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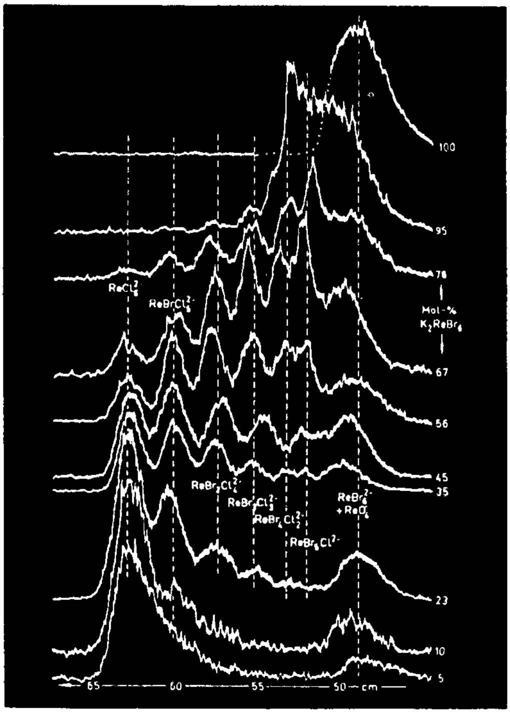

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SPECTROGRAPHIC DETERMINATION OF THE RARE EARTHS IN HIGH-PURITY GRAPHITE

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(*Received* 10 *September* 1970. *Accepted* 16 *December* 1970)

Summary—A spectrographic method has been developed for determination of the rare-earth elements in graphite. The rare earths are concentrated from ignited graphite on a calcium base. The impurities (Fe, V, Mn, Al, Ti) associated with the rare earths are separated by precipitation of the rare earths as hydroxides in the presence of Fe as a carrier, followed by precipitation of the rare earths as oxalates in the presence of Ca carrier. The mixture of calcium and rare-earth oxides obtained after ignition of the corresponding oxalates is mixed with graphite in 1:1 ratio and excited in a 15-A d.c. arc, with Nd as internal standard. The concentration ranges of determination are as follows: 0·006–0·125 ppm for Eu, 0·006–0·25 ppm for Gd, 0·006–0·06 ppm for Dy, 0·06–0·5 ppm for Sm. This sensitivity is achieved with 35-g samples of graphite. Higher enrichment factors are needed in order to enhance the sensitivity of the method.

REQUIREMENTS for high-purity graphite arise from the application of this material as a moderator in nuclear reactors, and the impurity tolerances are set by the high absorption cross-section for neutrons of some elements such as gadolinium and boron, which even in small concentrations could shift the nuclear balance of reactors.

In developing methods for determination of the rare earths in graphite it is possible to restrict them to those for elements of high cross-sections for neutron absorption, *e.g.* Gd, Sm, Eu and Dy. These elements, as well as boron, appear in electrographite at relatively high concentrations, whereas most of the other impurities evaporate as chlorides or fluorides during the procedure of simultaneous production and purification of graphite.

Simultaneous detection and quantitative determination of two or more rare earths is very difficult, as very few selective methods are available. It is possible to separate trace amounts of rare earths from a matrix by the use of ion-exchange resins. Chemical methods are not applicable, owing to their low sensitivity and selectivity. The most suitable method appears to be spectrochemical analysis.

Four principal methods have been used for spectroscopic determination of the rare earths: isolation of the rare earths as oxides, and excitation in craters,[1–4] the use of Feldman's porous cup electrode,[5] evaporation of the rare-earth solution on carbon electrodes[6] and excitation of the rare earths by copper spark or arc.[7]

The sensitivity of determination of the rare earths by these methods varies from 1 to 10 μg/g of matrix. Only the method of Feldman and Ellenburg[6] reaches a sensitivity of 0·1 μg/g of matrix. However, this method is limited to a determination of $>1\%$ of rare earths in solutions in hydrochloric acid. Thus, the methods described are either not sensitive enough, or are limited in scope because they require a particular medium.

Another difficulty arises from the low concentration of the rare earths in graphite, which makes it impossible to use direct spectrographic determination. In order to increase the sensitivity of the determination, it is necessary to use a preconcentration technique, but as this procedure is generally accompanied by a simultaneous increase in the concentration of other impurities in the analysed sample, a subsequent separation of the rare earths from these impurities is required.

The first work on this subject was by Goleb[8] who determined the rare earths together with the other refractory elements by igniting the graphite sample, then dissolving the residue in hydrochloric acid and using a copper spark for excitation. The method is semiquantitative, with a sensitivity ranging from 0·02 ppm for Eu to 0·5 ppm for Sm.

In Golling's method,[9] the graphite sample is ignited at 800° in the presence of thulium oxide. Fe and Ti are separated by distillation from chloride solution, in a stream of carbon tetrachloride. The impurities are separated by precipitation of the rare earths with sodium and ammonium hydroxides in the presence of thulium as carrier. The oxides are mixed with sodium fluoride and graphite and excited in a 15-A d.c. arc. The method gives a sensitivity of the order of $10^{-8}\%$ if 100-g samples are used.

The purpose of the present work was to develop a simple method for determination of trace amounts of rare earths in graphite. In trying to find an adequate procedure, attention was focused on a method which combines a chemical separation, a preconcentration of the rare earths on a calcium matrix and excitation in a d.c. arc.

EXPERIMENTAL

Procedures

Preparation of standards. Dissolve spectroscopically-pure Gd, Dy, Sm and Eu oxides in nitric acid to yield solutions containing 10, 0·5 and 0·125 μg of rare earth per ml. Dissolve calcium oxide in hydrochloric acid to give a solution containing 5 ml of Ca/ml. Then prepare standards containing 0·006–0·5 ppm of rare earths in a calcium matrix solution, as follows. Add 10 mg of Fe(III) carrier and 6 mg of Nd internal standard to the solution containing a given concentration of a rare earth. Heat the solution and precipitate rare earths at pH 8–9 with ammonia solution. Dissolve the hydroxides in diluted hydrochloric acid and evaporate the solution to dryness. Add 50 ml of water and 100 mg of Ca to the residue, heat to near boiling and precipitate the rare earths and Ca with oxalic acid. Leave overnight and filter off the oxalates, wash them with 5% oxalic acid solution, dry, and ignite at 950°. Mix the resultant oxides with graphite in 1:1 proportion and ignite 10 mg of this mixture in a 15-A d.c. arc.

The spectrochemical conditions and apparatus used are given in Table I, and the analytical line-pairs in Table II.

TABLE I.—APPARATUS AND OPERATING CONDITIONS

Spectrograph	Jarrell-Ash with flat grating
Wavelength region	270–370 nm (second order)
Slitwidth	20 μm
Analytical gap	4 mm
Excitation source	Jarrell-Ash Varisource, d.c. arc
Current	15 A
Electrodes	Counter (cathode) graphite rod, spectral grade, 3·1 mm diameter, used as obtained. Sample (anode) shallow thin-walled graphite electrode, 2-mm deep crater, 5·2 mm diameter, wall thickness 0·5 mm. The anode is supported on a 3·1-mm diameter graphite pedestal.
Preburn time	None
Exposure	30 sec
Emulsion, *etc.*	Kodak SA_I, developer D-19, 4 min at 20°

TABLE II.—ANALYTICAL LINE-PAIRS AND CONCENTRATION RANGES

Wavelength, *nm*	Concentration range, *ppm*
Eu 272·77/Nd 311·614	0·006–0·06
Eu 290·67/Nd 311·614	0·006–0·12
Gd 342·25/Nd 342·89	0·006–0·12
Gd 310·05/Nd 311·614	0·12–0·25
Dy 340·78/Nd 342·89	0·006–0·06
Sm 366·135/Nd 342·89	0·06–0·56

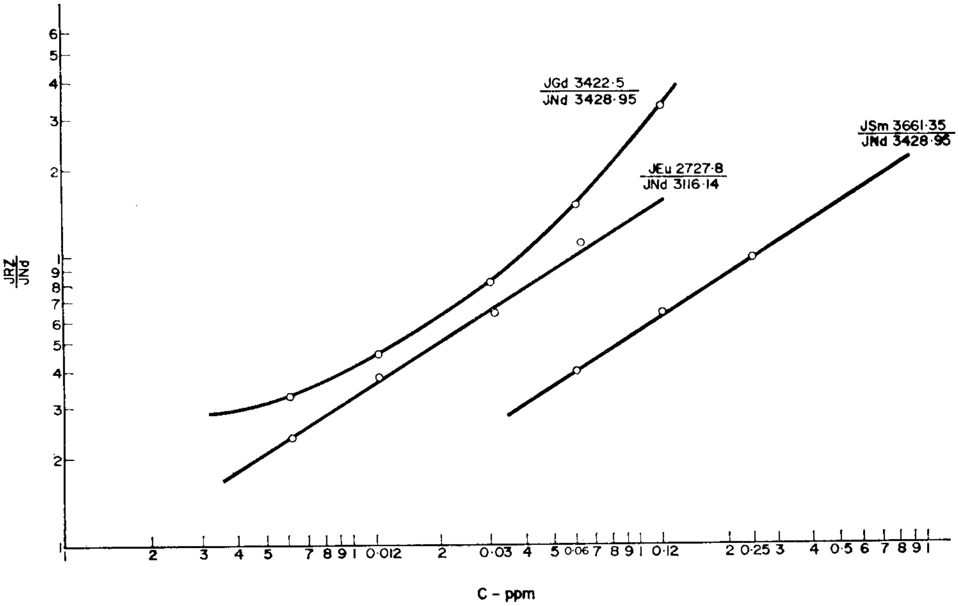

FIG. 1.—Analytical working curves for Eu, Gd and Sm.

Figures 1 and 2 show the analytical working curves as intensity ratio of the element determined and the internal standard (Nd) vs. concentration.

The precision of the method, expressed as relative standard deviation, is ±8–19% for Eu, ±4–18% for Gd, ±4–15% for Dy and ±10–22% for Sm.

Preparation of samples. Place 35 mg of graphite sample in a platinum beaker and add 1 ml of 5 mg/ml Fe(III) solution and 1 ml of 0·260 mg/ml Nd solution. Ignite the sample at 800° and dissolve the residue so obtained, in dilute sulphuric acid. Then add hydrofluoric acid and heat to dryness to remove silicon. Dissolve the residue in dilute hydrochloric acid and precipitate the rare earths at pH 8–9 with ammonia solution. Then precipitate the rare earths with oxalic acid in the presence of calcium as carrier. The other conditions are the same as in the procedure for the preparation of the standard.

RESULTS AND DISCUSSION

The concentration of the rare earths in graphite is so small that it makes a direct spectrographic determination impossible. A high preconcentration of the rare earths is needed in order to achieve good sensitivity. However, during this preconcentration procedure a simultaneous concentration of the impurities occurs. These impurities dilute the rare earths and the internal standard, increase the background and the spectral interference and change the excitation performance of the residue.

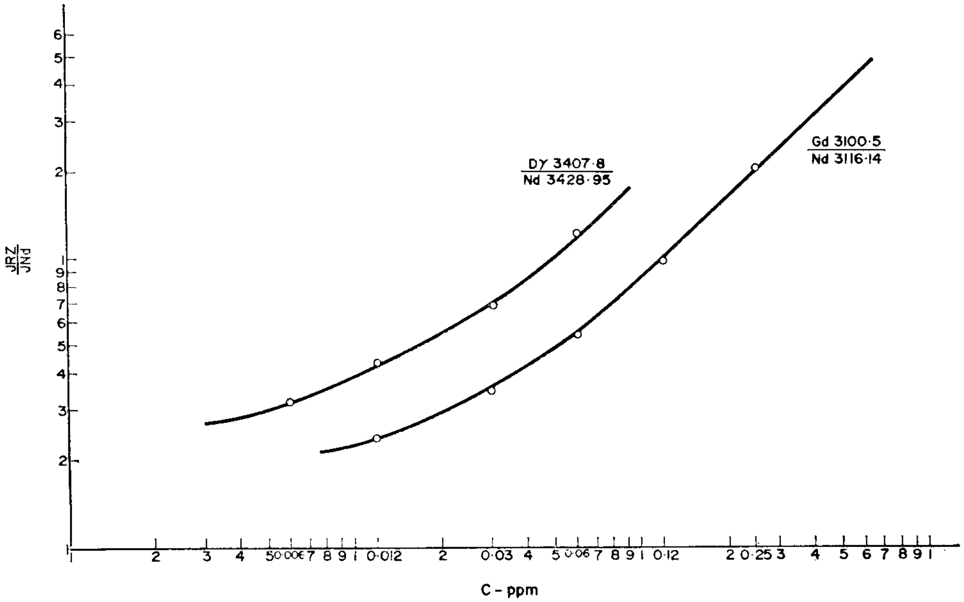

FIG. 2.—Analytical working curves for Gd and Dy.

In order to avoid these disturbing effects of the impurities, we have used a method of separation of rare earths as hydroxides and oxalates in the presence of iron and calcium as carriers, iron during precipitation of hydroxides, and calcium for the oxalate precipitation, because iron(III) will not precipitate as oxalate under these conditions.

The main features an element should have in order to be successfully used as a carrier in this method are to be precipitated quantitatively with oxalic acid and to have convenient spectrochemical properties similar to those of the rare earths (volatility, ionization potential, low background and simple spectrum). The rare-earth elements are not suitable for this purpose as they affect the lower limit of the determination, owing to the rare-earth content of the matrix. This was the reason for using calcium as a carrier. This element precipitates quantitatively under the conditions of our experiment and has the desired spectrochemical properties.

TABLE III.—RELATIVE INTENSITY OF THE SPECTRAL LINES OF Eu AND Gd IN La_2O_3 AND CaO MATRICES

Matrix	Eu	Gd
La_2O_3	0·19	0·31
CaO	0·67	0·55

Table III shows the relative intensity of the spectral lines of Eu and Gd when La_2O_3 and CaO matrices are used, Nd being used as an internal standard. Nd was used as internal standard since it has similar chemical and spectroscopic properties to the elements determined and also compensates for losses occurring during the chemical operations.

TABLE IV.—RECOVERY OF THE METHOD

Element	Added, μg	Recovered μg	%
Gd	0·006	0·0061	102
	0·012	0·0125	104
Eu	0·006	0·0064	104
	0·012	0·0115	96
Dy	0·006	0·0058	97
	0·012	0·0124	103

Several ratios of graphite and CaO have been explored in order to find the best ratio for stabilizing the arc. These studies showed that a 1:1 ratio is best. With this ratio and Nd as internal standard good reproducibility is obtained.

The recovery is illustrated in Table IV.

Zusammenfassung—Ein spektrographisches Verfahren zur Bestimmung der seltenen Erden in Graphit wurde entwikkelt. Die seltenen Erden werden aus geglühtem Graphit in einer Calciummatrix angereichert. Die mit den seltenen Erden zusammen vorkommenden Verunreinigungen (Fe, V, Mn, Al, Ti) werden durch Fällen der seltenen Erden als Hydroxide in Gegenwart von Fe als Träger und nachfolgende Fällung als Oxalate in Gegenwart von Ca-Träger abgetrennt. Das durch Verglühen der Oxalate erhaltene Gemisch der Oxide von Calcium und den seltenen Erden wird im Verhältnis 1:1 mit Graphit gemischt und in einem 15 A-Gleichstrombogen mit Nd als innerem Standard angeregt. Die Konzentrationsbereiche für die Bestimmung sind: 0,006–0,125 ppm für Eu, 0,006–0,25 ppm für Gd, 0,006–0,06 ppm für Dy, 0,06–0,5 ppm für Sm. Diese Empfindlichkeit wird mit 35 g-Graphitproben erreicht. Zur Erhöhung der Empfindlichkeit des Verfahrens werden höhere Anreicherungsfaktoren benötigt.

Résumé—On a élaboré une méthode spectrographique pour la détermination des éléments des terres rares dans le graphite. Les terres rares sont concentrées du graphite porté à l'incandescence sur une base de calcium. Les impuretés (Fe, V, Mn, Al, Ti) associées aux terres rares sont séparées par précipitation des terres rares à l'état d'hydroxydes en la présence de Fe comme support, suivie de la précipitation des terres rares à l'état d'oxalates en la présence de Ca support. Le mélange de calcium et d'oxydes de terres rares obtenu après calcination des oxalates correspondants est mélangé avec du graphite dans le rapport 1:1 et excité dans un arc 15 A courant continu, avec Nd comme étalon interne. Les domaines de concentration du dosage sont les suivants: 0.006–0,125 p.p.m. pour Eu, 0,006–0,25 p.p.m. pour Gd, 0,006–0,06 p.p.m. pour Dy, 0,06–0,5 p.p.m. pour Sm. Cette sensibilité est obtenue avec des échantillons de 35 g de graphite. Des facteurs d'enrichissement plus élevés sont nécessaires pour accroître la sensibilité de la méthode.

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3,5,7,4′-TETRAHYDROXYFLAVONE (KAEMPFEROL) AS A CHROMOGENIC REAGENT FOR GALLIUM AND INDIUM

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(*Received* 19 *January* 1970. *Revised* 27 *November* 1970. *Accepted* 13 *December* 1970)

Summary—3,5,7,4′-Tetrahydroxyflavone (kaempferol) forms yellow chelates with indium and gallium. Based on this reaction, a sensitive spectrophotometric method for the determination of gallium and indium alone and in presence of other metals and alloys has been developed. Beer's law is obeyed up to 2·8 and 1·44 ppm for indium and gallium respectively.

NUMEROUS reagents have been investigated for spectrophotometric determination of gallium and indium.[1–28] The present paper deals with investigations on the use of kaempferol as a chromogenic reagent for gallium and indium. This ligand is known to form more stable complexes than the other flavones.[29] On addition of a kaempferol solution in ethanol to gallium or indium solutions (pH = 3–5), a deep yellow colour is developed instantaneously. The reaction is sensitive and can be successfully used for the determination of micro amounts of gallium and indium, alone or in the presence of many foreign ions.

EXPERIMENTAL

Reagents

Gallium and indium stock solutions were prepared by dissolving the metals (spectroscopically pure) in perchloric acid and diluting to known volumes with doubly distilled water. Other chemicals used were of reagent-grade quality and their solutions were prepared in doubly distilled water. A stock solution of kaempferol was prepared in 95% ethanol.

Spectral behaviour of the complexes

The effect of pH, time, solvent, *etc.* on the colour systems was investigated.

A series of solutions containing a fixed amount of metal and excess of kaempferol was prepared at different pH values adjusted by means of dilute perchloric acid and sodium hydroxide. The final v/v ethanol concentration was 50%. The absorption spectra were recorded against reagent blanks (Figs. 1 and 2). In both cases the absorbance rises as the pH is raised, becoming maximum and practically constant at pH 4·0–4·75 for indium, and 4·0–5·6 for gallium, then falling again at higher pH (at which the ligand itself becomes highly coloured). The nature of the spectral curves and the position of λ_{max} (between 420 and 430 nm for indium and at 425 nm for gallium) indicate formation of only one complex in each case. The absorption spectrum for reagent alone is shown in Fig. 3. The adjustment of pH in the indium system is very important. If the pH is adjusted from low to high there is no abnormal behaviour, but if it is too high and has to be lowered, the absorbance is lowered. Furthermore, if the hydroxide of indium is precipitated, it cannot be dissolved readily by addition of perchloric acid. For the gallium system the direction of adjustment of pH is immaterial.

Maximum colour formation takes place immediately and the colour remains stable for about 8 hr and then slowly fades. Temperature variation between 15 and 30° had no effect.

Variation in the concentration of ethanol had no effect on the absorbance, but a minimum concentration of 30% v/v ethanol was necessary to keep the complexes and ligand in solution. A 50% v/v concentration of ethanol was chosen for safety.

Other organic solvents such as ethers do not enhance the absorbance as they do when PAN is used as reagent.[30]

For the indium–kaempferol system, a minimum of 100-fold molar excess of reagent is required for full colour development (20-fold for gallium).

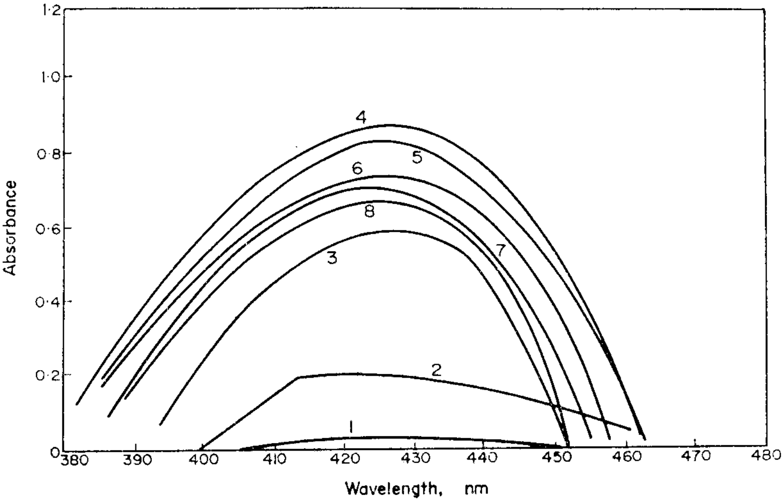


FIG. 1.—Absorption spectra of indium-kaempferol complex. *1*, pH 2·0; *2*, pH 3·0; *3*, pH 3·5; *4*, pH 4·0, 4·5, 4·75; *5*, pH 5·1; *6*, pH 5·5; *7*, pH 6·0; *8*, pH 7·0.

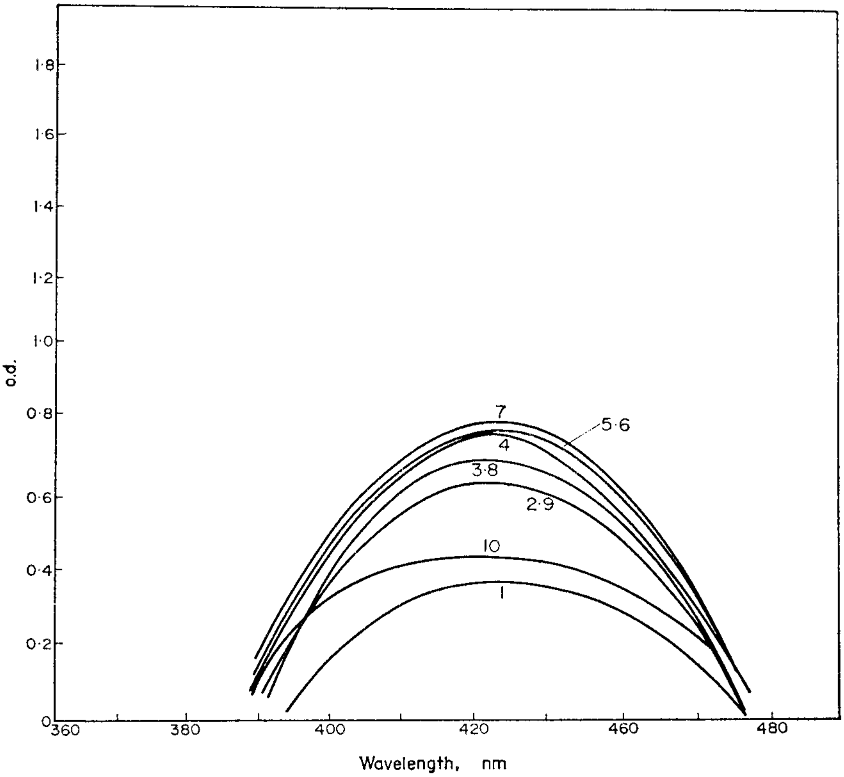


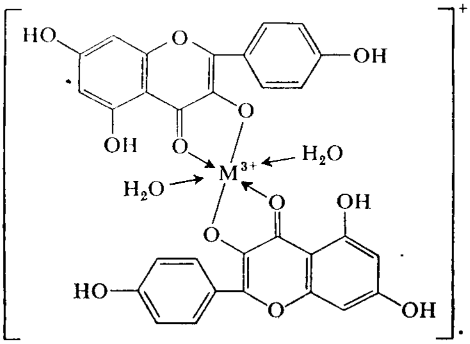
FIG. 2.—Absorption spectra of gallium-kaempferol complex. *1*, pH 2·0; *2*, pH 3·0; *3*, pH 3·6, 4·0; *4*, pH 4·0; *5*, pH 4·6; *6*, pH 5·0; *7*, pH 5·5; *8*, pH 6·0; *9*, pH 6·4; *10*, pH 7·5.

Linearity between the absorbance and metal ion concentration was observed up to 2·8 ppm (430 nm, pH 4·5) and 1·44 ppm (425 nm, pH 5·0) for indium and gallium respectively. The optimum ranges for accurate determination as deduced from Ringbom plots are 0·6–2·8 ppm and 0·5–1·0 ppm for indium and gallium respectively.

Composition of the complexes

The stoichiometric ratios of metals to ligand in the complexes under the conditions mentioned above, were determined by the methods of continuous variations,[31] Asmus,[32] slope-ratio[33] and Bent and French.[34] These methods all confirmed that the metal to ligand ratio in the complexes is 1:2.

Because indium and gallium generally form octahedral complexes, the structure of the complexes is tentatively suggested to be



That the 3-hydroxy group takes part in chelation is shown by the fact that dimethylkaempferol, in which the 3- and 4′-positions are blocked, does not give a colour reaction with gallium or indium. The complexes can be extracted into chloroform, ether, *etc*., presumably as perchlorate ion-association compounds.

Recommended procedure

To a suitable aliquot containing 6–28 μg of indium or 5–10 μg of gallium add excess of 0·3% ethanolic solution of kaempferol (1 ml for indium; 0·5 ml for gallium). Adjust the pH to 4·5 (indium) or 5·0 (gallium), paying heed to the note above on direction of adjustment. Dilute to 10 ml in a standard flask to yield a final ethanol concentration of 50% v/v. Measure the absorbance against a reagent blank.

RESULTS

From measurements on a number of solutions containing 2·30 ppm of indium or 0·697 ppm of gallium and excess of reagent, the average and maximum relative errors were 0·3% and 0·5% respectively for indium and 0·4% and 0·8% respectively for gallium.

Interferences

Interference due to iron(III) is avoided by reducing it to iron(II); zirconium(IV) can be masked to some extent with tartrate or citrate. Some anions, *viz*. fluoride, thiosulphate, iodate, EDTA and NTA interfere seriously. Sulphate, citrate, tartrate, oxalate, phosphate and borate do not interfere even if present in 50–60-fold molar ratio relative to In or Ga. Acetate, nitrate, chloride, iodide, bromide, thiocyanate and sulphite are tolerated in up to 100–1000-fold amounts. Large amounts of hydroxylamine hydrochloride and thiourea have no effect.

At pH values above 4·5 rare earth ions interfere, but at pH 4·5, 10-fold amounts are tolerated. The alkaline earths, mercury(II), thallium(I), silver and lead do not interfere in up to 200-fold amounts, and cobalt(II), nickel, copper(II), cadmium and

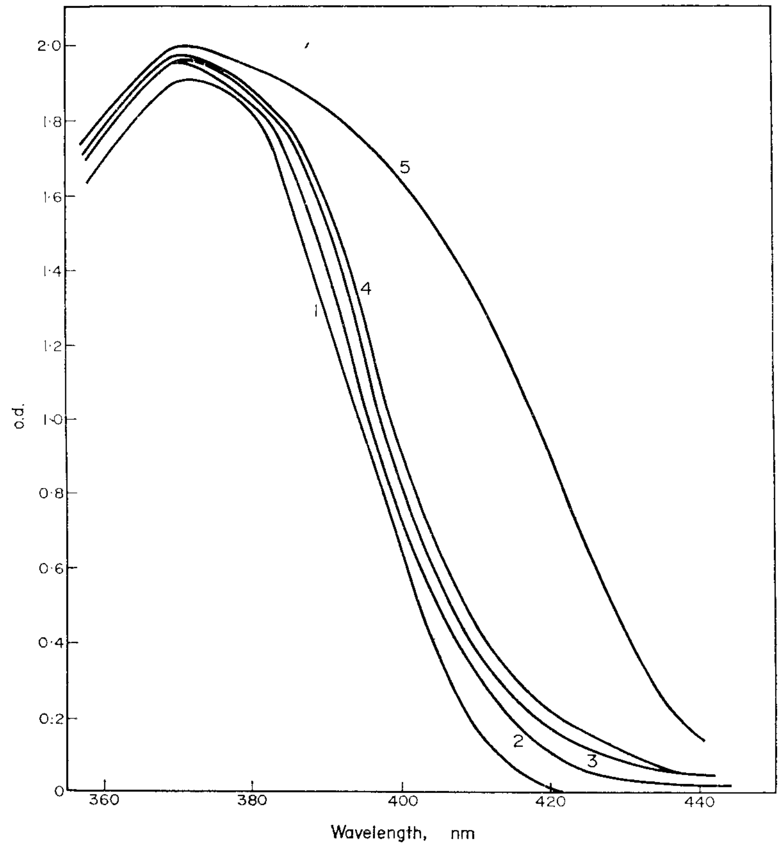


FIG. 3.—Absorption spectra of kaempferol in 50% v/v ethanol. Concentration of kaempferol = 1·6 × 10^{-4}*M*. *1*, pH 3·5, 4·0, 4·5, 5·0, 5·5; *2*, pH 6·0; *3*, pH 6·5; *4*, pH 7·0; *5*, pH 8·0.

zinc are tolerated in up to 80-fold amounts. Aluminium, beryllium, iron(III), thorium, uranium(VI), molybdenum(VI), tungsten(VI), antimony(III), tin(IV), zirconium, titanium(IV) and vanadium(IV) or (V) interfere owing to formation of coloured chelates with kaempferol.

APPLICATIONS

Determination in metals and alloys

Since alloys containing gallium and indium were not available, synthetic mixtures containing these and other metals were prepared and analysed as described below.

In presence of lead, tin and antimony (e.g., *in cylindrite*). Decompose the sample by heating with 2–3 ml each of conc. sulphuric, perchloric and nitric acids with dropwise addition of hydrobromic acid (40%, 5 ml) and shaking during at least 30–40 min. Evaporate the solution to small volume, to remove most of the acids, cool the solution, dilute it to 50 ml with doubly distilled water and again evaporate it to small volume. Cool, add 1 ml of 0·6% solution of kaempferol in ethanol, adjust the pH to 4·5, and dilute to 25 ml (final ethanol concentration 50%). Measure the absorbance against a reagent blank.

Results are shown in Table I for indium. The same procedure also gives accurate results for gallium. It has been shown by radioactive tracer technique[34] that no indium or gallium is lost under the conditions used, and tin and antimony are quantitatively volatilized as the volatile bromides.

TABLE I.—DETERMINATION OF INDIUM IN SYNTHETIC MIXTURES

In(III) present, *ppm*	Pb, *ppm*	Sb, *ppm*	Sn, *ppm*	In(III) found, *ppm*
28·7	518	30·3	29·7	28·8
45·9	828	60·6	59·3	46·0
57·4	1036	90·9	89·0	57·0

Determination of gallium and indium in cadmium. Recently, Flaschka and Butcher[35] have used iodide as masking agent for cadmium in the EDTA titration of cadmium and zinc in a mixture. The masking property of iodide for cadmium ions has been utilized for determination of indium and gallium in cadmium without prior separation of cadmium. In the study of interferences, it was observed that cadmium does not interfere when it is present to the extent of 80 ppm. Also iodide does not interfere when it is present up to 400 ppm. By advantage being taken of these facts, indium and gallium have been determined in presence of large quantities of cadmium.

Varying amounts of gallium or indium solutions were taken and different amounts of cadmium solution were added. To the mixture were added 1–2 g of potassium iodide, 10 ml of 0·3% kaempferol in ethanol and sufficient ethanol to give a final concentration of 50% v/v. The pH was adjusted to 4·5 for indium or 5·0 for gallium and the total volume made up to 100 ml. The absorbance was measured against a reagent blank. Some results are shown in Table II.

TABLE II.—DETERMINATION OF GALLIUM AND INDIUM IN CADMIUM (2 g OF KI ADDED)

Cd,	In, *μg*		Cd,	Ga, *μg*	
mg	present	found	*mg*	present	found
0	22·9	22·9	0	6·90	6·91
5	22·9	23·0	5	5·50	5·55
10	28·7	28·8	10	6·90	6·95
15	22·9	23·1	15	10·00	10·15

Discussion

PAR and PAN are claimed to be the best reagents for spectrophotometric determination of gallium and indium. PAN can be successfully employed for the determination of these metals in presence of cadmium and some other metals. The λ_{max} for PAN lies at 560 nm which is very near to that of the In–PAN complex (545 nm). In the kaempferol method, λ_{max} for the reagent lies at 360–370 nm, while its value for the complex is 430 nm, at which wavelength absorption by the ligand is very low. Also appreciable amounts of cadmium are tolerated without the use of masking agent. The sensitivity of the colour reaction is better than that with PAN. Gallium and indium can also be satisfactorily determined in presence of zinc, lead and many other ions. However, prior separation of antimony and tin by volatilization as the bromides is necessary as in the case of other methods. Thiocyanate, thiourea and hydroxylamine hydrochloride do not interfere even if they are present in large excess (~1000-fold) and may be useful to mask some of the interfering ions.

The major disadvantage is that if gallium and indium are present together, a preliminary separation is necessary. For this purpose gallium can be extracted as chlorogallic acid into isopropyl ether from 6–7*M* hydrochloric acid[36] and then determined with kaempferol. Indium is retained in the aqueous phase. The average error is then ±2·5% for each metal.

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Zusammenfassung—3,4,7,4′-Tetrahydroxyflavon (Kaempferol) bildet gelbe Chelate mit Indium und Gallium. Auf Grund dieser Reaktion wurde eine empfindliche spektrophotometrische Methode zur Bestimmung von Gallium und Indium allein und in Gegenwart anderer Metalle und Legierungen entwickelt. Das Beersche Gesetz gilt bis maximal 2,8 bzw. 1,44 ppm Indium bzw. Gallium.

Résumé—La 3,5,7,4′-tétrahydroxyflavone (kaempferol) forme des chélates jaunes avec l'indium et le gallium. En se basant sur cette réaction, on a élaboré une méthode spectrophotométrique sensible pour le dosage du gallium et de l'indium seuls et en présence d'autres métaux et alliages. La loi de Beer est suivie jusqu'à 2,8 et 1,44 p.p.m. pour l'indium et le gallium respectivement.

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CATION-EXCHANGE SEPARATION OF URANIUM IN DIMETHYLSULPHOXIDE MEDIUM

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Summary—Cation-exchange chromatography in a dimethylsulphoxide (DMSO) medium is a suitable means for separating uranium from metal ions, including copper, iron, nickel and molybdenum. Quantitative separations of uranium from 26 elements can best be effected on a column of Dowex 50W-X8 (200–400 mesh), using as the eluent a 20% v/v DMSO solution which is 0·6*M* in hydrochloric acid and 0·25*M* in sodium acetate. Only calcium is eluted with the uranium and all other elements studied are eluted either before or after uranium. The elution characteristics of uranium and of other metal ions were investigated with respect to changes in eluent and resin compositions. Separations were much less effective at higher concentrations of sodium ion or DMSO. None of the organic solvents methanol, ethanol, methyl glycol, acetone, dioxan or acetic acid was found to produce favourable separation conditions. Results with Dowex 50 resins of lower or higher cross-linkage were inferior to those obtained with the X8 resin.

As PART of a systematic investigation of the factors which control cation-exchange selectivity in DMSO–water systems[1,2] analytical applications of these media have recently been explored in this laboratory. The solvent system DMSO–water differs from most binary solvent media previously used[3–5] in that the bulk dielectric constants of mixtures are relatively high, and the selective swelling of resins is quite small. These facts and other remarkable properties of DMSO–water systems have been previously discussed.[1,2,6,7].

Mixed aqueous–organic solvents have already proven to be of great utility for separations of uranium by ion-exchange methods.[3,8] Recent research on DMSO media has shown that various ions can be separated by anion-exchange[9,10] or by cation-exchange[2,11] procedures. Some distribution data for the uranyl ion in the system DMSO–hydrochloric-acid–Dowex 50-X8 were reported earlier.[12] However, none of these results suggested conditions for selective separation of uranium by cation-exchange. The present study reveals the feasibility of highly selective separations for uranium from numerous cations on very short columns when an acidic 20% v/v DMSO medium containing alkali metal ions is used.

EXPERIMENTAL

Reagents

Ion-exchange resins. The air-dried cation-exchange resin (Bio-Rad) Dowex 50W-X8, 200–400 mesh, hydrogen form, was used for most separations and studies of the ion-exchange characteristics of the elements, although experiments were also carried out with X8 resin of larger particle size (100–200 mesh) as well as with X4 and X12 resins (100–200 mesh).

Standard solutions of the elements. 0·1*M* solutions in hydrochloric acid of the chlorides, nitrates or other suitable salts (6*M* of the following metal ions) were prepared: UO_2(II), Fe(III), Cr(III), Cu(II), Co(II), Ni(II), Mo(VI), V(V), Cd(II), Zn(II), Mn(II), Pb(II), Th(IV), Sc(III), Al(III), Mg(II), Ca(II), Sr(II), Ba(II), Be(II), Pd(II), Hg(II), Bi(III), Ga(III), In(III), Zr(IV), Ti(IV), and Sn(II).

Organic solvents. The following reagent grade (or purest commercial grade) solvents were used: dimethylsulphoxide (DMSO), methanol, ethanol, methyl glycol (ethylene glycol monomethyl ether), acetone, dioxan, and glacial acetic acid.

Eluent solution. The solution was prepared by mixing 6*M* hydrochloric acid (100 ml), 2·5*M* sodium acetate (100 ml) and water (600 ml), and diluting to 1 litre with DMSO.

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Determination of distribution coefficients

Distribution coefficients (K_d) of uranium and other metal ions were determined by the column method, using the relationship

$$K_d = \frac{\mathrm{VEP} - V}{m}$$

where VEP = volume of elution peak (in ml), m = mass of resin (1 g in all cases) and V = void volume (0·7 ml for a 1-g column). The volumes corresponding to the elution peaks and to the breakthrough and terminal elution volumes (BTV and TEV respectively) were determined by means of the separation procedure described below. The fractions collected were 1 ml in volume in the case of readily eluted elements (otherwise 5 ml). The breakthrough volume corresponded to a concentration of $\geqslant$ 5 ppm of the ion in question in the column effluent, and the terminal volume to $\leqslant$ 5 ppm.

Determination of the elements

Standard colorimetric procedures were employed for the detection and determination of uranium and most other elements in the eluate fractions. Sr, Ba and Hg were determined by atomic-absorption spectrophotometry.

Separation procedure

Preparation and pretreatment of resin column. Soak 1 g of the resin for 1–2 hr in a few ml of the eluent and then transfer it to an ion-exchange column (glass tube of suitable length and 7 mm bore) with 10–15 ml of the same solution as a rinse and for pretreatment.

Sorption. Combine 1 ml of $6M$ hydrochloric acid, containing the elements to be separated, 1 ml of $2{\cdot}5M$ sodium acetate solution and 6 ml of demineralized water and dilute the mixture to 10 ml with DMSO. Pass this solution through the resin column at a flow-rate of 1 ml/6 min. (Usually 1 ml is used as the sorption volume.)

