analytical aim, whereas the rest has been concerned primarily with the kinetics and mechanism of the electrode processes. In consequence this book is also something of a hybrid and contains a good deal that some analytical chemists may regard as difficult or superfluous. Actually, if A.C. polarographic methods are to be used analytically, the user must understand something of the relevant electrochemical and diffusion theory. Such a background is presented, in a reasonable compromise between simplicity and theoretical rigour, in Chapter 2 (67 pp.). An understanding of this theoretical background is more necessary for the avoidance of error than it is in ordinary polarography. In particular, for example, the alternating current due to a given concentration of a depolariser is often far more sensitive to minor changes in the composition of the base electrolyte than is the ordinary polarographic diffusion current; only a proper understanding of why and when anomalous variations in the alternating current are likely will guard the analyst against misinterpretations.

In addition to the chapter on theory, there is one on Instrumentation (30 pp.) and the largest chapter (120 pp.) is on Analytical Applications. Much of the latter is at present rather tentative but should serve as a basis for development. A final chapter on the elucidation of electrode processes does not contain much of value.

As a whole, the book should serve well its intended purpose of introducing A.C. polarography to analytical chemists with some electrochemical knowledge.

J. E. B. Randles (Birmingham)

Anal. Chim. Acta, 32 (1965) 98

H. LUX, *Praktikum der quantitativen anorganischen Analyse*, 4. Auflage, Verlag J. F. Bergmann, München, 1963, viii + 204 S., Geheftet DM 15.80.

Diese nunmehr in der vierten verbesserten Auflage vorliegende Buch is eine Anleitung für das Praktikum der quantitativen anorganischen Analyse; es werden die wichtigsten Arbeitsmethoden der Makroanalyse beschrieben und mit gut ausgewählten Beispielen erläutert.

Nach der Beschreibung der Geräte und Grundoperationen des analytischen Laboratoriums folgt eine Reihe von Beispielen zur gravimetrischen Analyse, wobei allerdings nur zwei organische Fällungsreagenzien berücksichtigt werden (8-Oxychinolin und Tetraphenylborat). Der Abschnitt „Massenanalyse" bringt Beispiele aus den wichtigsten Gruppen der Volumetrie: Neutralisationsverfahren, Fällungs- und Komplexbildungstitrationen (einschliesslich eines Beispieles einer Titration mit EDTA), Oxidations- und Reduktionsverfahren. Die theoretischen Einleitungen zu den einzelnen Abschnitten sind übersichtlich und sehr klar verständlich dargestellt. Im Kapitel „Trennungen" werden einige der wichtigsten Trennmethoden der quantitativen Analyse (Fällung, Komplexierung, Ionenaustausch, Destillation, Fest–Flüssig-Extraktion) durch eine Anzahl von praktischen Beispielen erläutert. Die heute so wichtige Flüssig–Flüssig-Extraktion wird nur äusserst kurz erwähnt, was wohl auf den begrenzten Umfang des Buches zurückzuführen ist. In dem der Kolorimetrie gewidmeten Abschnitt wird das Beer'sche Gesetz in äusserster Kürze abgehandelt und die Methode selbst an einigen wenigen üblichen Beispielen erläutert. Im letzten Kapitel werden Vorschriften zu vollständigen Analysen von Mineralien und technischen Produkten gegeben.

Das Buch kann als Anleitung zum analytischen Grundpraktikum empfohlen werden; es wird sicherlich wiederum, wie seit längerer Zeit seine Vorgänger (ist es doch die achte Auflage seit seiner Begrünung durch ALFRED STOCK) nützlich sein.

H. WEISZ (Freiburg i. Br.)

Anal. Chim. Acta, 32 (1965) 99

Advances in Mass Spectrometry, Vol. 2, Edited by R. M. ELLIOTT, Pergamon Press, Oxford–London–New York–Paris, 1963, xvii + 628 pp., price 140 s.

