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THE NEUTRON ACTIVATION DETERMINATION OF LITHIUM IN THE PRESENCE OF ALKALI METALS AND MAGNESIUM

A neutron activation method for lithium in the presence of alkali metals or magnesium has been developed, utilizing the $^6Li(n,\alpha)^3H$ and $^{18}O(t,n)^{18}F$ nuclear reactions. After a short thermal neutron irradiation with a lithium standard, 112-min fluorine-18 is separated by a lead chlorofluoride precipitation. The annihilation photons from the separated fluorine-18 are counted using 2 sodium iodide detectors, a fast–slow coincidence system and a multichannel analyzer. Precision in a synthetic 1% lithium-in-sodium matrix was found to be $\pm 2.0\%$ standard deviation, whereas the accuracy of the method is estimated to be $\pm 3\%$ or better. The ultimate sensitivity in pure solution is estimated to be about 0.2 p.p.b. and in a sodium matrix about 0.5 p.p.m. The only interferences are several positron emitters, easily discriminated from by chemical separation, decay or by means of other nuclear parameters. Three hours are required for a duplicate determination, following initial sample preparation and dilution. To use the method, the lithium isotopic abundance must be known or determined by mass spectrometry because of the prevalence of depleted lithium in metal and salts.

G. W. SMITH, D. J. SANTELLI AND H. FIESS,
Anal. Chim. Acta, 33 (1965) 1–12

NEUTRON ACTIVATION ANALYSIS OF SCANDIUM

A neutron activation method is proposed for the determination of trace quantities of scandium, down to submicrogram level, in rocks, ores and meteorites. The sample and standard are irradiated intermittently for a total of 30 h, at a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec; the radiochemical separation consists essentially of a one-step anion exchange. The induced γ-activity of ^{46}Sc, 85 days, isolated from the sample is measured and compared with that of a standard. The chemical yield averages 85% and there is a considerable saving of time in the radiochemical work. Results are quoted for the scandium contents of 2 standard rocks, cassiterite and several stony meteorites. Details of conflicting nuclear reactions are also given.

H. HAMAGUCHI, T. WATANABE, N. ONUMA, K. TOMURA AND R. KURODA,
Anal. Chim. Acta, 33 (1965) 13–20

THE ABSORPTIOMETRIC DETERMINATION OF MOLYBDENUM AS MOLYBDENUM(V) THIOCYANATE IN STEEL

The absorptiometric thiocyanate method for molybdenum has been thoroughly studied with regard to the role of the following reagents: HCl, H_2SO_4, $HClO_4$, KSCN, $SnCl_2$, and Fe. A method is described, which allows the determination of 0.01–10% Mo in steel with a relative standard deviation of less than 0.5%. The only interferences (slight) are Nb and the combination V and W. The method gives better than 99.8% recoveries. Results for the determination of molybdenum in standard samples are presented.

N. LOUNAMAA,
Anal. Chim. Acta, 33 (1965) 21–35
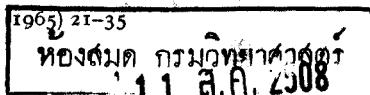
THE DETERMINATION OF SELENIUM IN SEA WATER, SILICATES AND MARINE ORGANISMS

Spectrophotometric procedures are described for the determination of selenium in sea water, silicates (especially marine sediments) and marine organisms. Coprecipitation with iron(III) hydroxide at pH 4–6 is used to concentrate selenium and to separate it from many of the commoner elements. Separation from iron and other cations is achieved by ion exchange. Selenium is determined photometrically with diaminobenzidine. Isotope dilution with selenium-75 is used to correct results for the small losses occurring during the analysis. Silicates can be decomposed without loss of selenium by means of a mixture of hydrofluoric and nitric acids. The method of CUMMINS *et al.*, with sulphuric and perchloric acids in presence of molybdate ion, is highly satisfactory for the decomposition of bio-materials. For sea water, which contains *ca.* 0.4–0.5 μg Se/l, a standard deviation of 0.03 μg/l was obtained. A silicate sediment and a sea weed containing *ca.* 1.5 μg Se/g and 0.8 μg Se/g respectively gave coefficients of variation of 8.0% and 4.7%. The U.S. Geological Survey standard granite G1 was found to contain 2.5 $\pm$ 0.1 μg Se/g.

Y. K. CHAU AND J. P. RILEY,

PHOTOMETRIC TITRATIONS WITH INDICATORS

Various types of photometric titration curves are discussed. If a metal M is titrated compleximetrically using a metal indicator and the absorbance is plotted *vs.* the titrant consumed, the inflection point appears at a pM value defined by the equation
$$3 \, pM_{\text{infl}} = pM_{\text{trans}} + 2 \, pM_{\text{eq}}$$
This expression is valid when M combines in a 1 : 1 ratio with the complexing agent and the indicator and when the indicator concentration is small compared to the total metal concentration.

The difference between the pM values at the inflection and equivalence points can be calculated from the equation
$$\Delta pM = pM_{\text{infl}} - pM_{\text{eq}} = \tfrac{1}{3}(pM_{\text{trans}} - pM_{\text{eq}}) =$$
$$\tfrac{1}{6}\log(C_M K_{MI}^2/K_{MY})$$
If the inflection point is taken as the equivalence point, the error arising can be calculated from ΔpM, or more simply, read from a diagram.

If transmittance, instead of absorbance, is plotted as a function of the titrant volume, the inflection point depends on the added amount of indicator. However, at high transmittance values, *i.e.*, at low indicator concentrations, the inflection point of a transmittance curve occurs practically at the same volume of added titrant as the inflection point of an absorbance curve. Rules are given for applying an indicator correction for the amount of metal bound to the indicator at the end-point.

The derived equations and discussions can also be applied to acid–base titrations.

E. STILL AND A. RINGBOM,

A COMPARISON OF THREE ABSORPTIOMETRIC METHODS FOR THE DETERMINATION OF COPPER IN BIOLOGICAL MATERIALS

Absorptiometric methods for traces of copper based on dithizone, 2,9-dimethyl-1,10-phenanthroline (neocuproine) and bis-cyclohexanone-oxalyldihydrazone (BCOD) were compared by carrying out replicate analyses on specimens of liver; the amount of sample taken was varied so as to provide a means of detecting systematic errors. Agreement between the results by the different methods was poor, the neocuproine method giving higher and more variable results than the other two. A systematic error, inconsistent with the sample size, was detected in the BCOD method. The dithizone method showed no systematic error and possessed better precision and sensitivity.