Chromatographic separation. Following the sorption step, wash the resin with 4 ml of eluent and combine this wash with the (1 ml) effluent previously obtained. (This constitutes the first 5-ml fraction.) Continue elution and collecting 5-ml fractions (or sometimes 1-ml fractions—see above) at a rate of 1 ml/6 min. The first 45 ml thus collected contain Cr(III), Cu(II), Co(II), Ni(II), Mo(VI), V(V), Cd(II), Zn(II), Mn(II), Pb(II), Mg(II), Be(II), Pd(II), Hg(II), Bi(III), In(III), Ti(IV) and Sn(II) as well as Mo(IV/V), V(IV), and Sn(IV) [these last three being formed by partial reduction or oxidation of Mo(IV), V(V) and Sn(II) respectively]. The following 7 fractions (a total of 35 ml) contain the uranium and most of the calcium (if present) while strontium and iron are not eluted until 100 and 115 ml respectively of the eluent solution have passed through the resin column. Th(IV), Sc(III), Al(III), Ba(II), Ga(III) and Zr(IV) are also very strongly retained by the resin. Breakthrough of these elements is still not observed after the passage of more than 100 ml of eluent.

RESULTS AND DISCUSSION

Preliminary investigations of the effect of DMSO on the adsorption of uranium(VI) and iron(III) on Dowex 50W-X8 showed that a medium containing 20% v/v of DMSO is the most suitable for separations involving these two metal ions. At DMSO concentrations corresponding to 30, 40, 60 and 80% v/v or higher these elements have low distribution coefficients but show practically identical adsorption behaviour so that separations are impossible. On the other hand, a decrease of the DMSO concentration (*e.g.* to 10% v/v) entails a considerable increase of the distribution coefficients which makes impossible the separation of uranium from iron within a reasonable period of time. The same observation is made when the hydrochloric acid concentrations of the mixtures is decreased. Strong buffering with sodium acetate above the level in the suggested eluent solution has the same effect as the use of DMSO concentrations greater than 20% v/v. On the basis of these results the eluent solution described was chosen as the most suitable medium for effecting clean-cut separations of uranium from iron and from numerous other elements. The efficiency of separations is similar when instead of the recommended eluent a 20% v/v DMSO solution is used which is $0{\cdot}35M$ in hydrochloric acid and $0{\cdot}25M$ in sodium chloride. Thus, the separability of the elements is not affected by the presence of free acetic acid (formed by protolysis of acetate) in the eluent. However, the elution characteristics of uranium depend on the alkali metal ion concentration of the eluent. This effect is shown in Table I. It is seen that an increase of the sodium ion concentration decreases BTV, VEP and TEV. This effect is essentially independent of the accompanying anion. The displacement of uranium is more pronounced with potassium ion than with sodium ion of the same concentration, owing to the stronger sorption of potassium ion on the cation exchanger: the Hofmeister series is maintained in DMSO media, but the selectivity differences for alkali metal ions are significantly increased.[2,6] The ammonium ion in this medium shows the same sorption (and displacement) behaviour as does the sodium ion (see Table I). The strong solvation of the hydrogen ion in DMSO media makes its solutions rather weak displacing agents in comparison with the alkali metal ions.

TABLE I.—EFFECT OF ADDITIONAL SALT CONCENTRATION ON ADSORPTION OF URANIUM (0·01*M*) ON DOWEX 50W-X8 (200–400 MESH) OF SODIUM ACETATE

Additional salt concentration	Elution characteristics		
	BTV	VEP	TEV
0·1*M* NaCl	35	50	65
0·25*M* NaCl	20	30	50
0·50*M* NaCl	10	15	35
0·1*M* $NaNO_3$	35	50	65
0·25*M* $NaNO_3$	20	30	50
0·50*M* $NaNO_3$	15	20	35
0·25*M* Na_2SO_4	5	10	20
0·50*M* Na_2SO_4	5	5	15
0·1*M* KCl	25	35	55
0·1*M* NH_4Cl	35	50	65

BTV = breakthrough volume, *ml.*
VEP = volume of elution peak, *ml.*
TEV = terminal elution volume, *ml.*
Eluent: 20% v/v DMSO, 0·60*M* in HCl, 0·25*M* in CH_3CO_2Na; 5-ml fractions.

Among many systems studied the chosen eluent solution proved to be the most efficient mixture for achieving separations of uranium from iron. Therefore, the elution characteristics of numerous other elements were investigated with this medium. Table II shows that complete separations of uranium from all metal ions listed (except calcium) are possible. Chromium, copper, cobalt, nickel, molybdenum, vanadium, cadmium, zinc, manganese, lead, magnesium, beryllium, palladium, mercury, bismuth, indium, titanium and tin are eluted completely before the BTV of uranium is reached. On the other hand the TEV of uranium is considerably lower than the BTV of iron, strontium, thorium, scandium, aluminium, barium, gallium and zirconium so that quantitative separations of uranium from these elements are possible too. Numerous separations involving 0·01*M* solutions of uranium and of the elements listed in Table II have been carried out by the working procedure described above. The results showed that in all cases complete separations of uranium from these metal ions were achieved.

If pure aqueous solutions of corresponding composition (*i.e.* 0·25*M* in sodium chloride and 0·35*M* in hydrochloric acid are used, uranium cannot be separated from copper and nickel although its separation from iron is possible. The results of these investigations are shown in Table III. It follows that the presence of DMSO greatly increases the selectivity of separation of uranium from copper, nickel and other

TABLE II.—ELUTION CHARACTERISTICS OF METAL IONS*

Metal ion (0·01*M*)	BTV, *ml*	VEP, *ml*	TEV, *ml*
Mo(IV/V)	1	2	2
Pd(II)	1	2	3
Hg(II)	1	2	5
Bi(III)	1	3	10
Cd(II)	3	3	5
In(III)	3	4	6
V(V)	3	4	7
Sn(II/IV)	6	8	12
Mo(VI)	5	9	17
Cr(III)†	10	11	13
Pb(II)	14	15	20
Zn(II)	18	20	23
Be(II)	20	20	25
V(IV)	20	23	26
Ti(IV)	20	24	31
Mg(II)	23	24	30
Cu(II)	22	25	31
Mn(II)	24	30	40
Co(II)	26	31	39
Ni(II)	29	34	40
UO_2(II)	50	65	85
Ca(II)	60	75	90
Fe(III)	115	140	195
Sr(II)	100	—	—
Ba(II)	>100	—	—
Al(III)	>100	—	—
Ga(III)	>100	—	—
Sc(III)	>100	—	—
Zr(IV)	>100	—	—
Th(IV)	>100	—	—

* Eluent: 20% DMSO–10% 6*M* HCl–10% 2·5*M*–60% H_2O) Dowex 50W-X8 (200–400 mesh).

† This experiment was performed two days after preparation of the sorption solution, so that all rapid solvation equilibria could be assumed as being attained.

TABLE III.—ELUTION CHARACTERISTICS ON DOWEX 50W-X8 (200–400 MESH)

Metal ion, 0·01*M*	BTV, *ml*	VEP, *ml*	K_d	TEV, *ml*
UO_2(II)	35	40	39·3	55
Cu(II)	35	40	39·3	55
Ni(II)	40	45	44·3	70
Fe(III)	120	140	139·3	200

Eluent: aqueous 0·25*M* NaCl which is 0·35*M* in HCl.

bivalent metal ions such as cobalt, zinc, manganese and lead which cannot be separated from uranium in the absence of DMSO.

A comparison of the elution characteristics of copper and uranium in media containing a number of other solvents in place of DMSO is presented in Table IV. These results show that DMSO is by far the most suitable solvent. In all other organic solvents a considerable overlap of the elution curves of uranium and copper is observed. This once more proves the superiority of the chosen eluent.

To study the possible effects of particle size and cross-linkage the elution experiments outlined in Fig. 1 were performed. From the elution curves shown it is seen

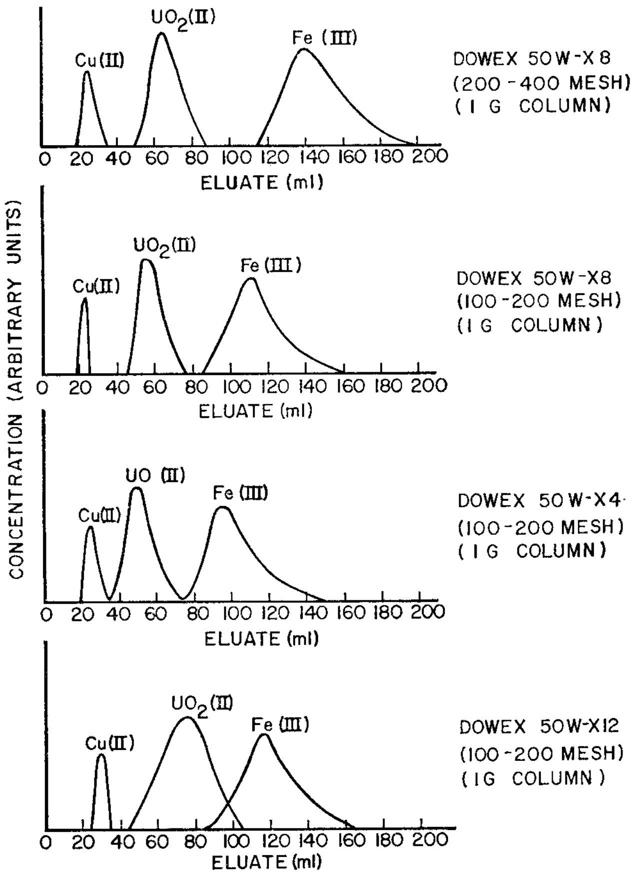

FIG. 1.—Effects of particle size and cross-linkage on separation of Cu, U and Fe in 20% DMSO–10% 6*M* HCl–10% 2·5*M* CH_3CO_2Na–60% H_2O (eluent solution).

TABLE IV.—EFFECT OF VARIOUS SOLVENTS

Solvent, 20% v/v	Elution characteristics					
	Cu(II), 0·01*M*			UO_2(II), 0·01*M*		
	BTV	VEP	TEV	BTV	VEP	TEV
DMSO	20	25	35	50	65	85
Water (*i.e.*, purely aqueous medium)	35	40	55	35	40	55
Methanol	30	30	35	35	40	55
Ethanol	25	30	40	30	40	55
Methyl glycol	30	35	40	30	40	55
Acetone	30	35	40	40	45	60
Dioxan	25	30	35	35	40	50
Acetic acid	30	35	45	45	55	70

BTV = breakthrough volume, *ml*.
VEP = volume of elution peak, *ml*.
TEV = terminal elution volume, *ml*.
Eluent: 20% solvent–10% 6*M* HCl–10% 2·5*M* CH_3CO_2Na–60% H_2O. Resin: Dowex 50W-X8 (200–400 mesh).

that the most efficient separation of copper–uranium–iron is obtained by using Dowex 50W-X8 (200–400 mesh) while with the lower and higher cross-linked resins (as well as with the 100–200 mesh X8 resin) less satisfactory results were obtained. The least effective separation of uranium from iron was found with the X12 resin. In this case a considerable overlap of the elution curves of uranium and iron was observed.

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Zusammenfassung—Die Kationenaustauschchromatographie in einem Dimethylsulfoxid-(DMSO)Medium ist geeignet, Uran von anderen Metallionen wie Kupfer, Eisen, Nickel und Molybdän abzutrennen. Quantitative Uranabtrennungen von 26 Elementen erzielt man am besten auf einer Säule Dowex 50W-X8 (200–400 mesh) mit einer 20% (Volumenanteil) DMSO-Lösung, die 0,6*M* Salzsäure und 0,25*M* Natriumacetat enthält, als Elutionsmittel. Nur Calcium wird mit dem Uran eluiert, alle anderen untersuchten Elemente entweder vorher oder nachher. Die Elutionseigenschaften von Uran und anderen Metallionen wurden im Hinblick auf Änderungen in der Zusammensetzung der Elutionslösung und des Harzes untersucht. Bei hohen Natrium- oder DMSO-Konzentrationen waren die Trennungen weit weniger wirkungsvoll. Von den organischen Lösungsmitteln Methanol, Äthanol, Methylglykol, Aceton, Dioxan oder Essigsäure ergab keines vorteilhafte Trennbedingungen. Ergebnisse mit Dowex 50-Harzen von niedrigerem oder höherem Vernetzungsgrad waren denen mit dem X8-Harz unterlegen.

Résumé—La chromatographie d'échange de cations dans un milieu diméthylsulfoxyde (DMSO) est un moyen convenable pour séparer l'uranium d'ions métalliques, y compris le cuivre, le fer, le nickel et le molybdène. Les séparations quantitatives d'uranium de 26 éléments peuvent être effectuées au mieux sur une colonne de Dowex 50W-X8 (200–400 mesh) en utilisant comme éluant une solution à 20% v/v de DMSO qui est 0,6*M* en acide chlorhydrique et 0,25*M* en acétate de sodium. Seul le calcium est élué avec l'uranium et tous les autres éléments étudiés sont élués soit avant ou après l'uranium. Les caractéristiques d'élution de l'uranium et d'autres ions métalliques ont été étudiées par rapport aux changements dans l'éluant et la composition de la résine. Les séparations ont été beaucoup moins efficaces à des concentrations plus élevées en ion sodium ou DMSO. On a trouvé qu'aucun des solvants organiques méthanol, éthanol, méthylglycol, acétone, dioxane ou acide acétique ne produit des conditions de séparation favorables. Les résultats avec des résines Dowex 50 à enchaînement transversal plus faible ou plus élevé ont été inférieurs à ceux obtenus avec la résine X8.

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A TITRIMETRIC METHOD FOR THE RAPID DETERMINATION OF CARBON IN STEEL WITH AN AQUEOUS TITRANT

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Summary—It is demonstrated that the addition of 5% of water to the non-aqueous solvent for the titrimetric determination of carbon in steel improves the performance of the titration. Modifications to the procedure are proposed which allow the normal titrant, tetra-n-butylammonium hydroxide dissolved in benzene-methanol, to be replaced by an aqueous solution of potassium hydroxide. The proposed procedure has been applied to the analysis of a wide range of standard steel samples.

ONE OF THE MORE popular current methods for the determination of carbon in steel involves the non-aqueous titration of the carbon dioxide resulting from the high-temperature combustion of the steel sample in a stream of pure oxygen. A number of workers[1–5] have described modifications to the titration procedure suggested by Blom *et al.*,[6,7] in which the carbon dioxide is absorbed in pyridine and titrated with a solution of sodium methoxide dissolved in a mixture of methanol and pyridine. Grant *et al.*[1] proposed that the pyridine be replaced by dimethylformamide and used potassium methoxide in a benzene–methanol mixture as titrant. Jones *et al.*[2,4] added small amounts of ethanolamine to the same absorbant to give more efficient absorption of carbon dioxide and used tetra-n-butylammoniumhydroxide in benzene–methanol or toluene–methanol as titrant. They demonstrated that their procedure was rapid, applicable to a wide range of steels, and of sufficiently high accuracy. The end-point of the titration in all cases was detected visually, with Thymol Blue or thymolphthalein as indicator, the latter apparently being preferable,[5] although potentiometric indication would be possible, particularly if it were desired to automate the determination.

During a recent investigation[8] into the feasibility of determining small quantities of carbon dioxide by coulometric titration in non-aqueous media but using small amounts of water for generation of the titrant (OH^-), it was found that the addition of water actually improved the sharpness of the end-point in a solvent consisting of 10% v/v ethanolamine in pyridine. Water cannot be added to dimethylformamide as hydrolysis occurs, resulting in the formation of formic acid which would also be titrated.[9] In the non-aqueous titration method for the determination of carbon in steel, the use of an efficient absorbant is essential, as the flow of the oxygen carrier gas must be kept high in order to facilitate a rapid determination. The use of an organic absorbant is therefore obligatory but the effect of water just mentioned makes possible replacement of the complex and costly organic titrant with an aqueous titrant. A modification to the existing procedure[2] and the use of aqueous potassium hydroxide as titrant are described in this communication.

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EXPERIMENTAL

Reagents

The purest available chemicals were used and water was distilled in an all-quartz still.

Absorbant/titrand solvent

For Procedure A. Dilute 50 ml of ethanolamine to 500 ml with pyridine. Separately dilute 50 ml of ethanolamine to 500 ml with distilled water. Mix known quantities of the aqueous and pyridine solutions of ethanolamine to obtain solutions of 10% v/v ethanolamine in pyridine containing known amounts of water.

For Procedures B and C. Dilute 11·5 ml of distilled water together with 6·0 ml of a 0·1% w/v methanolic solution of thymolphthalein and 50 ml of ethanolamine to 500 ml with pyridine.

Store all mixtures in tightly stoppered containers.

Procedures

(A) *Measurement of titration quality (Q).* Aliquots (5 ml) of sodium carbonate solution (0·04*M* aqueous) were transferred to a three-necked flask, and a slight excess of sulphuric acid (1*M*) was added from a dropping funnel. The carbon dioxide produced was swept out by a stream of oxygen (200 ml/min) and bubbled through 50 ml of previously neutralized absorbant/titrand solvent contained in a cylindrical 100-ml titration cell fitted with a Quickfit cap. The cap was provided with apertures through which a 0·1*M* calomel electrode, antimony indicator electrode, an Agla syringe burette, and gas inlet and outlet tubes were fitted and the solution was stirred by a magnetic stirrer. Small increments of titrant (1*M* potassium hydroxide) were added and when equilibrium was reached (after several minutes), potentials were measured on an E.I.L. 39A pH meter. Values of *Q* were determined from the titration curves, as described in the text.

(B) *Determination of carbon in steel.* The apparatus used was similar in construction to that described by Jones *et al.*,[2] and was made available by the Dalzell Steel Works of the British Steel Corporation. The procedure was altered only in that the titrand solvent consisted of pyridine with 10% v/v ethanolamine and 2·3% v/v water, and the titrant was 0·05*M* aqueous potassium hydroxide.

An accurately weighed sample of steel was transferred to a preignited refractory boat, and 1 g of pure tin was added to act as flux. The boat was ignited at 1250° in a stream of pure oxygen (2 l./min) and the gas stream passed through 20 ml of the absorbant solvent contained in the titration cell. The solution was then titrated manually to the sharp thymolphthalein end-point. A determination took 2 min.

(C) *Simulated procedure for repetitive carbon determinations.* Known quantities of carbon dioxide were generated and transferred to 20 ml of previously neutralized absorbant/titrand solvent as in Procedure A. The carbon dioxide was titrated to the thymolphthalein end-point with 1*M* potassium hydroxide from an Agla syringe burette.

RESULTS AND DISCUSSION

The effect of water on the quality of the titration

The sharpness of the end-point in a titration has been expressed quantitatively in a number of ways, for example, the sharpness index[10] and the quality of a titration (*Q*).[11] The latter was selected as most convenient for this investigation and, for this purpose, was defined as "the change in potential of the indicator electrode on the addition of an 0·01-ml increment of titrant symmetrically distributed about the end-point." Titrations were performed in a medium containing 10% v/v of ethanolamine in pyridine to which was added small amounts of water. The solvent was first neutralized to remove the carbon dioxide present initially and then procedure A was followed. The amount of water present changed slightly during the titrations, owing to the addition of titrant, so the titration quality was plotted as a function of water concentration at the end-point as shown in Fig. 1. The curve shows a distinct maximum for a medium containing approximately 5% of water. This may be explained by considering two properties of the solvent system which vary with the water concentration, namely, the basicity of the solvent and the dielectric constant of the

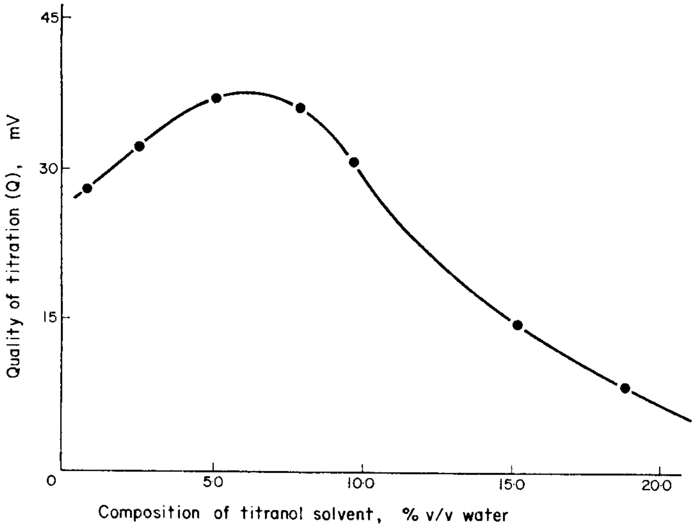

FIG. 1.—Variation of titration quality with the water content of a pyridine-based titrand solvent containing 10% v/v of ethanolamine.

medium. The first will increase with decreasing water concentration, and the dissociation constant of the acid K_a will therefore increase, *i.e.* the acid will become stronger as the water concentration decreases. The dielectric constant, however, would be expected to decrease with decreasing water concentration so that more work has to be done to separate the anion and the protonated species, with a consequent decrease in K_a and an apparent weakening of the acid. It is possible that at some optimum concentration of water, the value of K_a will reach a maximum and the sharpest end-point should then be observed. Semiquantitative equations supporting both of these hypotheses have been derived.[8]

In the present solvent system the sharpest end-points are obtained in a solvent containing approximately 5% v/v of water, but as the peak in Fig. 1 is broad, it is evident that small changes in water concentration will not seriously affect the sharpness of the end-points.

Determination of carbon in steel samples

The determination of carbon in a wide range of standard steels was carried out by procedure B and the results are given in Table I. Reproducibility tests were carried out on two samples and the results of these tests are given in Table II. The results show that the method is at least as accurate, convenient and rapid as that proposed by Jones *et al.*[2] Although the optimum water concentration was 5%, the concentration of water in the titrand was fixed at 2·3% to allow for the increase caused by the addition of titrant.

If the proposed changes in solvent system and titrant were to be adopted, it would be preferable to modify the apparatus of Jones *et al.*[2] The present cell design incorporates a 10-ml burette which necessitates the use of substantial volumes of titrant to obtain the necessary accuracy, and hence a dilute (0·05*M*) solution of potassium hydroxide. Addition of these quite large volumes of titrant, in the present

TABLE I.—DETERMINATION OF CARBON IN STANDARD STEELS BY PROCEDURE B

Sample	Carbon, certificate value, %	Sample weight, *g*	Carbon found, %
BCS 431	0·019	1	0·0180, 0·0195
BCS 265/2	0·048	1	0·049, 0·050
BCS 432	0·093	1	0·0935, 0·0935
BCS 294	0·145	1	0·1405, 0·139
BCS 433	0·19	1	0·185, 0·188, 0·190
BCS 270	0·22	0·5	0·228, 0·225
NBS 1168	0·26	0·5	0·268, 0·263
BCS 239/3	0·30	0·5	0·304, 0·304
BCS 212/1	0·36	0·5	0·369, 0·362
BCS 222	0·35	0·2	0·351, 0·351
BCS 225/1	0·385	0·2	0·388, 0·382
BCS 240/2	0·41	0·2	0·406, 0·412

Results standardized with respect to a 0·219% C standard from Mid-West Instrument Co. Inc., Belafield, Wisconsin, U.S.A. This gave results identical to those calculated from the known potassium hydroxide concentration.

TABLE II.—REPRODUCIBILITY OF ANALYSIS OF STANDARD STEELS BY PROCEDURE B

	Sample BCS 432 0·093% C	Sample BCS 239/3 0·30% C
Results (Same method of determination as in Table I).	0·091 0·091 0·092 0·092 0·093 0·093 0·093 0·093 0·093	0·309 0·307 0·297 0·306 0·301 0·305 0·294 0·301 0·304
Mean % C	0·0924	0·303
Standard deviation, % C	0·000866	0·00487
95% Confidence limits, % C	±0·0020	±0·0107

work, meant that the concentration of water increased considerably during titration and, except for the low-carbon steels, it was not practicable to carry out more than one determination in each aliquot of titrand/absorbant. The results in Tables I and II were therefore obtained with individual aliquots of solvent. In the nonaqueous method[2] it is usual to carry out several determinations in each aliquot of titrand and this factor would be considered a disadvantage of the present method. However, with suitable modification of the titration cell to include a standard microburette or, better, a microsyringe burette, a much more concentrated potassium hydroxide solution could be used with the consequent addition of much smaller amounts of water, enabling many successive titrations to be done in the same portion of solvent. To demonstrate this possibility procedure B was simulated in our own laboratory, by use of an Agla microsyringe burette and 1*M* potassium hydroxide (Procedure C). The results are shown in Table III. The weights of carbon taken are equivalent to 0·12% C, 0·06% C and 0·012% C in 1-g samples of steel. At least six consecutive analyses are possible at all concentration levels with more at lower levels. The limiting factor with respect to the continuous use of a single aliquot of solvent is undoubtedly the addition of water during the course of a titration. If this is reduced as described then the present method compares favourably with the standard method.[2] In no case was a precipitate detected, as has been reported elsewhere when potassium salts are used as titrants, presumably because of the presence of the water.

TABLE III.—CONSECUTIVE DETERMINATION OF SAMPLES OF CARBON USING THE SAME ALIQUOT OF ABSORBANT SOLVENT (PROCEDURE C)

Carbon taken, *mg*	1·2	0·6	0·12
Theoretical titration, *ml* of 1*M* KOH	0·1058	0·0529	0·0106
Observed titration, *ml* of 1*M* KOH	0·1057	0·0531	0·0120
	0·1056	0·0530	0·0100
	0·1056	0·0528	0·0106
	0·1056	0·0514	0·0108
	0·1054	0·0538	0·0096
	0·1062	0·0539	0·0108
	—	—	0·0106
	—	—	0·0102
	—	—	0·0107
Standard deviation, % C	0·00027	0·00090	0·00067
95% Confidence limits, % C	±0·0007	±0·0023	±0·0015

The main advantage of the proposed modification to the procedure of Jones *et al.*[2] is the replacement of the titrant, tetra-n-butylammonium hydroxide, and its solvent, benzene (or toluene)–methanol, with an aqueous solution of potassium hydroxide, and the consequent elimination of additional fire and toxicity hazards[12] in works laboratories, inherent in the use of a benzene-based titrant. The titrand is used under completely sealed conditions and does not contribute to these hazards. The use of the aqueous titrant also reduces the overall cost of the determination. The speed of the determination is not altered, since this is limited by the rate of combustion. The present procedure is most unusual in that the presence of small amounts of water in a basically non-aqueous titration system is shown to be beneficial to the performance of the titration.

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Zusammenfassung—Es wird gezeigt, daß die Zugabe von 5% Wasser zu dem nichtwäßrigen Lösungsmittel bei der titrimetrischen Bestimmung von Kohlenstoff in Stahl die Titration verbessert. Es werden Änderungen an der Vorschrift vorgeschlagen, die den Ersatz des normalen Titranten Tetra-n-butylammoniumhydroxid in Benzol-Methanol durch eine wäßrige Kaliumhydroxidlösung erlauben. Die angegebene Vorschrift wurde zur Analyse einer großen Anzahl von Standard-Stahlproben verwendet.

Résumé—On démontre que l'addition de 5% d'eau au solvant non aqueux pour le dosage titrimétrique du carbone dans l'acier améliore la marche du titrage. On propose des modifications à la technique qui permettent de remplacer l'agent de titrage normal, l'hydroxyde de tétra-*n*-butylammonium dissous en benzène-mèthanol par une solution aqueuse de potasse. La technique proposée a été appliquée à l'analyse d'une large gamme d'échantillons étalons d'acier.

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ZUR ANALYSE DES FLUßSPATS

DIE SCHNELLANALYSE DES FLUßSPATS DURCH DESTILLATIVE ABTRENNUNG UND ALKALIMETRISCHE BESTIMMUNG SEINES FLUORGEHALTES

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Zusammenfassung—Es wird eine Destillationsapparatur beschrieben, mit welcher innerhalb einer Stunde der Fluoridgehalt einer Flußspatprobe direkt bestimmt werden kann. Die Kinetik der Destillation wird durch potentiographische Aufzeichnung der Fluor-Transportkurve untersucht, Geschwindigkeitskonstante und Halbwertsdauer werden bestimmt, sowie eine Beziehung zwischen Bestimmungsfehler und Destillationsdauer angegeben. Umwandlung der Exponentialfunktion in eine geometrische Reihe ermöglicht die Berechnung des Gesamtfluorids einer Probe als Reihensumme und damit als Grenzwert für eine unendlich lange Destillationsdauer. Die Fehlerstatistik ergibt für Routinebestimmungen eine Standardabweichung $s \leq \pm 0{,}1\%$ CaF_2.

Die von H. H. Willard und O. B. Winter eingeführte Destillationsmethode[1] trennt das Fluor als Hexafluorokieselsäure (HFKS) von nichtflüchtigen Begleitern. Danach kann es direkt maßanalytisch bestimmt werden. Die Titration mit einem der zahlreichen in der Literatur vorgeschlagenen Titranten erfordert die Beachtung vielfältig wechselnder Titrationsbedingungen und die Hinnahme systembedingter Beschränkungen.

Die Stöchiometrie der Reaktionen ist die Resultante aus vielen Parametern, unter denen die absolute Menge des zur Titration gelangenden Fluorids, seine Konzentration, der pH-Bereich, Gegenwart von Puffer-bzw. Neutralsalzen, Kieselsäure und Spuren der zur Destillation verwendeten Mineralsäure vor allem genanne seien. Jede im Titriermedium neu auftretende oder wegfallende Komponentt erfordert eine neue Eichung. Der Titer einer Maßlösung ist nur innerhalb des engen Bereiches der bei seiner Feststellung eingehaltenen Bedingungen gültig. Im Anschluß an eine Destillation wird er zwangsläufig auch von der Destillationsausbeute abhängig. Diese wird u.a. von der Geometrie und den Betriebsbedingungen der Destillationsapparatur mitbestimmt. Bei Apparaturen gleichen Typs und konstanten, optimierten Betriebsbedingungen ist sie reproduzierbar und wird zweckmäßig in den Titer der Maßlösung mit einbezogen.[2,3] Um im Bereich linearer Beziehungen zwischen Fluoridgehalt und Titrantverbrauch zu bleiben, ist entweder eine Aliquotierung des Destillats oder eine einschneidende Reduzierung der Einwaage notwendig. Letztere muß in jedem Falle einen repräsentativen Querschnitt durch die zu untersuchende Lieferung oder Charge darstellen und kann deswegen bei festem Material nicht ohne Gefahr beliebig verkleinert werden. Ein weiteres ungünstiges Moment der gebräuchlichen Titrationsverfahren für Fluorid ist die durchweg schwierige Feststellung des genauen Titrationsendpunktes durch visuelle Beobachtung. Durch die kontrastarmen

Farbumschläge der wenigen brauchbaren Indikatoren wird das Meßergebnis zusätzlich noch von Beleuchtungsfaktoren und der individuellen Farbtüchtigkeit des Ausführenden abhängig. Wenn auch eine registrierende, photometrische Titration (Metrohm-System) von den subjektiven Einflüssen befreit, die anderen oben genannten Beschränkungen bleiben bestehen. Auch für die Photozelle ist nicht jeder Indikatorumschlag gleichwertig. Eine sorgfältige Auswahl geeigneter Verbindungen und ein genaues Studium der während der Titration einzuhaltenden Milieubedingungen ist unumgänglich und für eine Anzahl Indikator-Titrantpaare von uns kürzlich beschrieben worden.[2–5]

Abgesehen davon, daß die apparative Ausrüstung nicht überall vorhanden ist oder unter Umstünden nicht eingesetzt werden kann, umgeht man die meisten der genannten Schwierigkeiten, wenn die durch Destillation abgetriebene HFKS alkalimetrisch titriert wird. Es war jedoch notwendig geeignete Destillationsapparaturen zu bauen und Betriebsbedingungen für diese aufzufinden, welche es gestatten, bei einer zwischen 0,5 und 1 g betragenden Einwaage das gesamte Destillat zu einer alkalimetrischen Bestimmung heranzuziehen.

Die Titration kann mit Bürette und Indikator oder an der Glaselektrode ausgeführt werden. Neue Möglichkeiten bietet die Potentiometrie insofern, als es mit ihrer Hilfe möglich ist den Fluortransport aus dem Sumpf in das Destillat im pH-stat-Verfahren potentiometrisch während der Destillation mitzuschreiben. Um unverzerrte Kurven zu erhalten, muß die Titriergeschwindigkeit etwas größer gehalten werden als die Transport-(Destillations-)geschwindigkeit. Die Transportkurven bestätigen das von R. Valach [Zitat 20, mit umfassender Bibliographie älterer Arbeiten.] hergeleitete Geschwindigkeitsgesetz 1. Ordnung für diesen Vorgang. Fraktionierte Vermessung der Transportkurven, gleichbedeutend mit einer Umformung der e-Funktion in eine unendliche, konvergente, geometrische Reihe liefert deren Gliedquotienten q. Dieser gestattet die Berechnung des Gesamtfluorgehaltes als Reihensumme, der Halbwertszeit und der effektiven Geschwindigkeitskonstanten K des Transportvorganges. Durch die Reihensumme wird man vom Zwang der Zuendeführung einer Destillation befreit. Vorzeitiger Abbruch einer Destillation—im Hinblick auf den Funktionscharakter und die Beschränkung auf praktikable Transportzeiten bzw.—volumina wird jede Destillation vorzeitig abgebrochen—spielt keine wesentliche Rolle mehr, weil die Reihensumme das Ergebnis für eine unendliche Transportzeit ergibt. Das Verhältnis Transportzeit:Halbwertszeit gibt einen ersten Anhaltspunkt bezüglich des bei einer Destillation zu erwartenden Fehlbetrages. Der Bestimmung entgehen nur 0,1 bzw. 0,01% CaF_2 sofern die Destillationsdauer 10 bzw. 14 Halbwertszeiten umfaßt.

EXPERIMENTELLER TEIL

Destillationsapparaturen

In der Literatur sind eine ganze Anzahl Destillationsapparaturen teils für Fluor, teils für andere mit Wasserdampf flüchtige Verbindungen beschrieben worden.[6–17] Die übliche Anordnung des Wasserdampfentwicklers außerhalb der eigentlichen Destillationsapparatur erfordert Platz und Maßnahmen zur ausreichenden Überhitzung des Wasserdampfes, um eine Verdünnung des Destillationssumpfes durch Kondensat zu verhindern. Der Kondensatbildung läßt sich durch eine Schachtelung von Dampfentwickler und Destillationsblase am wirksamsten begegnen. Hohe Destillationstemperatur und Mitreißeffekte durch zu große Dampfgeschwindigkeit haben übermäßige und schwankende Blindwerte im Gefolge. Eine alkalimetrische Bestimmung des Fluors hat nur dann

Aussicht auf Anwendung im Routinebetrieb eines Laboratoriums, wenn der durch übergehende WWS* verursachte Blindwert so klein und reproduzierbar gehalten werden kann, daß er keine zeitraubende zusätzliche Korrekturbestimmung erfordert. Mäßigung der Dampfgeschwindigkeit und Herabsetzung der Destillationstemperatur waren damit angezeigt.

Destillationsapparatur für schnelle Reihenbestimmungen des Fluors in Flußspat

Die Abbildung 1 zeigt schematisch Form und Aufbau der Destillationsapparaturen, mit welchen die Untersuchungen ausgeführt wurden. Das Destilliergefäß (*1*) hat zylindrische Form. Der Wasserdampfentwickler (*2*) (bei 80% Füllstand 1,4 l. Fassungsvermögen) umschließt es allseitig und dämmt es gegen stärkere Wärmeverluste an die Umgebung ab. Gleichzeitig wirkt der Wärmeübergang vom Destilliergefäß zum Wasserdampfentwickler einer unerwünschten, hohen Überhitzung des Destillationsgutes entgegen. Der Füllstutzen (*3*) des Wasserdampfentwicklers kann während der Destillation durch einen Hahn (*3a*) verschlossen werden. Der Hahn bleibt bis zum gleichmäßigen Sieden des Wassers offen. Der Steuerhahn (*4*) befindet sich während der Destillation in Stellung (*4a*). Nach Schließen des Hahnes (*3a*) strömt der Dampf durch eine seitliche Öffnung des Steuerhahnes (*4*)

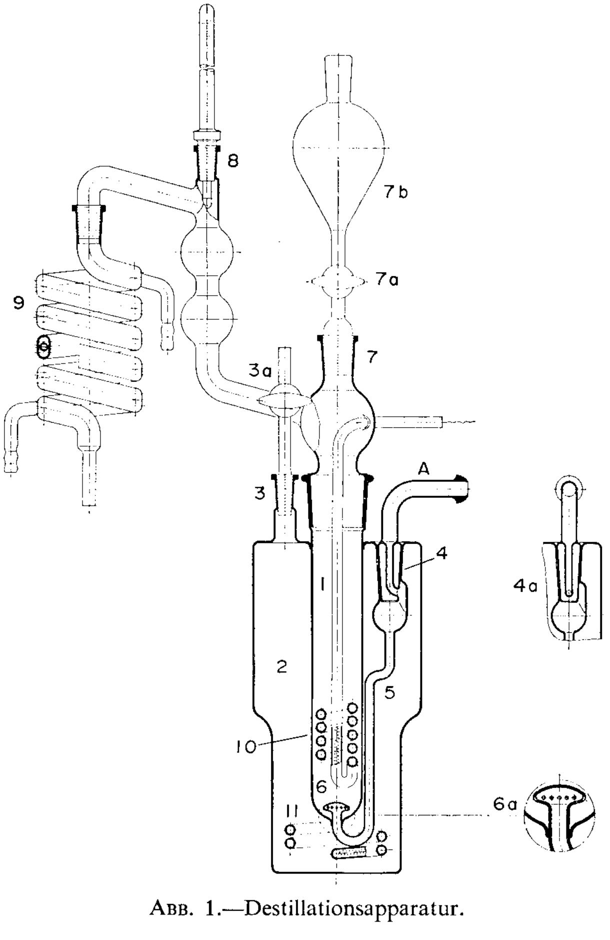

Abb. 1.—Destillationsapparatur.

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* Im weiteren Text wird für die zur Destillation des Fluors angewendete Mineralsäure die Abkürzung WWS = Willard-Winter-Säure verwendet. Bei Flußspat verwenden wir ausschließlich 50%ige Perchlorsäure.

† DBGM 69 28232 (A. Döhr). Hersteller: Glusapparatebau Herbert Miethke, D 509 Leverkusen-Bürrig, Kyllstraße 11. Unsere Apparaturen sind seit Jahren in Betrieb. Der Tauchsieder (Nr. *10*, Abb. 1), dessen überhitzte wandung durch primär entstehende Fluorwasserstoffsäure bevorzugt angegriffen wird, ist leicht zu ersetzen.

in die Zuleitung (*5*) zum pilzförmigen Verteiler (*6*). Dieser hat auf seinen Umfang gleichmäßig verteilte, schräg nach unten gerichtete, *ca.* 1-mm große Öffnungen, wie in Abb. 1, (*6a*) angedeutet ist. Der zum Boden des Destilliergefäßes gerichtete Dampfstrom reißt das zu Beginn der Destillation am Boden liegende Analysenmaterial mit sich hoch, so daß es in feiner Verteilung mit der WWS ausreagieren kann. Gleichzeitig drückt er, für einen Augenblick fast den gesamten Querschnitt des Destilliergefäßes beanspruchend, den Sumpf eine kurze Strecke vor sich her, bevor er sich in einzelne Blasen auflöst. In dem durch die Beheizung (*10*) verengten Querschnitt verzögert sich der Rücklauf der geförderten Flüssigkeit. Das Zusammenwirken von kurzzeitiger, mammutpumpenähnlicher Förderung und Rücklauf erzeugt eine Zone intensiver Wirbelung. Dadurch bleibt die Einwaage in ständigem Kontakt mit unverbrauchter WWS und die große Berührungsfläche zwischen Dampf und Sumpf begünstigt die schnelle Entfernung des flüchtigen Reaktionsproduktes aus dem Reaktionsraum. Drei Umlenkungen und zwei kugelförmige Erweiterungen des Dampfweges zum Kühler (*9*) halten vom Dampfstrom mitgerissene Flüssigkeitströpfchen wirksam zurück. Die leichte Kondensation in diesem weder wärmeisolierten noch beheizten Apparateteil erzeugt einen geringen Rücklauf, welcher die abgefangenen Tröpfchen in den Sumpf zurückspült. Die Beschickung der Apparatur mit Analysengut geschieht durch den Schliff (*7*). Die WWS wird aus dem Tropftrichter (*7b*) durch Öffnen des Hahnes (*7a*) in das Destilliergefäß gegeben.