This volume records the proceedings of the triennial international conference on mass spectrometry which was held at Oxford in September 1961, under the joint auspices of both British and American organisations. Forty-four original papers are contributed and each is followed by an edited version of the ensuing discussion. The scope of the material presented by leading workers from 8 countries is extremely diverse, ranging from nuclear physics to the mass spectra of large organic compounds, and although the book is a valuable and interesting one to have in the reference library it cannot, at the price, be genuinely recommended for the personal collection of even a specialist in mass analysis, let alone a research student.

Broadly speaking, the contents may be classified under 5 sub-titles, namely, mass spectrometry in research, mass spectrometry of inorganic compounds, new instruments and techniques, mass spectrometry of organic compounds, and ionization and dissociation processes. The miscellaneous group of special applications of mass analysis in research includes studies on field ionization, ion-sputtering of surfaces, free radical reactions, ions in flames, nuclear reaction cross-sections and adsorption of oxygen on tungsten. In the inorganic section there is some emphasis on vapour pressure studies at elevated temperatures, a field of growing importance, whilst the papers on new instruments are essentially for the specialist interested in high resolution analysis. The section on organic compounds is by far the largest (14 papers). The first part contains a review of the current statistical theory of mass spectra together with studies on the initial energy of fragment ions and the effects of temperature on mass spectra. The second part is essentially on the determination, and correlation with structure, of the mass spectra of large molecules such as waxes and oils, alkaloids, steroids, carbohydrates and borazoles. Finally, there is the usual fundamental section on the ionization and dissociation of molecules by electron or ionic impact.

A comprehensive index ot all the papers published in the volume is a most welcome feature. Further, there is a valuable classified bibliography, with a name index, covering all aspects of mass spectrometry during the period 1958–60. This supplements a previously published bibliography for the years 1938–57 inclusive.

D. W. THOMAS (Birmingham)

Anal. Chim. Acta, 32 (1965) 99–100

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Handbuch der Spurenanalyse

Die Anreicherung und Bestimmung von Spurenelementen unter Anwendung extraktiver, photometrischer, spektrochemischer, mikrobiologischer und anderer Verfahren

Von **Othmar G. Koch**
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Neunkirchen/Saar

und **Gertrud A. Koch-Dedic**
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XVI, 1232 Seiten Gr.-8°. 1964
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Die Entwicklung der letzten Jahre hat gezeigt, daß Spurenelemente, d. h. Elemente in Gehalten von 0,01% abwärts, auf vielen Gebieten der Lebensvorgänge und der Technik eine wichtige Rolle spielen. Ihre Berücksichtigung auf Grund der bisherigen Erkenntnisse sowie die Erforschung ihrer erst teilweise bekannten Wirkungsmechanismen erfordern eine genaue Erfassung der im einzelnen vorhandenen Menge. Zu deren quantitativer Bestimmung ist die Anwendung einer besonderen Arbeitstechnik notwendig. Das Buch gibt unter Berücksichtigung von über 3800 aus der weit verzweigten Literatur zusammengestellten Zitaten eine umfassende Darstellung der als Spurenanalyse bezeichneten Arbeitsweise, die es ermöglichen soll, an Hand der angeführten Vorschriften ohne langwierige Literatursuche Spurenelemente in den verschiedensten Materialien quantitativ zu bestimmen. Darüber hinaus will es Anregungen bei der Ausarbeitung neuer Verfahren vermitteln. Ganz besonders wird dabei auf die Arbeitstechnik eingegangen, da ihre richtige Durchführung für den Erfolg von Spurenanalysen ausschlaggebend ist. Unter den Trennverfahren wird die Extraktion mit organischen Lösungsmitteln eingehend besprochen. Durch die ausführliche Behandlung der wichtigsten photometrischen Reagentien ist es außer zur Bestimmung von Spurenelementen auch auf dem Gebiet der photometrischen Analyse allgemein anwendbar.