E. J. BUTLER AND D. H. S. FORBES,

COMPLEX FORMATION OF COPPER(II) WITH TRIETHYLENETETRAMINEHEXAACETIC ACID

The interaction between copper(II) and triethylenetetraminehexaacetic acid (TTHA) was investigated by polarographic, spectrophotometric and potentiometric methods. The existence of chelates with the formulae $CuH-TTHA$, $Cu-TTHA$ and Cu_2-TTHA was shown. The polarographic behaviour and absorption curves of the chelates are described and the equilibrium constants defining the formation of the various species, are reported.

K. S. KLAUSEN, G. O. KALLAND AND E. JACOBSEN,

EFFECT OF COBALT-60 GAMMA RADIATION ON THE DETERMINATION OF URANIUM(VI) IN PHOSPHORIC ACID SOLUTIONS OF URANIUM(IV) OXIDE

The effect of ^{60}Co γ-radiation on aerated and deaerated phosphoric acid solutions of uranium(IV) oxide (UO_2) was studied as a function of temperature, concentration of UO_2, and radiation dose rate. The effect was measured in terms of the radiolytic yield of uranium(VI), $G_{U(VI)}$. For solutions of high initial UO_2 concentration, $G_{U(VI)}$ is largest for the aerated solutions at 25°; it is lowest for the deaerated solutions at 140°. The $G_{U(VI)}$ is lower for the solution of low initial UO_2 concentration than for any of the solutions of high initial UO_2 concentration. At the high starting UO_2 concentration, the initial $G_{U(VI)}$ values are always higher than the succeeding values; this effect is attributed to the depletion of oxygen originally present in the solution. Gamma radiation causes an error in the determination of the stoichiometry of UO_2; the error is a function of the radiation dose. This error can be minimized by excluding oxygen from solutions of UO_2 and by keeping the initial UO_2 concentration as low as possible.

G. L. KOCHANNY, JR.,

SEPARATION OF AMINES BY LIGAND EXCHANGE

PART III. A COMPARISON OF DIFFERENT CATION EXCHANGERS

The elution behavior of 4 amines, ethanolamine, diethanolamine, dimethylamine and *n*-butylamine, was studied on 4 cation-exchange resins and zirconium phosphate, all loaded with nickel ions. Aqueous ammonia was used for elution. Different selectivity orders were found with exchangers of different types. The carboxylic cation-exchange resin gave the sharpest bands, but 2% cross-linked sulfonic resin gave the best separation of these amines.

A. G. HILL, R. SEDGLEY AND H. F. WALTON,

ANION-EXCHANGE BEHAVIOR OF RARE EARTHS, THORIUM, PROTACTINIUM AND URANIUM IN THIOCYANATE–CHLORIDE MEDIA

The anion exchange of rare earths, thorium(IV), protactinium(V) and uranium(VI) from thiocyanate–chloride media was investigated. The equilibrium distribution study showed that the rare earths(III) and yttrium(III) were not significantly adsorbed on a basic anion-exchange resin, while thorium(IV), protactinium(V) and uranium(VI) were strongly adsorbed. Adsorption from the thiocyanate–chloride solutions is in the order, U(VI) > Pa(V) > Th(IV). The separation of rare earths or yttrium(III), thorium(IV), protactinium(V) and uranium(VI) was successfully accomplished by column elution in thiocyanate–chloride media. A rapid and effective ion-exchange method for separating protactinium-233 from irradiated thorium(IV) is also presented.

H. HAMAGUCHI, K. ISHIDA AND R. KURODA,

THERMODILATOMETRIC ANALYSIS: SOME CHEMICAL APPLICATIONS

Some applications of thermodilatometric analysis are discussed. The technique may be used for the determination of *solid–solid* phase transitions and decomposition reactions. An inexpensive recording dilatometer is described.

W. W. WENDLANDT,

THERMOGRAVIMETRIC CHARACTERISTICS OF SOME SALTS OF VIOLURIC ACID AND 1,3-DIMETHYLVIOLURIC ACID

The thermolysis curves of the various salts of violuric acid and 1,3-dimethylvioluric acid with sodium and potassium are described. These salts form hydrates in all cases. 1,3-Dimethylvioluric acid forms 1:1 salts with sodium or potassium; violuric acid may form either 1:1 or 1:2 salts with these metals.

M. E. TAYLOR, A. BERLIN AND R. J. ROBINSON,

QUANTITATIVE ANALYSIS OF SOLID MIXTURES BY DIFFUSE REFLECTANCE MEASUREMENTS

The factors affecting the reflectance of an absorbing substance mixed with material not absorbing at the wavelength of measurement were investigated and it was found that the effect of particle size could be eliminated by prolonged grinding. It is shown that the percentage by weight of the absorbing substance is directly proportional to the quantity $(A/R)^{1.383}$ (R = percentage reflectance; A = 100 − R) and that this quantity is additive for 2 absorbing substances. A method is developed for the accurate determination of low concentrations of one and two absorbing substances mixed with non-absorbing material. The method is applicable to poorly crystallized substances which give no characteristic X-ray powder diffraction patterns as well as to crystalline solids. The reflectance of some substances is shown to be dependent on the previous history of the particular sample. The method is not applicable if there is physical interaction between the components of the mixture.

W. P. DOYLE AND F. FORBES,
Anal. Chim. Acta, 33 (1965) 108–114

THE USE OF THE RING OVEN IN THIN-LAYER CHROMATOGRAPHY

(Short Communication, in German)

L. J. OTTENDORFER,
Anal. Chim. Acta, 33 (1965) 115–116

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THE NEUTRON ACTIVATION DETERMINATION OF LITHIUM IN THE PRESENCE OF ALKALI METALS AND MAGNESIUM*

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(Received October 2nd, 1964)

A method was needed by the Argonne Chemical Engineering Division for the determination of lithium in alkali or magnesium matrices with lithium concentrations ranging from several percent down to 100 p.p.m. or lower. The flame spectrophotometric method, though its sensitivity is 0.1 p.p.m.[1], had shown poor accuracy, presumably due to matrix effects. Also, the possible presence of traces of plutonium in the sample was a potential health hazard.

Lithium is traditionally a difficult element to determine. High concentrations require time-consuming and difficult separations based either on extraction of lithium chloride from other alkali chlorides or on precipitation of the other alkalies before gravimetric or titrimetric methods can be used[2]. Precipitation as the complex periodate[3] would be inapplicable in the presence of high concentrations of magnesium or at low lithium concentrations. The thoron spectrophotometric method[4], while sensitive to 0.1 p.p.m., is worthless at high lithium concentrations, and sodium or magnesium interfere in the strongly alkaline medium used.