Das Thermometer (*8*) dient zur Messung der Dampftemperatur vor Eintritt in den Kühler. Es ist die Meßstelle der Kopftemperatur. Der Henkelkühler (*9*) ist ein zur Wendel aufgerollter Liebigkühler. Das Gefälle der Wendel muß so steil gehalten werden, daß das Kondensat gleichmäßig ablaufen kann. Auch andere Intensivkühler sind brauchbar.

Die Beheizungen (*10*) und (*11*) sind so aufeinander abzustimmen, daß der Inhalt jedes Gefäßes nach 8–10 Minuten zu sieden beginnt. Die Heizleistungen von *ca.* 270 W für (*10*) und *ca.* 750 W für (*11*) werden mit Regeltransformatoren eingestellt und brauchen nur gelegentlich nachreguliert zu werden. Die Innenbeheizung (*10*) des Destilliergefäßes hält die Sumpftemperatur immer etwas über der Wassertemperatur im Wasserdampfentwickler. Der Sumpf hat bei Siedebeginn des Wassers eine Temperatur von *ca.* 128°, also den Siedepunkt der WWS (126–128°) erreicht. Damit wird eine Verdünnung der WWS (*ca.* 50%ige Perchlorsäure) durch anfänglich kondensierenden Wasserdampf vermieden. Die Sumpftemperatur hält sich während der Destillation etwa bei 125°. Erst gegen Ende, bei abgesunkenem Wasserstand im Wasserdampfentwickler, steigt sie langsam wieder gegen 128° hin an. Die Kopftemperatur bewegt sich zwischen 104–110°, meistens bleibt sie zwischen 107–109° stehen. Unter diesen Bedingungen stellen sich Dampfgeschwindigkeiten um 22 ml/Minute, als Kondensat gemessen, ein. Das Sumpfvolumen (*ca.* 120 ml) bleibt praktisch unverändert.

Die Destillation wird beendet durch Abschaltung der Beheizungen und sofortiges Öffnen der Hähne (*3a*) und (*7a*), um Druckausgleich mit der Atmosphäre zu ermöglichen. Alle Schliffkerne der Apparatur, außer dem Steuerhahn (*4*) und dem Kugelschliff an (*A*) tragen Plastikmanschetten. Durch sie wird ein Schmiermittel zur Dichtung der Schliffe entbehrlich und ein Festsetzen sicher verhindert.

Reinigung der Apparatur

Nach Entfernung des Destillates wird der Steuerhahn aus der Destillationsstellung (*4a*) um 90° in Stellung (*4*) gedreht (in Abb. 1 ist die Apparatur in Spülstellung gezeichnet). Die in Stellung (*4a*) bestehende Verbindung vom Wasserdampfentwickler (*2*) zum Destilliergefäß (*1*) wird dadurch gesperrt und dieses mit dem Absaugstutzen (*A*) des Steuerhahnes verbunden. Nach Entfernen einer in Abb. 1 nicht gezeichneten, während der Destillation als Verschluß dienenden kleinen Kugelschliffkappe, wird die Apparatur an eine Wasserstrahlpumpe angeschlossen. Ohne die weitere Abkühlung der Apparatur abzuwarten saugt man nach Schliessen des Hahnes (*7a*) vom Kühlerende her, also entgegen der Destillationsrichtung, stoßweise destilliertes Wasser durch die Apparatur bis alle Destillationsrückstände entfernt sind. Der Hahn (*3a*) bleibt während der Reinigungsoperation offen. Sofort nach beendeter Reinigung kann die Apparatur neu beschickt und die nächste Destillation begonnen werden, nachdem der Steuerhahn in Destillationsstellung (*4a*) zurückgedreht und der Absaugstutzen (*A*) mit seiner Kappe verschlossen worden ist.

Die Ausführung der Destillation mit Flußspat

Reagenzien und Lösungen.

Perchlorsäure *p.a.* (1,67) oder auf 50% Säuregehalt verdünnte Perchlorsäure.
Natronlauge, 1*M*.
Silberperchlorat.

Geräte.

Magnetrührwerk.
Laborlift, Untersatz für die Vorlage.

Plastikbecher, Mindestfassungsvermögen 1 Liter.
Mikrokugelmühle, Typ Grindomat MM (Fa. Retsch) oder ähnliche Typen.
Radiometer Titrator und Titrigraph.
Motorbürette ABU 1 S 1 oder ABU 12 (Radiometer).
Kombinierte Glas-Kalomelelektrode GK 202 B (Einstabmeßkette) von Radiometer.
Sieb mit 100 Maschen/mm², Gewebe Nr. 100, DIN 1171, lichte Maschenweite 0,06 mm.

Beschickung der Destillationsapparatur. Vom Analysenmuster werden 3 g in der Mikrokugelmühle gemahlen bis alles Material das Sieb passiert (Zeitbedarf max. 15 Minuten, Kornfeinheit ⩽0,06 mm). Auf der Analysenwaage werden 700 mg des gesiebten Materials abgewogen. Durch einen langhalsigen Pulvertrichter wird die Einwaage in das Destillationsgefäß geschüttet und der Trichter mit wenig Wasser saubergespült. Nach Verschließen des Schliffs (*7*, Abb. 1) durch den Aufsatz (*7a*, *b*) gibt man 70 ml Perchlorsäure (1,67) und soviel Wasser (*ca.* 50 ml) in den Tropftrichter (*7b*), daß die Mischung nach dem Einlaufen in das Destilliergefäß etwa 10–20 mm über der obersten Windung des Tauchsieders (*10*, Abb. 1) steht, oder direkt 50%ige Perchlorsäure bis zur gleichen Höhe. Ein Zusatz von Silberperchlorat zur Eliminierung von Chloridionen ist bei Flußspat nicht unbedingt erforderlich. Soll er gemacht werden, gibt man 0,5–1 g des Salzes in fester Form zuerst in das Destilliergefäß oder bringt es in der WWS gelöst mit dieser ein. Der Wasserdampfentwickler ist über den in Stellung *4a*, (Abb. 1) stehenden Steuerhahn mit dem Destillationsgefäß verbunden. Unter den Kühler setzt man einen Plastikbecher, welcher 100 ml Wasser enthält, so daß die Mündung des verlängerten Kühlerablaufrohres und die Einstabmeßkette eintauchen (in Abb. 1 nicht gezeichnet). Das Kühlwasser wird angestellt und die Beheizungen (*10*, *11*, Abb. 1) eingeschaltet. Nach 8–10 Minuten (6–8 Minuten bei noch durchgewärmter Apparatur) beginnt das Sieden in beiden Gefäßen. Sobald Kondensat in die Vorlage gelangt, wird die Titrierautomatik gestartet (Kopftemperatur 100°).

Einstellungen an der Titrierautomatik zur potentiographischen Aufzeichnung des Fluortransports im pH-stat-Verfahren (Transportkurve)

Titrator (Radiometer TTT 1c).

Schalter
End-point pH 7.6
Delay of shut-off ∞
Selector: Titration up-scale
Range: pH 20°C
Proportional band: 0.1

Titrigraph (Radiometer SBR 2c).

Schalter

Registrierung:	pH-stat
Kompensation:	0
Temp. Berichtigung:	20°C
Papiervorschub:	10 mm/Minute

Motorbürette, 25 ml
Schalter: Speed (Titriergeschwindigkeit, Kolbenvorschub) 10 oder 20%/Minute.

Während oder nach der Destillation kann auch eine normale Titration durchgeführt werden. Die dazu nötigen Einstellungen am Gerät werden als bekannt vorausgesetzt und hier nicht weiter darauf eingegangen. Der Verbrauch an Natronlauge wird von der Motorbürette digital angezeigt, bzw. an den mitgeschriebenen Kurven bei pH 7,6 abgelesen (Abb. 2) und nach der Formel (*a*) oder (*b*) der gesuchte Prozentgehalt berechnet.

$$\%\,\mathrm{F} = \frac{(\mathrm{ml\ 1N\ NaOH} - 0{,}04\ \mathrm{ml}) \cdot 1{,}900}{\mathrm{Einwaage\ (g)}} \tag{a}$$

$$\%\,\mathrm{CaF_2} = \frac{(\mathrm{ml\ 1N\ NaOH} - 0{,}04\ \mathrm{ml}) \cdot 3{,}904}{\mathrm{Einwaage\ (g)}} \tag{b}$$

Sind keine Geräte vorhanden, kann gegen Bromthymolblau (Umschlagsbereich pH 6–7,6) titriert werden. Die Indikatorlösung ist 0,1%ig und wird mit 20%igem Alkohol angesetzt. Auf ein Destillatvolumen von *ca.* 1 Liter nimmt man 10 Tropfen Indikatorlösung. Es wird heiß (60°) auf ein reines Blau titriert. Der Umschlag ist auch bei Lampenlicht gut zu sehen.

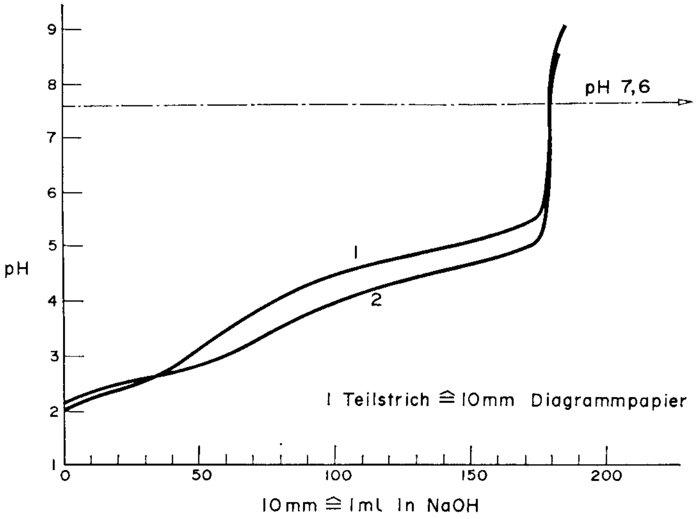

ABB. 2.—Titrationskurven.
1—Titration während der Destillation; *2*—Titration nach der Destillation.

DISKUSSION

Die potentiometrische und photometrische Bestimmung des Destillationsblindwertes bei Verwendung von Perchlorsäure als WWS

Mit und ohne Flußspat wurde für diese Bestimmungen eine *ca.* 50%ige Perchlorsäure eingesetzt. Destilliert wurde ohne Silberperchloratzusatz, so daß der alkalimetrisch ermittelte Blindwert nicht nur die mitgeführte Perchlorsäure sondern auch deren flüchtige Verunreinigungen erfaßt, sofern diese Säuren sind oder zu solchen hydrolysiert werden. Die Titrationen wurden mit der oben erwähnten Titrierkombination von Radiometer (0,25 ml Kolbenbürette) ausgeführt. Anschließend an die potentiographische Titration des Destillates wurde das Perchlorat photometrisch-nach bestimmt.[18,19] Blindwertsunterschiede zwischen Destillationen ohne und mit Flußspat, an mehreren Apparaturen, von mehreren Mitarbeitern unter Einsatz von Flußspat verschiedener Provenienz durchgeführt, ergaben sich innerhalb der Meßgenauigkeiten nicht. Die statistische Auswertung[24,25] der in einem Zeitraum von 4 Jahren vorgenommenen Bestimmungen lieferte ein Blindwertmittel $\bar{x} = 0{,}035$ mMol $HClO_4$/Liter Destillat mit einer Standardabweichung $s = \pm\, 0{,}007$ mMol $HClO_4$/Liter aus $n = 95$ Bestimmungen; davon sind 70 Bestimmungen photometrisch mit, 25 alkalimetrisch ohne Flußspateinsatz ausgeführt worden.

Das Reaktionsprodukt der Willard-Winter-Destillation

Den Untersuchungen liegen routinemäßig ausgeführte Destillationen zugrunde. Mit Rücksicht auf die nachfolgende Verarbeitung der Destillate wurde potentiometrisch, teilweise auch im pH-stat-Verfahren neutralisiert.

Die Kieselsäure im Destillat wurde nach Maskierung des Fluors mit Borsäure als Molybdatokieselsäure aus perchlorsaurer Lösung mit MIBK extrahiert, der Extrakt mit verdünnter Perchlorsäure gewaschen, die Heteropolysäure anschließend mit

Natronlauge reextrahiert. Nach Ansäuren und anschließender Reduktion des Molybdän(VI) zu Molybdän(V) mittels überschüssiger Titan(III)-Lösung wurde das entstandene Molybdän(V) potentiometrisch mit Cer(IV)-sulfat titriert. Es treten zwei Potentialsprünge auf. Der erste zeigt die Beseitigung des Titan(III)-Überschusses an; alles Molybdän liegt jetzt fünfwertig vor. Der zweite Potentialsprung beendet die Oxidation zu Molybdän(VI). Die Bestimmung hat im Bereich 3,2–32 mg Molybdän eine Standardabweichung von $s = \pm 0{,}045$ mg Mo. Als Mittelwert ergaben 21 untersuchte Destillate ein Molverhältnis $F:Si = (5{,}9 \pm 0{,}16):1$. Die Destillationen wurden ohne Zusatz von Glas-bzw. Quarzpulver als Siliciumlieferanten ausgeführt. Abbildung 2 zeigt potentiographische Titrationskurven von Destillaten, welche nach Verlauf und Sprungbereich mit der von M.L. Malaprade[21] angegebenen Neutralisationskurve der Hexafluorokieselsäure übereinstimmen. Mit einem Testflußspat von 99,7% CaF_2-Gehalt durchgeführte Destillationen lieferten Titrationskurven, welche bei pH = 7,6 ausgewertet, nach Abzug von 0,04 ml Blindwert für mittransportierte WWS, $\bar{x} = 99{,}7\%$ CaF_2, $s = \pm 0{,}10$ aus $n = 35$ zeitlich verteilten Bestimmungen ergaben.

Die apparativen Formparameter der Transportkurve

Die Transportreaktion des Fluors folgt einem Geschwindigkeitsgesetz 1. Ordnung.[20] Die Titration dagegen wird mit konstanter Geschwindigkeit ausgeführt. Sie folgt einem Fahrstrahl f (Abb. 3), dessen Steigung durch das Verhältnis Titriergeschwindigkeit/Papiervorschub gegeben ist. Ist $m_{D,t}$ die zur Zeit t im Destillat anzutreffende Fluor-, $m_{OH',t}$ die bis dahin zugeführte Natronlaugemenge, dann bestimmt das Verhältnis $m_{D,t}/m_{OH',t}$ die graphische Wiedergabe der Transportreaktion. Zu Beginn einer Destillation wird viel Fluor in die Vorlage transportiert, daher ist $m_{D,t}/m_{OH',t} > 1$, d.h. das Gerät titriert zu langsam, die Exponentialkurve und damit der Soll-pH-Wert 7,6 wird nicht erreicht, das Destillat bleibt sauer. Erst im Schnittpunkt von Transportkurve und Fahrstrahl $(t_S, m_{D,ts})$ ist $m_{D,ts}/m_{OH',ts} = 1$. Alle im Destillat vorhandene HFKS ist umgesetzt und die Exponentialkurve erreicht.

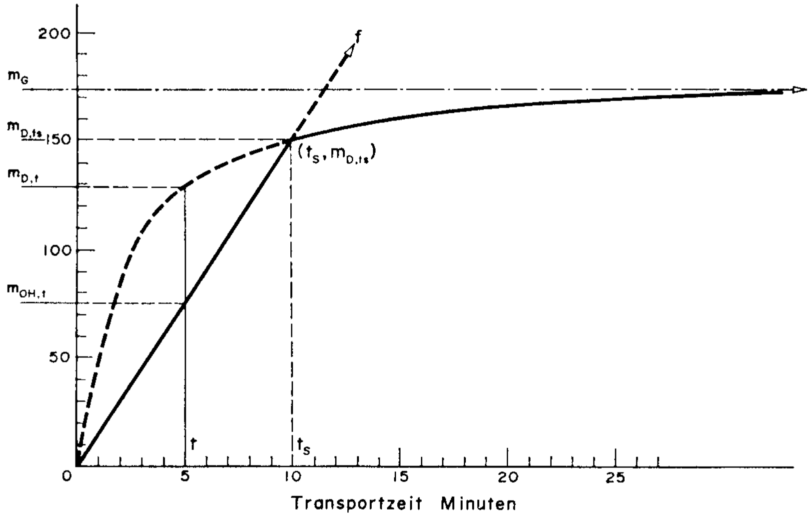

ABB. 3.—Wiedergabe der Transportreaktion.

Für $t > t_s$ schreibt das Gerät die unverzerrte Transportkurve mit. Die Titriergeschwindigkeit ist nun größer als die Transportgeschwindigkeit, aber der Fall $m_{D,t}/m_{OH',t} < 1$, welcher ein Übertitrieren bedeutete, wird nicht realisiert, weil das Gerät die Bürette stoppt, sobald der Soll-pH-Wert erreicht ist. Abbildung 4 zeigt einige Kurven, welche das verdeutlichen: Je steiler die linearen Fahrstrahlabschnitte der Diagramme verlaufen, umso länger wird das erfaßte Transportkurvenstück.

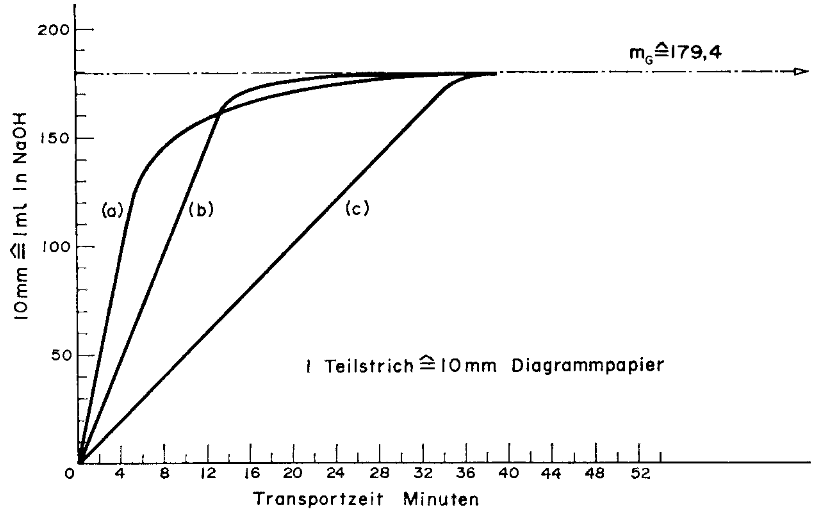

Abb. 4.—Einfluß des Kolbenvorschubs.
Kolbenvorschub: Kurve A—10%/min; Kurve *B*—5%/min; Kurve *C*—2%/min.
Papiervorschub 5 mm/min.

Greift man zu höheren Titriergeschwindigkeiten (>50% Büretten-Vol./Minute), so werden die Fahrstrahlabschnitte und die Kurve treppenförmig aufgezeichnet und können nicht exakt vermessen werden. Die mäßig verzögerte Aufzeichnung mit Titriergeschwindigkeiten von 20% oder 10% Kolbenvorschub/Minute (Nachlauftitration) bedeutet jedoch keinen Nachteil. Bei der theoretischen Herleitung der Transportkurvengleichung wird davon ausgegangen, daß die Anfangskonzentration des Fluors im Sumpf eine feste Größe ist. Weil Flußspat in der WWS ohne Wärmeeinwirkung nicht löslich ist, ist in der Praxis diese Bedingung nur angenähert erfüllt. Zwar löst sich die Flußspateinwaage während der Heizperiode zum größten Teil in der noch unbewegten Säure. Ein Rest, wahrscheinlich der resistentere Teil der Probe, löst sich vollständig erst, nachdem die Wirbelung des Sumpfes durch den Dampf eingesetzt hat, wodurch die Substanz mit unverbrauchter Säure in Berührung kommt. Gleichzeitig verarmt der Sumpf durch die Transportreaktion, so daß die Anfangskonzentration des Fluors infolge Verlust und Nachlieferung undefiniert bleibt. Der Anfangsteil einer Transportkurve wäre daher wertlos, auch wenn er graphisch faßbar wäre.

Die Transportgleichung der Willard-Winter-Destillation

Das mit der Einwaage eingebrachte Gesamtfluor (m_G) verteilt sich während der Destillation auf Sumpf und Destillat. Die Fluormenge im Destillat wächst um den gleichen Betrag um welchen der Sumpf verarmt, so daß stets die Beziehung

$$m_G = m_{D,t} + m_{S,t} \tag{1}$$

erfüllt ist. Mit $m_{D,t}$ und $m_{S,t}$ sind die zur Zeit t im Destillat bzw. Sumpf vorhandenen Fluormengen bezeichnet. Der glatte Verlauf der Destillation mit Flußspat unterschiedlicher Qualitäten, die gute Reproduzierbarkeit der Ergebnisse, ihre Übereinstimmung mit den Werten anderer Methoden beweist in ausreichendem Maße, daß die Abtrennung des Fluors ohne Komplikationen vor sich geht, d.h. die Bildung von Fluorokomplexen in einem das Meßergebnis beeinträchtigenden Maße ist nicht anszunehmen. Ausgehend von der allgemeinen Differentialgleichung einer Reaktion 1. Ordnung ergibt die Rechnung, daß die Fluormenge im Sumpf nach

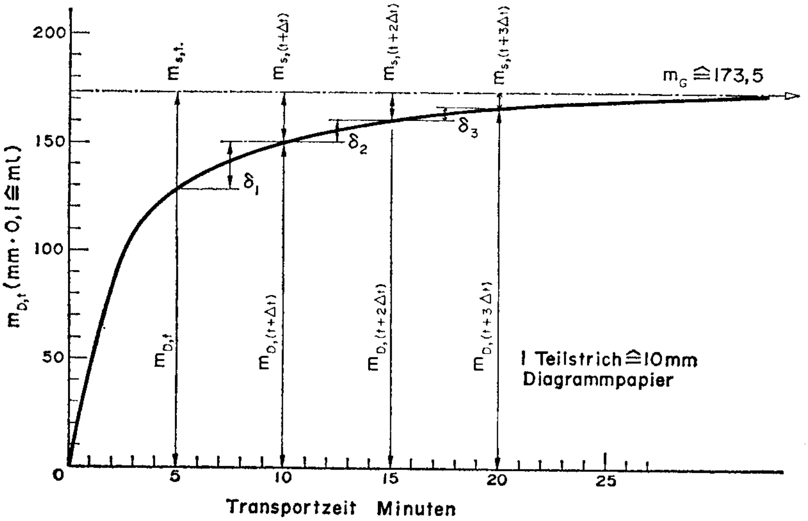

Abb. 5.—Auswertung der Titrationskurve.
Papiervorschub 10 mm/min; Kolbenvorschub 10%/min.

$$m_{S,t} = m_G \cdot \exp(-Kt) \tag{2}$$

abnimmt. K bezeichnet die Geschwindigkeitskonstante der Transportreaktion, t die Destillationsdauer.

Wird Gl. (2) in Gl. (1) eingesetzt und diese nach $m_{D,t}$ aufgelöst, so erhält man als Transportgleichung

$$m_{D,t} = m_G[1 - \exp(-Kt)]. \tag{3}$$

Auswertung der Transportkurve

Während die Fluorbestimmung in diskreten Fraktionen einer Destillation nur ein grobes Näherungsverfahren darstellt, bietet die Transportkurve einen mathematisch einwandfreien Übergang von der Exponentialfunktion zur geometrischen Reihe (Abb. 5).

Der Gl. (1) ist zu entnehmen, daß das Glied $m_{S,t}$ den Fehler darstellt, den man machen würde wenn die Destillation zum Zeitpunkt t abgebrochen wird. Geht man von einem beliebig gewählten Kurvenpunkt der Abb. 5 mit den Koordinaten $(t, m_{D,t})$

in gleichen Zeitinkrementen Δt auf der Zeitachse weiter (Fraktionierung), so wächst der Natronlaugeverbrauch innerhalb der Zeitspanne Δt jeweils um:

$$\delta_1 = m_{\mathrm{S,t}}[1 - \exp(-K\,\Delta t)] \tag{4}$$

$$\delta_2 = m_{\mathrm{S,t}} \cdot \exp(-K\,\Delta t)[1 - \exp(-K\,\Delta t)] \tag{5}$$

$$\delta_n = m_{\mathrm{S,t}} \cdot \exp(-(n-1)K\,\Delta t)[1 - \exp(-K\,\Delta t)]. \tag{6}$$

Aus den Gl. (4) bis (6) ergibt sich der Gliedkoeffizient der geometrischen Reihe zu

$$q = \delta_n/\delta_{n-1} = \exp(-K\,\Delta t) \tag{7}$$

Weil stets $\delta_n < \delta_{n-1}$ ist, wird auch $q < 1$ und damit ist das Konvergenzkriterium der Reihe erfüllt. Die zur Umsetzung erforderlichen Natronlaugevolumina $\delta_1 \ldots . \delta_n$ verringern sich nach δ_1; $\delta_1 \cdot q$; $\delta_1 q^2 \ldots$ usw.; ihre Summe ergibt den im Destillat am Punkt $(t, m_{\mathrm{D,t}})$ noch nicht abdestillierten Fluorrest im Sumpf:

TABELLE I.—BEISPEIL FÜR DIE BERECHNUNG EINER TITRATION

t_{tr}, Min	$m_{\mathrm{D,t}}$, mm	δ_n, mm	q	$m_{\mathrm{S,t}}$, mm	m_{G} (Gl. 1), mm
10	150,5	10,3		23,4	173,9
15	160,8	5,7	0,554	12,9	173,7
20	166,5	3,2	0,562	7,3	173,8
25	169,7	1,8	0,565	4,1	173,8
30	171,5	1,0	0,555	2,3	173,8
35	172,5	0,6	0,600	1,4	173,9
40	173,1				
			$\bar{q} = 0{,}57$		$\bar{m}_{\mathrm{G}} = 173{,}8$ mm $= 17{,}38$ ml

Fraktionierintervall $\Delta t = 5$ Minuten, ab 10 Minuten Transportzeit (t_{tr}) Titriergeschwindigkeit 10%/Minute. 10 mm Ordinatenstrecke = 1 ml NaOH (1*N*). Digitalanzeige der Motorbürette = 17,36 ml NaOH (1*N*) bei Abbruch der Destillation nach $t_{\mathrm{tr}} = 55$ Minuten. Photometrischer Blindwert 0,03 ml NaOH (1*N*).

$$m_{\mathrm{S,t}} = \sum_{n=1}^{\infty} \delta_n = \delta_1/(1-q). \tag{8}$$

Das Gesamtfluor m_{G} einer Probe kann somit als Reihensumme berechnet werden. In der Tabelle I ist ein Beispiel zusammengefaßt.

Weil die Reihensummierung sich auf eine unendlich lange Destillationsdauer erstreckt, müßte der errechnete m_{G}-Wert immer etwas größer ausfallen, als der durch Titration des Destillates praktisch bestimmte Fluorgehalt, der durch "vorzeitigen" Abbruch mit einem systematischen Minusfehler behaftet anzunehmen ist, solange *K*, die effektive Geschwindigkeitskonstante in Gl. (2) unbekannt ist.

Die Ermittlung der effektiven Geschwindigkeitskonstanten K *aus der Transportkurve*

Löst man Gl. (2) nach *K*, so erhält man

$$K = -\frac{\log m_{\mathrm{S,t}}/m_{\mathrm{G}}}{0{,}43_4 \cdot t} \tag{9}$$

Nach Substitution von $m_{S,t}/m_G$ durch den aus Gl. (1) folgenden Ausdruck $m_{S,t}/m_G = (1 - m_{D,t}/m_G)$, wird

$$K = -\frac{\log(1 - m_{D,t}/m_G)}{0{,}43_4 \cdot t} \qquad (10)$$

erhalten, womit eine Aufzeichnung der Transportkurve in der bekannten halblogarithmischen Darstellungsweise ermöglicht wird (Abb. 6, die Zahlenwerte sind in Tab. II, Spalte 2 zu finden). Graphisch wurde aus Abb. 6 $K = 0{,}111_6$ gefunden, in guter Übereinstimmung mit dem berechneten Wert $K = 0{,}111_4$. Letzterer wurde den weiteren Berechnungen zugrunde gelegt.

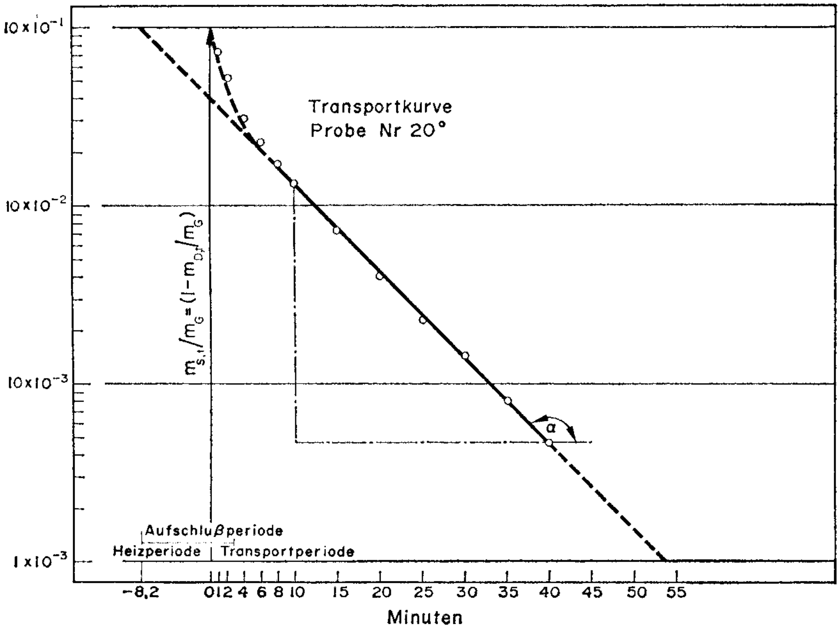

Abb. 6.—Auswertung der Transportkurve bezgl. *K*.

Die Heizperiode (t_H) von 8,2 Minuten läßt sich durch Verlängerung der Geraden nach negativen Transportzeiten (t_{tr}) bis zum Schnitt mit der 100% Ordinate ($m_{S,t}/m_G = 1$) aus Abb. 6 ermitteln und damit die Zeitdifferenz zwischen Destillations- und Transportbeginn korrigieren. Die Gleichung der Transportkurve ist mit $t = (t_{tr} + t_H)$

$$m_{D,t} = m_G \cdot e^{-0{,}1114(t_{tr}+8{,}2)} \qquad (11)$$

Die nach dieser Gleichung mit $m_G = 173{,}5$ berechneten Werte sind in Tabelle II den experimentellen Werten gegenübergestellt.

Durch Verlängerung der Geraden in Richtung wachsender Transportzeit bis zum Schnitt mit der 0,1% Ordinate ($m_{S,t}/m_G = 10^{-3}$), kann der Abb. 6 entnommen werden, daß für die Transportperiode dieses Versuches $t_{tr} = 53$ Minuten erforderlich waren, um das Restfluor im Sumpf auf 0,1% zu drücken.

TABELLE II.—VERGLEICH ZWISCHEN BERECHNETEN UND ABGELESENEN $m_{D,t}$-WERTEN

Transportzeit, t_{tr}, *Min*	$m_{D,t}/m_G$	$m_{S,t}/m_G = (1 - m_{D,t}/m_G)$	$m_{D,t}$ berechnet nach Gl. (11), *mm*	$m_{D,t}$ Meßwerte von der Kurve, *mm*
	1	2	3	4
0			103,4	0
1	0,2662	0,7338	111,2	46,2
2	0,4904	0,5906	117,6	85,1
4	0,6956	0,3044	128,9	120,7
6	0,7775	0,2225	137,8	134,9
8	0,8293	0,1707	146,4	143,9
10	0,8674	0,1326	150,6	150,5
15	0,9268	0,0732	160,4	160,8
20	0,9596	0,0404	166,0	166,5
25	0,9769	0,0231	169,2	169,7
30	0,9855	0,0115	171,0	171,5
35	0,9912	0,0088	172,1	172,0
40	0,9953	0,0047	172,7	172,6
45	0,9973	0,0027	173,0	173,1

Transportzeit von 100° Kopftemperatur an gerechnet. Titriergeschwindigkeit 10%/Minute, 25-ml Kolbenbürette. pH-stat-Titration.

Die Halbwertszeit τ der Destillation ist bestimmt durch

$$\tau = \ln 2/K \tag{12}$$

Mit τ als Maßeinheit für die Destillationsdauer t läßt sich berechnen, welche Fluorfehlbeträge auftreten können, wenn eine Destillation in Unkenntnis des individuellen Ablaufs zu früh beendet wird. Weil während jeder Halbwertsdauer die Fluormenge im Sumpf halbiert wird, folgt aus $(1/2)^n = 1/10^{-3}$ bzw. $1/10^{-4}$, daß für 99,9 bzw. 99,99%igen Fluortransport in das Destillat $n = 10$ bzw. 14 Halbwertszeiten für die Destillationsdauer t anzusetzen sind.

TABELLE III

t/τ	Nickt erfasstes Fluor %
5	3,12
6	1,56
7	0,78
8	0,39
9	0,2
10	0,1
14	0,01

Statistische Angaben zur Fluordestillation

Durchgeführt wurden stets Doppelbestimmungen in mehreren Apparaturen und mit wechselnden Mitarbeitern. Ausrechnung und Bezeichnung der statistischen Größen sind nach Doerffel vorgenommen worden,[24] während von Gottschalk einige tabellierte Funktionswerte entnommen wurden.[25] Vor der Destillation wurde das Probematerial restlos durch ein Sieb mit 10^2 Maschen/mm^2 gebracht. Die Kurvenauswertung geschah mit einem Koinzidenzlineal. Ohne Kurvenaufzeichnung wurde

TABELLE IV.—STATISTISCHE ERGEBNISSE

Meßmethode	Zahl der Freiheitsgrade, n	Standardabweichung, s % CaF_2	Streubereich $\Delta x = (99, n) \cdot s$ % CaF_2	Flußspatqualität
Kurvenauswertung	14	±0,016	±0,05	Säurespat
Digitalanzeige	34	±0,036	±0,11	
Titration gegen Bromthymolblau	90	±0,07	±0,2	Säurespat
	35	±0,10	±0,3	Testspat 99,7 % CaF_2
	10	±0,10	±0,3	Testspat 49,0 % CaF_2
	19	±0,10	±0,3	Testspat 10,5 % CaF_2

die Digitalanzeige der Motorbürette verwendet. Der Vollständigkeit halber sind auch die älteren Ergebnisse der Indikatormethode (s.S. 783) in die Tabelle mit aufgenommen. Die Testspatproben sind zur Kontrolle der Destillationsergebnisse nach Zitat[23] analysiert worden.

Summary—A still is described by means of which fluoride in fluorspar may be determined within an hour, finishing with an alkalimetric titration. Recording transport of fluoride potentiographically proves the kinetics to be first-order and makes the reaction rate constant and half-life accessible by converting the exponential rate law into a geometric progression. Summation of this gives total fluoride as the limiting value for an infinite distillation period. Precision of a determination depends on the ratio of distillation period to half-life period. The standard deviation in practice is $\leq \pm 0{\cdot}1$ % CaF_2.

Résumé—On décrit un appareil à distillation au moyen duquel on peut déterminer le fluorure dans la fluorine en une heure, en terminant avec un titrage alcalimétrique. L'enregistrement potentiographique du transport du fluorure établit que la réaction est du premier ordre et rend la constante de vitesse de réaction et la demi-vie accessibles en convertissant la loi de vitesse exponentielle en une progression géométrique. La sommation de ceci donne le fluorure total comme la valeur limite pour une période de distillation infinie. La précision d'un dosage dépend du rapport de la période de distillation à la période de demi-vie. L'écart type en pratique est $\leqslant \pm 0{,}1$ % CaF_2.

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UNIFIED AUTOMATED DETERMINATION OF SILICON IN IRON ORES, SINTERS, SLAGS, IRON AND STEEL*

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Summary—An automatic absorptiometric method is presented for the determination of silicon in iron ores, sinters, slags, iron and steel. The last two are dissolved in dilute sulphuric acid; the others are fused with sodium peroxide, then dissolved in hydrochloric acid. After suitable additions and dilution, the resulting solutions are treated identically in a Technicon AutoAnalyzer. The silicomolybdate formed is reduced to molybdenum blue with iron(II). Fluoride is added to provide a redox buffering system. The novelty of the method lies in selecting the sample sizes, conditions of fusion and/or dissolution and dilutions so that this universality is attained. Thus a single programme for the analyzer serves to determine, in any sequence, silicon in iron ores or sinters (1–6%), slags (3–10%), iron (0·4–2·5%) or steel (0·005–2%), the only change being in the tables used to translate transmittance into per cent silicon. Both the precision and accuracy are satisfactory.

BISRA[1] employed the AutoAnalyzer for silicon determination in steels, and the details of several methods suitable for use with this equipment have been published. The procedures differ widely, according to the matrix and silicon content, so that the apparatus has to be programmed differently for each material. This is inconvenient in a quality-control laboratory which must process large numbers of varied samples arriving in an unpredictable sequence. The term "unified" is used in the title to suggest that the automated features of the analysis have been standardized so as to be the same for any of the materials listed, the necessary variations being introduced during the weighing, dissolution and dilution steps. Thus a single AutoAnalyzer can handle these solutions in identical fashion, regardless of the sample material. To achieve this goal, a number of changes have been made in the procedure for each material, and are reported in this paper.

Silicon may be determined by measuring the colour intensity of the yellow or blue complex formed by silicon with molybdate ions, the sensitivity being higher if the molybdenum blue is used. Sanders and Cramer[2] investigated various reducing agents such as tin(II) chloride, oxalic acid, iron(II) sulphate, sodium sulphite and 1-amino-2-naphthol-4-sulphonic acid. With iron(II), there is neither reduction of free molybdate nor interference from phosphorus or arsenic, as is possible with tin(II) chloride. Also, its use is not temperature-sensitive as that of sulphite is. Finally, since iron is present in the samples anyway, it may as well be used as the reducing agent.

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EXPERIMENTAL

Apparatus

Technicon AutoAnalyzer manifold. Schematically illustrated in Fig. 1, and used with 660-nm interference filters and tubular flow-cell with 15-mm light path.

Zirconium crucibles, 55 ml capacity.