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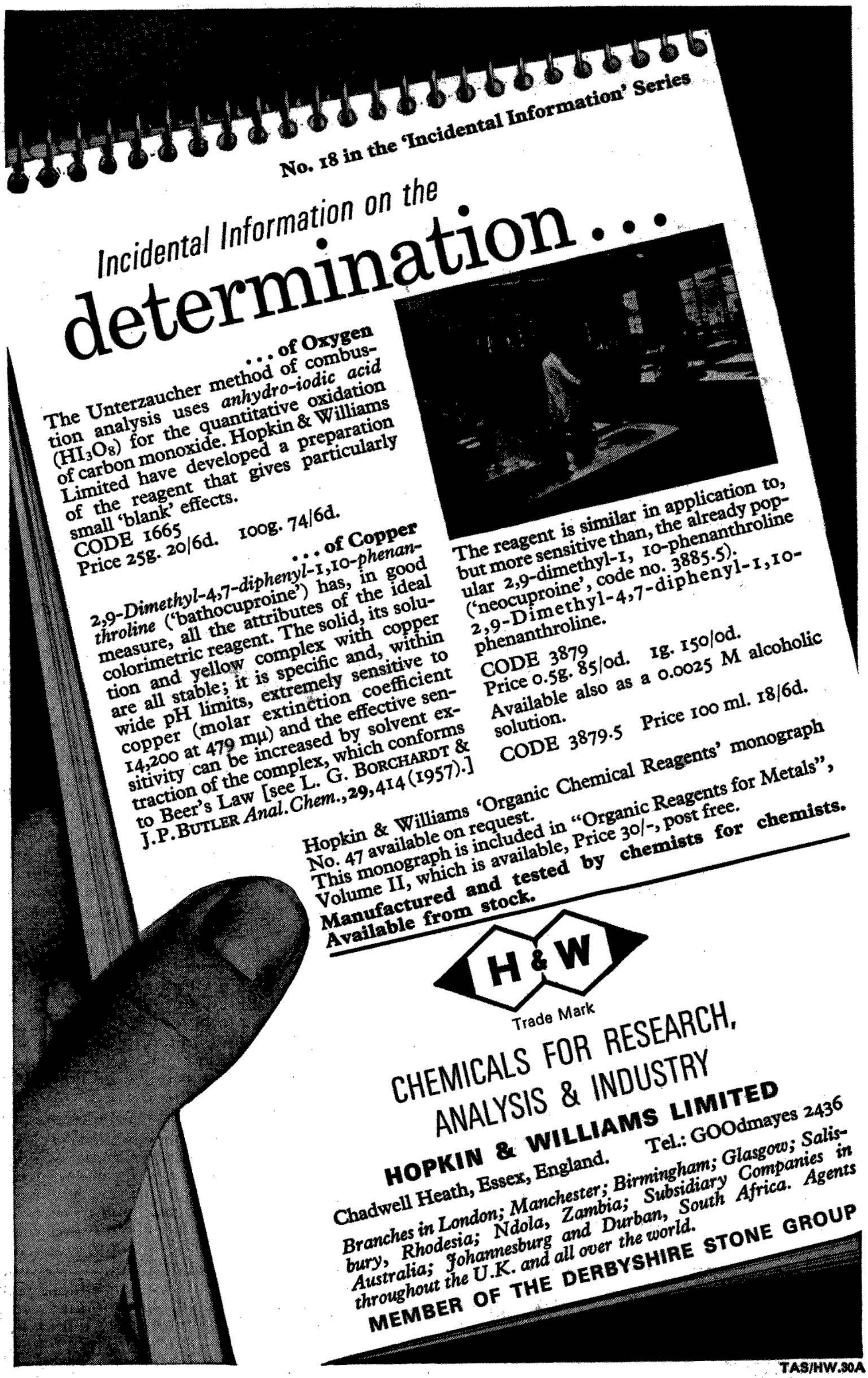

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