It was suggested that lithium might be determined in the desired wide range of concentration by neutron activation. The (n,γ) cross-section of lithium-6 for thermal neutrons is 945 barns, producing tritium (12.3 y) which has been counted in the gas phase to determine lithium[5]. Though tritium can readily be counted more conveniently by liquid scintillation, a much higher sensitivity may be obtained, especially at low concentrations in matrix elements, by utilizing the tritium recoil reaction $^{16}O(^{3}H,n)^{18}F$ first suggested by JENKINS AND SMALES[6]. (Fluorine-18 decays with 97.7% branching ratio and 112-min half-life through a 0.65 MeV positron, giving rise only to 0.51 MeV annihilation radiation.) This principle had earlier been used by OSMOND AND SMALES[7] for the determination of oxygen in powdered metals. Later BROWNLEE[8] utilized the same reaction for the determination of oxygen in organic compounds. Instead of excess of oxygen, as required for the determination of lithium in aqueous solution, excess of lithium as fluoride was mixed intimately with the powdered materials. Difficulties were experienced by BROWNLEE in non-uniform mixing and with high oxygen blanks in the lithium fluoride.

COLEMAN[9] determined the isotopic abundance of lithium by means of the above nuclear reactions, obtaining an accuracy of 1–2%. He sandwiched a lithium

hydroxide source between two 1/8″ pieces of aluminum to insure complete positron annihilation. For counting the fluorine-18, sodium iodide scintillation detectors were placed on opposite sides of the source, since almost 100% of the annihilation photons are emitted simultaneously at 180° from each other. The pulses from the detectors were amplified and conducted into a single-channel analyzer adjusted to admit only the 0.51 MeV peak, in coincidence. With lithium of the purity used, no separation was required, though 5 mg of lithium were needed, and at least one mass spectrometer analysis was required, since the method was not absolute. WINCHESTER et al.[10] determined lithium in aqueous solution by well-type scintillation counting of fluorine-18 and stated that a sensitivity of 0.7 μg of normal lithium could be obtained. BATE AND LEDDICOTTE[11] also used this principle to determine microgram quantities of oxygen in zirconium by placing thin zirconium foils in lithium chloride solution or powder. Recently BORN AND AUMANN[12] determined lithium in various compounds and in magnesium metal, taking into account a "matrix" effect as well as induced activity by fast neutrons.

This paper discusses the development of a method for lithium in the range of from several percent (in alkali or magnesium matrices) down to 0.2 p.p.b. in pure aqueous solution. A two-scintillation detector system is used, counting the positron annihilation radiation from fluorine-18 in coincidence, with backgrounds routinely in the 1–3 counts/min range. Unseparated matrix radioactivities, such as small amounts of sodium-24, are corrected for by counting after decay of fluorine-18. Precision and accuracy are of the order of $\pm 1\%$ relative at 1% lithium concentration in a synthetic sodium matrix, minimizing flux variations during irradiation by careful positioning of samples and standards in the rabbit.

EXPERIMENTAL

The irradiation of lithium

As pointed out by others, excessive concentrations of lithium must be avoided to prevent neutron self-shadowing due to the 945-barn cross-section of lithium-6. WINCHESTER et al.[10] specified an upper limit of 0.2 M lithium (of normal isotopic abundance), whereas COLEMAN[9] stated that no self-absorption was found below 0.1 g-atoms ^{6}Li/l*. We were careful to maintain all solution concentrations well below 0.2 M in normal lithium and to use irradiation containers with a diameter of about 1 cm.

At CP-5** activation analyses are customarily done using a calibration curve prepared from standards in capsules carefully centered in the large 1.5 × 3″ polyethylene rabbit. Gold foils weighing about 100 μg are placed at each end of the rabbits to monitor the flux. However, it is often necessary to wait for 24 h or longer to allow the gold foil to "cool" before counting. To eliminate this delay, and the time-consuming weighing of gold foils, standards and samples were irradiated simultaneously in the present study.

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* Corresponding to a 1.5 M normal lithium solution. Both WINCHESTER and COLEMAN used sample irradiation containers of 1 cm or smaller diameter.
** Chicago Pile No. 5 located at the Argonne National Laboratory: a heavy water-moderated experimental reactor, with a power level of 4.6 MW and a flux maximum of about $5 \cdot 10^{13}$ n/cm²/sec.

Tests were made of arrangements of sets of standard solution capsules within the rabbit. Capsules containing about 1.5 ml of solution were placed in the rabbits, parallel to the axis of the tube, using either 3 or 4 arranged symmetrically around the rabbit center as in Fig. 1. The percentage standard deviation in counts in solutions in the capsules after irradiation averaged ±4.0. However, if the average of the fluorine-18 activity from 2 opposite capsules of 4 was compared with the average of the other two opposite, the standard deviation was 1.5%. The 4-capsule arrangement was used in all comparisons of standards with samples or unknowns.

3 CAPSULE CONFIGURATION   4 CAPSULE CONFIGURATION

←—NEUTRON FLUX   ←—NEUTRON FLUX
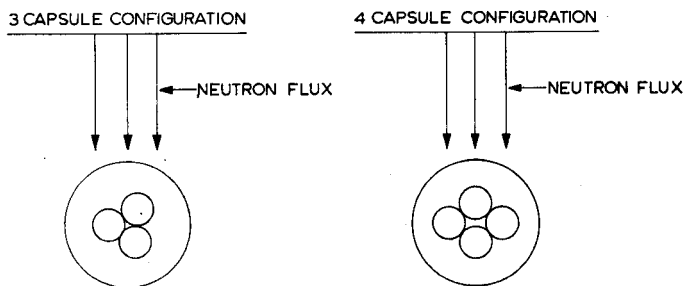
Fig. 1. Arrangement of capsules in large rabbit. (View from end of rabbit)

It is pertinent to note that capsules fabricated from Lusteroid (nitrated cellulose) were initially used at CP-5 because of their low cost and easy availability. Because the need for a better material had been recognized since the inception of the "rabbit laboratory", several prototype rabbits of polystyrene and polyethylene were designed and tested. The best design, developed in cooperation with the CP-5 group, was a 1–15/32" diameter by 3–5/8" long rabbit of hardened polyethylene*, incorporating a snap-fit cap. These rabbits gave about one-tenth the induced β–γ activity of the Lusteroid on irradiation and were not inflammable at the temperatures usually encountered. After die fabrication, they were manufactured inexpensively by injection molding, and are now in use.