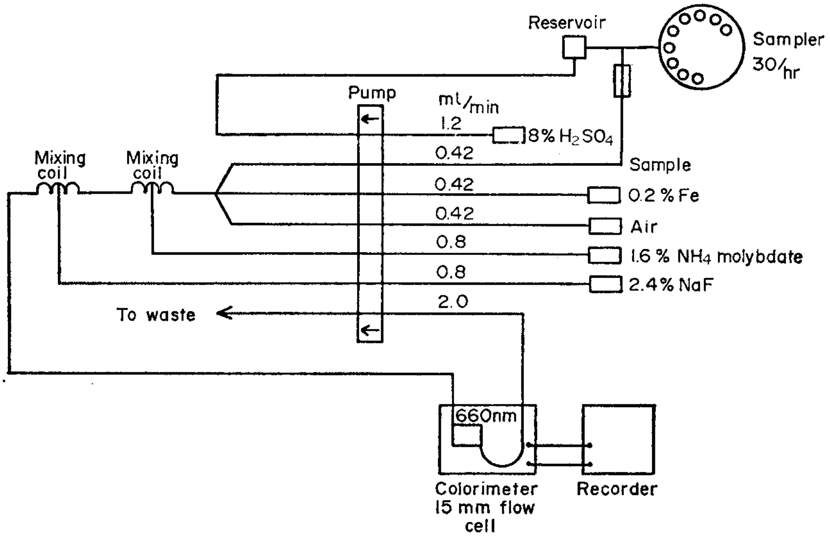

FIG. 1.—Schematic diagram for colorimetric determination of silicon.

Reagents

All reagents must be of analytical reagent grade.

Sulphuric acid, 8% v/v.

Hydrochloric acid, 6*M*.

Sodium peroxide.

Ammonium persulphate solution, 3% *w/v*. Freshly prepared.

Ammonium molybdate solution, 1·6% *w/v*. Prepared and stored in a polyethylene bottle.

Sodium fluoride solution, 2·4% *w/v*. Prepared and stored in a polyethylene bottle.

Pure iron solution 0·2%. Dissolve 1·00 g of pure iron (Ferrovac E is suitable) in 80 ml of 8% sulphuric acid. Add 10 ml of 3% ammonium persulphate solution and boil for 2 min. Cool and dilute to 500 ml in a volumetric flask.

Standards

Appropriate NBS and/or BCS standard steels, iron ores, sinters and slags.

Sample dissolution

Steel and iron. Weigh the appropriate sample of steel or iron and add 8% v/v sulphuric acid (Table I). Simmer to dissolve. When the reaction ceases, add 10 ml of 3% w/v ammonium persulphate solution and boil for 2 min. Cool to room temperature, dilute to the mark with water in a

TABLE I.—SAMPLE WEIGHT AND DILUTION

Matrix	Silicon range, %	Sample weight, *g*	Sulphuric acid 8% v/v, *ml*	Final dilution, *ml*
Steel	0·01–0·35	1·000	60	500
Iron	0·2–2·5	0·200	50	500
Iron ore or sinter	1–6	0·200	40	1000
O.H. Slag	3–10	0·100	40	1000

500-ml volumetric flask, and mix. In the case of iron samples, filter a portion of the solution through a dry Whatman No. 40 or equivalent filter paper.

Iron ore, sinter or O.H. slag. Add 2 g of sodium peroxide to a clean zirconium crucible. Weigh accurately the appropriate size of sample (Table I), transfer it to the crucible, mix until homogeneous, then fuse at red heat over a burner, swirling the crucible, until a clear melt is obtained (no specks should be visible). Keep at red heat and swirl for about 30 sec. Cool somewhat, place the crucible in a 400-ml beaker and cover with a watch-glass. Cautiously and quickly add about 20 ml of water to the crucible and quickly replace the watch-glass. When the reaction ceases remove the crucible and wash its contents into the beaker. Add 30 ml of 6*M* hydrochloric acid to the beaker and warm until a clear solution is obtained. Rinse the crucible with the warm acidic sample solution, then with water. Transfer the solution to a 1-litre volumetric flask, washing the beaker with water, and add about 500 ml of water. After mixing add 40 ml of 8% v/v sulphuric acid with swirling, and then dilute to volume with water and mix. The solution can be analysed directly either by manual colorimetry or automatically on the AutoAnalyzer. Occasionally, it may be desirable to filter the portion to be utilized through a dry filter paper.

Procedures

Manual colorimetry. Transfer by pipette a 10-ml aliquot into a 50-ml volumetric flask containing 5 ml of 0·2% pure iron solution. Add 10 ml of ammonium molybdate solution and mix. After 3 min add 10 ml of sodium fluoride solution, mix and immediately dilute to volume with water. Mix well. Measure absorbance in a 10-mm cuvette with water as reference, at 665 nm.

AutoAnalyzer. Set up the AutoAnalyzer manifold with the flow pattern shown in Fig. 1. Use a sample rate of 30/hr and a 2:1 ratio of wash time to sample time on the sampler. The wash solution is 8% v/v sulphuric acid. Three tubes (0·42 ml/min) are used for sample solution, iron solution and air. Two tubes (0·8 ml/min) carry ammonium molybdate and sodium fluoride solutions and mix into the stream in mixing coils of 4-mm outside diameter tubing with a centre take-off. The molybdenum blue is conducted to the flow-cell of the colorimeter (660 nm filter, 15-mm light-path) through transmission tubing of 1·65-mm bore. The waste solution from the flow-cell is conveyed by the 1·85-mm bore tube to the drain. The transmittance is recorded on the strip-chart recorder.

Calibration

Calibrate exactly as described under the procedures, using sets of appropriate NBS, BCS, or local standard samples.

RESULTS AND DISCUSSION

Effect of iron concentration

Since the method was developed to cover a wide range of silicon in iron and steel it was important to know the precise effect of the iron concentration. Pure iron or NBS 55e was dissolved in 8% v/v sulphuric acid; carbides were destroyed by the addition of persulphate and finally the solution was diluted to provide iron concentrations of 1 and 2 g/l. Suitable aliquots were placed in 50-ml volumetric flasks and known amounts of silicon were added. The colour was developed as discussed earlier. Table II shows the results.

TABLE II.—EFFECT OF IRON

Silicon added, *μg*	Iron present, *mg* 50*	25*	10†
	Net absorbance		
0	0·015	0·009	0·011
5	0·035	0·036	0·036
10	0·070	0·072	0·072
20	0·136	0·145	0·145
40	0·280	0·283	0·289

* In 0·144*N* sulphuric acid.
† In 0·057*N* sulphuric acid.

It is evident that 5–40 mg of iron has no effect on the silicon determination. Also the acidity is not too critical. However, when determining above 2% of silicon it was found that only a bluish tinge appeared, indicating incomplete reduction to molybdenum blue. The effect of low concentrations of iron was investigated, with the results shown in Table III.

TABLE III

Fe, *mg*	Si, *μg*	Absorbance	Fe, *mg*	Si, *μg*	Absorbance
0·2	10·2	0·085	4·0	10·2	0·100
0·5	10·2	0·095	0·2*	4·82	0·035
1·0	10·2	0·097	0·2*	4·82 + 80·0	0·030
2·0	10·2	0·100	0·2* + 2·0	4·82 + 80·0	0·360

* Fe contributed by using NBS cast iron standard 7 g, containing 2·41 % Si.

There is a rise in the absorbance for 10 μg of silicon as the concentration of iron is increased from 0·2 to 2 mg, but even 2·2 mg of iron is inadequate to give complete reduction for 80 μg of silicon.

As already shown, up to 40 mg of iron have no adverse effect, so a standard addition of 10 mg of iron was incorporated before the addition of ammonium molybdate. This overcomes the insufficiency of iron when highly siliceous materials such as slags lack the iron necessary for reduction to molybdenum blue, without affecting those solutions already containing an adequate iron concentration. With this modification, the AutoAnalyzer can be programmed to deal with solutions of iron, steel, sinter, ore or slag, containing silicon levels between 0·005% (in a steel) and 10% in O.H. slag.

Standard steel, sinter and iron ore samples containing 0·02–10% silicon, were then analysed by the recommended procedure. The results are recorded in Table IV with the standard deviation at each level. The silicon contents listed are the NBS certificate or other acceptable standardization values.

The BISRA automatic method for determining silicon in steel is applicable to a wide variety of steels containing up to 1·6% silicon, but a shorter path-length flow-cell is necessary if the concentration of silicon exceeds 1%. This is acceptable for batch analysis but not convenient in a control laboratory where time is a vital factor and the silicon level has a wide range. There are two time-delay coils, 7 min each, employed in the BISRA method and it requires 21 min for a sample to go through the system. In the system presented here the solution is made in such a way that one programme on the AutoAnalyzer can cover a range of 0·005–10% silicon in a variety of matrices. No delay coils are required, and the sample can go through in 7 min. The BISRA solution technique would solubilize high-alloy steels to a larger extent, but the system presented here is satisfactory for most of the grades produced by our Company.

Low carbon rimmed steel takes the longest time to dissolve, as much as 40 min. However, low-alloy steel, Cr-steels, semi-killed and killed steels are in solution in 15–20 min. The time needed to dissolve cast iron varies from 2–5 min. In our previous studies[3] a scheme was devised for the rapid dissolution of iron ores, sinters and open hearth slags after fusion with sodium peroxide in a nickel crucible, but because the solutions were greenish in colour, (causing high blanks) it was thought desirable to avoid nickel. Fusion in a zirconium crucible provided an almost colourless solution.

TABLE IV.—PRECISION AND ACCURACY TESTS

Sample	Si, %				Sample	Si, %			
	Cert.	Found	$s(n)$*			Cert.	Found	$s(n)$*	
Steels					*Cast irons*				
NBS 10g	0·020	0·020 0·019			NBS 122d	0·62	0·63 0·62	0·005	10
BDS 292	0·060	0·053 0·055			NBS 4j	1·31	1·28 1·30	0·01	10
NBS 15g	0·095	0·095 0·095			NBS 6f	1·85	1·84 1·85		
NBS 14d	0·126	0·127 0·126			NBS 82a	2·07	2·05 2·05		
NBS 16e	0·20	0·202 0·202			NBS 7g	2·41	2·45 2·47	0·04	10
					Iron ores				
NBS 100b	0·210	0·210 0·212							
NBS 13g	0·355	0·355 0·355			BCS 175/2	2·58	2·55 2·58		
NBS 8i		0·02	0·001	10	Sweden-7	3·34	3·45 3·42		
NBS 50g		0·100	0·001	10	NBS 27e Sibley	3·65	3·64 3·67		
NBS 32e		0·280	0·002	10	Canadian	5·04	5·03 5·01		
Sinters									
Stelco—I		3·07	0·034	51	Marcona	5·47	5·47 5·45		
Stelco—II		4·73	0·037	51	Sweden-2	6·52	6·50 6·52		
Stelco—III		8·60	0·028	51	Minette	9·31	9·30 9·32		

* s = standard deviation; n = number of variates.

Fusion and dissolution of the iron ores, sinters and O.H. slags can be completed in about 5 min. Calibrations are carried out with standard samples of steel, cast iron. sinter, iron ore and open hearth slag. These standard solutions are stable for at least two weeks.

The silicomolybdate formed is reduced to molybdenum blue with iron(II). In the oxidation of carbides a deficit of ammonium persulphate is used so that not all the iron(II) is oxidized. The result is that the potential of the iron(III)/iron(II) couple is too high for it to be able to reduce either free molybdate or silicomolybdate and sodium fluoride is added to buffer the redox system to a potential at which it can reduce the latter but not the former molybdate species.

Acknowledgement—We wish to thank J. F. Donovan for carrying out some of the experimental work and the Steel Company of Canada for permission to publish.

Zusammenfassung—Ein automatisches absorptiometrisches Verfahren zur Bestimmung von Silicium in Eisenerzen, Lunkern, Schlacken, Eisen und Stahl wird angegeben. Die letzten beiden Produkte werden in verdünnter Schwefelsäure gelöst, die anderen mit Natriumperoxid geshmolzen und dann in Salzsäure gelöst. Nach Zugabe der entsprechenden Reagentien und Verdünnung werden die erhaltenen Lösungen alle in gleicher Weise in einem Technicon Autoanalyzer verarbeitet. Das gebildete Silicomolybdat wird mit Eisen(II) zu

Molybdänblau reduziert. Um einen Redoxpuffer zu erhalten, wird Fluorid zugegeben. Die Neuheit des Verfahrens liegt in der Auswahl der Probengrößen, der Schmelz- bzw. Lösungsbedingungen und der Verdünnungsoperationen, sodaß diese universelle Anwendbarkeit resultiert. So kann man mit einem Program für den Analyzer in jeder beliebigen Reinfolge Silicium in Eisenerzen oder Lunkern (1–6%), Schlacken (3–10%), Eisen (0,4–2,5%) oder Stahl (0,005–2%) bestimmen. Der einzige Unterschied besteht im Wechsel det Tabelle, die den Zusammenhang zwischen Durchlässigkeit und Prozent Silicium angibt. Genauigkeit und Richtigkeit sind zufriedenstellend.

Résumé—On présente une méthode absorptiométrique automatique pour le dosage du silicium dans les minerais de fer, les sornes, les scories, le fer et l'acier. Ces deux derniers sont dissous en acide sulfurique dilué; les autres sont fondus avec du peroxyde de sodium, puis dissous en acide chlorhydrique. Après additions et dilution convenables, les solutions résultantes sont traitées identiquement dans un Autoanalyseur Technicon. Le silicomolybdate formé est réduit en bleu de molybdène par le fer(II). On ajoute du fluorure pour fournir un système tampon redox. La nouveauté de la méthode réside dans la sélection des dimensions de l'échantillon, des conditions de fusion et/ou dissolution et dilutions de sorte que cette universalité est atteinte. Ainsi un seul programme pour l'analyseur sert à déterminer, dans n'importe quel ordre, le silicium dans les minerais de fer et sornes (1–6%), scories (3–10%), fer (0,4–2,5%) ou acier (0,005–2%), le seul changement étant dans les tables utilisées pour convertir la transmission en pour cent de silicium. La fidélité et la précision sont toutes deux satisfaisantes.

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DETERMINATION OF CHLORIDE BY DISPLACEMENT OF HYDROGEN CYANIDE FROM MERCURY(II) CYANIDE

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Summary—A method, based on the passivity of mercury(II) cyanide in dilute sulphuric acid and its reaction with hydrochloric acid to produce hydrogen cyanide, has been developed for the determination of small amounts of chloride. Hydrogen cyanide, distilled from a mercury(II) cyanide–halide–dilute sulphuric acid system is found by iodometric measurement to be directly proportional to the amount of chloride or bromide and of hydrogen ion in acids such as sulphuric acid. A linear correlation also holds for iodide but the stoichiometry is different, the titration values being about three times larger than expected. By conversion of the cyanide into a dye by means of the pyridine–pyrazolone reagent, 0·014–0·43 μg/ml chloride concentrations have been determined. The method is also applicable to bromide and sulphuric acid in small amounts but not to fluoride and iodide. Results are reproducible to within $\pm 2\%$.

THE HALIDE and pseudohalide ions (Cl^-, Br^-, I^-, SCN^-, CN^-) can be determined by several standard methods which employ mercury(II) nitrate, perchlorate and oxycyanide, but little use has been made of mercury(II) cyanide in quantitative analysis. However, as the salt is soluble in water and its solution is only slightly ionized, it has been used in a number of ways in qualitative spot tests.[1]

Pure mercury(II) cyanide, unlike other cyanides, is affected only slightly by dilute sulphuric, phosphoric or nitric acids even on prolonged boiling, but if it is warmed with dilute hydrochloric acid it decomposes to give hydrogen cyanide. A similar reaction also occurs on warming dilute sulphuric acid solutions of mercury(II) cyanide with anions which form acid-resistant mercury(II) salts, according to the following reaction:

$$Hg(CN)_2 + 2X^- + 2H^+ \rightarrow HgX_2 + 2HCN \quad (X^- = Cl^-, Br^-, I^-, SCN^-)$$

These anions and their acids or complexes have thus been detected by the evolution of hydrogen cyanide.[2] The possibility of determining small amounts of the halides in general, and chloride in particular, by this reaction appears promising, especially as cyanide has been determined at very low concentrations in industrial effluents, water, sewage, biological materials, vitamin B_{12}[3] *etc.* There are a number of colorimetric reagents and chromatographic methods[4] for the determination of trace amounts of cyanide which might also be applied to the determination of small amounts of chloride by the mercury(II) cyanide reaction.

The results presented here show that small quantities of chloride, bromide and sulphuric acid can be determined by such a colorimetric procedure and relatively larger amounts of these and also of iodide can be determined by an iodometric titration based on the hydrogen cyanide generated. Fluoride does not react with mercury(II) cyanide in dilute sulphuric acid.

EXPERIMENTAL

Reagents

Distilled cyanide-free water was used throughout.

Pyridine–pyrazolone reagent. Prepared[3] from reagent grade chemicals by mixing five volumes of aqueous 3-methyl-1-phenyl-5-pyrazolone solution (0·25%) with one volume of bis(3-methyl-1-phenyl-5-pyrazolone) solution in pyridine (0·1%).

Mercury(II) cyanide. Reagent grade.

Di-isopropyl ether. Reagent grade, purified by drying over sodium wire, followed by fractional distillation. All other reagents used were of analytical-reagent grade.

Buffer solution (pH 6·9)[5]. A mixture of 0·066*M* potassium dihydrogen phosphate and 0·066*M* disodium hydrogen phosphate in water.

Apparatus

Distillation apparatus. An all-Pyrex glass microdistillation apparatus (Noonan-Scorah apparatus[6]) was used for the distillation of hydrogen cyanide. The distillate containing cyanide was collected and titrated in 250-ml ground-glass stoppered conical flasks.

Standardization.

Distillation of the cyanide. Transfer to the distillation apparatus a 2–10 ml portion of 0·005*M* halide, with *ca.* 2-ml portions of water. Add 10 ml each of mercury(II) cyanide solution and 0·05*M* sulphuric acid. Wash down with water to give a final volume of about 40 ml. Place 25 ml of 1% potassium hydroxide solution in the receiving flask, and adjust the tip of the distillation-apparatus condenser to touch the bottom. Begin distillation and collect 100 ml of the distillate with the condenser-tip in the solution. Lower the flask to lift the condenser clear of the solution and collect a further 25 ml. Finally wash the condenser tip and remove the flask; the distillate may then be analysed by iodometric titration or colorimetric determination. Use 10 ml each of 0·2% mercury(II) cyanide solution and 0·05*M* potassium bromide when standardizing with 0·005*N* sulphuric acid.

Iodimetric method. The Schulek method[7] was modified according to the following procedure. Acidify the distillate with 10 ml of 20% orthophosphoric acid and treat the solution with an excess of saturated bromine water. Stopper the flask, shake the solution thoroughly and let it stand for 10 min. Add 2 ml of 90% formic acid, stopper the flask once more and destroy the excess of bromine by repeatedly shaking the solution and allowing it to stand for a few minutes. Wash down the stopper and the sides of the flask and add 0·5 g of solid potassium iodide. Wash down the solid and stopper the flask immediately. Mix the solution thoroughly and allow to stand for 10 min. Titrate with 0·01*N* sodium thiosulphate, using Thyodene indicator.

Determine blanks by the same method for either halide or the acid.

Colorimetric method. The Epstein method[3,8] was modified as follows. Dilute the distillate to 1 litre. Measure out appropriate volumes of the diluted solution into a series of 25-ml volumetric flasks and add 5 ml of the buffer solution to each. Add 2 ml of 0·1% freshly prepared aqueous chloramine-T solution, stopper the flasks and mix thoroughly, allow to stand for 5 min and add 5 ml of the mixed pyridine–pyrazolone reagent. Mix thoroughly and dilute to the mark. Record the absorbance at 618 nm after 25 min, against a reagent blank, and construct a calibration curve from the readings for the series.

RESULTS AND DISCUSSION

There are several possible ways in which the hydrogen cyanide evolved from the reaction of chloride with mercury(II) cyanide in dilute sulphuric acid may be determined. It could be distilled and the residual cyanide titrated, it could be measured colorimetrically *in situ* as there should be little interference from mercury(II) cyanide, or it could be distilled and determined titrimetrically or colorimetrically. Each of these possibilities was investigated.

To determine chloride by analysing for the residual mercury(II) cyanide, a solution containing 5 ml each of 0·005*M* sodium chloride, 2% mercury(II) cyanide solution and 0·2*N* sulphuric acid was boiled for about 1 min and then cooled. The residual cyanide was determined iodometrically with 0·01*N* sodium thiosulphate. It was possible, by careful boiling of the solution, to obtain an almost stoichiometric recovery of the chloride. When however, the strength of the mercury(II) cyanide reagent was decreased from 2% to 0·4%, the recovery decreased but the titration values were proportional to the amount of added chloride; thus for 2, 4, 6 and 8 ml of 0·005*M* sodium chloride added, the decreases in mercury(II) chloride titre were 1·4, 3·4, 5·3 and 7·4 ml of 0·01*N* sodium thiosulphate respectively. Furthermore, any change in the sulphuric acid concentration, the volume of the solution or the time of boiling affected the linearity of the results.

The colorimetric method for the determination of cyanide is based on the König reaction. The cyanide is first converted into cyanogen chloride which then reacts with the pyridine–pyrazolone reagent to form a blue dye. The problem found here in determining small amounts of cyanide generated *in situ*, and the blanks obtained later in the distillation procedure, is obviously caused by the small amount of cyanide which results from the ionization of mercury(II) cyanide in dilute sulphuric acid, the equilibrium amount being governed by the concentration of mercury(II) cyanide added. As a result Beer's law is not obeyed and calibration curves are difficult to reproduce unless the colour is developed under rigidly controlled conditions, particularly with respect to the reaction time with chloramine-T.

In view of the difficulties thus encountered in the direct determination of chloride, distillation of the hydrogen cyanide was examined in detail. Distillation was adopted because it is easy to control conditions and the recoveries of cyanide are always reproducible. In addition this method provided a pure cyanide solution whose analysis was relatively straightforward by the available titrimetric and colorimetric methods. Further, distillation could readily be applied to coloured, contaminated or opaque samples. The efficiency of distillation was proved by iodimetric titration of distilled hydrogen cyanide; for a set of five distillations of 10 ml of 0·01*M* potassium cyanide, recoveries of the cyanide between 99% and 100% of the theoretical amount were obtained.

The procedure was first studied for the chloride ion by distillation of hydrogen cyanide fromt he mercury(II) cyanide–chloride–dilute sulphuric acid system. The recoveries of the cyanide and the reagent blanks were found to be dependent upon the concentration of both mercury(II) cyanide and sulphuric acid. Further, complete recoveries of the halide in terms of the distilled cyanide were difficult to obtain. Nevertheless, they were directly proportional to the amount of chloride added (Fig. 1), and tended to the stoichoimetric values for 4% mercury(II) cyanide.

The reagent blanks were also high at such a higher concentration of mercury(II) cyanide. For 0·2% mercury(II) cyanide in 0·05*N* sulphuric acid, the recovery of the cyanide was linear up to 8 ml of 0·005*M* sodium chloride but fell off above this value. However, whatever the reagent concentrations, the recoveries were reproducible to within 0·1 ml of 0·01*N* sodium thiosulphate in repeated tests, provided that the volumes of the distillate and the solution distilled were kept approximately constant.

The distillation procedure was then applied to 0·005*M* solutions of chloride, bromide, iodide and hydrogen ion in sulphuric acid. The recoveries of hydrogen cyanide in all cases were again linear with respect to the added ions (Fig. 2). However, in the case of iodide the volumes of thiosulphate consumed were approximately three times larger than for the other ions. For more than 8 ml of 0·005*N* potassium iodide recovery also fell off, probably because of the depletion of the mercuric cyanide reagent. The lines for iodide and sulphuric acid in Fig. 2 do not pass exactly through the origin, despite the deduction of blank values, because the reactions in the blank

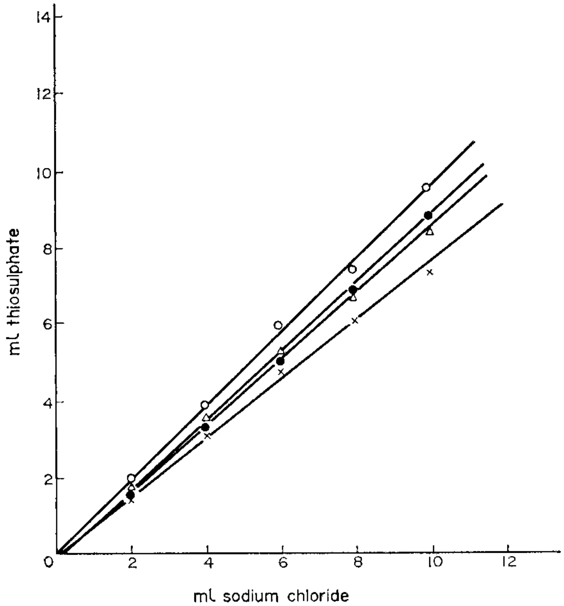

FIG. 1.—Hydrogen cyanide displaced by sodium chloride from (*i*) (○), 4% mercury(II) cyanide in 0·2*N* sulphuric acid, (*ii*) (△), 2% mercury(II) cyanide in 0·2*N* sulphuric acid, (*iii*) (●), 0·4% mercury(II) cyanide in 0·4*N* sulphuric acid, (*iv*) (×), 0·2% mercury(II) cyanide in 0·005*N* sulphuric acid.

determinations do not proceed in the same way as in actual determinations which involve the formation of mercury(II) bromide or iodide compounds.

A solvent extraction method[3] using di-isopropyl ether was also examined, but proved less than one tenth as efficient as distillation. Although this method might prove useful in some instances it was not investigated further because of the low recoveries at the required concentration level.

As the distillation procedure gave reproducible recoveries of hydrogen cyanide which could be determined colorimetrically, the application of the mercuric cyanide reagent to the determination of small amounts of halides and sulphuric acid was investigated. Several sensitive colorimetric reagents for cyanide have been proposed and any such might be employed.[3,9,10] In the present study the pyridine–pyrazolone reagent was chosen chiefly because it has been frequently applied and has sufficient sensitivity (0·2–1·2 ppm CN^-), although the reagent is not stable for more than three days and the best results were obtained when it was freshly prepared daily. Generally, of existing procedures for the determination of cyanide at low concentrations, the colorimetric methods are claimed to be preferred to titrimetric, polarographic or chromatographic procedures.[9]

Hydrogen cyanide, equivalent to 10 ml of 0·005*M* chloride was distilled out under fixed distillation conditions and reagent concentration. The distillate was diluted to 1 l. and suitable volumes of the dilute solution reacted with the pyridine–pyrazolone reagent. The resulting absorbances were plotted against chloride concentrations, a straight line being obtained (Fig. 3). The method worked equally well for bromide and sulphuric acid but could not be applied to iodide because of interference from iodine co-distilled with the hydrogen cyanide. This probably also accounts for the

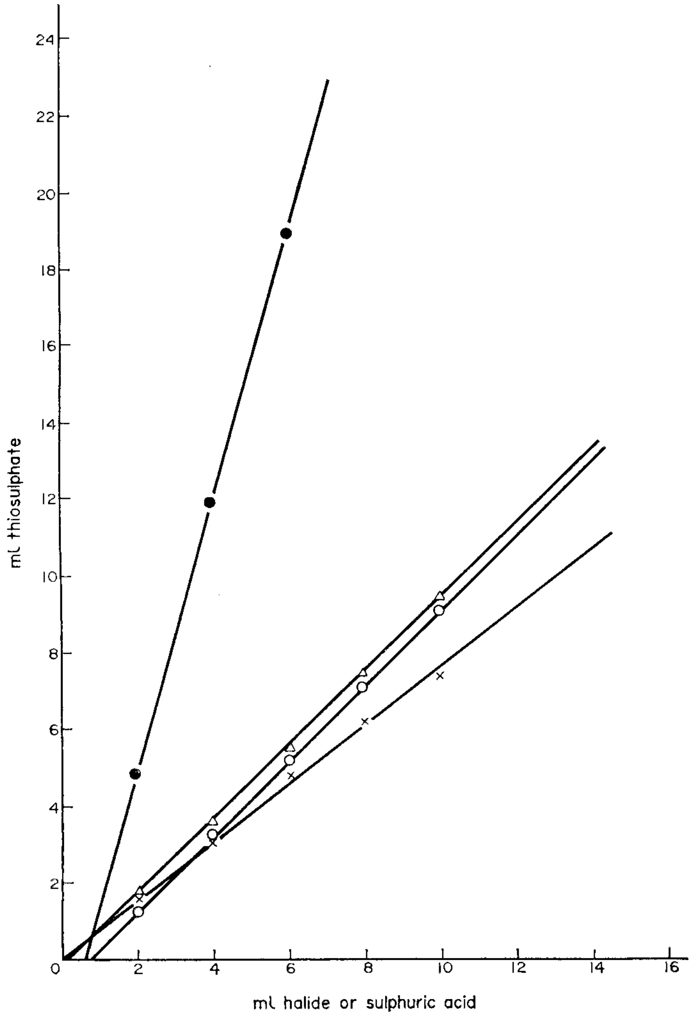

FIG. 2.—Distillation recoveries of hydrogen cyanide, using 10 ml each of 0·2% mercury-(II) and 0·05*N* sulphuric acid for the halides and 0.2% of mercury(II) and 0·05*N* potassium bromide for sulphuric acid. (*i*) (×), Chloride, (*ii*) (△), bromide, (*iii*) (●), iodide, (*iv*) (○), sulphuric acid.

consumption of the unusually large volumes of sodium thiosulphate in the titrimetric procedure.

Chloride ion in the range 0·014–0·426 μg/ml was determined by this method. Bromide and sulphuric acid were determined between 0·16–0·48 μg/ml and 0·098–0·39 μg/ml respectively. From the calibration curves, practical lower concentration limits for bromide of *ca.* 0·04 μg/ml and for sulphuric acid of *ca.* 0·025 μg/ml were indicated.

Anions which produce hydrogen cyanide in ca. 0·2N sulphuric acid or from mercuric cyanide in sulphuric acid will interfere in the determination of chloride by this method. The most common of these are bromide, iodide, cyanide, thiocyanate, ferricyanide and ferrocyanide.

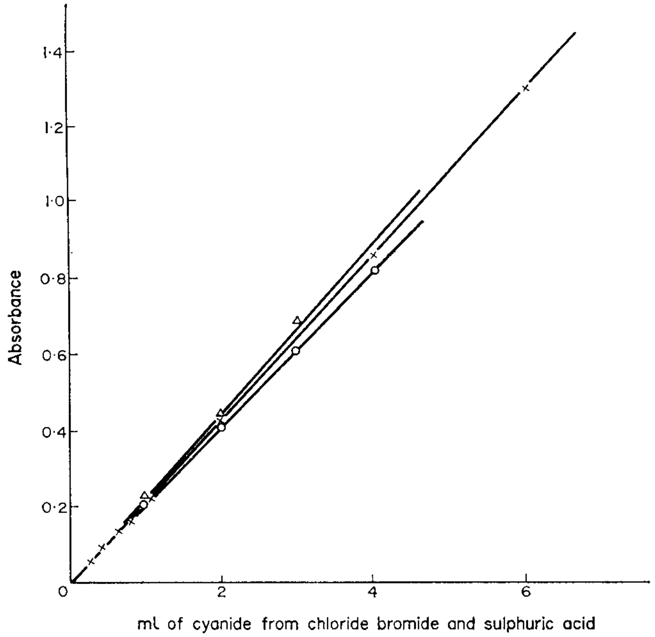

FIG. 3.—Absorbance of cyanide as distilled from chloride, bromide and sulphuric acid, (*i*) (×), chloride, (*ii*) (△), bromide, (*iii*) (○), sulphuric acid.

There are, however, several ways for the removal of these interferences.[11–14] Both cyanide and thiocyanate can be measured separately on an aliquot of the test solution and the extent of their interference assessed. Alternatively, cyanide can be destroyed with hydrogen peroxide and thiocyanate with nitrous acid. Bromide and iodide are removed by oxidation to bromine and iodine which are then volatilized. Ferricyanide and ferrocyanide are removed by the addition of a copper salt, the excess of which is eliminated with hydrogen sulphide.

The reproducibility of the results for 8 consecutive runs of 0·284 μg/ml of chloride, which resulted in an absorbance of 0·85, was within $\pm 2\%$. The subsequent decrease in absorbance over 2 hr was 0·02 when fresh pyridine–pyrazolone reagent was used. The range of the method may be extended by dilution at higher concentrations and by solvent extraction of the colour at lower concentrations of the cyanide.

The reagent blanks with mercuric cyanide can always be accounted for if necessary, for they as well as the sample distillations are reproducible.

Acknowledgements—We gratefully acknowledge the help and keen interest of Professor R. Belcher. One of us (M. K. B.) thanks the Pakistan Government and the P.C.S.I.R. for leave of absence and the Nuffield Foundation for the award of a Research Fellowship.

Zusammenfassung—Zur Bestimmung kleiner Chloridmengen wurde ein Verfahren entwickelt, das auf der Reaktionsträgheit von Quecksilber(II) cyanid in verdünnter Schwefelsäure und seiner Reaktion mit Salzsäure zu Blausäure beruht. Destilliert man Blausäure aus einer Lösung mit Quecksilber(II) cyanid, Halogenid und verdünnter Schwefelsäure ab, so findet man durch jodometrische Titration, daß ihre Menge direkt proportional ist der Chlorid- oder Bromidmenge und der Anzahl von Wasserstoffionen in Säuren wie Schwefelsäure. Eine lineare Beziehung gilt auch für Jodid, doch ist die Stöchiometrie anders: man erhält etwa dreimal größere Titrationswerte als erwartet. Durch Überführen des Cyanids in einen Farbstoff mit dem Pyridin-Pyrazolon-Reagens wurden Chloridkonzentrationen von 0,014–0,43 μg/ml bestimmt. Das Verfahren läßt sich auch auf Bromid und Schwefelsäure in kleinen Mengen anwenden, nicht jedoch auf Fluorid und Jodid. Die Ergebnisse sind auf ±2% reproduzierbar.

Résumé—Une méthode, basée sur la passivité du cyanure de mercure(II) en acide sulfurique dilué et sa réaction avec l'acide chlorhydrique pour produire de l'acide cyanhydrique, a été élaborée pour le dosage de petites quantités de chlorure. Par mesure iodométrique, on trouve que l'acide cyanhydrique, distillé d'un système cyanure de mercure(II)-halogénure-acide sulfurique dilué, est directement proportionnel à la quantité de chlorure ou de bromure et d'ion hydrogène dans les acides tels que l'acide sulfurique. Une relation linéaire s'applique aussi à l'iodure mais la stoechiométrie est différente, les valeurs de titrage étant environ trois fois plus grandes qu'attendu. Par conversion du cyanure en un colorant au moyen du réactif pyridine-pyrazolone, on a dosé 0,014–0,43 μg/ml de concentration en chlorure. La méthode est aussi applicable au bromure et à l'acide sulfurique en petites quantités, mais non au fluorure et à l'iodure. Les résultats sont reproductibles à ±2%.

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APPLICATION OF THE ZONE MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—V*

ZONE CHROMATOGRAPHIC SEPARATION OF METAL CHELATES ON COLUMNS OF SOME INERT SOLID SOLVENTS

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Summary—Binary mixtures of acetylacetone and 8-hydroxyquinoline chelates of copper(II), nickel(II), cobalt(II) and cobalt(III) were processed by zone-chromatography on columns of some naphthylalkyl ethers as inert solid solvents. The metal chelates were separated to give chromatograms on the columns according to the ratio of their distribution coefficients. Distribution coefficients of metal ions varied with the type of chelating agent used and the solid solvent, and were found to be strongly affected by operating conditions, especially zone length, zone travelling speed and initial concentration of the metal chelate.

THE ZONE-REFINING TECHNIQUE has been applied by Imamura[1] and by the present authors to the separation of mixtures of metal chelates. A completely satisfactory procedure has not yet been worked out, however, and the present paper presents further work on the zone chromatography of metal chelates on a column of an inert solid solvent.

The theoretical basis of zone chromatography has been presented by Pfann[2] and Reiss,[3] though very few experimental applications have been reported. This technique was applied to the separation of a mixture of metal chelates on a column of an inert organic solvent which was solid at room temperature. In practice, a mixture of metal chelates and the solid solvent is placed on the upper end of a column of the pure solid solvent and molten zones are repeatedly passed slowly downwards. The metal chelates separate into bands, each of which travels at a rate determined by the distribution coefficient of the metal chelate. Separation of the chromatographic bands depends upon the distribution coefficient and number of zone-passes.

The metal chelates need not be stable at their melting points nor show clear melting points. The melting point of the solid organic solvent, however, should be low enough for the metal chelates to dissolve without any thermal decomposition. In addition, the organic solvent needs to be chemically inert but must be a good solvent for metal chelates.

Preliminary investigation of organic solvents showed that some naphthylalkyl ethers were satisfactory. The present paper is concerned with an investigation on some factors influencing zone-chromatographic separation of binary mixtures of 8-hydroxyquinolinates on 2-methoxynaphthalene and naphthodioxane columns.

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EXPERIMENTAL

Metal chelates

The metal derivatives of acetylacetone and 8-hydroxyquinoline were prepared by standard procedures,[4] and analysed as described previously.[5]

Solubility

Organic solid solvents investigated in the present work were 2-methoxynaphthalene (β-MN), m.p. 72°; 2,3-dimethoxynaphthalene[6] (DMN), m.p. 116°; naphthodioxan[7] (NDO), m.p. 82°; and diphenylenedioxide[8] (DPO), m.p. 121°.

A mixture of a solid solvent and sufficient of the metal chelate was heated in a glass tube (8 mm in diameter and 100 mm long) at a constant temperature with occasional stirring until equilibrium was attained (about 10 hr). Further chelate was added as required, to maintain some of it undissolved. The saturated mixture was quickly frozen in an ice–salt bath to give a solid column, which was analysed for the metal ion (except the bottom part containing the undissolved metal chelate). Copper(II), cobalt(II) and nickel(II) ions were determined by atomic absorption and visible absorption spectrophotometry, and other metal ions by the latter method.

Distribution coefficients

The distribution coefficients of the metal chelates were determined by Sorensen's method,[10] with a column of a solid solvent. The distribution of the metal ion in the column was determined by atomic absorption or visible absorption spectrophotometry.

Apparatus

The zone chromatography apparatus was constructed in our laboratory. The glass tube is held vertically and moved upwards so that molten zones move downwards. Around the tube, ten heaters and ten coolers are placed alternately, 1 mm apart. The heater is a sheathed Nichrome ring, having inside it a brass collar 4 mm high and 7 mm in inner diameter. The cooler is a rectangular brass block, with a hole 7 mm in diameter. One end of the block is welded to a tank through which cooling water is circulated.

Procedure

A weighed amount of solid solvent was packed into a Pyrex glass tube (4·0 mm bore) stoppered at its lower end by a piece of silicone rubber, and was completely melted. The molten content was then solidified from the lower end gradually so that air bubbles in the melt could be excluded from the congealed solid. The resulting solid column was then zone-refined (ten passes). Impurities swept to the lower end were cut off together with the glass tube, and the resulting opening was closed by a silicone rubber stopper inserted about 10 mm into the tube.

On the upper end of the solid solvent column, a mixture of metal chelates and the solid solvent was placed, one zone-length high, the concentration of each metal chelate being insufficient to give a saturated solution in the molten solvent.

The resulting column, topped with the mixture of metal chelates and solid solvent, was zone melted (ten passes). The metal chelates travelled downwards and separated into widely diffused bands. The zone-processed column was cut into pieces about 8 mm long, and a sample from each piece was weighed and then dissolved in an appropriate solvent. These solutions were analysed for the metal ions by atomic absorption.

RESULTS AND DISCUSSION

The solubilities of the metal chelates in the solid solvents are summarized in Tables I and II. The solubilities in naphthalene are included for comparison. The results indicate that diethers are better solvents than monoethers and that the solubility of acetylacetonates is higher than that of 8-hydroxyquinolinates. This tendency is especially outstanding for the octahedrally hexaco-ordinate tervalent metal ions.

Visible region spectra of the metal chelates in molten solvents reveal no solvent interactions. The visible absorption spectrum of copper(II) acetylacetonate in molten β-methoxynaphthalene is almost identical with that obtained in chloroform and not with that obtained in pyridine [a strongly co-ordinating solvent (Fig. 1)]. In the case of nickel(II) 8-hydroxyquinolinate, the visible pectrums in molten naphthodioxan

TABLE I.—SOLUBILITIES (IN PPM) OF THE OXINATES IN THE SOLID SOLVENTS

Metal ion	Solid solvent			
	β-MN*	DMN†	NDO§	Naphthalene‡
Cr^{3+}	410			88
Mn^{2+}	170			51
Fe^{3+}	210			22
Co^{2+}	340	960	1370	65
Ni^{2+}	240	690	830	57
Cu^{2+}	350	1470	760	152
Zn^{2+}	290			203
MoO_2^{2+}	340			570
Th^{4+}	480			

* At 75°C.
† At 125°C.
§ At 85°C.
‡ At 81°C.

TABLE II.—SOLUBILITIES OF THE ACETYLACETONATES IN 2-METHOXYNAPHTHALENE AT 75°C

Metal ion	Solubility, % w/w
Cu^{2+}	0·21
Ni^{2+}	0·76
Co^{2+}	0·55
Co^{3+}	1·70
Fe^{3+}	1·30
Cr^{3+}	2·50
Mn^{3+}	1·30

(Fig. 2), showing an absorption maximum at 740 nm, which corresponds to that observed at 760 nm in chloroform at room temperature, has a very close resemblance to that in molten naphthalene.[9] Figure 2 also shows the spectrum in molten 8-hydroxyquinoline and that in quinoline at an elevated temperature for comparison. Ligand-field bands of the nickel chelate in the two donating solvents are affected strongly, though in different ways. Thus, the naphthyl ethers are very unlikely to be concerned in the coordination about the central metal ion even at an elevated temperature in a molten zone. Also, in the visible spectrum of the nickel chelate in naphthyl ethers, no change was observed upon prolonged or repeated heating, suggesting that no thermal decomposition took place.

Table III shows some examples of distribution coefficients of the metal chelates in the solid solvents. For a binary mixture of metal chelates shown in Table III, the higher the ratio of their distribution coefficients, the more effective is the separation. A component having a lower distribution coefficient travels faster towards the lower end of the column. On the other hand, the same metal chelate shows various distribution coefficients in a variety of solid solvents, and the same metal ion in the same oxidation state shows a different distribution coefficient if the chelating agent is changed. Furthermore, the data in Table III indicate that a change in oxidation state of a metal ion (*e.g.*, cobalt) may facilitate the separation of one metal ion from another.

The values obtained depend upon operating conditions although ideally they should be independent. The zone length, *l*, the zone travelling speed, *v*, and the

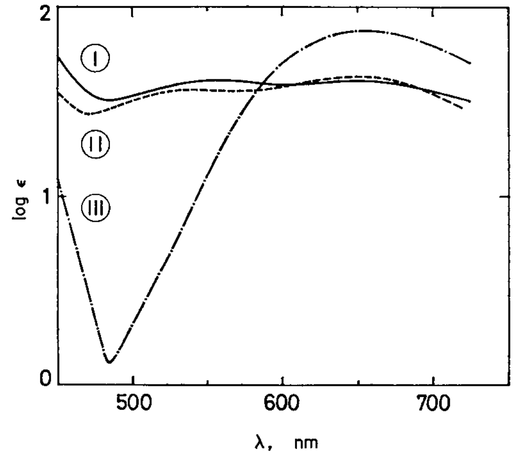

FIG. 1.—Visible absorption spectra of copper acetylacetonate in various solvents. I—molten β-MN at 77°; II—chloroform; III—pyridine.

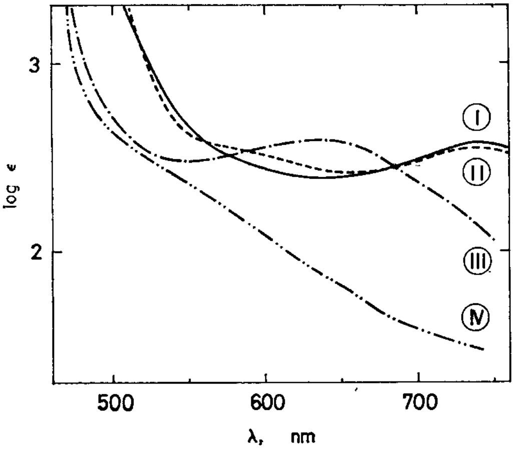

FIG. 2.—Visible absorption spectra of nickel 8-hydroxyquinolinate in various solvents at 97°.
I—molten NDO; II—molten naphthalene; III—quinoline; IV—molten 8-hydroxyquinoline.

initial concentration of a metal chelate, C_i, are important factors, and these conditions should be defined when values of distribution coefficients are given. In practice, the last two conditions may easily be kept constant but zone length is difficult to maintain constant.

The Sorensen method[10] of plotting metal ion concentration against the distance in zone lengths (x/l) gave a fairly good linear relation for every system studied here, and these results indicate that a constant distribution relationship is established at least within a region of several zone lengths near the upper end of a column, where the distribution of metal ions would be governed only by the distribution coefficient and not by the solubility.

Some typical examples of the chromatographic separation of metal ions after the zone melting process are shown in Figs. 3–8. The ratio of metal ion concentration, C_x, at a distance, x, to its initial concentration, C_i is plotted against the distance

TABLE III.—THE DISTRIBUTION COEFFICIENTS, k, OF THE OXINATES AND ACETYLACETONATES IN THE SOLID SOLVENTS

Chelate	Metal ion	Solvent	k	Zone-length, l, *mm*	Zone-speed, v, *mm/hr*	Initial concn., C_i, *ppm*
Oxinates	Cr^{3+}	β-MN	0·21	40	27	
	Fe^{3+}	β-MN	0·19	15	27	
	Co^{2+}	β-MN	0·57	15	15	
			0·47	15	27	
			0·66	8	27	186
		NDO	~1	13·5	27	
			>1	10·5	27	22
	Ni^{2+}	β-MN	0·86	15	15	
			0·41	15	27	
		NDO	~1	15	27	
	Cu^{2+}	β-MN	0·31	15	27	
			0·55	15	40	
			0·86	6	27	890
		NDO	~1	30	30	
		DMN	0·1	16	27	
		DPO	0·1	24	27	
	Zn^{2+}	β-MN	0·23	15	27	
	MoO_2^{2+}	β-MN	0·41	25	27	
Acetylacetonates		β-MN	0·48	5	27	
			0·92	10	27	13·5 × 10³
	Co^{3+}		>1	8	27	206
	Co^{2+}	β-MN	1	20	27	
	Ni^{2+}	β-MN	0·90	12	27	
	Cu^{2+}	β-MN	0·50	12	27	
			0·77	10	27	2500

in zone lengths, x/l. Individual points in the plots are of observed values of metal concentration and the curved lines are drawn for convenience just to show general tendencies in the metal ion distributions, and are not based on any algebraic assessment. In most examples metal ions were observed to be concentrated at the lower end. This is caused by processing on a column of a finite length, and if an infinitely long column were used, the curve would be close to the ideal one with a Poisson distribution.

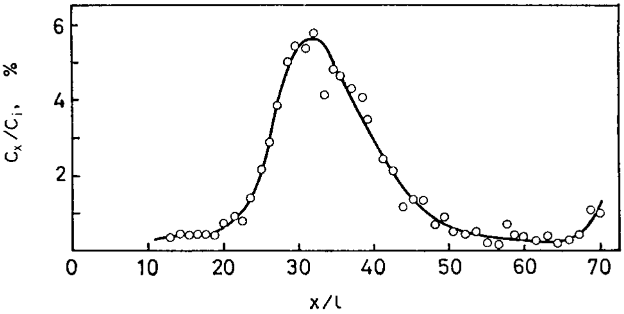

FIG. 3.—Distribution of the metal ion after the zone melting process in the copper 8-hydroxyquinolinate–β-MN system.
C_i, 156 ppm; L, total length of the column; 0·56 m; l, 8 mm; n, number of zone passes, 10; v, 27 mm/hr.

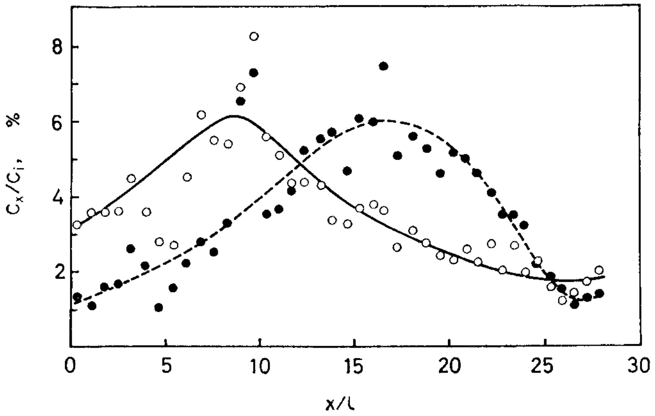

FIG. 4.—Distribution of the metal ions after the zone melting process in the copper 8-hydroxyquinolinate–cobalt 8-hydroxyquinolinate–β-MN system
Cu, ●; Co, ○; C_i(Cu), 213 ppm; C_i (Co), 63 ppm; *L*, 0·42 m; *l*, 15 mm; *n*, 30; *v*, 27 mm/hr.

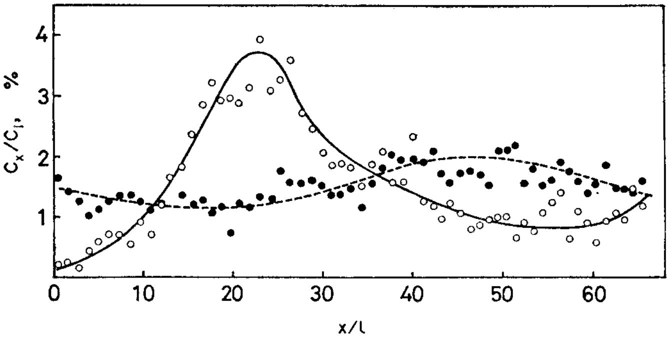

FIG. 5.—Distribution of the metal ions after the zone melting process in the copper 8-hydroxyquinolinate–cobalt 8-hydroxyquinolinate–NDO system.
Cu, ○; Co, ●; C_i(Cu), 182 ppm; C_i(Co), 383 ppm; *L*, 0·49 m; *l*, 7 mm; *n*, 60; *v*, 27 mm/hr.

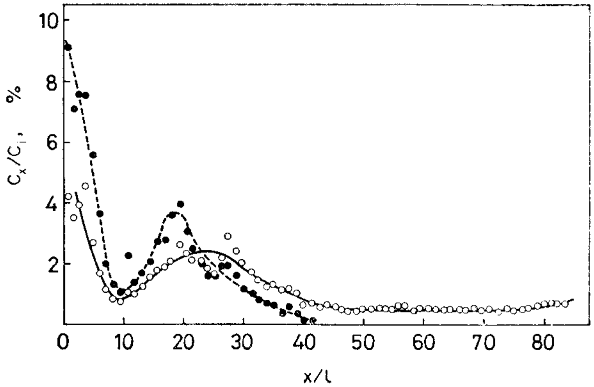

FIG. 6.—Distribution of the metal ions after the zone melting process in the copper acetylacetonate–cobalt acetylacetonate–β-MN system.
Cu, ○; Co, ●; C_i(Cu), 234 ppm; C_i(Co), 1160 ppm; *L*, 0·67 m; *l*, 8 mm; *n*, 20; *v*, 27 mm/hr.

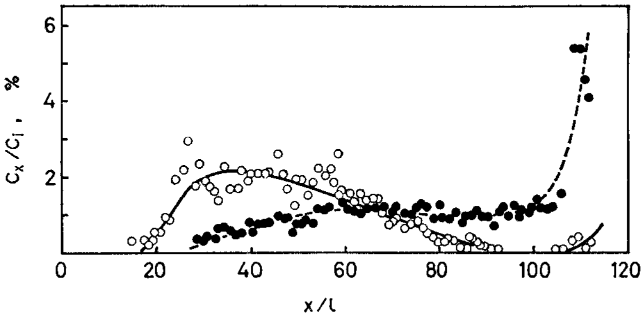

FIG. 7.—Distribution of the metal ions after the zone melting process in the copper acetylacetonate–cobalt acetylacetonate-β-MN system;
Cu, ●; Co, ○; C_i(Cu), 373 ppm; C_i(Co), 1010 ppm; *L*, 0·79 m; *l*, 7 mm; *n*, 60; *v*, 27 mm/hr.

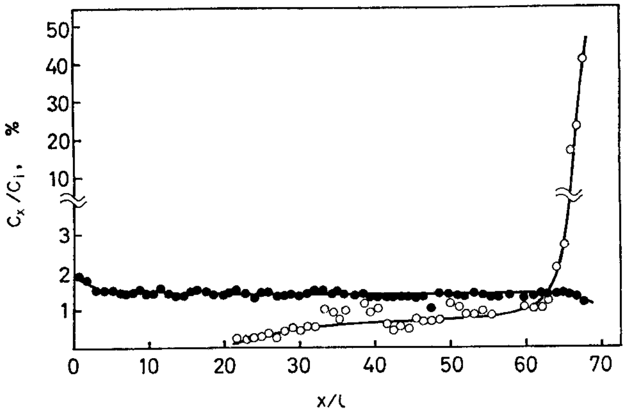

FIG. 8.—Distribution of the metal ions after the zone melting process in the copper 8-hydroxyquinolinate–nickel 8-hydroxyquinolinate–NDO system;
Cu, ○; Ni, ●; C_i(Cu), 337 ppm; C_i(Ni), *ca.* 400 ppm; *L*, 0·47 m; *l*, 7 mm; *n*, 80; *v*, 27 mm/hr.

According to theoretical calculation, based on assumption of ideality, the position of the chromatographic peak after *n* zone passes can be expressed as follows:

$$(x/l)_{\max} = (n - 1)[(1/k) - 1] \tag{1}$$

where the subscript max means a value at the chromatographic peak of the metal ion under discussion. For a binary mixture, the ratio, *R*, of the migrating lengths of each chromatographic peak of both components, 1 and 2, is

$$R = \frac{(x_1/l)_{\max}}{(x_2/l)_{\max}} = \frac{k_2(1 - k_1)}{k_1(1 - k_2)}. \tag{2}$$

Except at the lower end, every system shows a chromatographic band for each metal ion. However, between the calculated and observed values of $(x/l)_{\max}$ and the ratio, *R*, in some binary systems, there can be found considerable differences as summarized in Table IV. This discrepancy is most probably due to the inconstancy of the molten zone length during the operation as well as variation of the distribution

TABLE IV.—COMPARISONS OF THE CALCULATED AND OBSERVED POSITIONS OF CHROMATOGRAPHIC PEAKS

System	k	$(x/l)_{\max}$		R	
		Calcd.	Obsd.	Calcd.	Obsd.
Cu(Ox)$_2$ in β-MN	0·86*	1·4	32		
Cu(Ox)$_2$ +	0·31	64·7	17	2·0	2
Co(Ox)$_2$ in β-MN	0·47	31·8	8·5		
Cu(acac)$_2$ +	0·77*	5·7	24	3·5	1·2
Co(acac)$_3$ in β-MN	0·92*	1·65	20		

* Values under the nearest operation conditions are used, since those under the same conditions are not available from Table III.

coefficient caused by variation in operation conditions. Also, in some instances, the observed values were found to be widely scattered, and not lying on a smooth curve. One of the main reasons for this may be the inconstancy of the zone length as mentioned previously. Thus, the theoretical treatment of the observed results is not very meaningful at this stage. Accordingly the technique is being improved so that the zone length can be maintained constant. Thus, a more reasonable distribution coefficient could be determined by the position of its chromatographic peak and use of equation (1), instead of Sorensen's method.

In Fig. 6 the distribution curve shows a rise at the upper end, and this abnormality may be due to quick solidification; when a molten zone passed the upper end of the column, the melt behind the molten zone would not solidify immediately, remaining as a supercooled melt, and after a while (once a crystallization nucleus had occurred) the melt would solidify very quickly. This corresponds to fast travelling of a molten zone, and as a consequence there is an apparent rise in the distribution coefficient of the metal ion near the upper end. This effect would disturb a normal distribution process, resulting in a poor separation of the components in a mixture.

Figure 8 shows the distribution of nickel ions in a column after apparently abnormal zone chromatography. Nickel ions were determined by an atomic-absorption method, and in the course of elucidating this abnormality we found that the presence of large amounts of aromatic compounds could interfere with the determination of some metal ions by atomic-absorption spectrophotometry. The sample solutions in this work contain a large amount of the aromatic solvent together with a trace of metal ions, and the aromatic compounds, which show strong absorption in the region below 250 nm, were found to show considerable absorption in an atomic-absorption measurement in this region. Intensity of the absorption due to a burning aromatic compound, though proportional to concentration in the absence of nickel, decreases with increase in the amount of the metal ion present. Consequently, the error in nickel determination would be much higher when a trace of nickel ion was present in a large amount of an aromatic solid solvent. The species responsible for this absorption is not known, but it is probably one of the thermal decomposition products of the solid solvents in the flame. The effect of the metal ions is to catalyse the thermal decomposition.

The interference could be significant in the determination of a metal which has its characteristic resonance line in the short wavelength region (*e.g.*, nickel 237 nm and cobalt 240·7 nm), and no appreciable interference could be observed for a metal having an absorption line at >300 nm (*e.g.*, copper, 324·7 nm).

Acknowledgements—The authors wish to thank the Ministry of Education, Japanese Government, for financial support of this work.

Zusammenfassung—Binäre Gemische von Acetylaceton- und 8-Hydroxychinolinchelaten von Kupfer(II), Nickel(II), Kobalt(II) und Kobalt(III) wurden an Säulen aus Naphthylalkyläthern als inerten festen Lösungsmitteln der Zonenchromatographie unterworfen. Die Metallchelate wurden getrennt und lieferten Chromatogramme in den Säulen, die dem Verhältnis der jeweiligen Verteilungskoeffizienten entsprachen. Die Verteilungskoeffizienten der Metallionen änderten sich je nach der Art des verwendeten Chelatbildners und des festen Lösungsmittels; sie wurden auch stark von den Arbeitsbedingungen beeinflußt, besonders von der Zonenlänge, der Wanderungsgeschwindigkeit der Zone und der Anfangskonzentration der Metall chelate.

Résumé—Des mélanges binaires d'acétylacétone et de chélates de 8-hydroxy quinoléine avec les cuivre(II), nickel(II), cobalt(II) et cobalt-(III) ont été traités par chromatographie de zone sur des colonnes de quelques naphtylalkyléthers en tant que solvants solides inertes. Les chélates métalliques ont été séparés en donnant des chromatogrammes sur les colonnes selon le rapport de leurs coefficients de partage. Les coefficients de partage des ions métalliques varient avec le type d'agent chélatant utilisé et le solvant solide, et l'on a trouvé qu'ils sont fortement affectés par les conditions opératoires, spécialement la longueur de zone, la vitesse de mouvement de zone et la concentration initiale du chélate métallique.

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PURIFICATION AND CHARACTERIZING PROPERTIES OF ANALYTICAL REAGENT QUINIZARIN-2-SULPHONIC ACID AND ITS SODIUM SALT

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Summary—Quinizarin-2-sulphonic acid and its sodium salt have been purified for analytical use. The thermal analysis behaviour and the infrared and NMR spectra of the reagent have been recorded. Absorptiometry at 465 nm is recommended for the assay of solutions. Spectrophotometric measurements, corrected for fading, are treated by a PITMAP-type procedure to obtain acid dissociation constants for the reagent. Finally, some reactions with metal ions are surveyed briefly.

QUINIZARIN-2-SULPHONIC ACID (1,4-dihydroxy-9,10-anthraquinone-2-sulphonic acid) is an intensely-coloured compound which reacts with certain metal ions to produce coloured complexes. This reagent came to our attention during a survey of *bis*-bidentate ligands. It has been recommended for several analytical applications[1–6] but no procedure for its assay or adequate criteria for its purity could be found. The present paper deals with our findings concerning the purification of quinizarin-2-sulphonic acid, and with various characterizing measurements performed on the purified acid and its sodium salt.

EXPERIMENTAL

Apparatus and reagents

Only Class A volumetric ware was used, and all transfer pipettes were calibrated. A Radiometer PHM4 pH-meter was used, with the manufacturer's G 200B and K 100 electrodes. The meter was standardized with two buffer solutions to compensate for the actual Nernst slope of the glass electrode. Readings greater than pH 12 were corrected for sodium ion error by using the alignment chart supplied with the electrode. The meter was calibrated as a hydrogen ion concentration probe.[7] At the levels of concentration used in this work, no instability of readings attributable to the precipitation of potassium perchlorate at the liquid junction of the reference electrode was observed.

Differential thermal analysis (DTA) was performed on a DuPont 900 Differential Thermal Analyser at a heating rate of 15°/min and sensitivities of 0·02°/mm and 2°/mm on the differential and programmed temperature axes respectively. The cell atmosphere was static air, and 5 mg of microglass beads were used as reference. Thermogravimetric analysis (TGA) was performed on the DuPont 950 Thermogravimetric Analyser module at the same heating rate. Samples of 10–25 mg were used with a programmed temperature sensitivity of 4°/mm. The atmosphere was dry air flowing at 1000 ml/min, and the balance was operated with a 1-sec damping constant. Temperatures were corrected for the non-linearity of chromel–alumel thermocouples.

Spectrophotometric measurements were made at 25·0 ± 0·1° in 10-mm matched silica cells with a Beckman DU spectrophotometer when fixed wavelengths were to be observed, and with a dual-beam Cary 14 recording spectrophotometer (purged with dry nitrogen) when spectra were to be scanned. All solutions used in the reference beam were verified as giving no spectrum when scanned against a water reference. Absorbance values were estimated to 0·001. Measured values were key-punched, and processed by an IBM 360/75 computer, with graphical output plotted by a Calcomp 763 digital incremental plotter.

Infrared spectra were recorded at the slow scan speed of a Beckman IR10 instrument as Nujol or Fluorolube mulls held between silver chloride plates. The JEOL C-60 NMR spectrometer was used to examine the sample dissolved in deuterium oxide.

Quinizarin-2-sulphonic acid was purchased from a number of suppliers, and found to be of inadequate purity. It was also synthesized from technical grade quinizarin. Eventually, the reagent supplied as the sodium salt by Harmon Colors, Industrial Chemical Division, Allied Chemical Corp., was found to be most suitable and was purified in the manner described below and used to prepare aqueous solutions.

Metal ion solutions were prepared from the hydrated perchlorates. Other chemicals were of analytical-reagent grade.

Purification of quinizarin-2-sulphonic acid

The literature refers to the sodium salt as orange-red needles,[9,10] orange-red plates[10] and orange-red.[6] The first material examined by us was deep brownish red. It displayed colour changes from yellow to pink to blue with increasing pH in agreement with the literature. The uncorrected melting range was 145–149°. The only melting point found recorded was in a manufacturer's catalogue, as 145–145·5°. No common solvent dissolved this material completely. An aqueous solution was prepared and filtered, and a published procedure for purification was attempted.[5] Only when sodium chloride was added did a small crop of orange-red crystals, not melting at 160°, appear. It was concluded that these were the sodium salt. Elemental analysis confirmed this conclusion, but revealed that both the free acid and the sodium salt were impure, the former being no more than 66% pure.

Literature reports of variation of the analytical sensitivity of quinizarin-2-sulphonic acid with the source[6] were confirmed when large variations in purity were found. One product purchased was found to be contaminated with 20% iron.

The sodium salt obtained from Harmon Colors contained a quantity of sodium chloride but was chosen as most suitable for further purification: 5 g of this salt were dissolved in 300 ml of hot water and the solution filtered immediately through a medium glass frit, which was washed with further hot water. The filtrate and washings were reduced in volume to about 90 ml, then 1 g of sodium chloride and 1 drop of 12*M* hydrochloric acid were added. The solution was allowed to cool slowly, and finally chilled on ice. The resulting crystals were collected on a medium glass frit and washed with 100 ml of ice-cold water. The last portion of these washings showed no chloride ion when tested with 0·2*M* silver nitrate. Filtered air was drawn through the frit for 1 hr and the crystals were then oven-dried for 2–3 hr at 110°. The solid gave a negative test for chloride ion. This product was believed to be the sodium salt in a highly pure state.

The free acid was prepared by dissolving 5 g of the Harmon sodium salt in 300 ml of hot water and passing the solution at a rate of 2 ml/min through a cation-exchange column in the hydrogen form. The column was washed with hot water until the effluent was colourless, and the volume of the eluted solution was then reduced to about 175 ml. After a flame test for sodium proved negative, the solution was passed through a medium glass frit, and further concentrated to 100 ml. Slowly, 25 ml of 12*M* hydrochloric acid were stirred in, giving an orange-red precipitate, which was digested for 1 hr at 70°, cooled in an ice-bath, and filtered off on Whatman No. 40 paper. The precipitate was washed with 75 ml of ice-cold 1*M* hydrochloric acid. Filtered air was drawn through the crystals for 2 hr, four 20-ml portions of cold ether being passed through after the first 10 mins. The crystals were oven-dried for 3–4 hr at 110°. The recrystallization was twice repeated, with final oven-drying for 2 hr. The resulting solid gave negative tests for sodium and for chloride ion. The melting point was 281·5–282·5° (uncorrected), and further recrystallization caused no change in melting point.

Identification of the free acid

The melting point reported above is 137° higher than that reported previously for quinizarin-2-sulphonic acid. Related hydroxyanthraquinones show melting points over the entire range, and thus do not cast doubt on either value. Several experiments were carried out to verify the identity of the purified material.

Qualitative examination of the purified material showed that it agreed with literature descriptions in displaying appropriate pH-dependent colour changes and fading rapidly from blue to yellow in strongly alkaline solution.[6,11] The acid solutions faded slowly in light, but not in a dark cupboard.[12–14]

Approximately equivalent solutions of the two prepared materials were titrated with sodium hydroxide. Considered as a strong monobasic acid, the purified "free acid" showed a titre equivalent to a molecular weight of 315 (theoretical 320).

Starting from quinizarin, the sodium salt of quinizarin-2-sulphonic acid was prepared by the method of Marshall[10] and then transformed into "free acid" by ion-exchange. Without recrystallization, this product melted at 279–281°, and gave a visible spectrum closely approximating to that of the two purified substances. DTA and infrared results were also in agreement.

The free acid showed a double NMR signal in the ratio of 4:1 in the aromatic region 2·6 ppm downfield from the water absorption. Signals from hydroxyl protons were not expected in a room temperature spectrum, and were not observed.

The infrared spectrum showed a strong band at 1625 cm^{-1} (C=O stretch) and no hydroxyl band at 3300 cm^{-1}. This is consistent with studies of other hydroxyanthraquinones[15,16] and is taken to indicate strong hydrogen bridging between carbonyl and hydroxyl groups. The absence of a band at

2950 cm^{-1} shows that the reduction product, leucoquinizarin-2-sulphonic acid, has not been formed. Bands at 1213 cm^{-1} and 1058 cm^{-1} in the free acid, and at 1210 cm^{-1} and 1050 cm^{-1} in the sodium salt correspond to reported S=O stretching bands (1229 and 1058 cm^{-1}).[17]

The free acid was submitted to thin layer chromatography with methanol as solvent, and was found to be chromatographically homogeneous. The R_f value was approximately 0·7. Solutions which were first exposed for some time to room air and fluorescent light showed a weak slower-running spot as well.

Elemental analysis of the recrystallized free acid gave a formula $C_{14}H_9O_7S$ (based on the carbon result). This is in good agreement with $C_{14}H_8O_7S$ required.

It is concluded that the purified free acid is authentic and that the previous melting point value is incorrect.

Thermal analysis studies and hygroscopicity

To determine the best pre-treatment of reagent for preparing standard solutions, DTA and TGA studies were made to detect the loss of both hygroscopic and hydrated water which might be present.

The sodium salt which had been dried was left exposed to ambient humidity, and then subjected to DTA and TGA. Figure 1 shows a DTA curve. A modified TGA experiment is shown in Fig. 2. The sample was heated to 60° and then held isothermally for 60 min while weight loss was recorded against time. The temperature was then set to advance normally to 950°, completing a conventional TGA experiment.

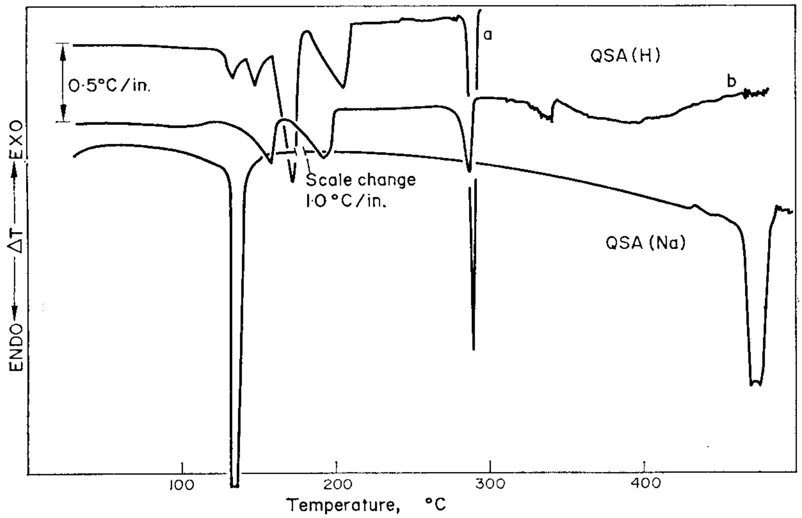

FIG. 1.—Results of differential thermal analysis: (*a*) triply-recrystallized free acid (*b*) once-recrystallized free acid.

The free acid was also studied. The thrice-recrystallized material, heated to 60° for 3 hr and stored over phosphorus pentoxide, was submitted to DTA (Fig. 1), and a singly-recrystallized sample, oven-dried for more than 3 hr at 110° and stored in room atmosphere, was examined by both DTA and TGA (Figs. 1 and 3).

A standard procedure for drying pure material at 110° before weighing was adopted. A drying time of 1 hr was adequate. On a day of high humidity a 1-g portion of dried free acid gained 2 mg in 10 min when exposed during weighing, and showed no gain in a closed weighing bottle.

Spectrophotometric assay of quinizarin-2-sulphonic acid

The fading of alkaline solutions of the reagent made it desirable to work with acid media, and an equimolar acetic acid–sodium acetate buffer maintained at a free acetate ion concentration of 0·1*M* was selected. A stock solution of the free acid was prepared from which appropriate portions were taken, placed with glacial acetic acid and anhydrous sodium acetate in volumetric flasks, and made up to volume with water. The calibration curve was prepared with a slitwidth of 0·065 mm and a wavelength of 465 nm (Beckman DU spectrophotometer) with buffer as reference. Three or more aliquots

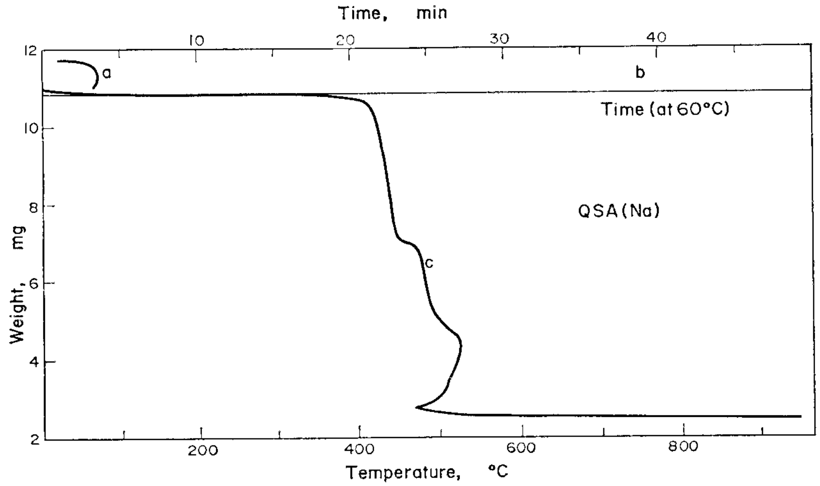

FIG. 2.—Thermogravimetric analysis with temperature arrest: (*a*) thermogram during temperature advance to 60° showing weight loss attributed to adventitious water, (*b*) stability of weight while a temperature of 60° was maintained for 1 hr. (*c*) thermogram during subsequent temperature advance from 60°, showing no weight loss up to 300°.

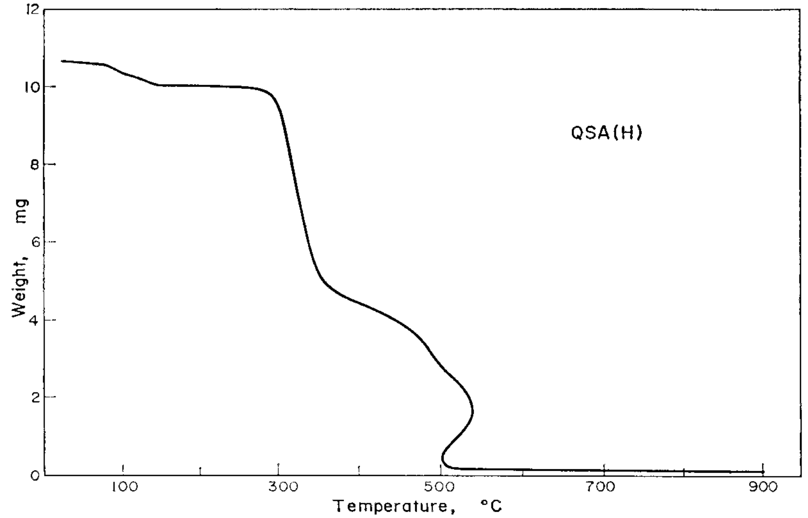

FIG. 3.—Thermogravimetric analysis.

of each solution were read. Beer's law was found to be obeyed and the following equation derived by least-squares analysis: $A = 8865C + 0{\cdot}001$ where A is the absorbance at 465 nm and C is the analytical concentration of the reagent.

Portions of the solutions used in preparing the calibration curve were stored in a cupboard away from light, and remeasured at intervals until 1700 hr had elapsed. No change in absorbance was observed. After 194 hr, one solution was stored on the bench, routinely exposed to visible light (daylight through double-glazing, and fluorescent lights through ultraviolet filtered lamp units). This sample then faded slowly, losing half its absorbance in 430 hr.

In practice, the concentrations of solutions of the free acid and of the sodium salt were determined by transferring a suitable aliquot to a 250-ml volumetric flask, partially neutralizing any mineral acid present with 0·1M sodium hydroxide, adding 2·1 g of sodium acetate and 1·45 ml of glacial acetic acid and making up to the mark with water. The absorbance was read and the concentration obtained from the calibration curve. One sample, prepared in 0·1M perchloric acid, was standardized four times over a period of 33 weeks (5500 hr) with identical results. When this method was used to analyse commercial quinizarin-2-sulphonic acid, purities as low as 44% were found.

Species contributing to the absorbance

Five media of varying pH were prepared to give approximate values as shown: sulphuric acid (pH 2·3), acetic acid–sodium acetate (pH 5·8), ammonium acetate–ammonium hydroxide (pH 8·6), ammonium chloride–ammonium hydroxide (pH 10·3) and sodium hydroxide (pH 12·3). In each of these media, solutions of quinizarin-2-sulphonic acid were prepared to be $4{\cdot}4 \times 10^{-5}M$ and spectra from 700–300 nm were recorded. By recording of spectra of mixtures of the five starting solutions, nine measured pH values were studied.

After inspection of the spectra, absorbance readings at 10-nm intervals from 660 to 410 nm for solutions from pH 5·69 to 12·30 were digitized and treated by computer program RANK, which is a slight modification of the program of Varga and Veatch.[18] Baseline corrections were negligible and were not applied. The entries in the error matrix, representing the postulated uncertainty of the absorbances being operated upon, were derived from the expression

$$S_{ij} = 0{\cdot}43429\ \Delta T \text{ antilog } A_{ij}$$

where S_{ij} is an error matrix entry corresponding to absorbance entry A_{ij} and ΔT is a postulated uncertainty of the observed transmittance. The programme automatically operates on a range of successive values of ΔT from 0·5% to 7·0%. All values of ΔT between 1·5% and 4·0% gave a value of 3 for the apparent rank of the absorbance matrix, and hence for the number of absorbing species contributing. The three contributing species are presumably the unprotonated, monoprotonated and diprotonated forms of the ligand, the sulphonic acid group always being completely dissociated at these pH values.

Acid dissociation constants

By use of standard solutions of perchloric acid and sodium hydroxide, unbuffered solutions about $1 \times 10^{-4}M$ in quinizarin-2-sulphonic acid were prepared at pH values from 1 to 13. The stock solutions were kept at 25° for at least 30 min in subdued light before mixing. The time of mixing was taken to be the time at which the bulk of any necessary addition of base was made. For each solution, spectra were recorded from 700 to 300 nm at various times up to 2 hr after mixing, depending on the instability of the absorbance (which was greater at higher pH values), the first spectrum being recorded about 5 min after mixing.

The spectra and related baselines were digitized at 5-nm intervals and the computer program ZERO TIME SPECTRUM was used to derive absorbances at time of mixing by linear least-squares extrapolation, from the set of up to six recorded spectra. These extrapolated spectra were plotted by the computer (Figs. 4 and 5).

Absorbance and pH data, the former corrected to zero time and the latter converted into concentration of hydrogen ion were presented to a group of programmes prepared by modifying Metzler's programme PITMAP[19] based on Sillén's LETAGROP VRID.[20] A model allowing the two acid dissociations was fitted to the data, and acid dissociation constants for the two phenolic protons were derived. Spectra for the individual species were calculated and plotted (Fig. 6) and their calculated mixtures were compared with the original experimental data. The values obtained were:

$$HQ^{2-} = H^+ + Q^{3-} \quad pK_a = 12{\cdot}14 \pm 0{\cdot}01$$
$$H_2Q^- = H^+ + HQ^{2-} \quad pK_a = 8{\cdot}71 \pm 0{\cdot}01$$
$$H_3Q = H^+ + H_2Q^- \quad \text{strong acid}$$

(Temperature: 25·0°; ionic strength: 0·10 – 0·05M; reagent concentration: $0{\cdot}998 \times 10^{-4}M$)

Owens and Yoe[11] give ~12 and 8·7 ± 0·1 for the pK_a values.

Reactions with metal ions

Solutions ($2 \times 10^{-2}M$) of five metal ions, in 0·1M perchloric acid, were tested for reaction with the reagent at five pH values. Results are shown in Table 1. For iron(III) the colour and the acidity at which it developed were different from those for the other systems.