The counting of fluorine-18

Counting of the fluorine-18 annihilation photons in coincidence was done with 4"-diameter sodium iodide detectors on opposite sides of the source in close geometry. The source was enclosed in a 1-mm thick aluminum cup to insure complete annihilation of the 0.65 MeV positron. The signals produced were led from Nuvistor cathode followers into one of the completely transistorized fast–slow coincidence systems developed by STRAUSS[13]. The above system was coupled with a Victoreen Instrument Company 400-Channel analyzer. A block diagram (Fig. 2) gives the entire assembly.

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* Agilene-H.T., obtained from the American Agile Corp., Cleveland, Ohio.

Both single-channel analyzers (Fig. 2) were gated to count essentially only the 0.51 MeV peak counts occurring in coincidence (actually during a finite time interval of 30 nanosec). The detectors were shielded on all sides by 4″ of lead and backgrounds were routinely in the range 1–3 counts/min with the CP-5 reactor operating.
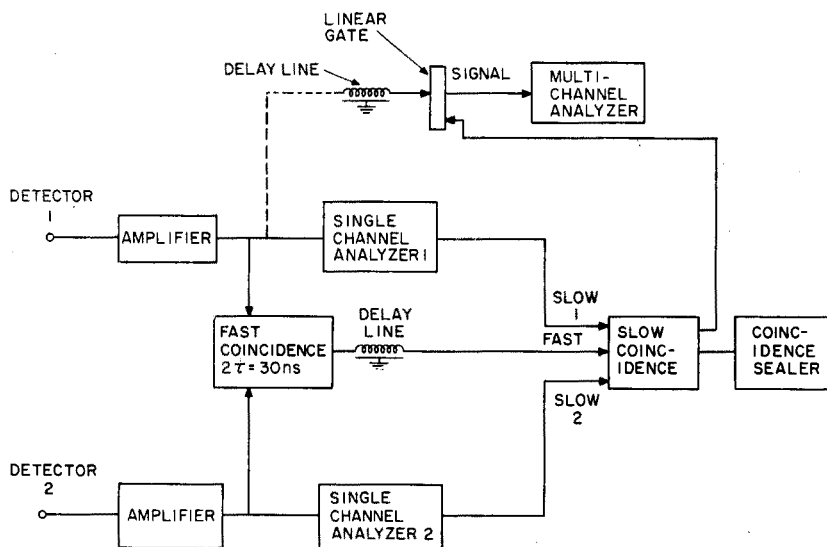
Fig. 2. Block diagram of fluorine-18 counting system.

It is of interest to note the approximate efficiency of this system. A sodium-22 source about 0.5 cm in diameter was prepared on Mylar from a National Bureau of Standards calibrated solution. It was then sandwiched between 1/16″ of aluminum to insure annihilation, in the approximate geometry for fluorine-18 counting. At a coincidence-counting rate of about 4200 counts/min, where the random background contribution to the 0.51 MeV peak was negligible, the counting efficiency was 8%. Incidentally, with this system, at a coincidence counting rate as high as $2.5 \cdot 10^5$ counts/min, the random coincidence rate is only 390 counts/min.

The radiochemical separation of fluorine-18

Though highly specific in its counting of fluorine-18 in coincidence, the above-described counting equipment does not discriminate completely against high levels of induced matrix activity, such as sodium-24. For example, with 0.1 p.p.m. lithium in 0.4 g sodium, about $3 \cdot 10^3$ d.p.m. fluorine-18 and $1 \cdot 10^{11}$ d.p.m. sodium-24 would be induced in a 20-min irradiation. This would require a discrimination factor in the order of 10^7. Since the counting system at the geometry used gave a discrimination

of only 10^3, it was therefore necessary to make a radiochemical separation of fluorine-18 from the bulk of the interfering sodium-24 radioactivity.

Methods which were considered for the separation of fluorine included micro-diffusion as hydrofluoric acid[14], collection of the fluoride by exchange with insoluble rare earths such as lanthanum[15], removal of impurity radioactivity by preferential absorption on cellulosic support materials[16], by anion exchange[17], or by precipitation as lead chlorofluoride ($PbCl_2$–PbF_2)[18]. Micro-diffusion and the use of the cellulose-type support material for impurity removal were considered too time-consuming. Experiments with anion exchange showed that low concentrations of other anions caused fluoride breakthrough. It was finally decided to compare precipitation of lead chlorofluoride with that of lanthanum fluoride. It was suggested that a quantitative method be developed which would avoid the necessity for a chemical yield determination.

Lanthanum fluoride was precipitated in a 3-ml Lusteroid tube by the addition of excess lanthanum fluoride carrier (as NH_4F) in *ca.* 0.01 *M* nitric acid solution. To coagulate the precipitate, ammonium acetate was added and heat applied. A slightly acidic lanthanum solution containing acetate was used for washing, by centrifugation and decantation with a small transfer pipet. By carrying out a second precipitation in the combined supernate and washings from the first precipitation, a 99.8% recovery was obtained, as determined by the use of fluorine-18 tracer.

Lead chlorofluoride was precipitated in a 3-ml Lusteroid tube at room temperature by addition of excess lead nitrate solution to fluoride carrier solution with excess of sodium chloride. The precipitate was washed by centrifugation with a solution containing sodium chloride and lead nitrate. Again with a second precipitation in the combined supernate and washings as above, an over-all recovery of 99.2% was realized.

To test the effectiveness of the two separation procedures, microgram amounts of irradiated sodium and copper were carried through the procedure. Milligram amounts of fluoride and holdback carriers were added after irradiation and separations were made. Results are summarized in Table I. It is evident that the lead chlorofluoride separation procedure was superior to the lanthanum fluoride method, probably because of the denser and less adsorptive chlorofluoride precipitate. If the lead chlorofluoride was dissolved, reprecipitated and washed, the decontamination was $5 \cdot 10^4$ with an additional factor of 10^3 afforded by the counting procedure (above). The over-all discrimination realized was therefore approximately $5 \cdot 10^7$.

TABLE I

DECONTAMINATION COMPARISON OF LANTHANUM FLUORIDE AND LEAD CHLOROFLUORIDE PROCEDURES

	Method			Method	
	LaF_3	$PbClF$		LaF_3	$PbClF$
Na irradiated (μg)	63	63	Cu irradiated	63	63
Na holdback carrier (mg)	4.6	4.6	Cu holdback carrier (mg)	6.3	6.3
Decontamination factor[a]	60	450	Decontamination factor[a]	140	1000

[a] Defined as $= \dfrac{\text{contaminating radioactivity present initially (counts/min)}}{\text{contaminating radioactivity present after separation (counts/min)}}$

To determine recovery by the lead chlorofluoride separation procedure in the presence of varying amounts of matrix elements, two-component mixtures of sodium, potassium or magnesium with lithium were prepared. Following the irradiation and separation procedure as outlined above, the fluorine-18 from aliquots was counted and lithium determined by comparison with aliquots of the standards*. Corrections for small amounts of the 15-h sodium-24 remaining in the lead chlorofluoride precipitates were made where necessary, by counting the next day after the fluorine-18 had decayed. Potassium-42 was not carried to any extent and the 9.5-h magnesium-27 was allowed to decay before counting the fluorine-18. Results are given in Table II and show that the method was quantitative.