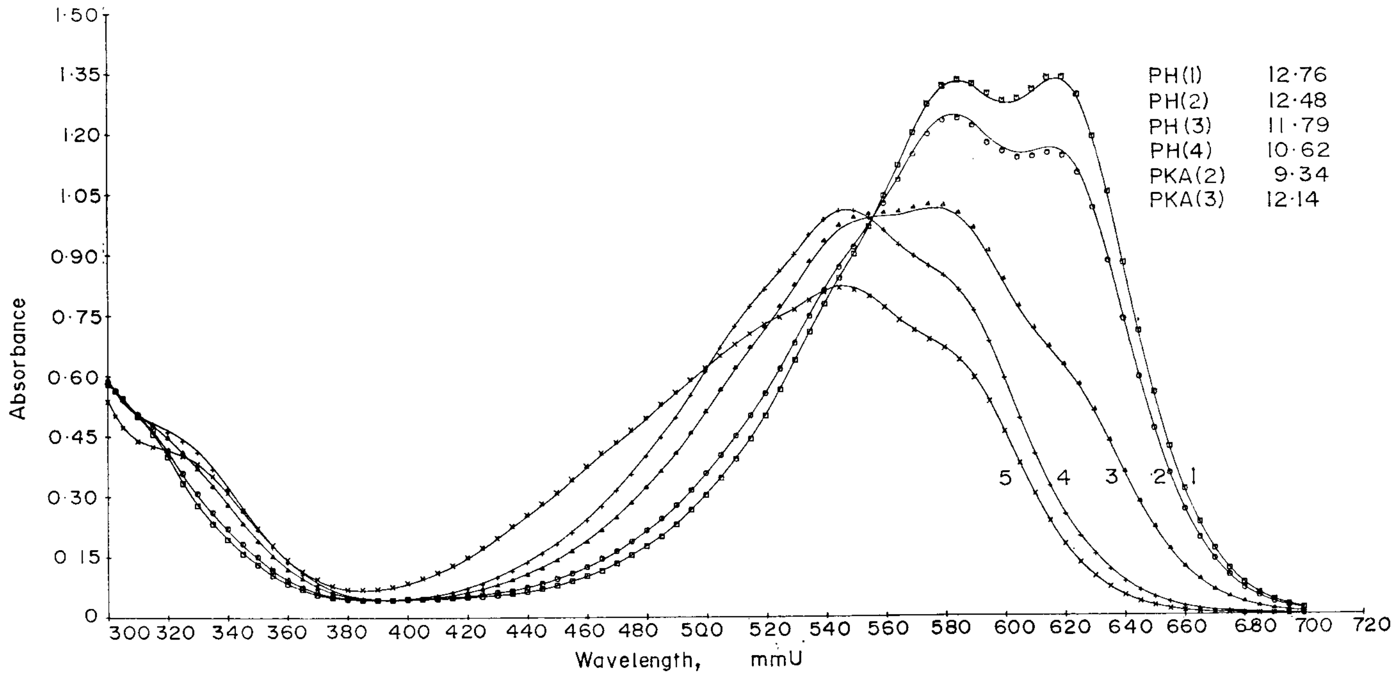

Fig. 4.—Spectra at various acidities, corrected for fading.

Symbol:	□	○	△	+	×
pH:	12·76	12·48	11·79	10·62	9·34

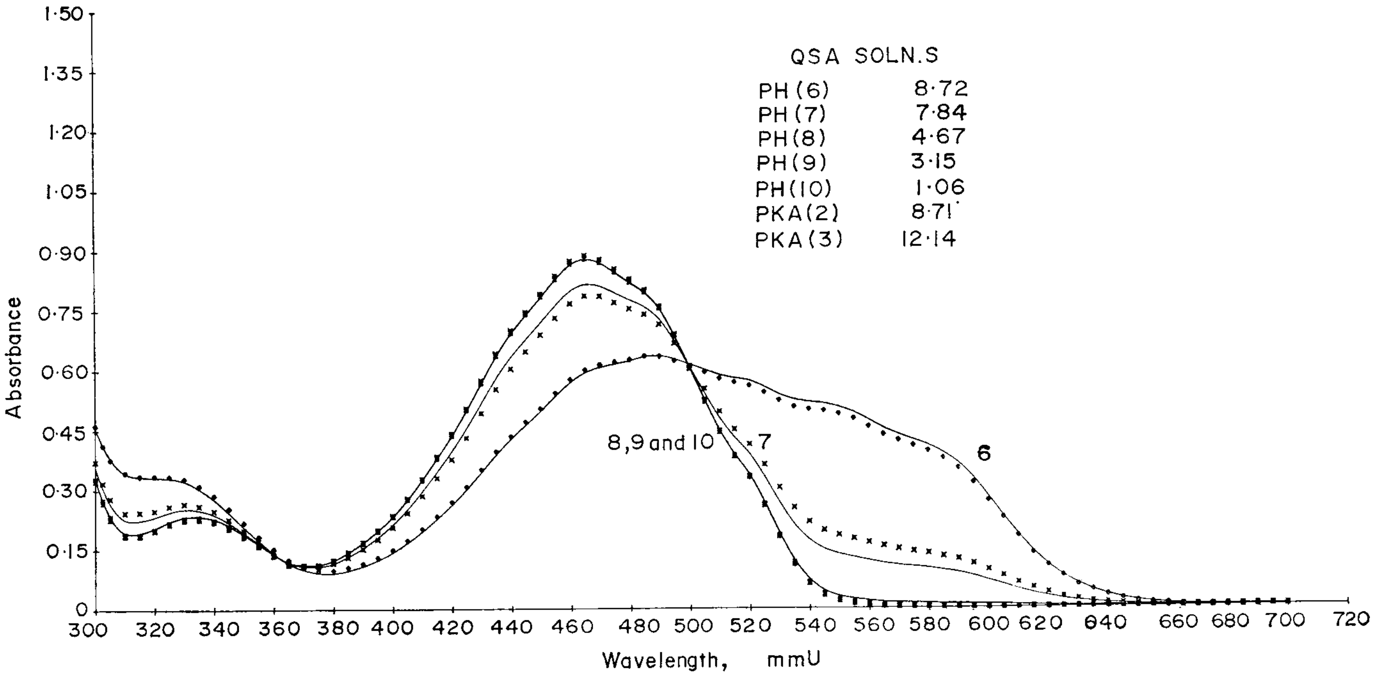

FIG. 5.—Spectra at various acidities, corrected for fading.

Symbol:	◇	⌧	⧗	*	Y
pH:	8·72	7·84	4·67	3·15	1·06

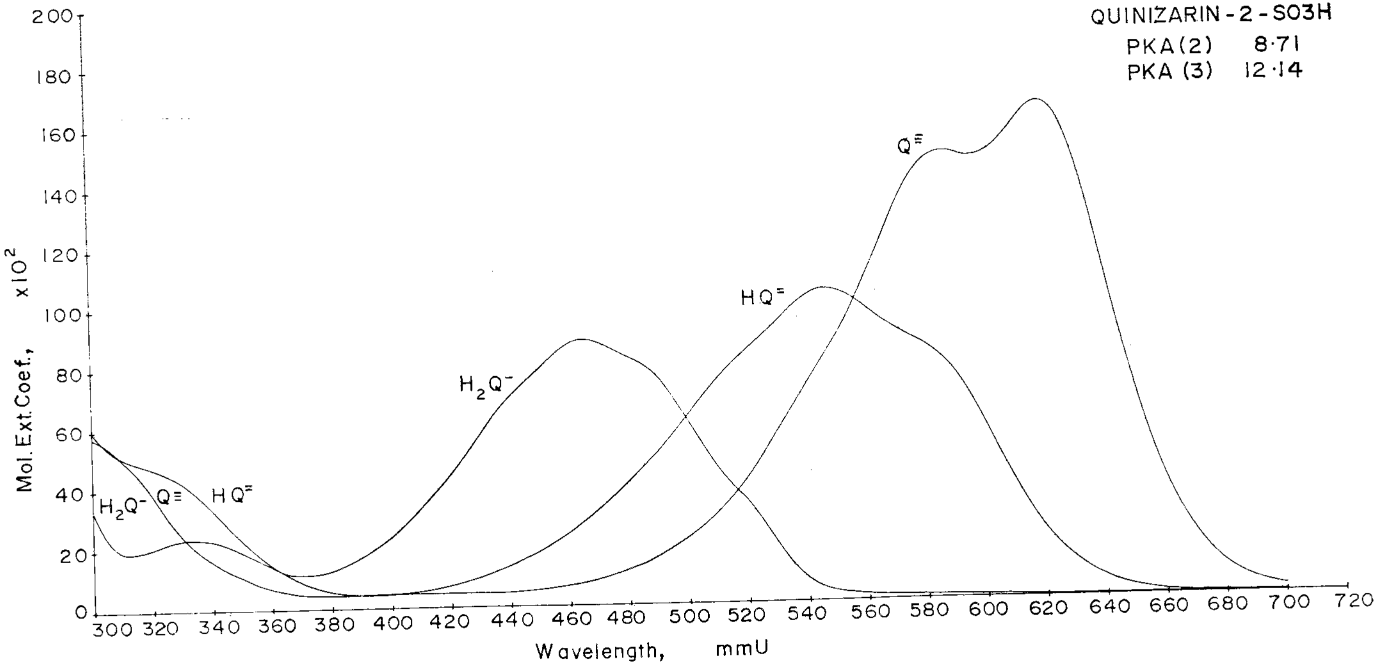

FIG. 6.—Computed spectra of pure species, $pK_{a_1} = 8{\cdot}71$; $pK_{a_2} = 12{\cdot}14$.

TABLE I.—REACTION OF QUINIZARIN-2-SULPHONIC ACID WITH CERTAIN METAL IONS

Test soln.*	Cation	Nominal pH of buffer solution				
		2	6	8	10	12
Average pH of test solns.	Co(II)	2·1	5·4	6·6	10·0	12·4
	Ni(II)	2·1	5·4	6·9	10·0	12·4
	Cu(II)	1·8	5·2	6·5	9·8	12·3
	Al(III)	1·8	5·3	6·8	9·9	12·5
	Fe(III)	1·8	5·3	6·3	9·9	12·4
Ligand only	—	OY	OY+	OR	P	B
Metal only	Co(II)	R−	R−	R−	PPTE(GB−)	PPTE(B)
	Ni(II)	NC	NC	NC	BG−	PPTE(BW)
	Cu(II)	NC	BG	GB	B	PPTE(B)
	Al(III)	NC	NC	PPTE(W)	PPTE(W)	NC
	Fe(III)	Y−	PPTE(BN)	PPTE(BN)	PPTE(BN)	PPTE(BN)
Metal plus ligand	Co(II)	OY	OR+	RP+	V, LK	B+, LK
	Ni(II)	OY	RO	PR+	V	B+, LK
	Cu(II)	OY+	PR, LK	PR, LK	P+, LK	V, LK
	Al(III)	OR+	P+, LK	P+, LK	P+	V+
	Fe(III)	R − BL	BN−, PPTE(BL)	BN−, PPTE(BL)	P, PPTE(BL)	B, PPTE(BL)

* Coding: O—orange, Y—yellow, R—red, P—purple, B—blue, G—green, BN—brown, BL—black, V—violet, W—white, NC—clear or no colour; PPTE indicates a precipitate, usually gelatinous, and its colour is given in parentheses; LK stands for formation of a coloured lake. Changes in intensity or hue are noted by + or − indicating deeper or lighter, respectively.

Digital data

Listings of the digitized spectra of each species are available on request.

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Zusammenfassung—Chinizarin-2-sulfonsäure und ihr Natriumsalz wurden für analytische Zwecke gereinigt. Das thermoanalytische Verhalten und die Infrarot- und NMR-Spektren des Reagens wurden registriert. Für die Gehaltsbestimmung von Lösungen wird Extinktionsmessung bei 465 nm empfohlen. Für den Ausbleicheffekt korrigierte spektrophotometrische Messungen werden nach einem Verfahren vom Typ PITMAP verarbeitet, um die Säuredissoziationskonstanten zu erhalten. Schließlich wird eine kurze Übersicht über einige Reaktionen mit Metallionen gegeben.

Résumé—L'acide quinizarine 2-sulfonique et son sel de sodium ont été purifiés pour usage analytique. On a enregistré le comportement à l'analyse thermique et les spectres infra-rouge et RMN du réactif. On recommande l'absorptiométrie à 465 nm pour le contrôle des solutions. Les mesures spectrophotométriques, corrigées pour l'affaiblissement de coloration, sont traitées par une technique du type PITMAP pour obtenir les constantes de dissociation acide pour le réactif. Finalement, on passe brièvement en revue quelques réactions avec des ions métalliques.

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KALIUMBESTIMMUNG IN SILIKATGLÄSERN DURCH THERMOMETRISCHE KONZENTRATIONSANALYSE

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Zusammenfassung—Eine rasche thermometrische Bestimmung des Kaliums wird beschrieben. Als Reaktionstyp wird die Fällung des Kaliums als Kaliumtetraphenylborat gewählt. Das Verfahren führt zu guten Ergebnissen und ist der gravimetrischen Methode überlegen. Eine Doppelbestimmung läßt sich in etwa einer Stunde durchführen.

DIE KONVENTIONELLEN gravimetrischen Bestimmungsverfahren sind meist recht zeitaufwendig und daher wenig geeignet für den Einsatz in der Betriebskontrolle. Die Anwendung der in den letzten Jahren bekanntgewordenen Methodik der "thermometrischen Konzentrationsanalyse"[1,2] erlaubt, die Analysenzeiten auf ein Minimum herabzusetzen und die täglich im Industrielaboratorium anfallenden Routinearbeiten rationell zu gestalten.

Die von Rondeau und Mitarbeitern[3] erhaltenen Befunde bei der Untersuchung der Kaliumtetraphenylborat-Fällungsreaktion durch thermometrische Titration gaben Anlaß zur Ausarbeitung einer brauchbaren Kaliumbestimmung in Silikatgläsern nach der Methode der thermometrischen Konzentrationsanalyse, über die im vorliegenden Beitrag berichtet wird.

Chemische Umwandlungen werden in fast allen Fällen von mehr oder weniger großen Reaktionswärmen exo- bzw. endothermen Charakters begleitet. Die durch die Reaktionswärmen verursachten Temperaturänderungen können mittels einer geeigneten apparativen Einrichtung meßbar verfolgt werden. Beim enthalpimetrischen Titrationsverfahren wird die Temperaturänderung eines Reaktionsgemisches als Funktion des zugegebenen Volumens einer Maßlösung verfolgt, während nach der Arbeitstechnik der thermometrischen Konzentrationsanalyse das Reagens in konzentrierter Form auf einmal und im Überschuß der Probelösung zugefügt wird.

Für die in einem wäßrigen System bei vernachlässigbarer Verdünnungswärme ablaufende selektive Reaktion

$$aA + (b + c)B = pP + cB \tag{1}$$

resultiert der integrale Wärmeeffekt

$$Q = n_A \cdot \Delta H, \tag{2}$$

wo n_A = Molzahl der zu bestimmenden Komponente A in der Analysenlösung, ΔH = molare Reaktionsenthalpie bezeichnen.

Wird dem in einer adiabatischen Meßzelle vorliegenden Lösungsmittel eine Wärmemenge Q zugeführt, so erhöht sich seine Temperatur T um einen bestimmten Betrag ΔT, dessen Größe von der Wärmekapazität k des Gesamtsystems abhängt:

$$Q = k \cdot \Delta T. \tag{3}$$

Nach Einsetzen des für Q gültigen Ausdrucks in Gleichung (2) wird für ΔT erhalten:

$$\Delta T = \frac{\Delta H}{k} \cdot n_A = \text{konst} \cdot n_A. \tag{4}$$

Die Temperaturänderung ΔT ist also proportional der Molzahl n_A der in einem bestimmten Lösungsmittelvolumen enthaltenen Komponente A und damit direkt proportional der zu ermittelnden Konzentration der Komponente A.

Die erfolgreiche Durchführung der thermometrischen Konzentrationsanalyse ist an folgende Hauptvoraussetzungen gebunden:

1. Die für die quantitativ zu bestimmende Komponente ausgewählte Reaktion muß selektiv sein, schnell und vollständig verlaufen sowie eine genügend große Wärmetönung liefern.
2. Die Wärmekapazitäten der Analysen-, Reagenslösung und der Meßeinrichtung müssen konstant gehalten werden.
3. Die Messungen müssen unter quasi-adiabatischen Bedingungen ausgeführt werden.
4. Das Reagens ist stets in konzentrierter Form anzuwenden und der Analysenlösung immer auf einmal und in derselben überschüssigen Menge zuzufügen.
5. Die Matrix der zu analysierenden Materialien darf nur in bestimmten, vorher zu ermittelnden Grenzen variieren.

Die bei einer Fällungsreaktion resultierende Wärme setzt sich aus zwei Anteilen zusammen: der molaren Wärme als Folge der Bildung einer schwerlöslichen Verbindung aus den in Lösung vorhandenen freien Ionen und der eigentlichen Fällungswärme. Diese Gesamtwärmemenge ist gewöhnlich nicht sehr groß und liegt bei etwa 40 kJ pro Mol. Für die Kaliumtetraphenylborat-Fällungsreaktion konnte $\Delta H_{298K} = -40{,}3$ kJ/Mol ermittelt werden.[4]

EXPERIMENTELLER TEIL

Reagentien

Flußsäure 38–40%-*ig p.a. Salzsäure ca.* 37%-*ig p.a. Natriumacetatlösung.* $CH_3COONa \cdot 3H_2O$ kristallisiert *p.a.* (800 g) wird in destilliertem Wasser gelöst, und die Lösung wird in einem 2-Litermeßkolben mit Wasser bis zur Eichmarke ergänzt.

Reagensmittel nahezu ohne Verdünnungswärme. Natriumtetraphenylborat *p.a.* (100 g) wird in 1750 ml destilliertem Wasser unter Erwärmen gelöst (5,40%-ige Lösung).

Kaliumchlorid p.a. Als Eichsubstanz.

Meßeinreichtung, Meßprinzip und optimale Meßbedingungen

Anwendung findet das von der Firma Ungarische Optische Werke Budapest kommerziell erhältliche Analysengerät Directhermom, dessen Kernstück die in der Abb. 1 schematisch dargestellte Wheatstone'sche Brückenschaltung bildet.

Als Temperaturfühler dient der NTC-Thermistor R3. Im abgeglichenen Zustand der Brücke gilt die Beziehung:

$$R_1 : R_2 = R_4 : R_3, \tag{5}$$

womit die Diagonalspannung $U = 0$ ist. Bei Änderung des Brückenwiderstandes R_3 (Thermistor) wird die abgeglichene Brücke um einen Wert R_x verstimmt, und es tritt eine Potentialdifferenz, d.h. $U \neq 0$ auf. Als Folge fließt ein Strom I durch das Anzeigeinstrument G (Skalengalvanometer) in der Brückendiagonalen. Mittels des Spannungsteilers ST läßt sich eine Justierung der Galvanometerskala in °C vornehmen, wobei durch Hinzuschalten parallel zum Anzeigeinstrument liegender Festwiderstände einzelne Empfindlichkeitsstufen erhalten werden.

Vier Reihen zu je fünf bzw. eine Reihe zu vier parallel zum Anzeigeninstrument einschaltbare Lineardrahtpotentiometer $P_1 - P_{24}$ gestatten bei entsprechender Empfindlichkeitsvorwahl die Eineichung der Galvanometerskala in analytische Konzentrationsdaten.

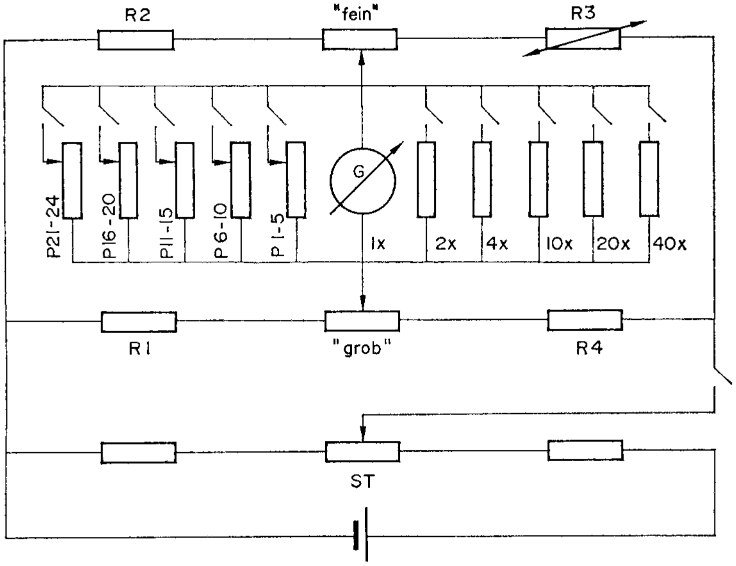

ABB. 1.—Wheatstone'sche Brückenschaltung des thermometrischen Analysengerätes Directhermom (Prinzipschaltbild).

ST	Spannungsteiler
$1\times, 2\times, 4\times, 10\times, 20\times, 40\times$	Empfindlichkeitsstufen
R_1, R_2, R_4	Festwiderstände
R_3	NTC-Thermistor
"grob", "fein"	Brückenabgleichpotentiometer
G	Skalengalvanometer
P_1–P_{24}	Konzentrations-Eichpotentiometer

Damit sind mit dem Directhermom zwei Arbeitsweisen möglich: Ausführung der thermometrischen Analysen (*a*) nach dem Eichkurvenverfahren und (*b*) durch Direktanzeige des Konzentrationswertes. Als optimale Meßbedingungen gelten:

1. Der Meßzellenraum wird durch ein Dewargefäß gebildet (Abb. 2), in das ein etwa 400-ml Plastikbecher zur Aufnahme der Analysenlösung eingesetzt werden kann. Der Meßkopf trägt einen Schaumstoffdichtungsring und gewährleistet nach Einführen der Meßelemente in die Analysenlösung einen hermetischen Abschluß zur Umgebung. Dadurch sind quasi-adiabatische Bedingungen während des Meßvorganges gegeben.
2. Die Rührgeschwindigkeit wird konstant gehalten.
3. Analysen-, Reagenslösung und Meßzelleninnenraum sollen gleiche Ausgangstemperatur (±0,1°) aufweisen; ein vollständiger Temperaturausgleich erfolgt nach 5-minutigem Rühren.
4. Die Tauchpipette wird stets mit konstanter Reagensmittelmenge gefüllt. Ebenso wird die zur Entleerung der Tauchpipette erforderliche Luftmenge immer konstant dosiert.

Arbeitsvorschrift

Glas-Aufschluß. Die dem zu erwartenden K_2O-Gehalt bemessene Einwaage des feinpulverisierten Glases wird in einer 100-ml Platinschale mit Wasser befeuchtet, zweimal mit je 15 ml Flußsäure und einmal mit 15 ml konzentrierter Salzsäure auf dem Wasserbad eingedampft. Der Abdampfrückstand wird in verdünnter Salzsäure (3 ml konzentrierte Salzsäure und 25 ml Wasser) unter Erwärmen gelöst. Die Lösung wird in einen 250-ml Meßkolben überführt, 10 ml Natriumacetatlösung werden zugegeben, und der Meßkolben wird mit destilliertem Wasser bis zur Eichmarke aufgefüllt.

Arbeitsweise nach dem Eichkurvenverfahren. Zum Aufstellen der Eichkurve bzw. Eichfunktion y[Skalenteile oder $\Delta T = \mathrm{K}$] $= f(x)$[mg K_2O] wird Kaliumchlorid verwendet. Die den K_2O-Mengen von 25, 50, 75 und 100 mg entsprechenden Kaliumchloridmengen werden in 250-ml Meßkolben eingewogen, in destilliertem Wasser gelöst, jeweils mit 3 ml konzentrierter Salzsäure und 10 ml Natriumacetatlösung versetzt, und die Meßkolben werden mit Wasser bis zu den Eichmarken aufgefüllt. Die so vorbereiteten Eichlösungen und das Reagensmittel werden in einem Thermostaten

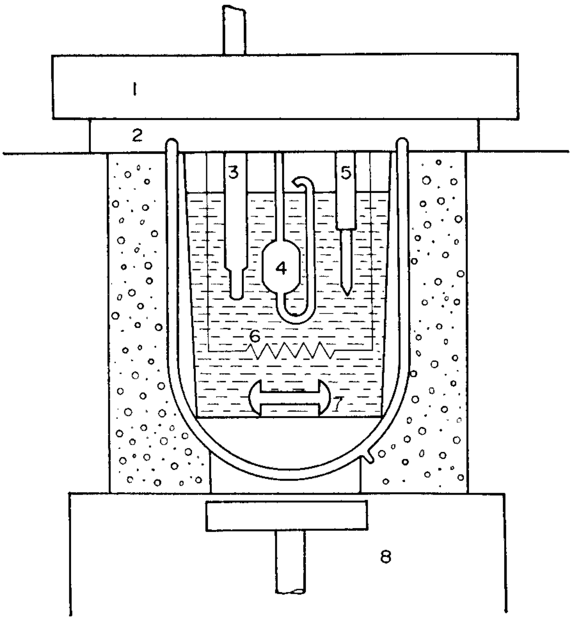

ABB. 2.—Meßzelleneinrichtung des thermometrischen Analysengerätes Directhermom.

1 Meßkopf
2 Schaumstoffdichtung
3 Kontroll- bzw. Beckmann-Thermometer
4 Tauchpipette
5 NTC-Thermistor
6 Elektrische Widerstandsheizung
7 Magnetrührstab
8 Magnetrührwerk

auf die vorher gemessene Ausgangstemperatur des Meßzelleninnenraumes mit ±0,1° eingestellt. Die einzelnen Eichlösungen werden in den als Meßgefäß dienenden Plastbecher, in dem sich der Magnetrührkern befindet, überführt. Der mit 250 ml Probelösung gefüllte Plastbecher wird sodann in den Meßzellenraum eingesetzt. Die 15-ml Tauchpipette wird mit 5,40%-iger Natriumtetraphenylboratlösung gefüllt, außen mit wenig destilliertem Wasser abgespült, mit einem Zellstoffbausch kurz abgetupft und in die am Meßkopf vorgesehene Halterung eingebracht. Durch Absenken des Meßkopfes werden die Meßelemente in die Analysenlösung eingeführt und die Meßzelle verschlossen. Das Magnetrührwerk wird in Betrieb gesetzt; der Temperaturausgleich zwischen Analysen-, Reagenslösung in der Tauchpipette und Meßzellenraumumgebung ist nach 5 Minuten beendet. Der Meßkreis wird eingeschaltet. Nach Kontrolle auf Temperaturausgleich wird der Galvanometerausschlag bei der Empfindlichkeitsstufe "2-mal" (1000 Skalenteile = 0,50°) mit dem "Grob"- und "Fein"-Potentiometer auf Null einreguliert, das Reaengs aus der Tauchpipette in die Analysenlösung eingespritzt und der sich einstellende Galvanometerausschlag in Skalenteilen abgelesen.

Die Einwaagen der zu analysierenden Gläser werden so berechnet, daß ihre K_2O-Gehalte in den Konzentrationsbereich der Eichkurve zu liegen kommen; am günstigsten ist der Bereich zwischen 30 und 70 mg K_2O. Der Meßvorgang an den durch Flußsäureaufschluß vorbereiteten Analysenlösungen gestaltet sich gleichermaßen wie oben beschrieben. Das Analysenergebnis wird entweder durch Auswerten nach der Eichkurve oder durch Berechnen aus der Eichfunktion erhalten.

Arbeitsweise bei Direktanzeige des Konzentrationswertes. Bei Arbeit nach dem Verfahren der Direktanzeige des Konzentrationswertes wird eines der Lineardrahtpotentiometer P_{21}–P_{24} mit nur einer K_2O-Eichlösung justiert, wobei die Empfindlichkeitsstufe "1-mal" Anwendung findet. Der Konzentrationswert der Eichlösung wird auf der Galvanometerskala durch Verändern des Widerstandes des Lineardrahtpotentiometers fest eingestellt. Der gesuchte Analysenwert kann dann direkt in mg oder masse-% K_2O am Galvanometer abgelesen werden.

ERGEBNISSE UND DISKUSSION

Die Eichfunktion für die Kaliumtetraphenylborat-Fällungsreaktion ergibt sich zu $y = 2 + 1{,}48x$. Der relativ hohe Wert des Regressionskoeffizienten mit $b = 1{,}48$ Skalenteile pro mg K_2O gilt als Maß dafür, daß der gewählte Reaktionstyp in der thermometrischen Konzentrationsanalyse mit Erfolg eingesetzt werden kann. Bei Kenntnis der Größe von b läßt sich der Wert für die molare Enthalpieänderung nach Gleichung (6) leicht errechnen:

$$\Delta H = M \cdot b \cdot E \cdot k. \tag{6}$$

in dieser Gleichung bedeuten: M = Mol- bzw. Äquivalentmasse [g], b = Regressionskoeffizient [Skt · g^{-1}], E = Empfindlichkeitsstufe (Meßbereich) [K], k = Wärmekapazität der Meßzelleneinrichtung [kJ. K^{-1}].

Kationen, wie NH_4^+, Ag^+, Tl^+, Hg^{2+}, die ebenfalls mit Natriumtetraphenylborat schwerlösliche Niederschläge bilden, müssen abwesend sein, während die Gegenwart von Cl^-, NO_3^-, F^-, SO_4^{2-} und PO_4^{3-} keinen Einfluß ausübt.

TABELLE I.—VERGLEICHZ WISCHEN THERMOMETRISCH, FLAMMENPHOTOMETRISCH UND GRAVIMETRISCH ERMITTELTEN K_2O-GEHALTEN SOWIE DEN SYNTHESEWERTEN EINIGER SILIKATGLÄSER

	K_2O, *Masse-%*			
	Synthese	thermometrisch	flammenfotometrisch	gravimetrisch*
Alkalisilikatglas Nr. 1	28,0	27,9	27,5	28,2
Alkalisilikatglas Nr. 2	20,0	18,6	19,0	19,1
Alkalisilikatglas Nr. 3	17,5	16,9	17,1	17,3
Zink-Baryt-Glas (Standardglas[5])	—	7,1	—	7,7
Borosilikatglas (Pyrextyp)	1,5	1,1	1,2	—

* Als Kaliumtetraphenylborat.

Die Tabelle I enthält die Analysenergebnisse der thermometrischen K_2O-Bestimmung für einige Silikatgläser. Die Gegenüberstellung zu den durch Flammenfotometrie und auf gravimetrischem Wege erhaltenen Analysendaten sowie den Synthesewerten läßt Übereinstimmung erkennen. Diese gute Reproduzierbarkeit wird auch durch die in der Tabelle II zusammengestellten Maßzahlen für den Zufallsfehler der thermometrischen Kaliumbestimmung bestätigt.

Nach dem Verfahren der thermometrischen Konzentrationsanalyse sind bei Arbeit mittels Eichkurve noch K_2O-Gehalte bis herab zu 10 mg quantitativ bestimmbar. Das ermöglicht die äußerst rasch, eindeutig und vollständig verlaufende Fällung des Kaliums mit Natriumtetraphenylborat und zeigt andererseits die Leistungsfähigkeit des Analysengerätes Directhermom, sehr geringe Temperaturänderungen reproduzierbar zu erfassen.

Das Reagensmittel kann auf Grund der Schwerlöslichkeit des Natriumtetraphenylborats als eine nur 5,40%-ige wäßrige Lösung bereitet werden. Bei Anwenden von 15 ml (Tauchpipette) ist das Reagens noch in ausreichendem Überschuß in der Analysenlösung vorhanden und gestattet die Bestimmung bis 150 mg K_2O. Die Erweiterung des Konzentrationsbereiches ist möglich:

—durch Verwenden einer Tauchpipette größeren Fassungsvermögens oder

TABELLE II.—MATHEMATISCH-STATISTISCHE BEWERTUNG DES VERFAHRENS DER THERMOMETRISCHEN KONZENTRATIONSANALYSE ZUR K_2O-BESTIMMUNG IN SILIKATGLÄSERN

Standardabweichung[6]	$s = 0{,}17$ Masse-% K_2O
$s = \sqrt{\frac{\Sigma(x' - x'')^2}{2m}}$	für $f = 10$ Freiheitsgrade
mit $f = m$ Freiheitsgraden	
Vertrauensintervall des Mittelwertes[7]	$\Delta\bar{x} = \pm 0{,}2$ Masse-% K_2O
$\Delta\bar{x} = \frac{t(P,f)\,.\,s}{n}$	für $n = 4$ Parallelbestimmungen
Streubereich des Einzelwertes	$\Delta x = \pm 0{,}4$ Masse-% K_2O
$\Delta x = t(P,f)\,.\,s$	
Maximal zulässige Differenz zwischen zwei Parallelbestimmungen[8]	$x_D = 0{,}5$ Masse-% K_2O
$x_D = t(P,f)\,.\,s\,.\,\sqrt{2}$	
	Statistische Sicherheit $P = 95\%$

—bei umgekehrter Arbeitsweise, indem die Analysenlösung aus der Tauchpipette in die in großem Überschuß vorgelegte Reagenslösung gegeben wird.

Wesentlich ist der für die thermometrische Kaliumbestimmung in Silikatgläsern benötigte geringe Zeitbedarf: eine Doppelbestimmung ist innerhalb einer Stunde ausführbar. Im Gegensatz dazu werden für das gravimetrische Verfahren etwa 6 Stunden benötigt. Die thermometrische Kaliumbestimmung reiht sich so in die Gruppe der rationellen Analysenmethoden ein und dürfte für die Betriebslaboratorien der Glas- und Silikatindustrie von Interesse sein.

Summary—A rapid thermometric determination of potassium is described in which the element is precipitated as the tetraphenylborate, and the change in enthalpy of the solution system is measured. Results obtained for the analysis of glasses were satisfactory and the method is superior to the usual gravimetric one.

Résumé—On décrit une détermination thermométrique rapide du potassium, dans laquelle l'élément est précipité à l'état de tétraphénylborate, et l'on mesure la variation d'enthalpie de la solution. Les résultats obtenus pour l'analyse de verres ont été satisfaisants, et la méthode est supérieure à la méthode gravimétrique usuelle.

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SHORT COMMUNICATIONS

Liquid–liquid extraction of lead(II) with tributyl phosphate

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THE EXTRACTION COEFFICIENT of lead with tributyl phosphate (TBP) from hydrochloric acid has been determined,[1] and is not affected by the presence of iron.[2] Several transition metals are quantitatively extracted by diluted TBP.[3] Extension of these studies revealed that lead can also be quantitatively extracted with 30% TBP in isobutyl methyl ketone (IBMK) from 3*M* hydrochloric acid/2*M* lithium chloride. It was further observed that the diluent IBMK is incapable of extracting lead. Lead can be stripped from the organic phase with water and determined photometrically as its orange-red complex with 4-(2-pyridylazo) resorcinol (PAR) at 520 nm.[4]

EXPERIMENTAL

Reagents

Tributyl phosphate.

4-(2-Pyridylazo)resorcinol. Aqueous solution, 0·01%.

Buffer solution, pH ~10·0. Ammonium chloride (7 g) and conc. ammonia solution (57 ml) in 1 litre of water.

Stock solution of lead. Lead nitrate (analytical grade ~0·8 g) dissolved in 1 litre of distilled water, and standardized gravimetrically as chromate,[5] then diluted tenfold to obtain the working solution.

General procedure

An aliquot of solution containing 49·5 μg of lead was taken. Enough hydrochloric acid and lithium chloride were added to make their respective concentrations 3*M* and 2*M* respectively in a volume of 25 ml. The solution was then transferred to a 250-ml separatory funnel and 10 ml of 30% TBP in IBMK was added and it was shaken briskly for about 5 min. The layers were allowed to separate and the aqueous layer was carefully withdrawn. Lead from the organic phase was stripped with 10 ml of water. The resulting aqueous phase was mixed with 10 ml of buffer solution (pH ~10·0), 0·5 ml of 0·01% PAR solution was added and the total volume was made up to 25 ml. After about 15 min the absorbance of the orange–red complex was measured at 520 nm. The concentration of lead was found from the calibration curve. The extractions and colorimetric determination were carried out at room temperature (28°).

RESULTS AND DISCUSSION

Effect of TBP and acid concentration

The concentration of TBP was varied from 0 to 100% (0–3·66*M*) with IBMK as the diluent. The acid concentration was varied between 0·5 and 8*M*, and in each extraction, unless otherwise specified, 2*M* lithium chloride was used as the salting-out agent (Table I). It was observed that in the absence of TBP, the diluent is incapable of extracting lead at any concentration of hydrochloric acid. Similarly 100% TBP in the absence of salting-out agent does not extract more than 70·8% of lead from 4*M* hydrochloric acid. With 30% TBP in IBMK the extraction is again incomplete at any acidity in the absence of salting-out agent, but is quantitative from 3*M* hydrochloric acid with 2*M* lithium chloride as the salting-out agent. Thus this TBP–IBMK mixture was taken as the optimum because it gave the lowest TBP concentration at which lead was quantitatively extracted from 3*M* hydrochloric acid/2*M* lithium chloride.

The composition of the extractable species was investigated by plotting log *D vs.* log [TBP] at a fixed acidity (1*M* hydrochloric acid). The slope was 1·73, suggesting the most probable composition of the extractable species may be $PbCl_2 \cdot 2TBP$.

Effect of salting-out agents

Various salting-out agents, such as lithium, sodium, potassium and ammonium chlorides were tested for their effect on extraction (Table II). It was not possible to use multivalent salting-out

Table I.—Effect of TBP and acid concentrations on extraction of lead
Pb = 49·5 μg; 2*M* LiCl as salting-out agent

[TBP]	Initial [HCl], *M*	% Extraction	Distribution ratio
100% (3·66*M*) in absence of 2*M* LiCl	0·5	25·0	0·83
	1·0	41·6	0·71
	2·0	54·2	1·18
	3·0	66·7	2·00
	4·0	70·8	2·42
	5·0	66·7	2·00
	6·0	62·5	1·67
	7·0	58·3	1·40
	8·0	50·0	1·00
100% (3·66*M*)	0·5	66·7	2·00
	1·0	79·3	3·83
	2·0	91·7	11·05
	3·0	100·0	∞
75% (2·74*M*)	0·5	64·6	1·82
	1·0	77·1	3·37
	2·0	89·6	7·86
	3·0	100·0	∞
50% (1·83*M*)	0·5	82·5	1·67
	1·0	75·0	3·00
	2·0	87·5	7·00
	3·0	100·0	∞
30% (1·09*M*)	0·5	54·2	1·18
	1·0	70·8	2·42
	1·5	77·1	3·37
	2·0	85·4	5·85
	2·5	91·7	11·05
	3·0	100·0	∞
30% (1·09*M*) in absence of 2*M* LiCl	0·5	16·7	0·20
	1·0	37·5	0·60
	2·0	45·8	0·85
	3·0	62·5	1·67
	4·0	58·3	1·40
20% (0·73*M*)	0·5	29·3	0·41
	1·0	45·8	0·85
	2·0	58·3	1·40
	3·0	70·8	2·42
0% (0*M*)	0·5–8·0	0	—

agents such as magnesium or aluminium chloride as they showed strong interference[6,7] in the determination of lead with PAR.

The results in Table II showed that it is possible to extract lead quantitatively with 30% TBP–IBMK from 3*M* hydrochloric acid only in the presence of 2*M* lithium chloride as the salting-out agent. Other salting-out agents have no pronounced effect.

The period of equilibration was varied from 1 to 15 min. Extraction is quantitative in 5 min.

Effect of diverse ions

Several ions were studied for their effect on extraction of lead (Table III). The tolerance limit was set as the amount of foreign ion required to cause ±2% error in lead recovery. It was observed that ions such as thallium, bismuth, thorium, alkali metals and alkaline earths, arsenate, bromide,

TABLE II.—EFFECT OF SALTING-OUT AGENTS
Pb = 49·5 μg; 30% TBP IN IBMK

Salting-out agent		Initial [HCl], *M*	% Extraction	Distribution ratio
LiCl	1*M*	0·5	45·8	0·85
		1·0	58·3	1·40
		2·0	70·8	2·42
		3·0	83·3	4·99
	2*M*	0·5	62·5	1·67
		1·0	75·0	3·00
		2·0	87·5	7·00
		3·0	100	∞
NaCl	1*M*	0·5	39·6	0·65
		1·0	30·0	1·00
		2·0	62·5	1·67
		3·0	75·0	3·00
	2*M*	0·5	41·6	0·71
		1·0	54·2	1·18
		2·0	68·4	2·17
		3·0	81·1	4·29
KCl	1*M*	0·5	39·6	0·65
		1·0	52·1	1·09
		2·0	60·4	1·53
		3·0	70·8	2·42
	2*M*	0·5	45·8	0·85
		1·0	58·3	1·40
		2·0	68·4	2·17
		3·0	79·3	3·83
NH_4Cl	1*M*	0·5	29·3	0·41
		1·0	41·6	0·71
		2·0	54·2	1·18
		3·0	66·7	2·00
	2*M*	0·5	45·8	0·85
		1·0	54·2	1·18
		2·0	66·7	2·00
		3·0	79·3	3·83

chlorate and fluoride are tolerated in ratio of 100:1 weight ratio to lead. Ions tolerated in 50:1 weight ratio are mercury, beryllium, zirconium, cerium, selenite, tellurite, thiocyanate *etc.* Silver, platinum, gold, iridium, ruthenium are tolerated at 20:1 ratio. Ions showing strong interference are copper(II), iron(III), zinc, cobalt(II) and chromate. Cadmium, nickel and uranium show interference which can be eliminated by masking them with about 2·5 mg of tartaric, malonic and ascorbic acid respectively, before extraction.

Application to analysis of gun-metal

About 0·2 g of gun-metal was dissolved in 15 ml of concentrated nitric acid. The solution was evaporated almost to dryness to remove excess of acid. The residual mass was leached with water and diluted to 250 ml in a standard flask. Then 1 ml of this diluted solution was taken and adjusted to pH 2·5, then extracted with five 10-ml portions of 0·10*M* acetylacetone in benzene to remove copper.[8,9] The aqueous phase was then carefully separated, adjusted to about pH 4·5, and extracted

Table III.—Effect of diverse ions
Pb = 49·5 μg; 3*M* HCl + 2*M* LiCl; 30% TBP in IBMK

Foreign ion	Added as	Tolerance limit, *mg*	Foreign ion	Added as	Tolerance limit, *mg*
Ag^{+}	$AgNO_3$	1·0	Ca^{2+}	$CaCl_2{\cdot}2H_2O$	5·0
Hg^{2+}	$Hg(NO_3)_2$	2·5	Sr^{2+}	$SrCl_2{\cdot}6H_2O$	5·0
Tl^{+}	$Tl(NO_3)$	5·0	Ba^{2+}	$BaCl_2{\cdot}2H_2O$	5·0
Cu^{2+}	$CuSO_4{\cdot}5H_2O$	nil	Rb^{+}	$RbCl$	5·0
Cd^{2+}	$CdCl_25H_2O$	0·5*	Cs^{+}	$CsCl$	5·0
Sn^{2+}	$SnCl_2{\cdot}2H_2O$	2·5	AsO_4^{3-}	Na_3AsO_4	5·0
Bi^{3+}	$Bi(NO_3)_3$	5·0	CrO_4^{2-}	K_2CrO_4	nil
Ru^{3+}	$RuCl_3{\cdot}3H_2O$	1·0	ClO_3^{-}	$KClO_3$	5·0
Pd^{2+}	$PdCl_2{\cdot}2H_2O$	1·0	F^{-}	NaF	5·0
Ir^{3+}	$IrCl_3{\cdot}3H_2O$	1·0	Br^{-}	$NaBr$	5·0
Pt^{4+}	$H_2PtCl_6{\cdot}6H_2O$	1·0	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	2·5
Au^{3+}	$HAuCl_4{\cdot}xH_2O$	1·0	SeO_3^{2-}	Na_2SeO_3	2·5
Fe^{3+}	$FeCl_3{\cdot}6H_2O$	nil	TeO_3^{2-}	Na_2TeO_3	2·5
Ce^{3+}	$Ce_2(SO_4)_3$	2·5	SCN^{-}	NH_4SCN	2·5
Th^{4+}	$Th(NO_3)_4{\cdot}4H_2O$	5·0	$S_2O_3^{2-}$	$Na_2S_2O_35H_2O$	1·0
Be^{2+}	$Be(NO_3)_2{\cdot}4H_2O$	2·5	PO_4^{3-}	Na_3PO_4	1·0
Ti^{4+}	$TiCl_4{\cdot}4H_2O$	0·25	$EDTA^{4-}$	Na_2H_2EDTA	2·5
Zr^{4+}	$Zr(NO_3)_4$	2·5	Ascorbate	Ascorbic acid	2·5
UO_2^{2+}	$UO_2(NO_3)_2{\cdot}6H_2O$	0·25†	Citrate	Citric acid	2·5
Zn^{2+}	$ZnSO_4{\cdot}7H_2O$	nil	Malonate	Malonic acid	2·5
Mn^{2+}	$MnCl_2{\cdot}4H_2O$	nil	Oxalate	Oxalic acid	2·5
Co^{2+}	$CoCl_2{\cdot}6H_2O$	nil	Tartrate	Tartaric acid	2·5
Ni^{2+}	$NiCl_2{\cdot}6H_2O$	0·25‡			

* Complexed with 2·5 mg tartaric acid.
† Complexed with 2·5 mg of absorbic acid.
‡ Complexed with 2·5 mg of malonic.

with three 10-ml portions of 0·01*M* hydroxyquinoline in chloroform to remove zinc.[10,11] The aqueous phase containing the lead was then made 3*M* in hydrochloric acid and 2*M* in lithium chloride and shaken with 30% TBP in IBMK for about 5 min. The organic phase was separated and lead stripped from it with water and determined photometrically with PAR at 520 nm. Lead found was 4·90, 4·95 and 4·90% (certificate value 5·0%).

It is thus possible to extract microgram amounts of lead. The method is rapid, simple, selective and permits extraction and determination of lead in about 30 min. The average recovery of lead is 99·8 ± 0·2%. The standard deviation is ±1·0%.

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Summary—Tributyl phosphate [30% solution in isobutyl methyl ketone (IBMK)] is used for the quantitative extraction of microgram amounts of lead from 3*M* hydrochloric acid containing lithium chloride (2*M*) as salting-out agent. It is then stripped from the organic phase with water and determined colorimetrically as its orange-red complex with 4-(2-pyridylazo)resorcinol at 520 nm. TBP alone cannot quantitatively extract lead in the absence of salting-out agents. The IBMK used as diluent does not extract lead under the conditions used. The period of equilibration needed is 5 min. Lead can be extracted in the presence of up to 100 times as much of certain other ions. The method is found to be applicable to analysis of gun-metal.

Zusammenfassung—Tributylphosphat [30% gelöst in Isobutyl-methylketon (IBMK)] wird zur quantitativen Extraktion von μg Blei aus 3*M* Salzsäure verwendet, die Lithium-chlorid (2*M*) als aussalzendes Agens enthält. Das Blei wird dann mit Wasser aus der organischen Phase zurückextrahiert und kolorimetrisch als orangeroter Komplex mit 4-(2-Pyridylazo) resorcin bei 520 nm bestimmt. TBP allein ist nicht in der Lage, Blei ohne Aussalzmittel quantitativ zu extrahieren. Das als Verdünnungsmittel verwendete IBMK extrahiert Blei unter den angewandten Bedingungen nicht. Die zur Gleichgewichtseinstellung notwendige Zeit beträgt 5 min. Blei kann in Gegenwart eines bis zu 100-fachen Überschusses bestimmter anderer Ionen extrahiert werden. Das Verfahren läßt sich für die Analyse von Kanonenbronze verwenden.

Résumé—On utilise le tributyl phosphate [solution à 30% dans l'isobutylméthylcétone (IBMK)] pour l'extraction quantitative de quantités de plomb de l'ordre du microgramme à partir d'acide chlorhydrique 3*M* contenant du chlorure de lithium (2*M*) comme agent de relargage. Il est alors extrait de la phase organique avec de l'eau et dosé colorimétriquement sous forme de son complexe orangé rouge avec le 4-(2-pyridylazo) résorcinol à 520 nm. Le TBP seul ne peut pas extraire quantitativement le plomb en l'absence d'agents de relargage. L'IBMK utilisée comme diluant n'extrait pas le plomb dans les conditions utilisées. La période nécessitée pour la mise en équilibre est de 5 nm. On peut extraire le plomb en la présence de quantités jusqu'à 100 fois supérieures de certains autres ions. On a trouvé que la méthode est applicable à l'annalyse du bronze industriel.

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Determination of nickel and selenium by direct injection enthalpimetry

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THE PRESENT-DAY requirements of analytical chemistry are for simple and rapid methods of analysis that, for routine work, can be easily automated. Thermometric titrimetry[1,2] and direct injection enthalpimetry (DIE) meet these requirements. The principles, instrumentation, and applicability of thermometric methods of analysis have been reviewed in two recent monographs.[1,3]

This paper describes the construction of a simple, robust and inexpensive thermometric titrator similar to that of Snelson *et al.*[4] It has been applied in the complexometric determination of nickel and selenium by direct injection enthalpimetry. The titrant was the disodium salt of quinoxaline-2, 3-dithiol. The reactions are rapid and the reaction enthalpies are large enough to make direct injection enthalpimetry appropriate.

EXPERIMENTAL

Titrator

The essential features of the apparatus are shown in Fig. 1. The calorimeter consists of a 50-ml beaker encased in a "Styrofoam" jacket. The cap is a rubber bung with holes for entry of a thermistor (STC, type F2C, nominal resistance 2000 Ω at 25°) and the burette delivery tip. Solutions are stirred magnetically (plastic-sheathed iron follower). The thermistor forms one arm of a Wheatstone bridge. Sensitivity of the bridge is controlled *via* variable resistor R_3. The output of the bridge is fed to a 1-mV chart-recorder operated at a chart speed of 50 mm/min.

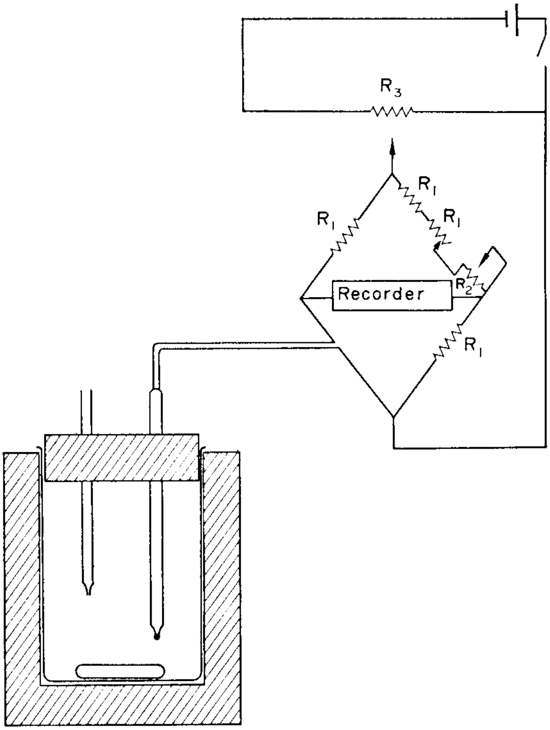

FIG. 1.—Titration vessel and Wheatstone Bridge.
$R_1 = 2\ \text{k}\Omega$; $R_2 = 10\ \Omega$; $R_3 = 50\ \Omega$

In the DIE procedure titrant was added by manual injection, in one rapid stroke, from a short 1-ml glass syringe (capacity in use 0·6 ml). Conventional thermometric titrations are performed with a motor-driven burette (*e.g.* an Agla all-glass syringe driven by a synchronous motor) substituted for the syringe.

The whole was placed in a draught-free enclosure maintained at 25 ± 0·5°.

Reagents

Quinoxaline-2,3-dithiol (disodium salt) solution, 1M. Prepared by dissolving 27·4 g reagent (dihydrate) in 100 ml of water. The preparation of the disodium salt has been described.[5] Solutions stored in the dark remained suitable for use for 1 week.

Metal ion solutions. Aqueous 0·01*M* solutions prepared from the analytical-grade nitrates; 0·01*M* solutions of selenium(IV) were prepared from selenium(IV) oxide.

Perchloric acid. Approximately 0·5M solution prepared by dilution of analytical grade reagent and standardized with sodium carbonate.

Sodium hydroxide solution, 2M. Prepared by dilution of a concentrated carbonate-free analytical-grade reagent.

Buffer solution, pH 10. Ammonium chloride (7 g) dissolved in conc. aqueous ammonia (57 ml) and diluted to 100 ml.

Procedure

Charge the calorimeter with 25 ml of the appropriate titrand solution. Fill and adjust the burette (in practice a titrant volume of 0·6 ml was used) so that the delivery needle is full. Mount the burette in the cap, ensuring that the needle is just above the surface of the titrand. (If the burette was positioned so that the needle projected below the surface of the titrand, reaction visibly occurred around the needle owing to slight mixing of the solutions before injection.) Commence stirring. Start the recorder and adjust the variable resistors in the Wheatstone bridge to obtain a suitable base line and optimum sensitivity. Inject the titrant at one stroke. Record the temperature rise and keep the recorder on for a bit longer. Measure the recorded deflection, which is proportional to the temperature rise, and convert it into concentration or heat units by reference to the appropriate calibration data.

RESULTS AND DISCUSSION

To obtain the approximate enthalpies of the reactions investigated, the calorimeter was calibrated by neutralization of a strong acid by strong base, with a correction for heat of dilution effects (0·6 ml of 2M sodium hydroxide injected into 25 ml of water). A calibration factor was calculated from 4 replicates, as follows, the enthalpy of neutralization for strong acid–strong base being assumed[6] to be −56 kJ/mole. The negative sign of the correction indicates an exothermic dilution. By the same method, with use of the calibration data, the approximate reaction enthalpies for the reagent and several metal ions and selenium(IV) were measured. The results are summarized in Table I.

Sensitivity setting	Perchloric acid, *μmole*	Temperature rise, *chart divisions* Mean	Rel. std. devn., %	Dilution correction *chart div.*	Factor, *J/chart div.*
60	243·5	71·2	0·24	−2·0	0·197
20	487·0	47·1	0·55	−1·0	0·592

Table I.—Approximate enthalpies of reaction for reaction of quinoxaline-2,3-dithiol and metal ions

Titrand*	Amount *μmole*	Sensitivity setting	Chart divisions (mean)	Dilution correction†	No. of replicates	$-\Delta H$, *kJ/mole* (corrected for dilution effects only)
Co^{2+}	150	60	70·0	+18·8	6	116
Ni^{2+}	250	60	65·9	+18·8	6	67
Cu^{2+}	125	60	32·0	+18·8	6	80
Zn^{2+}	250	60	16·5	+18·8	6	28
Se^{4+}	150	20	70·2	−45·2	6	99

* 25 ml of titrand plus 0·5 ml of buffer (pH 10) except in the case of Se^{4+} which was prepared in 0·03M $HClO_4$.

† + denotes endothermic dilution.

The corrections for the heat of dilution of reagent are quite large, but this does not matter if they are reproducible and precise. In the experiments with selenium the dilution effect was exothermic and large; this resulted in an experimental measurement of 70·2 chart divisions of which only one third was due to reaction with selenium itself. The high dilution correction results from the partial neutralisation of the alkaline titrant by the acid present in the titrand. These conditions were found necessary to ensure precipitation of the selenium–quinoxaline dithiol complex only. Variation of these conditions results in the precipitation of the excess of reagent added as titrant. Soluble complexes result from reactions involving Ni(II) and Zn(II). Se(IV) yields an insoluble complex. Co(II) and Cu(II)

TABLE II.—DIE DETERMINATION OF NICKEL AND SELENIUM (TITRANT 0·6 ml OF 1·0M REAGENT)

Titrand	Amount *μmole*	Chart divns., mean	No. of replicates	Rel. std. devn. of mean, %
Nickel(II) + 0·5 ml of buffer pH 10	250	65·9	6	1·0
	200	44·8	6	1·2
	150	34·1	6	1·4
	100	12·7	6	2·6
Selenium(IV) in 0·03M $HClO_4$	150	70·2	5	0·3
	60	56·6	5	0·6

occasionally gave partial precipitation and were therefore not subjected to analytical determination by DIE. The reactions and the composition of the resulting complexes have been discussed.[5]

The results of the DIE determination of nickel and selenium are given in Table II.

A calibration curve constructed by least-squares analysis of the results for the nickel solution is linear and passes through the origin. Typical enthalpograms are shown in Fig. 2. For comparison purposes the nickel solutions were also titrated by the continuous thermometric titration procedure.[1] The relative standard deviations were 0·4, 1·0 and 1·7% for 250, 200 and 100 μmole of nickel respectively (3 replicates for each). An absorptiometric method has been proposed[5] for the determination of nickel and selenium with quinoxaline-2,3-dithiol. The procedure for nickel is claimed to be superior to the standard dimethylglyoxime method.[7] The procedure for selenium proved to be less successful, owing to the slowness of colour formation and the relative instability of the solution of the complex in organic solvents. In contrast, thermometric titrimetry with the highly water-soluble form of the reagent, *i.e.*, the disodium salt, is shown to be successful; 10^{-2}–$10^{-3}M$ solutions of selenium can be analysed rapidly; the relative standard deviation of the results is about 0·5%. The same procedure has been applied to the determination of nickel within a similar concentration range. Here again the method has high precision.

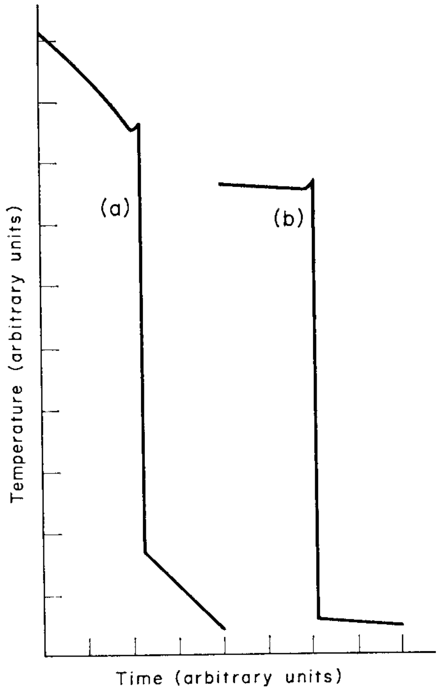

FIG. 2.—Typical enthalpograms.
A—nickel(II); B—selenium(IV)

The thermometric methods described here possess the typical advantages of the method, namely, simplicity, rapidity (total titration time *ca.* 1 min) and the possibility of adaptation to routine control and automation in chemical processes.

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Summary—The construction of a simple thermometric titrator is described. The titrator has been used in a direct injection enthalpimetric procedure to determine nickel and selenium with precisions of 1·0 and 0·3% respectively at a concentration of $10^{-2}M$. The titrant was quinoxaline-2,3-dithiol (disodium salt). The thermometric procedure is shown to be successful in the determination of selenium in contrast to an absorptiometric method using the same reagent.

Zusammenfassung—Die Konstruktion eines einfachen thermometrischen Titrationsgeräts wird beschrieben. Es wurde in einem enthalpimetrischen Verfahren mit Direkteinspritzung zur Bestimmung von Nickel und Selen bei einer Konzentration von $10^{-2}M$ mit Genauigkeiten von 1,0 bzw. 0,3% benutzt. Titrationsmittel war Chinoxalin-2,3-dithiol (Dinatriumsalz). Es wird gezeigt, daß das thermometrische Verfahren im Gegensatz zu einer absorptiometrischen Vorschrift mit dem selben Reagens erfolgreich ist.

Résumé—On décrit la construction d'un appareil de titrage thermométrique simple. L'appareil de titrage a été utilisé dans une technique enthalpimétrique à injection directe pour doser le nickel et le sélénium avec des précisions de 1,0 et 0,3% respectivement à une concentration de $10^{-2}M$. L'agent de titrage est le quinoxaline 2,3-dithiol (sel disodique). On montre que la technique thermométrique est satisfaisante dans le dosage du sélénium à l'opposé d'une méthode absorptiométrique utilisant le même réactif.

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Separation of rhodium from iridium with sodium borohydride and standardization of rhodium(III) solutions

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The separation of rhodium from iridium is the most difficult of the separations involving platinum group metals. There are potential interferences in every known method of separation and determination of these metals. Gravimetric separations of rhodium from iridium have been reviewed by Beamish.[1]

Although Schaeffer and colleagues[2] used sodium borohydride to reduce Pt(IV) to Pt(0) and Pd(II) to Pd(0), the reagent was not applied to the separation of any of the platinum-group metals. This paper describes a method in which an aqueous solution of sodium borohydride is used for the separation of milligram amounts of Rh(III) from Ir(IV).

EXPERIMENTAL

Reagents

Rhodium(III) chloride and iridium(IV) chloride were used to prepare the stock solutions. Each salt was dissolved in a small amount of distilled water, to which 5 ml of conc. hydrochloric acid were added. The solution was transferred to a volumetric flask and diluted to volume with distilled water. Both solutions were initially standardized by the method of Gilchrist and Wichers.[3] In each case the metal was oxidized to the +4 state and then precipitated as the hydrous oxide by the addition of sodium bicarbonate. The oxide was reduced to the metal by heating in a stream of hydrogen gas in a Rose crucible.

The 0·1% solution of sodium borohydride, $NaBH_4$ was prepared 100 ml at a time immediately before use.

Acetoxime, $HON{=}C(CH_3)_2$, was synthesized according to the method of Semon,[4] and a 0·2% aqueous solution (50 ml) was prepared just before use. The reagent hydrolyses to produce hydroxylamine.

All other chemicals were reagent grade.

Procedure

Aliquots of the stock solutions of rhodium and iridium were mixed in a 400-ml beaker with 50 ml of conc. perchloric acid. The solution was evaporated to near dryness on a hot-plate. Then 10 ml of dilute perchloric acid (1 + 4) were added and again the solution was evaporated. Addition of water and evaporation was repeated two or more times until no insoluble residue remained. Approximately 200 ml of the dilute perchloric acid were added and the mixture was heated to near boiling. Acetoxime solution was added dropwise until no further change in colour was observed, and then an additional 5 ml. The solution was kept close to boiling for about 5 min, after which time sodium borohydride solution was added slowly and with stirring until about 5 ml in excess had been added. (Excess of reagent causes the precipitated rhodium metal to coagulate readily.) The precipitate was digested for 10 min, filtered off on a Whatman No. 42 paper and washed with hot distilled water, and transferred to a tared porcelain crucible. It was dried, ignited in air and then in a stream of hydrogen gas and weighed as the metal.

Detection of rhodium in the filtrate and iridium in the precipitate

After filtration, filtrates containing the iridium were evaporated to near dryness, 10 ml of conc. hydrochloric acid were added and the rhodium was determined spectrophotometrically according to the method of Ayres and co-workers.[5] The rhodium precipitate was mixed with graphite and determined spectrographically with a Jarrel-Ash 2·5-m spectrograph.

Results are shown in Table I.

Effect of medium

Media studied, other than perchloric acid, were hydrochloric acid and sulphuric acid. When hydrochloric acid was used, only one evaporation to near dryness was required before addition of the

TABLE I.—SEPARATION OF RHODIUM FROM IRIDIUM WITH SODIUM BOROHYDRIDE IN PERCHLORIC ACID IN PRESENCE OF ACETOXIME

Rh taken, *mg*	Ir taken, *mg*	No. of samples	Average Rh found, *mg*
18·5	5·2	5	18·6
18·5	10·4	5	18·7
18·5	15·6	2	18·7
37·0	10·4	2	37·1
37·0	15·6	2	37·1
92·5	5·2	2	92·4
92·5	35·5	2	92·7
92·5	71·0	2	92·9
92·5	106·5	2	94·5

acetoxime solution and subsequent precipitation. With sulphuric acid as medium, however, two or three evaporations to near dryness were necessary before all of the rhodium and iridium were converted into completely soluble compounds. The number of evaporations was proportional to the amount of rhodium present when either perchloric or sulphuric acid solution was the medium. Precipitations were also carried out in the presence of EDTA and hydroxylamine. Results are shown in Table II.

TABLE II.—EFFECT OF MEDIUM ON THE REACTIONS OF RHODIUM AND IRIDIUM WITH SODIUM BOROHYDRIDE

Medium	Rh taken, *mg*	Ir taken, *mg*	Rh found, *mg*
HCl	50·0	0·0	50·1
H_2SO_4	50·0	0·0	50·4
$HClO_4$	50·0	0·0	50·4
H^+ + EDTA	50·0	0·0	44·5
$HClO_4 + HONH_2$	50·0	0·0	50·1
HCl	0·0	36·5	1·9
H_2SO_4	0·0	36·5	1·0
$HClO_4$	0·0	36·5	1·4
H^+ + EDTA	0·0	36·5	0·9
$HClO_4 + HONH_2$	0·0	82·3	0·0

Effects of heating time

It was found that the rhodium metal precipitated by sodium borohydride was finely divided, but heating coagulated the metal and decreased the filtering time. To determine the effect of heating on precipitation of rhodium and iridium, a series of perchlorate solutions was prepared. The samples, containing either rhodium or iridium, were treated in the usual manner with sodium borohydride and heated for varying lengths of time, then the precipitates were filtered off, washed with water, and finally ignited.

Table III shows that heating time had no effect on solutions containing only rhodium. Some iridium, however, was precipitated when solutions were heated, and for larger amounts of iridium the precipitation tended to increase with an increase in heating time. For rhodium alone, therefore, heating did not hinder precipitation; in the case of iridium, heating had a detrimental effect, and caused more metal to precipitate.

TABLE III.—EFFECT OF HEATING ON THE REACTIONS OF RHODIUM AND IRIDIUM WITH SODIUM BOROHYDRIDE

Rh taken, *mg*	Ir taken, *mg*	Rh found, *mg*	Heating time, *min*
37·5	0·0	37·5	10
37·5	0·0	37·3	20
37·5	0·0	37·7	30
46·5	0·0	46·5	15
0·0	36·5	1·4	60
0·0	64·5	0·7	0
0·0	64·5	2·9	15

Standardization of Rh(III) *solutions*

An aliquot of rhodium chloride solution was transferred to a 400-ml beaker and diluted to approximately 200 ml with distilled water. The solution was heated to near boiling on a hot-plate. $NaBH_4$ solution was added dropwise with stirring until precipitation was complete. The end-point of pre-precipitation is readily detected since rapid coagulation of metallic rhodium occurs. The precipitate was digested for 15 min, then filtered off on a Whatman No. 42 paper, dried in an oven at 110° and ignited first in air in a Rose crucible and then to the metal in a hydrogen atmosphere.

An identical aliquot was treated according to the method of Gilchrist.[3] Results are shown in Table IV. The average deviation for the method is 0·03 mg.

TABLE IV.—COMPARISON OF THE GILCHRIST–WICHERS METHOD WITH THE SODIUM BOROHYDRIDE METHOD

Rh^{3+} solution, *ml*	Gilchrist-Wichers		Sodium borohydride	
	Rh pptd., *mg*	Rh, *mg/ml*	Rh pptd., *mg*	Rh, *mg/ml*
5·0	20·9	4·18	19·7	3·94
	18·1	3·62	19·4	3·88
	20·5	4·10		
	18·4	3·68		
10·0	39·0	3·90	38·9	3·89
	38·4	3·84	38·5	3·85
15·0	58·0	3·87	57·0	3·80
	58·2	3·88	59·0	3·93
			58·6	3·90
20·0	78·3	3·91	77·4	3·87
			77·0	3·85
25·0	96·0	3·84	96·6	3·85
	96·2	3·85		
30·0			116·0	3·87
Average:		3·88		3·88

CONCLUSIONS

Sodium borohydride in aqueous solution quantitatively reduces Rh(III) to Rh(0) and Ir(IV) to Ir(III). In mixtures of the two metals some co-precipitation of iridium is observed when the amount of iridium present is greater than twice that of rhodium. As the amount of iridium in the mixture increases, more iridium is co-precipitated. Addition of acetoxime decreases the amount of co-precipitation and in samples containing less than 10 mg of iridium the rhodium precipitate has been found to be spectrographically free from iridium. Direct addition of hydroxylamine, as the hydrochloride or sulphuric acid salt, causes larger co-precipitation of indium, and it is best to generate it by hydroxylis of acetoxime. In comparison to other separation schemes, the present one is rapid and is easily carried out. Conditions for the separation are not critical. Close control of pH is not required. For a separation involving rhodium in the presence of large amounts of iridium, dissolution of the reduced rhodium metal, followed by a second precipitation with sodium borohydride, is necessary. By a modification in procedure, Rh(III) solutions can be standardized with an accuracy equal to that of other methods of gravimetric analysis.

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Summary—Of the platinum group metal separations, that of rhodium from iridium is the most difficult. The existing gravimetric methods are too lengthy or make use of organic reagents which ultimately need to be removed before iridium can be determined. The proposed method of separation is rapid, needs no pH control, and easy to carry out. Rh(III) ions are quantitatively reduced to Rh(0) by the action of aqueous sodium borohydride. The separation is best achieved in perchlorate medium in the presence of hydroxylamine. The separation is dependent on the concentration ratio of iridium to rhodium; if this is high, some iridium is co-precipitated; if low, the rhodium obtained is free from even spectrographic traces of iridium. A new method for standardization of Rh(III) solutions with sodium borohydride is proposed.

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Zusammenfassung—Unter den Trennungen in der Gruppe der Platinmetalle ist die schwierigste die Trennung von Rhodium und Iridium. Die vorhandenen gravimetrischen Methoden sind zu langwierig oder verwenden organische Reagentien, die zuletzt vor der Iridiumbestimmung entfernt werden müssen. Das vorgeschlagene Trennverfahren geht rasch, braucht keine pH-Kontrolle und ist leicht auszuführen. Rh(III)-Ionen werden mit wäßrigem Natriumborhydrid quantitativ zu Rh(0) reduziert. Die beste Trennung erreicht man in Perchloratmedium in Gegenwart von Hydroxylamin. Die Trennung hängt ab vom Konzentrationsverhältnis Iridium zu Rhodium; ist es groß, so wird einiges Iridium mitgefällt; ist es klein, so ist das erhaltene Rhodium sogar spektrographisch frei von Iridiumspuren. Ein neues Verfahren zur Einstellung von Rh(III)-Lösungen mit Natriumborhydrid wird vorgeschlagen.

Résumé—Des séparations des métaux du groupe du platine, celle du rhodium de l'iridium est la plus difficile. Les méthodes gravimétriques existantes sont trop longues ou utilisent des réactifs organiques qui finalement doivent être éliminés avant qu'on puisse déterminer l'iridium. La méthode de séparation proposée est rapide, ne nécessite pas de contrôle de pH, et est aisée à mener. Les ions Rh(III) sont quantitativement réduits en Rh(O) par l'action de borohydrure de sodium aqueux. La séparation est réalisée au mieux en milieu perchlorate en la présence d'hydroxylamine. La séparation dépend du rapport de concentration entre iridium et rhodium; si celui-ci est élevé, on coprécipite de l'iridium; s'il est faible, le rhodium obtenu est exempt même de traces spectrographiques d'iridium. On propose une nouvelle méthode pour l'étalonnage de solutions de Rh(III) avec le borohydrure de sodium.

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Spectrophotometric determination of germanium with Catechol Violet and cetyltrimethylammonium bromide

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CATECHOL VIOLET has only a low sensitivity as a reagent for germanium[1] and is inferior[2] to other reagents such as trihydroxyfluorone, hydroxyflavones or hematin. West and co-workers[3–5] have sensitized Catechol Violet by adding cetyltrimethylammonium bromide (CTAB). CTAB has now been used to sensitize the germanium–Catechol Violet reaction.

EXPERIMENTAL

Reagents

Germanium(IV) 1000 ppm stock solution. Dissolve 0·360 g of pure germanium dioxide in the minimum needed of 0·1*M* sodium hydroxide, acidify with hydrochloric acid and dilute to 250 ml.

Germanium(IV) 10 ppm solution. Prepared by dilution of the 1000-ppm solution.

Catechol Violet solution, $10^{-3}M$. Dissolve 0·0286 g of Catechol Violet in 100 ml of distilled water.

Cetyltrimethylammonium bromide solution, $10^{-3}M$. Dissolve 0·3644 g of CTAB in 1 litre of distilled water.

Procedure

To prepare the calibration curve, transfer 0·5, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of 10-ppm germanium solution to 100-ml separatory funnels. Dilute to 5 ml with distilled water and add 20 ml of conc. hydrochloric acid to bring the acidity to about $9M$. Keep the solutions cool (preferably below 20°) to prevent loss of germanium tetrachloride by volatilization. Add 20 ml of carbon tetrachloride and shake vigorously for 2 min. Run the carbon tetrachloride layer into a second 100-ml dry separatory funnel. Add 5 ml of carbon tetrachloride to the acid solution in the first funnel, shake for another 10 sec, and run the lower layer into the second funnel. Wash the combined carbon tetrachloride solutions by shaking for 10 sec with 2 ml of $9M$ hydrochloric acid. Allow the layers to separate and transfer the lower layer to a third 100-ml separatory funnel which has been dried in an oven. Add 12·0 ml of water (burette) to the carbon tetrachloride solution in the third funnel. Stopper and shake vigorously for 2 min. Allow the layers to separate and discard the lower layer. Filter the aqueous layer through a small dry Whatman No. 40 filter paper into a dry 50-ml conical flask. Transfer 10·0 ml of the filtrate into a 50-ml volumetric flask. Add 2 ml of conc. hydrochloric acid, 5 ml of $10^{-3}M$ Catechol Violet, 5 ml of $10^{-3}M$ CTAB, dilute to the mark and mix. After 1 hr measure the absorbance at 655 nm against a reagent blank. Sample solutions should have a volume of about 25 ml and already be about $9M$ in hydrochloric acid, and be extracted as just described.

RESULTS AND DISCUSSION

Spectral characteristics

In Fig. 1, curve A shows the absorption spectrum of Catechol Violet in the presence and absence of germanium at an acid strength of about $0{\cdot}5M$ hydrochloric acid, indicating that there is no appreciable complex formation at this acidity (Nazarenko and Binarova[2] found pH 4·8 to be optimum for the formation of the complex in the absence of gelatin). Curve B shows the effect of the addition of CTAB.

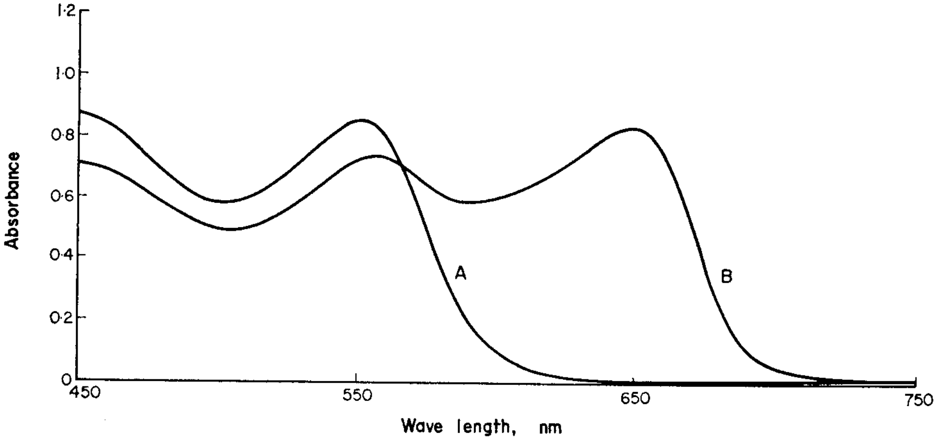

FIG. 1. Absorption spectra of Ge(IV)–Catechol Violet–CTAB system.

Curve *A*: 5 ml of $10^{-3}M$ Catechol Violet and 2·0 ml of conc. HCl, diluted to 50 ml with or without 5 ml of $10^{-4}M$ Ge and measured against distilled water. Curve *B*: 5 ml of $10^{-3}M$ Catechol Violet, 2·0 ml of conc. HCl, 5 ml of $10^{-4}M$ Ge and 5 ml of $10^{-3}M$ CTAB, diluted to 50 ml and measured against water.

Optimum conditions

Hydrochloric acid was chosen as medium because it is involved in the usual methods of separation of germanium by distillation and extraction. The absorbance is independent of the acid concentration over the range 0·1–$0{\cdot}6M$ but decreases at higher acidities. For convenience a final concentration of about $0{\cdot}5M$ is used.

The maximum colour intensity was obtained with an 8-fold molar excess of Catechol Violet and a 10-fold molar excess of CTAB relative to germanium. A greater concentration of both reagents slightly reduced the sensitivity of the reaction.

Colour development was essentially complete in 1 hr, the absorbance increasing by less than 0·5% in the next 45 min, and then remaining unchanged for at least 24 hr. The order of addition of reagents was immaterial. Colour development was independent of temperature over the range studied, 15–40°.

The complex is insoluble in carbon tetrachloride, chloroform, diethyl ether, pentanol, benzene, isobutyl methyl ketone, ethyl acetate and pentyl acetate.

Precision and sensitivity

The calibration curve is linear over the range 0·1–1·0 ppm of germanium. For the colour method alone the relative standard deviation was 2·3%, and for the whole procedure 3·7% (12 variates for both). The method has about the same sensitivity as the phenylfluorone–gum arabic method with carbon tetrachloride extraction.[6]

Interferences

A number of species likely to be present in a sample for analysis were investigated for interference in the colour reaction. No interference was found for a 1000-fold molar excess of As(III), a 100-fold molar excess of Na, K, Mg, Ba, Cu(II), Zn, Pb, Al, Ti(IV), Ni, Cd, Mn(II), Sb(III), nitrate, sulphate, citrate, tartrate, oxalate and phosphate. A 100-fold molar excess of the following caused the error given in brackets: Cr(VI)(−69%), Fe(III)(−24%), V(V)(−85%); 100-fold molar excess of W(VI), Bi(III) or Hg(II) gave rise to turbid solutions. Sn(IV) and Mo(VI) caused errors of +42% and +18% respectively when present in molar amounts twice that of the germanium.

TABLE I.—DETERMINATION OF GERMANIUM WITH CATECHOL VIOLET AND CTAB AFTER CARBON TETRACHLORIDE EXTRACTION

Foreign element added	Ge found, μg
Sn(IV) 10 mg	10·5
Fe(III) 10 mg	9·3
Cr(VI) 5 mg	9·3
As(III) 10 mg	10·0
W(VI) 10 mg	10·0
V(V) 5 mg	9·9
Mo(VI) 10 mg	10·0
Sb(III) 10 mg	9·9
Bi(III) 10 mg	9·9

The reaction is thus selective but not specific and separation of the germanium before photometric determination may sometimes by necessary. The separation of germanium by carbon tetrachloride extraction[6] was adopted for this purpose because of its speed and simplicity (compared with the distillation method) and because the germanium is finally obtained in aqueous solution relatively free from hydrochloric acid.

The findings of Luke and Campbell[7] that germanium was only about 95% recovered in a single carbon tetrachloride extraction was confirmed. To compensate for any loss, the extraction step is included in the procedure for calibration.

To test the specificity of the extraction method, the metals that were earlier found to interfere were tested again. Table I shows the results for 10 μg of germanium and various amounts of the interfering ions.