TABLE II

ANALYSES OF SYNTHETIC LITHIUM MATRICES

Mixture constituents				Holdback carrier present (mg)	Lithium recovered (μg/ml)	Error (%)
Matrix		Lithium				
Element	(μg/ml)	% in matrix	(μg/ml)			
Na	1124	0.30	3.40	7.7	3.38	−0.7
Na	502	3.3	17.0	7.6	16.7	−1.6
K	1916	0.18	3.40	0.6	3.42	+0.6
K	850	2.0	17.0	0.3	16.8	−1.2
Mg	1193	0.28	3.40	0.4	3.37	−0.9
Mg	530	3.1	17.0	0.2	16.8	−1.2

To determine the possible adverse effects of large amounts of high concentrations of added sodium holdback carrier, fluorine-18 tracer experiments were run. In the range 0–72 mg of added sodium (with 7.4 mg unavoidably present from reagents) an average recovery of 99.8% was obtained, indicating no deleterious effects.

Preliminary tests had also shown that after dissolution and reprecipitation of the lead chlorofluoride, recoveries of fluoride were about 97%. To confirm this, two irradiations were made, dissolving with nitric acid and reprecipitating at pH 4 with sodium hydroxide. Recoveries obtained averaged 96.9%.

It may be necessary, in certain cases of low lithium content samples requiring several dissolution and reprecipitation steps, to obtain the chemical yield of fluoride. This was carried out readily by means of an EDTA titration of the lead from the chlorofluoride precipitate dissolved in saturated ammonium acetate. The lead was titrated with eriochrome black T dye as indicator at pH 10 and tartaric acid was added to prevent precipitation. The fluoride carrier solution was standardized by precipitation of lead chlorofluoride using the method described in detail below, except for the dissolution and reprecipitation steps, with accurately standardized 0.05 M sodium-EDTA solution in a 10-ml microburet.

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* It was found unnecessary to separate fluorine-18 from the lithium standard solutions, since no significant impurity γ-rays were found upon irradiation, and its radioactivity decayed with a half-life of approximately 112 min, agreeing with values reported in the Table of Isotopes[19].

Standard lithium solutions

Standard lithium solutions were prepared from 99.99% pure lithium metal determined by mass spectrometry to be of normal isotopic abundance (Table IV). Stock solutions 0.25–0.35 M in lithium were made by carefully dissolving the metal in water and nitric acid in volumetric flasks. Excess acid was used to give a final concentration of about 1 M in nitric acid. Transfer was then made to polyethylene bottles for storage and dilutions were made for irradiation, usually in the range 17–65 μg of normal lithium per ml.

Method of analysis

The detailed procedure for the determination of lithium was as follows. Prepare a nitrate solution (using de-ionized water) of the pure aqueous solution, or of solutions containing sodium, potassium or magnesium, approximately 0.01 M in nitric acid, and containing not over 1 mg of normal lithium per ml. The isotopic composition of the sample must be known or be determined by mass spectrometric analysis (see p. 10).

Encapsulate 1.5-ml portions in carefully cleaned Intramedic polyethylene tubing, 12.7 mm I.D. and 14.2 mm O.D. (Clay-Adams Inc., Evanston, Ill., Catalog No. PE 450). Allow at least 50% of the total volume as void space, to prevent excessive build-up of pressure during irradiation, and heat-seal in 6-cm lengths. Arrange duplicate sample and standard capsules in a rabbit as discussed above (p. 3). Irradiate at a flux of about $2 \cdot 10^{13}$ n/cm²/sec for 20 min or for a comparable integrated flux. (Samples of pure solution extremely low in lithium should be irradiated for 60 min.) After removal of the rabbit from the pneumatic tube, cool to room temperature under running water before opening.

Open the capsules and pipet aliquots (with counting rates not over $2 \cdot 10^5$ counts/min at T_0) into 3-ml Lusteroid tubes. Add *ca.* 200 μl* of ammonium fluoride carrier (*ca.* 12 mg F per ml) and rinse the pipet with 0.1 M acetic acid–0.1 M sodium acetate solution. Add 0.70 ml of 0.2 M sodium chloride solution, milligram amounts of holdback carrier if necessary, 4 drops of 1% aerosol and mix with a Vortex Jr. mixer (Fisher Scientific Co., Chicago, Ill. Catalog No. 12-812V1). Add 0.90 ml of 0.15 M lead nitrate solution dropwise with mixing, centrifuge for 1 min and pipet the supernate by means of a small transfer pipet into a 10-ml Lusteroid tube. Add 2 drops of aerosol solution to the decanted precipitate. Wash the precipitate with 1 ml of water, 0.15 ml of 0.2 M sodium chloride and 0.15 ml of 0.15 M lead nitrate solutions. Mix, centrifuge and pipet the wash solution into the 10-ml Lusteroid tube. To this tube add 0.15 ml of fluoride carrier and 0.60 ml of 0.2 M sodium chloride solution and mix. Precipitate while mixing with 0.85 ml of 0.15 M lead nitrate solution. Centrifuge and discard the supernate. Wash the second precipitate with 1 ml of water, 0.15 ml of the sodium chloride and 0.15 ml of the lead nitrate solutions by mixing, centrifugation and decantation. Discard the supernate. (At this point, if the dissolution and reprecipitation steps are not required to remove extraneous radioactivies, omit the next paragraph.)

Dissolve the precipitate in the 3-ml Lusteroid tube by the addition of 1.0 ml

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* The solutions used are conveniently dispensed from dropping bottles with calibrated drop sizes of about 50 μl per drop.

of *ca.* 2.0 *M* nitric acid and heating on a water bath at boiling temperature. Add the contents of this Lusteroid tube to the 10-ml tube. Wash the 3-ml tube with 1 ml of 2 *M* nitric acid into the 10-ml tube. Add 4 drops of aerosol solution and heat to dissolve the precipitate. Neutralize the combined solution in the 10-ml Lusteroid tube to pH 4 (as determined by pH paper) by the addition of 0.75 ml of 8 *M* sodium hydroxide. (To adjust the pH more exactly, 2 *M* nitric acid and 2 *M* sodium hydroxide may be used at this point. The formation of a curdy yellow precipitate is an indication of too high a pH.) Add 0.5 ml of 0.2 *M* sodium chloride and 0.65 ml of 0.15 *M* lead nitrate solution with stirring, centrifuge and discard the supernate. Wash the precipitate with 1 ml of water, 2 drops of aerosol, 3 drops of 0.2 *M* chloride and 3 drops of 0.15 *M* lead solutions, centrifuge and discard the supernate. (As many dissolution and reprecipitation steps may be made as are necessary.)