Sn(IV), Fe(III), As(III), W(VI), Mo(VI), Sb(III), Bi(III) do not interfere when present to the extent of 1000 times the weight of germanium, while Cr(VI) and V(V) can be tolerated in amounts up to 500 times the weight of germanium.

Composition of the complex

Nazarenko and Binarova[2] have already established that the stoichiometric ratio of germanium to Catechol Violet is 1:2 at pH 4–5 both in the presence and absence of gelatin. The same ratio was found for the ternary complex and only one complex is formed.

Conclusion

In terms of sensitivity and selectivity, the method compares favourably with the phenylfluorone–gum arabic method, but is more time-consuming.

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Summary—A ternary complex between germanium, Catechol Violet (CV) and cetyltrimethylammonium bromide is proposed for the determination of germanium. The stoichiometric ratio Ge:CV is 1:2. Beer's law is obeyed from 0·1 to 1·0 ppm of Ge. The method is highly selective. Interference from Sn(IV), Fe(III), Bi(III), Cr(VI), Mo(VI), V(V) and Sb(III) in mg amounts is eliminated by extracting the germanium into carbon tetrachloride from 9*M* HCl and then stripping into water before the photometric determination.

Zusammenfassung—Zur Bestimmung von Germanium wird ein ternärer Komplex aus Germanium, Catechinviolett (CV) und Cetyltrimethylammoniumbromid vorgeschlagen. Das stöchiometrische Verhältnis Ge:CV beträgt 1:2. Das Beersche Gesetz gilt von 0,1 bis 1,0 ppm Ge. Die Methode ist sehr selektiv. Störungen durch Milligrammengen Sn(IV), Fe(III), Bi(III), Cr(VI), Mo(VI), V(V) und Sb(III) werden beseitigt, indem man das Germanium vor der photometrischen Bestimmung aus 9 M HCl in Tetrachlorkohlenstoff extrahiert und dann in Wasser rückextrahiert.

Résumé—On propose un complexe ternaire entre le germanium, le Catéchol Violet (CV) et le bromure de cétyltriméthylammonium pour le dosage du germanium. Le rapport stoechiométrique Ge:CV est 1:2. La loi de Beer est suivie de 0,1 à 1,0 p.p.m. de Ge. La méthode est hautement sélective. L'interférence de Sn(IV), Fe(III), Bi(III), Cr(VI), Mo(VI), V(V) et Sb(III) en quantités de l'ordre du mg est éliminée en extrayant le germanium en tétrachlorure de carbone à partir de HCl 9*M* puis en repassant dans l'eau avant la détermination photométrique.

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ANNOTATION

The stability of plutonium sulphate tetrahydrate, an analytical standard: A ten-year evaluation

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A PREVIOUS STUDY of the stability of plutonium sulphate tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, a proposed primary standard for plutonium, indicated that the material was stable for up to 28 months when stored in screw-capped glass bottles and that it was relatively unaffected by relative humidities of 17–75%.[1] The present investigation reports on the stability of the tetrahydrate over periods of up to 10 years and at relative humidities of 95% and less than 0·1%.

EXPERIMENTAL

Time stability

The plutonium content of several lots of plutonium sulphate tetrahydrate was determined periodically during 10 years to detect any change in composition with time. It had been suspected that this hydrated material might be susceptible to decomposition because of the effect of alpha-radiolysis on the water of crystallization. Constant-current potentiometry using National Bureau of Standards (NBS) potassium dichromate as titrant was used for the plutonium determination.[2,3] In all instances, the samples were stored in screw-capped glass bottles in glove-boxes when not in use. The relative humidity of the laboratory fluctuated from 30 to 80%.

Humidity stability

Although the stability of plutonium sulphate tetrahydrate at relative humidity (R.H.) between 17 and 75% had been studied previously,[1] it was considered important to learn the effect of exposure to the extremes of <0·1% and 95% R.H. Two series of tests were run in which three samples of the tetrahydrate (NBS No. 944) and empty glass weighing-bottles as controls were placed in desiccators maintained at the desired humidity. The 95% R.H. was obtained with sulphuric acid (9·2%) as humidistat and the <0·1% R.H. by desiccation with phosphorous pentoxide. Approximately 40% R.H. represented usual laboratory conditions. The tests were designed to disclose the magnitude and the reversibility of any weight changes caused by changes in humidity, and any possible change in stoichiometry caused by hydrolysis or decomposition resulting from the test conditions. In one series the samples were subjected to consecutive levels of humidities: 40%, 95%, <0·1% and 40% R.H. The second series consisted of long term exposure to <0·1% R.H.

RESULTS AND DISCUSSION

Stability with time

One lot of about 450 g of plutonium sulphate tetrahydrate was prepared at this laboratory in 1963 for evaluation purposes. In a co-operative evaluation programme sponsored by the U.S. Atomic Energy Commission,[4] four laboratories in addition to the New Brunswick Laboratory (NBL) used six different analytical methods to evaluate the stability of this lot of plutonium sulphate tetrahydrate for 32 months after preparation. The results of their plutonium determinations show the compound to be stable, Table I. (The NBL results also appear in more detail in Table II.) The plutonium-241 content of this material was 0·73% w/w at the time of preparation and this concentration would result in an estimated ^{241}Am growth (or plutonium loss) of about 350 ppm per year because of radioactive decay of ^{241}Pu to ^{241}Am. Accordingly, the results in the table are corrected for this change in plutonium content with time. Upon completion of this evaluation programme in 1966, NBL continued to study this material. The plutonium determinations on this same lot of plutonium sulphate tetrahydrate, shown in Table II and corrected for ^{241}Am growth, show this compound to be stable for at least 75 months.

Table I.—Stability of $Pu(SO_4)_2\cdot 4H_2O$, lot no. 7 (32-month period)

Date	Pu found, %* (Theoretical = 47·513%)						
	Lab A	Lab B	Lab C(1)	Lab C(2)	Lab D	NBL	Avg.
May 1, 1963	47·609	47·527	47·532	47·529	47·329	47·523	47·508
June 3, 1963	47·557	47·535	47·524	47·472	47·738	47·514	47·557
July 1, 1963	47·538	47·554	47·532	47·470	47·541	47·505	47·523
Sept. 3, 1963	47·530	47·507	47·499	47·485	47·514	47·515	47·508
Jan. 2, 1964	47·518	47·530	47·508	47·496	47·394	47·508	47·492
Sept. 1, 1964	47·555	47·507	47·509	47·494	47·379	47·510	47·492
Jan. 3, 1966	47·536	—	47·501	47·549	47·557	47·518	47·532
						Average	47·516

* Average of 3 determinations; Laboratory C used 2 methods: (1) (2).

Table II.—Stability of $Pu(SO_4)_2\cdot 4H_2O$, lot no. 7 (75-month period)

Date	Pu found, % (Theoretical = 47·513%)
May 1, 1963	47·527, 47·498, 47·543
June 3, 1963	47·475, 47·537, 47·531
July 1, 1963	47·502, 47·515, 47·499
Sept. 3, 1963	47·522, 47·513, 47·511
Jan. 2, 1964	47·500, 47·491, 47·533
Sept. 1, 1964	47·520, 47·506, 47·505
Jan. 3, 1966	47·523, 47·519, 47·513
June 1, 1969	47·510, 47·511, 47·517, 47·513, 47·469

Another investigation was made on portions of one lot of about 500 g of plutonium sulphate tetrahydrate prepared in March 1964 as an isotopic standard for plutonium. This material was subsequently accepted by the NBS for distribution as Standard Sample No. 948. Determination of the plutonium content of this material at the time of preparation and 63 months later shows the compound to be stable, Table III.

Table III.—Stability of $Pu(SO_4)_2\cdot 4H_2O$, NBS no. 948 (63-month period)

Date	Pu found, % (Theoretical = 47·513%)
March 1964	47·493, 47·505, 47·518, 47·506
June 1969	47·515, 47·524, 47·509, 47·500

In a final study, a small lot of plutonium sulphate tetrahydrate (15 g) prepared in October 1959, and containing 0·56% ^{241}Pu, was analysed again in October 1969. The plutonium content, after correction for ^{241}Am growth, was found to be essentially unchanged after 10 years, Table IV.

Table IV.—Stability of $Pu(SO_4)_2\cdot 4H_2O$, lot no. 6 (10-year period)

Date	Pu found, % (Theoretical = 47·514%)
October 1959	47·508, 47·536
October 1969	47·553, 47·532, 47·544

Stability and relative humidity

About 1·4 kg of plutonium sulphate tetrahydrate was prepared for the NBS in November 1967 for distribution at a later date as Standard Sample No. 944. After 8 months of study the compound was characterized as stoichiometric and stable with time. This material was then used for study of its stability at various extremes of humidity. The results in Table V indicate the following: plutonium sulphate tetrahydrate samples gained weight when exposed to 95% R.H. and lost weight in <0·1% R.H. but readjusted by an equivalent amount when returned to the original environment (40% R.H.). The plutonium content of the material after testing did not differ significantly from its initial value. The results of series 2 confirm the loss in weight at <0·1% R.H. and the fact that the weight loss is regained at 40% R.H. In both series of tests the original weight of the compound was obtained by overnight exposure (16 hr) to 40% R.H.

TABLE V.—THE EFFECT OF HUMIDITY EXTREMES ON THE STABILITY OF $Pu(SO_4)_2 \cdot 4H_2O$ (NBS NO. 944)

Series	Relative humidity, %*	Exposure, days	Average weight change, %†	Pu found, %§
1	40	initial	0	47·502
	95	22	+0·22	n.a.
	40	5	+0·01	47·521
	95	19	+0·24	n.a.
	<0·1	27	−0·05	n.a.
	40	5	+0·01	47·497
2	40	initial	0	47·496
	<0·1	55	−0·07	n.a.
	40	5	−0·01	47·510

* Consecutive exposure of sample.
† Relative to initial exposure at 40% R.H.
§ Average of one determination on each of 3 samples (theoretical = 47·505% Pu).
n.a. = no analysis.

All available results indicate that plutonium sulphate tetrahydrate is reasonably stable for periods of at least 10 years under the ordinary storage and handling conditions described. Although the material gains weight on exposure to high humidity it can be readily air-dried to its original weight without affecting its stoichiometry. The material can be used in "dry boxes" of extremely low humidity if an error of less than 0·1% is not required; loss of weight at very low humidities is readily reversible.

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Summary—The stability of plutonium sulphate tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, an analytical standard for plutonium, has been studied over periods of up to 10 years, and at relative humidities of 95% and less than 0·1%. The material was found to be stable with time; it was slightly affected by extremes of humidity but the changes were readily reversible.

Zusammenfassung—Die Stabilität von Plutoniumsulfat-Tetrahydrat $Pu(SO_4)_2 \cdot 4H_2O$, einem analytischen Standard für Plutonium, wurde in Zeiten bis zu 10 Jahren und bei relativen Feuchtigkeiten von 95% und unter 0,1% untersucht. Es wurde gefunden, daß der Stoff mit der Zeit stabil ist; seine Zusammensetzung wird durch extreme Feuchtigkeitsgrade schwach beeinflußt, aber diese Änderungen waren leicht reversibel.

Résumé—On a étudié la stabilité du sulfate de plutonium tétrahydraté, $Pu(SO_4)_2$, $4\,H_2O$, un étalon analytique pour le plutonium, pendant des périodes allant jusqu'à des humidités relatives de 95% et de moins de 0,1%. On a trouvé que la substance est stable dans le temps; elle est légèrement affectée par les valeurs extrêmes de l'humidité mais les variations sont aisément réversibles.

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A novel method for the estimation of arsenic(V) in organic compounds: Sarjit Singh Sandhu, Sarvinder Singh Pahil and Krishan Dev Sharma. (14 *June* 1971)

Use of the titanium(IV) chelate of salicylic acid for the absorptiometric determination of titanium in titaniferous materials: R. S. Ramakrishna and H. D. Gunawardena. (14 *June* 1971)

Precipitation of calcium oxalate from homogeneous solution by cation release: R. Grzeskowiak and T. A. Turner. (17 *June* 1971)

SUMMARIES FOR CARD INDEXES

Spectrographic determination of the rare earths in high-purity graphite: B. Zmbova, *Talanta*, 1971, **18**, 755. (The Boris Kidrich Institute of Nuclear Sciences, Belgrade, Yugoslavia.)

Summary—A spectrographic method has been developed for determination of the rare-earth elements in graphite. The rare earths are concentrated from ignited graphite on a calcium base. The impurities (Fe, V, Mn, Al, Ti) associated with the rare earths are separated by precipitation of the rare earths as hydroxides in the presence of Fe as a carrier, followed by precipitation of the rare earths as oxalates in the presence of Ca carrier. The mixture of calcium and rare-earth oxides obtained after ignition of the corresponding oxalates is mixed with graphite in 1:1 ratio and excited in a 15-A d.c. arc, with Nd as internal standard. The concentration ranges of determination are as follows: 0·006–0·125 ppm for Eu, 0·006–0·25 ppm for Gd, 0·006–0·06 ppm for Dy, 0·06–0·5 ppm for Sm. This sensitivity is achieved with 35-g samples of graphite. Higher enrichment factors are needed in order to enhance the sensitivity of the method.

3,5,7,4′-Tetrahydroxyflavone (kaempferol) as a chromogenic reagent for gallium and indium: B. S. Garg and R. P. Singh, *Talanta*, 1971, **18**, 761. (Chemistry Department, University of Delhi, Delhi-7, India.)

Summary—3,5,7,4′-Tetrahydroxyflavone (kaempferol) forms yellow chelates with indium and gallium. Based on this reaction, a sensitive spectrophotometric method for the determination of gallium and indium alone and in presence of other metals and alloys has been developed. Beer's law is obeyed up to 2·8 and 1·44 ppm for indium and gallium respectively.

Cation-exchange separation of uranium in dimethylsulphoxide medium: Gilbert E. Janauer, J. Korkisch and S. A. Hubbard, *Talanta*, 1971, **18**, 767. (Department of Chemistry, State University of New York at Binghamton, N.Y. 13901, U.S.A.)

Summary—Cation-exchange chromatography in a dimethylsulphoxide (DMSO) medium is a suitable means for separating uranium from metal ions, including copper, iron, nickel and molybdenum. Quantitative separations of uranium from 26 elements can best be effected on a column of Dowex 50W-X8 (200–400 mesh), using as the eluent a 20% v/v DMSO solution which is 0·6*M* in hydrochloric acid and 0·25*M* in sodium acetate. Only calcium is eluted with the uranium and all other elements studied are eluted either before or after uranium. The elution characteristics of uranium and of other metal ions were investigated with respect to changes in eluent and resin compositions. Separations were much less effective at higher concentrations of sodium ion or DMSO. None of the organic solvents methanol, ethanol, methyl glycol, acetone, dioxan or acetic acid was found to produce favourable separation conditions. Results with Dowex 50 resins of lower or higher cross-linkage were inferior to those obtained with the X8 resin.

СПЕКТРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В ВЫСОКОЧИСТОТНОМ ГРАФИТЕ:

B. Zmbova, *Talanta*, 1971, **18**, 755.

Резюме—Разработан спектрографический метод определения редкоземельных элементов в графите. Редкоземельные элементы концентрируют из обзоленного графита на кальциевой основе. Связанные с редкоземельными элементами примеси (Fe, V, Mn, Al, Ti) отделяют осаждением редкоземельных элементов в форме гидроокисей в присутствии железа в качестве носителя с последующим осаждением редкоземельных элементов в форме оксалатов в присутствии Ca в качестве носителя. Смесь кальция и редкоземельных окисей полученную после обзоления соответствующих оксалатов смешивают с графитом в отношении 1:1 и возбуждуют в дуге постоянного тока 15 а, с использованием Nd в качестве внутренного стандарта. Определения проводили в пределах: 0,006–0,125 мкг/г для Eu, 0,006–0,25 мкг/г для Gd, 0,006–0,06 мкг/г для Dy, 0,06–0,5 мкг/г для Sm. Приведенная чувствительность получена на пробах 35 г графита. Для улучшения чувствительности метода надо применять высшие факторы обогащения.

3,5,7,4′-ТЕТРОАКСИФЛАВОН (КЕМПФЕРОЛ) В КАЧЕСТВЕ ХРОМОГЕННОГО РЕАКТИВА ДЛЯ ГАЛЛИЯ И ИНДИЯ:

B. S. Garg and R. P. Singh, *Talanta*, 1971, **18**, 761.

Резюме—3,5,7,4′-Тетраоксифлавон (кемпферол) образует жёлтые хелаты с индием и галлием. На основе этой реакции разработан чувствительный спектрофотометрический метод определения галлия и индия самых и в присутствии других металлов и сплавов. Закон Бера соблюдается вплоть 2,8 и 1,44 мкг/г индия и галлия, соответственно.

ВЫДЕЛЕНИЕ УРАНА В РАСТВОРЕ ДИМЕТИЛСУЛЬФОКСИДА С ИСПОЛЬЗОВАНИЕМ КАТИОНИТА:

Gilbert E. Janauer, J. Korkisch and S. A. Hubbard, *Talanta*, 1971, **18**, 767.

Резюме—Катионообменная хроматография в растворе диметилсульфоксида (ДМСО) представляет собой подходящий метод отделения урана от других ионов металлов, включая медь, железо, никель и молибден. Самое лучшее отделение урана от 26 элементов осуществлено на колонке смолы Дауекс 50W-X8 (200–400 меш) пользуясь 20%-тным по объеме раствором ДМСО, содержащим 0,6M соляной кислоты и 0,25M ацетата натрия, в качестве элюента. Только кальций элюируется вместе с ураном; все остальные элементы элюируются или перед ураном или после его. Характеристики элюирования урана и других ионов металлов изучены в зависимости от состава элюента и типа смолы. Эффективност разделения гораздо меньше при больших концентрациях иона натрия или ДМСО. Получить удовлетворительные условия для разделения с использванием органических растворителей метанола, этанола, метилгликола, ацетона, диоксана или уксусной кислоты не удалось. Результаты полученные смолами Дауекс 50 с высшей или низшей степени поперечных связей более плохи чем результаты полученные смолой X8.

A titrimetric method for the rapid determination of carbon in steel with an aqueous titrant: J. M. Ottaway, D. W. Whymark, B. Metters and B. G. Cooksey, *Talanta*, 1971, **18**, 773. (Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow C.1.)

Summary—It is demonstrated that the addition of 5% of water to the non-aqueous solvent for the titrimetric determination of carbon in steel improves the performance of the titration. Modifications to the procedure are proposed which allow the normal titrant, tetra-n-butylammonium hydroxide dissolved in benzene–methanol, to be replaced by an aqueous solution of potassium hydroxide. The proposed procedure has been applied to the analysis of a wide range of standard steel samples.

Zur Analyse des Flußspats. Die Schnellanalyse des Flußspats durch destillative Abtrennung und alkalimetrische Bestimmung seines Fluorgehaltes: Ottmar Steinhauser and Paul von Fragstein, *Talanta*, 1971, **18**, 779. (Anorganisch-analytisches Laboratorium der Farbenfabriken Bayer AG, Leverkusen.)

Summary—A still is described by means of which fluoride in fluorspar may be determined within an hour, finishing with an alkalimetric titration. Recording transport of fluoride potentiographically proves the kinetics to be first-order and makes the reaction rate constant and half-life accessible by converting the exponential rate law into a geometric progression. Summation of this gives total fluoride as the limiting value for an infinite distillation period. Precision of a determination depends on the ratio of distillation period to half-life period. The standard deviation in practice is $\leq \pm 0{\cdot}1\%$ CaF_2.

Unified automated determination of silicon in iron ores, sinters, slags, iron and steel: Om. P. Bhargava, George F. Pitt and W. Grant Hines, *Talanta*, 1971, **18**, 793. (Chemical & Metallurgical Laboratories, Steel Company of Canada Ltd., Wilcox Street, Hamilton, Ontario, Canada.)

Summary—An automatic absorptiometric method is presented for the determination of silicon in iron ores, sinters, slags, iron and steel. The last two are dissolved in dilute sulphuric acid; the others are fused with sodium peroxide, then dissolved in hydrochloric acid. After suitable additions and dilution, the resulting solutions are treated identically in a Technicon AutoAnalyzer. The silicomolybdate formed is reduced to molybdenum blue with iron(II). Fluoride is added to provide a redox buffering system. The novelty of the method lies in selecting the sample sizes, conditions of fusion and/or dissolution and dilutions so that this universality is attained. Thus a single programme for the analyzer serves to determine, in any sequence, silicon in iron ores or sinters (1–6%), slags (3–10%), iron (0·4–2·5%) or steel (0·005–2%), the only change being in the tables used to translate transmittance into per cent silicon. Both the precision and accuracy are satisfactory.

ТИТРОМЕТРИЧЕСКИЙ МЕТОД ДЛЯ БЫСТРОГО ОПРЕДЕЛЕНИЯ УГЛЕРОДА В СТАЛИ С ИСПОЛЬЗОВАНИЕМ ВОДНОГО ТИТРАНТА:

J. M. Ottaway, D. W. Whymark, B. Metters and B. G. Cooksey, *Talanta*, 1971, **18**, 773.

Резюме—Показано что добавление 5% воды к неводному растворителю для титрометрического определения углерода в стали улучшает проведение титрования. Предложены модификации метода позволяющие заменять обыкновенный титрант—гидроокись тетра-н-бутиламмония растворен в смесе бензола-метанола—водным раствором гидроокиси калия. Предложенный метод применен в анализе широкого избора эталонов стали.

АНАЛИЗ ФЛЮОРИТА: БЫСТРЫЙ АНАЛИЗ БЛЮОРИТА ПУТЕМ ДИСТИЛЛЯЦИОННОГО ОТДЕЛЕНИЯ И АЛКАЛИМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ СОДЕРЖАННОГО В НЕМ ФТОРА:

Ottmar Steinhauser and Paul von Fragstein, *Talanta*, 1971, **18**, 779.

Резюме—Описан дистилляционный прибор который позволяет определять фтор в флюорите в течение одного часа с применением алкалиметрической титрации. Записывание переноса фторида потенциографическим методом показало что реакция первого порядка и позволило определить константу скорости реакции и полупериод, превращением экспоненциального закона скорости реакции в геометрическую прогрессию. Итог этих данных дает суммарный фторид в качестве предельного значения для бесконечного периода дистилляции. Воспроизводимость определения зависит от отношения периода дистилляции к полупериоде. Стандартная ошибка в практике составляет $\leq \pm 0{,}1\%$ CaF_2.

ОБЪЕДИНЕННОЕ АВТОМАТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КРЕМНИЯ В ЖЕЛЕЗНЫХ РУДАХ, НАТЕКАХ, ШЛАКАХ, ЖЕЛЕЗЕ И СТАЛИ:

Om. P. Bhargava, George F. Pitt and W. Grant Hines, *Talanta*, 1971, **18**, 793.

Резюме—Предложен автоматический абсорбциометрический метод определения кремния в железных, рудах, натёках, шлаках, железе и стали. Железо и сталь растворяют в разбавленной серной кислоте; остальные образцы плавят перекисью натрия а затем растворяют в соляной кислоте. После потребных добавлений и разбавления, полученные растворы обрабатывают объединенным методом на Ауто-Аналайзере фирмы Техникон. Образующийся кремнемолибдат восстанавливают до молибденового голубого железом(II). Раствору прибавляют фторид для установки восстановительноокислительной буфферной системы. Новость метода в отборе величины проб, условиях плавления и/или растворения и разбавления что бы получить объединенное конечное определение. Этим образом только одная программа прибора служит для определения кремния—в котором либо порядке следования—в железных рудах или натёках (1–6 %), шлаках (3–10 %), железе (0,4–2,5 %) или стали (0,005–2 %). Единственная разница состоится в таблицах использованных для перевода светопропускания в концентрацию кремния. Точность и воспроизводимость метода удовлетворительны.

Determination of chloride by displacement of hydrogen cyanide from mercury(II) cyanide: M. K. Bhatty and P. C. Uden, *Talanta*, 1971, **18**, 799. (Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.)

Summary—A method, based on the passivity of mercury(II) cyanide in dilute sulphuric acid and its reaction with hydrochloric acid to produce hydrogen cyanide, has been developed for the determination of small amounts of chloride. Hydrogen cyanide, distilled from a mercury(II) cyanide–halide–dilute sulphuric acid system is found by iodometric measurement to be directly proportional to the amount of chloride or bromide and of hydrogen ion in acids such as sulphuric acid. A linear correlation also holds for iodite but the stoichiometry is different, the titration values being about three times larger than expected. By conversion of the cyanide into a dye by means of the pyridine–pyrazolone reagent, 0·014–0·43 μg/ml chloride concentrations have been determined. The method is also applicable to bromide and sulphuric acid in small amounts but not to fluoride and iodide. Results are reproducible to within ±2%.

Application of the zone melting technique to metal chelate systems—V. Zone chromatographic separation of metal chelates on columns of some inert solid solvents: Nobuhiro Fukuda, Hiroshi Kobayashi and Keihei Ueno®, *Talanta*, 1971, **18**, 807. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.)

Summary—Binary mixtures of acetylacetone and 8-hydroxyquinoline chelates of copper(II), nickel(II), cobalt(II) and cobalt(III) were processed by zone-chromatography on columns of some naphthylalkyl ethers as inert solid solvents. The metal chelates were separated to give chromatograms on the columns according to the ratio of their distribution coefficients. Distribution coefficients of metal ions varied with the type of chelating agent used and the solid solvent, and were found to be strongly affected by operating conditions, especially zone length, zone travelling speed and initial concentration of the metal chelate.

Purification and characterizing properties of the analytical reagent quinizarin-2-sulphonic acid and its sodium salt: J. A. Thomson and G. F. Atkinson, *Talanta* 1971, **18**, 817. (Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.)

Summary—Quinizarin-2-sulphonic acid and its sodium salt have been purified for analytical use. The thermal analysis behaviour and the infrared and NMR spectra of the reagent have been recorded. Absorptiometry at 465 nm is recommended for the assay of solutions. Spectrophotometric measurements, corrected for fading, are treated by a PITMAP-type procedure to obtain acid dissociation constants for the reagent. Finally, some reactions with metal ions are surveyed briefly.

ОПРЕДЕЛЕНИЕ ХЛОРИДА ВЫТЕСНЕНИЕМ ЦИАНИСТОГО ВОДОРОДА ИЗ ЦИАНИДА РТУТИ(II):

M. K. Bhatty and P. C. Uden, *Talanta*, 971, **18**, 799.

Резюме—Разработан метод для определения небольших количеств хлорида основывающийся на пассивности цианда ртути(II) в разбавленной серной кислоте и на его реакции с соляной кислотой с выделением цианистого водорода. Иодометрическое определение цианистого водорода выделенного дистилляцией из системы цианид ртути(II)—галоид—разбавленная серная кислота показало что он прямо пропорциональный количеству хлорида или бромида и количеству ионов водорода в таких кислотах как серной кислоты. Обнаружена также прямолинейная зависимость для иодида но с различной стехиометрией: данные титрования в три раз больше чем ожиданные величины. Определены концентрации хлорида в пределах 0,014–0,43 мкг/мл получением окраски цианида с пиридин-пиразолоновым реактивом. Методом также возможно пользоватся для определения бромида и серной кислоты в небольших количествах, но не для определения фторида и иодида. Воспроизводимость результатов лучьше чем ±2 %.

ПРИМЕНЕНИЕ МЕТОДА ЗОНАЛЬНОГО ПЛАВЛЕНИЯ В СИСТЕМАХ ХЕЛАТОВ МЕТАЛЛОВ—V. ЗОНАЛЬНОЕ ХРОМАТОГРФАИЧЕСКОЕ РАЗДЕЛЕНИЕ ХЕЛАТОВ МЕТАЛЛОВ НА КОЛОНКАХ НЕКОТОРЫХ ИНЕРТНЫХ ТВёРДЫХ РАСТВОРИТЕЛЕЙ:

Nobuhiro Fukuda, Hiroshi Kobayashi and Keihei Ueno®, *Talanta*, 1971, **18**, 807.

Резюме—Двойные смеси хелатов меди(II), никеля(II), кобальта(II) и кобальта(III) с ацетилацетоном и 8-оксихинолином испытаны методом зональной хроматографии на колонках некоторых нафтилакилэфиров в качестве инертных твёрдых растворителей. Хелаты металлов разделились и дали хроматограммы согласно с отношением их констант распределения. Коэффициенты распределения ионов металлов изменялись с типом использованного хелатообразующего агента и с твёрдым растворителем. Опытные условия, в частности длина зоны, скорость движения зоны и начальная концентрация хелатов металлов имели резкое влияние на коэффициенты распределения.

ОЧИСТКА И ХАРАКТЕРИСТИКИ АНАЛИТИЧЕСКОГО РЕАКТИВА ХИНИЗАРИН-2-СУЛЬФОКИСЛОТЫ И ЕЕ НАТРИЕВОЙ СОЛИ:

J. A. Thomson and G. F. Atkinson, *Talanta*, 1971, **18**, 817.

Резюме—Проведена очистка хинизарин-2-сульфокислоты и ее натриевой соли с целью применения в анализе. Определены характеристики термического анализа, так как и инфракрасные и ЯМР спектры реактива. Предложено измерение светопоглощения при 465 нм в качестве обсуждения чистоты растворов. Спектрофотометрические данные, после поправки для потери цвета, обработаны по методе PITMAP для получения констант кислотной диссоциации реактива. Под конец приведен краткий обзор реакций с ионами металлов.

Kaliumbestimmung in Silikatgläsern durch thermometrische Konzentrationsanalyse: Klaus Doering, *Talanta*, 1971, **18**, 827. (Saale-Glas G.m.b.H., 69 Jena/DDR, Otto-Schott-Straße.)

Summary—A rapid thermometric determination of potassium is described in which the element is precipitated as the tetraphenylborate, and the change in enthalpy of the solution system is measured. Results obtained for the analysis of glasses were satisfactory and the method is superior to the usual gravimetric one.

Liquid-liquid extraction of lead(II) with tributyl phosphate: A. A. Yadav and S. M. Khopkar, *Talanta*, 1971, **18**, 833. (Department of Chemistry, Indian Institute of Technology, Bombay-76, India.)

Summary—Tributyl phosphate [30% solution in isobutyl methyl ketone (IBMK)] is used for the quantitative extraction of microgram amounts of lead from $3M$ hydrochloric acid containing lithium chloride ($2M$) as salting-out agent. It is then stripped from the organic phase with water and determined colorimetrically as its orange-red complex with 4-(2-pyridylazo)resorcinol at 520 nm. TBP alone cannot quantitatively extract lead in the absence of salting-out agents. The IBMK used as diluent does not extract lead under the conditions used. The period of equilibration needed is 5 min. Lead can be extracted in the presence of up to 100 times as much of certain other ions. The method is found to be applicable to analysis of gun-metal.

Determination of nickel and selenium by direct injection enthalpimetry: A. E. Beezer and A. K. Slawinski, *Talanta*, 1971, **18**, 837. (Chemistry Department, Chelsea College, Manresa Road, London S.W.3.)

Summary—The construction of a simple thermometric titrator is described. The titrator has been used in a direct injection enthalpimetric procedure to determine nickel and selenium with precisions of 1·0 and 0·3% respectively at a concentration of $10^{-2}M$. The titrant was quinoxaline-2,3-dithiol (disodium salt). The thermometric procedure is shown to be successful in the determination of selenium in contrast to an absorptiometric method using the same reagent.

ОПРЕДЕЛЕНИЕ КАЛИЯ В СИЛИКАТНЫХ СТЕКЛАХ МЕТОДОМ ТЕРМОМЕТРИЧЕСКОГО АНАЛИЗА:

Klaus Doering, *Talanta*, 1971, **18**, 827.

Резюме—Описано быстрое термометрическое определение калия основанное на осаждении элемента в форме тетрафенилбората и измерении перемены ентальпии раствора. Получены удовлетворительные резултаты в анализе стекел. Метод является лучшим обыкновенного весового метода.

ЖИДКОФАЗНАЯ ЭКСТРАКЦИЯ СВИНЦА(II) ТРИБУТИЛФОСФАТОМ:

A. A. Yadav and S. M. Khopkar, *Talanta*, 1971, **18**, 833.

Резюме—Трибутилфосфат в форме 30%-тного раствора в изобутилметилкетоне (ИБМК) использован для количественного извлечения микрограммовых количеств свинца из 3М соляной кислоты содержащей хлорид лития (2М) в качестве высаливающего агента. Свинец затем вымывают водой из органической фазы и определяют колориметрическим методом при 520 нм в форме его оранжево-красного комплекса с 4-(2-пиридилазо) резорцином. ТБП самый не позволяет количественно извлечать свинец в отсутствии высаливающих агентов. ИБМК, использованный в качестве растворителя, не экстрагирует свинец в использованных условиях. Время потребно для получения равновесия равно 5 мин. Метод позволяет экстрагировать свинец в присутствии 100-кратного избытка некоторых других ионов. Методом успешно пользовались в анализе орудийного металла.

ОПРЕДЕЛЕНИЕ НИКЕЛЯ И СЕЛЕНА МЕТОДОМ ЭНТАЛЬПИМЕТРИИ С НЕПОСРЕДСТВЕННЫМ ВПРЫСКИВАНИЕМ:

A. E. Beezer and A. K. Slawinski, *Talanta*, 1971, **18**, 837.

Рзеюме—Описана конструкция несложного термометрического титратора. Прибор использован в энтальпиметрическом методе с непосредственным впрыскиванием для определения никеля и селена при концентрации 10^{-2}M с воспроизводимостью 1,0 и 0,3%, соответственно. В качестве титранта использован хиноксалин-2,3-дитиол (динатриева соль). Термометрический метод позволил успешно определять селен, по сравнению с абсорбциометрическим методом, пользующимся тем же реагентом.

Separation of rhodium from iridium with sodium borohydride and standardization of rhodium(III) solutions: EDWARD S. MCKAY and RICHARD W. CORDELL, *Talanta*, 1971, **18**, 841. (Ohio University, Athens, Ohio, U.S.A.)

Summary—Of the platinum group metal separations, that of rhodium from iridium is the most difficult. The existing gravimetric methods are too lengthy or make use of organic reagents which ultimately need to be removed before iridium can be determined. The proposed method of separation is rapid, needs no pH control, and easy to carry out. Rh(III) ions are quantitatively reduced to Rh(0) by the action of aqueous sodium borohydride. The separation is best achieved in perchlorate medium in the presence of hydroxylamine. The separation is dependent on the concentration ratio of iridium to rhodium; if this is high, some iridium is co-precipitated; if low, the rhodium obtained is free from even spectrographic traces of iridium. A new method for standardization of Rh(III) solutions with sodium borohydride is proposed.

Spectrophotometric determination of germanium with Catechol Violet and cetyltrimethylammonium bromide: C. L. LEONG, *Talanta*, 1971, **18**, 845. (Geological Survey Federal Headquarters, P.O. Box 1015, Ipoh, Perak, Malaysia.)

Summary—A ternary complex between germanium, Catechol Violet (CV) and cetyltrimethylammonium bromide is proposed for the determination of germanium. The stoichiometric ratio Ge:CV is 1:2. Beer's law is obeyed from 0·1 to 1·0 ppm of Ge. The method is highly selective. Interference from Sn(IV), Fe(III), Bi(III), Cr(VI), Mo(VI), V(V) and Sb(III) in mg amounts is eliminated by extracting the germanium into carbon tetrachloride from 9*M* HCl and then stripping into water before the photometric determination.

The stability of plutonium sulphate tetrahydrate, an analytical standard: A ten-year evaluation: CHARLES E. PIETRI and ALBERT W. WENZEL, *Talanta*, 1971, **18**, 849. (New Brunswick Laboratory, United States Atomic Energy Commission, New Brunswick, New Jersey 08903, U.S.A.)

Summary—The stability of plutonium sulphate tetrahydrate, $Pu(SO_4)_2 \cdot 4H_2O$, an analytical standard for plutonium, has been studied over periods of up to 10 years, and at relative humidities of 95% and less than 0·1%. The material was found to be stable with time; it was slightly affected by extremes of humidity but the changes were readily reversible.

ОТДЕЛЕНИЕ РОДИЯ ОТ ИРИДИЯ БОРОГИДРИДОМ НАТРИЯ И УСТАНОВКА ТИТРА РАСТВОРОВ РОДИЯ(III):

Edward S. McKay and Richard W. Cordell, *Talanta*, 1971, **18**, 841.

Резюме—Среды разделений группы платиновых металлов наиболее трудным является отделение родия от иридия. Имеющиеся весовые методы слишком длинные или используют органические реактивы которые надо устранить перед определением иридия. Предложенный метод быстрый, не изыскует контроля pH и легко проводимый. Ионы Rh(III) восстанавливютсяколичественно до Rh(0) действием водного раствора борогидрида натрия. Разделение надо провести в хлорнокислой среде в присутствии гидроксиламина. Разделение зависит от отношения концентраций иридия и родия; в случае высокого отношения появляется в известной мере соосаждение иридия. В случае низкого отношения полученный родий свободен даже от спектрографических примесей иридия. Предложен новый метод установки титра растворов Rh(III) с использованием борогидрида натрия.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ГЕРМАНИЯ КАТЕХОЛОВЫМ ФИОЛЕТОВЫМ И ЦЕТИЛТРИМЕТИЛАММОНИЙБРОМИДОМ:

C. L. Leong, *Talanta*, 1971, **18**, 845.

Резюме—Троиной комплекс германия, катехолового фиолетового и цетилтриметиламмонийбромида предложен для определения германия. Стехиометрическое отношение Ge:КФ равно 1:2. Закон Бера соблюдается в пределах 0,1 до 1,0 мкг/мл Ge. Метод является высокочувствительным. Мешающее действие Sn(IV) Fe(III) Bi(III) Cr(VI) Mo(VI) V(V) и Sb(III) если присутствуют в миллиграммовых количествах устраняется извлечением германия тетрахлорметаном из 9N HCl и переносом в воду перед фотометрическим определением.

УСТОЙЧИВОСТЬ ТЕТРАГИДРАТА СУЛЬФАТА ПЛУТОНИЯ—АНАЛИТИЧЕСКОГО СТАНДАРТА: ДЕСЯТИЛЕТНЫЙ ОПЫТ:

Charles E. Pietri and Albert W. Wenzel, *Talanta*, 1971, **18**, 849.

Резюме—Устойчивость тетрагидрата сульфата плутония, $Pu(SO_4)_2 \cdot 4H_2O$, в качестве аналитического стандарта для плутония изучена в течение 10 лет и при относительных влажностях 95% и меньше чем 0,1%. Найдено что вещество не изменяется с временем; крайние влажности влияют в незначительной мере, но вызванные перемены обратимы.

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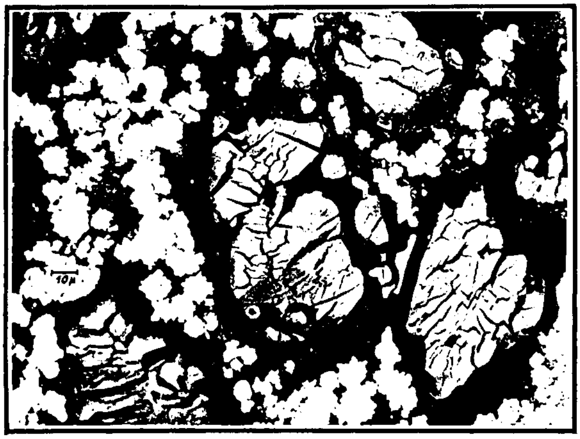

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