Dissolve the precipitate in the large Lusteroid tube by adding 1.0 ml of saturated ammonium acetate, mixing and heating. Transfer quantitatively, rinsing with water, to the small Lusteroid tube and dissolve any precipitate therein. The final volume should equal the standard dilution volume for the well-type γ-counting. Mix and count as described above. Allow the sample to decay overnight and count the residual matrix activity for correction of precipitate count. Gamma spectrometry and decay curves may be required for identification of radioactivities, especially if the impurity content is low. After counting, the chemical yield may be determined by EDTA titration.

From the fluorine-18 counting rate corrected to T_0 (out-pile time) calculate the p.p.m. or percentage of lithium, taking into account the weight percentage of lithium-6 in both standard and sample.

RESULTS AND DISCUSSION

Reproducibility

The reproducibility of the method was tested on a pure solution synthesized to simulate an approximately 1% lithium-in-sodium matrix. Ten determinations were made, separating fluorine-18 by a single chlorofluoride precipitation and normalizing flux variations by counting lithium standards which had been irradiated simultaneously. The average of 10 determinations was 0.96% lithium with a percentage standard deviation of ±1.2 for a single determination. Consistent with current statistical procedures[20], at the 95% confidence level the correct value for the standard deviation lies between ±0.81 and ±2.0%. This precision is considerably better than that of the usual radioactivation method, normally ±5–10%. On samples of progressively lower lithium concentration, the percentage standard deviation of course increases markedly, since precision must be sacrificed for sensitivity.

Accuracy

It is difficult to measure directly the accuracy of this method, since standards of known lithium content are not available in the matrices of interest. However, one measure of accuracy is by intercomparison of lithium standards, without radiochemical separation. Our first lithium standard, prepared from 99.9% lithium metal in January, 1963, was compared with 2 more standards of September, 1963, from the same metal lot. Portions of the earlier metal standard were irradiated, along with the

second or third standard. Flux variations were normalized by use of counting rates of the first standard, and specific activities of all standards compared, after duplicate irradiations. Satisfactory agreement between standards is shown in Table III. The accuracy of the method is estimated to be $\pm 3\%$ or better, taking into account the error shown in the separation experiments in Table II.

TABLE III

LITHIUM METAL STANDARD COMPARISON

Lithium standard no.	Specific activity (counts/min ^{18}F per μg Li)	% Deviation from standard no. 1
1	$3.46 \cdot 10^3$	0
2	$3.49 \cdot 10^3$	$+0.9$
2	$3.46 \cdot 10^3$	0
3	$3.49 \cdot 10^3$	$+0.9$
3	$3.48 \cdot 10^3$	$+0.6$

TABLE IV

LITHIUM MASS SPECTROMETRIC ANALYSES

Reagent material	^6Li concentration	
	Atom %	Wt. % [a]
LiCl	7.51	6.51
Li metal	7.42	6.43
LiNO$_3$	2.55	2.19
Normal LiNO$_3$[b]	7.42	6.43

[a] Calculated using isotopic masses of 6.01690 for ^6Li and 7.01818 for ^7Li.
[a] Salt which had been in the ANL Chemistry Division for approximately 20 years and is most probably in the usual range of normal isotopic abundance.

Sensitivity

The sensitivity of the method was determined in pure aqueous solution and in the presence of large amounts of sodium.

In de-ionized water, containing only lithium-free nitric acid (ca. 0.01 M) and 20 μg/ml concentrations of fluoride carrier (as ammonium fluoride), 10 p.p.b. was determined using a 20-min irradiation. It was estimated that the lower sensitivity limit was approximately 0.2 p.p.b., using a 60-min irradiation and counting a net 2 counts/min of ^{18}F over a background of 2 counts/min.

In the presence of large amounts of sodium, the sensitivity tests were limited by p.p.m. levels of lithium in the sodium metal or salts used (see below) requiring the subtraction of two relatively large numbers to obtain a small number. It was estimated that the sensitivity limit in sodium was 0.5 p.p.m. with long counting times, and several dissolution and reprecipitation steps. A 60-min irradiation would be required, yielding 5 counts/min of fluorine-18 over a background (including ^{24}Na) of 14 counts/min.

Interferences

The only interferences of importance, which cannot be discriminated from by counting, are positron-emitting nuclides induced by the (n,γ) reaction from minor impurities. From an examination of isotope charts, the most likely appear to be, in descending order of importance, copper-64 (12.8 h), bromide-80 (17.6 min), silver-108 (2.3 min) and zinc-65 (245 d). The low cross-section of zinc-64 and the relatively long half-life of zinc-65 prevent the formation of significant amounts of this isotope. Bromine-80, though coprecipitated as lead bromofluoride, is easily removed by nitric acid evaporation with bromide carrier and silver-108 may be allowed to decay before fluorine-18 is counted. Copper-64 can be largely separated by the lead chlorofluoride procedure, with any residual ^{64}Cu radioactivity corrected for by counting after fluorine-18 decay.

The isotopic abundance of lithium

The isotopic abundance of lithium-6 is listed by STROMINGER *et al.*[19] as 7.29 to 7.42 atom-% depending upon the source. The recent isotopes catalog from Oak Ridge National Laboratory (4th Revision, April, 1963) quotes an abundance of 7.52 atom-%, as determined by LU[21]. The latter value is 3.2% higher than the 7.29 quoted above, but the difference is unimportant when part per million levels of lithium are being determined. However, if percent levels of lithium were present, a mass spectrometric analysis for abundance would be required.

Early in our work with the method it was noticed that one lot of reagent-grade lithium nitrate gave fluorine-18 specific activities (counts/min per μg of lithium) low by about a factor of three. This was first believed to be an analysis error, but upon checking it became apparent that the lithium-6 isotopic composition must be low. Samples of the lithium nitrate, as well as of lithium chloride and metal were submitted to the Argonne Chemistry Division mass spectrometric group, who obtained the results shown in Table IV. It was evident that this lot of lithium nitrate was depleted in lithium-6.

CONCLUSIONS

As a demonstration of the capabilities of the method, a lithium salt and sodium metal and salts were analyzed for their lithium content.

The lot of reagent-grade lithium nitrate containing 2.19 weight-% of lithium-6 (Table I) was stated by the manufacturer to contain 99.9% lithium nitrate on the dry basis. Our analyses by activation were 99.4 and 99.6% $LiNO_3$ with moisture as determined by oven drying of less than 1%. Lots of reagent-grade sodium nitrate and metal, as well as of purified metal and sodium nitride, all of unstated or unknown lithium content, showed respectively 13, 46, 6 and 36 p.p.m.

It is believed that the method developed for lithium covers an extremely wide range of concentrations. It shows good precision and satisfactory accuracy, is reasonably specific and has high sensitivity. The method is rapid, allowing duplicate samples to be completed in 3 h (not including sample solution preparation time), unless impurity counting is required on the following day.

One disadvantage is the necessity for a mass spectrometric analysis or knowledge of the isotopic abundance of lithium-6 on each sample. Also, specialized count-

ing and γ-spectrometric equipment is required. However, the equipment has been stable and relatively trouble-free and its operation can easily be learned by personnel competent in counting techniques.

SUMMARY

A neutron activation method for lithium in the presence of alkali metals or magnesium has been developed, utilizing the $^6Li(n,\alpha)^3H$ and $^{16}O(t,n)^{18}F$ nuclear reactions. After a short thermal neutron irradiation with a lithium standard, 112-min fluorine-18 is separated by a lead chlorofluoride precipitation. The annihilation photons from the separated fluorine-18 are counted using 2 sodium iodide detectors, a fast–slow coincidence system and a multichannel analyzer. Precision in a synthetic 1% lithium-in-sodium matrix was found to be $\pm$ 2.0% standard deviation, whereas the accuracy of the method is estimated to be $\pm$ 3% or better. The ultimate sensitivity in pure solution is estimated to be about 0.2 p.p.b. and in a sodium matrix about 0.5 p.p.m. The only interferences are several positron emitters, easily discriminated from by chemical separation, decay or by means of other nuclear parameters. Three hours are required for a duplicate determination, following initial sample preparation and dilution. To use the method, the lithium isotopic abundance must be known or determined by mass spectrometry because of the prevalence of depleted lithium in metal and salts.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est proposée pour le dosage du lithium, en présence de métaux alcalins ou de magnésium, utilisant les réactions nucléaires $^6Li(n,\alpha)^3H$ et $^{16}O(t,n)^{18}F$. Après une courte irradiation aux neutrons thermiques, avec un lithium standard, le fluor-18 est séparé par précipitation sous forme de chlorofluorure de plomb. Les seules interférences sont des émetteurs de positrons, facilement décelés par séparation chimique, désintégration ou au moyen d'autres paramètres nucléaires. Trois heures suffisent pour effectuer un dosage à double. L' abondance du lithium doit être connue ou déterminée par spectrométrie de masse.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Bestimmung von Lithium in Gegenwart der Alkalimetalle oder des Magnesiums mit Hilfe der Neutronenaktivierungsanalyse entwickelt. Dabei wurden die Kernreaktionen $^6Li(n,\alpha)^3H$ und $^{16}O(t,n)^{18}F$ angewandt. Nach kurzer Bestrahlung mit thermischen Neutronen zusammen mit einem Lithiumstandard wurde das 112-min Fluor-18 durch eine Bleichlorofluoridfällung abgetrennt. Die Vernichtungsstrahlung des abgetrennten Fluor-18 wird mit 2 Natriumjodiddetektoren

gezählt, unter Anwendung eines Koinzidenz-Systems mit Vielkanalanalysator. Mit einer synthetischen Natriummatrix mit 1% Lithium wurde eine Standardabweichung von ±2% gefunden, während die Richtigkeit der Methode auf mindestens ±3% geschätzt wurde. Die absolute Empfindlichkeit in reiner Lösung wird auf etwa 0.2 p.p.b. geschätzt, in einer Natriummatrix auf etwa 0.5 p.p.m. Einige Positronenstrahler können Störungen hervorrufen, die sich jedoch leicht durch chemische Abtrennung, durch Zerfall oder mittels anderer nuklearen Parameter beseitigen lassen. Für eine Doppelbestimmung werden 3 Std. benötigt. Bei Anwendung der Methode muss wegen der Vorgeschichte des Lithium der Lithiumisotopenüberschuss bekannt sein oder mit Hilfe der Massenspektrometrie bestimmt werden.

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NEUTRON ACTIVATION ANALYSIS OF SCANDIUM

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Until recently the determination of trace quantities of scandium in rocks and related materials with a complex matrix has been hampered by the lack of suitable analytical methods; mainly spectrochemical methods have been employed. Recent development in neutron activation techniques has facilitated the determination of scandium, down to submicrogram quantities, with greater advantages over the other conventional methods. Thus, BATE et al.[1], WÄNKE[2], KEMP AND SMALES[3], and SCHMIDT et al.[4] have proposed procedures regarding the activation analysis of scandium in geochemical materials. Several methods for scandium in such materials as pure silicon[5], super-purity grade aluminum[6], cooling water of a reactor[7] and metallic beryllium[8] have also been reported. OKADA[9] has effected a non-destructive activation analysis of scandium in materials rich in rare earths using a short-lived ^{46m}Sc (19.5 sec). Although the non-destructive method has considerable advantages, it is not applicable to all samples which require analysis. The other methods involve chemical separations and many analytical separation steps must be inevitably incorporated to obtain radiochemically pure scandium from complicated matrices. In this study an effort was made to develop a simple and reasonably rapid procedure for the radio-chemical separation of scandium; a method involving a sufficiently high chemical yield and considerable saving of time for the radiochemical work is described below.

EXPERIMENTAL

Nuclear data

Scandium exists in nature as a mononuclide ^{45}Sc (100% abundance). The nuclear reaction ^{45}Sc(n,γ)^{46}Sc with an effective cross-section of 23 barns gives rise to 85-day ^{46}Sc. The 100% isotopic abundance of ^{45}Sc coupled with its high activation cross-section makes scandium a quite favorable element for determination by neutron activation. Competing nuclear reactions which might interfere will be discussed later.

Reagent and chemicals

Scandium stock solution. An appropriate amount of Sc_2O_3 (99.9% purity) was dissolved in a minimum amount of hydrochloric acid, evaporated to dryness

and finally taken up in 100 ml of 0.5 M hydrochloric acid. Scandium was determined by titration with 0.01 M EDTA solution standardized previously against zinc metal of primary standard quality. The stock solution contained 2 mg Sc/ml of 0.5 M hydrochloric acid, and served both as a carrier and as a comparative standard after appropriate dilution.

All the other chemicals used were of analytical grade quality.

Ion-exchange column. A strong base-type anion exchanger, Dowex 1-X8, 100–200 mesh, sulfate form, was used. Conventional glass tubes of 10 mm internal diameter, 20 cm long, packed at the bottom with glass wool were used. The columns were filled with a slurry of 10 g of the dried resin, the tops of the columns being fitted with conventional dropping funnels through a rubber stopper. The resulting bed was usually 18 cm high.

Irradiation and activity measurement

A sample of 0.1–0.4 g was weighed and sealed in a polyethylene tube. An aliquot of the standard scandium solution (40 μg Sc) was impregnated into a narrow strip of filter paper placed in a polyethylene tube and sealed. The sample and the comparative standard were then packed side by side in an aluminum can with aluminum packing foil. They were inserted in position in a rotary specimen rack mounted on the upper part of the graphite reflector of the Triga Mark II reactor of St. Paul's University and irradiated for 5 days (sometimes 10 days) at a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec and power level of 100 kW. The irradiation lasted 6 h a day. After cooling for 4 weeks the irradiated sample and the comparative standard were chemically processed to obtain radiochemically pure scandium activity in a solution form. Gamma-counting was performed using a standard well-type scintillation counter coupled with a 1.75 × 2″ thallium-activated NaI crystal.

Radiochemical procedures

Silicate rocks. Transfer 2 ml of the scandium carrier solution to a 50-ml nickel crucible, and add dilute ammonium hydroxide to precipitate scandium hydroxide. Evaporate to dryness. Put an irradiated sample into the crucible and fuse with 10 g of sodium peroxide for 10 min. Leach the melt with 100 ml of water and centrifuge. Discard the supernate. Dissolve the residue in a small amount of hydrochloric acid and add 3–4 ml of thioglycolic acid. Precipitate hydroxide by the addition of ammonium hydroxide. Centrifuge and discard the supernate. Wash the residue with small portions of 0.2% ammonium hydroxide solution. Dissolve the residue in 10 ml of 0.5 M sulfuric acid and evaporate with 1 ml of hydrofluoric acid. Take up the residue in 20 ml of 0.025 M sulfuric acid–0.07 M ammonium sulfate solution. If any precipitate appears, filter it off. Load the solution on to the ion-exchange column. Remove foreign activities by elution with 60 ml of the acid ammonium sulfate solution at a flow rate of 0.5–1 ml per min. Elute scandium with 60 ml of 2 M ammonium sulfate solution at the same flow rate. Add ammonium hydroxide to the eluate to precipitate scandium hydroxide. Dissolve the hydroxide in 5 ml of 6 M hydrochloric acid and transfer to a screw-cup vial. Count the total γ-activity of [46]Sc. Check, if necessary, the radiochemical purity by a proper multichannel analyzer. Obtain the chemical yield after the measurement of γ-activity by titration with

0.01 M EDTA solution using xylenol orange as indicator. Treat the comparative standard in a similar way.

Ores — cassiterite. The principle of the separation is almost the same as above. Fuse 0.1–0.3 g of the cassiterite in the presence of scandium carrier with 5 g of sodium peroxide. Leach the resulting melt with a little water. Add enough nitric acid, 3 ml of perchloric acid and 2 ml of hydrofluoric acid. Evaporate to dryness until the white fumes of perchloric acid disappear. Add 20 ml of 1:1 nitric acid to the residue and evaporate to 2–3 ml. Dilute with water and centrifuge. Add 1:1 ammonium hydroxide to the supernate to precipitate hydroxide. Dissolve the hydroxide in a little hydrochloric acid, add 2 ml of thioglycolic acid and again precipitate scandium hydroxide by the addition of 1:1 ammonium hydroxide. Dissolve the precipitate in 10 ml of 0.5 M sulfuric acid and evaporate to dryness. Take up the residue in 20 ml of 0.025 M sulfuric acid–0.07 M ammonium sulfate solution and then proceed as described for silicate rocks.

RESULTS

The results of determination of scandium in the 2 rock standards G-1 and W-1 are given in Table I along with those which have briefly been published before[10]. For comparison earlier literature values for scandium are quoted in Table II. It can

TABLE I

DETERMINATION OF SCANDIUM IN STANDARD ROCKS G-I AND W-I (p.p.m.)[a]

| G-1 | 2.8, 2.7 (3.0, 2.5, 2.6) |
| W-1 | 35, 36, 37 (28, 37, 37) |

[a] Values in parentheses were obtained by the "old method" published briefly before[10].

TABLE II

PREVIOUS DATA OF THE CONTENT OF SCANDIUM IN G-I AND W-I (p.p.m.)

G-1	W-1	Method	Reference
4[a] (1–6)	43[a] (5–70)	Spectr.	11
2	—	Spectr.	12
Trace	25[b] (10)	Spectr.	13
<10[b] (20)	38[b] (21)	Spectr.	14
13[b] (21)	120[b] (22)	Spectr.	15
<10	40[b] (2)	Spectr.	16
2.8[b] (5)	34[b] (4)	Activation	3
—	31[b] (2)	Activation	17

[a] Values recommended by AHRENS AND FLEISCHER based on the data published before (1960). Values in parentheses show the range.
[b] Values in parentheses represent the range or the number of determinations.

be seen that the range of spectrochemical values for scandium in W-1 involves a factor of more than 20. Spectrochemical information on the scandium in G-1 is also unsatisfactory. On the other hand there is good agreement among the activation values given by us, KEMP AND SMALES and MORRIS AND ROGERS[17]. The results on the determination of scandium in a cassiterite are indicated in Table III along with those in stony meteorites.

TABLE III

DETERMINATION OF SCANDIUM IN CASSITERITE AND METEORITES

Sample	Sc (p.p.m.)		
	This work	Other data by activation method	
		Bate et al.[1] (1960)	Schmidt et al.[4] (1963)
Cassiterite	4.6, 4.3, 4.3		
Meteorite:			
Nuevo Laredo	41	45	43
Forest City	7.4[a], 6.0[a], 6.8[a]	8.9	
Modoc	12[a], 9.6[a]	9.2	8.1
Admire (silicate phase)	1.7		

[a] Values obtained by the "old method".

DISCUSSION

In the past we used a radiochemical procedure involving a fluoride cycle as well as many other steps of purification (abbreviated to "old method"), like the other available methods, for determining scandium in a variety of samples by neutron activation analysis.

In most cases scandium fluoride precipitation, which is effective for a gross separation of scandium, lowers the chemical yield of scandium considerably. A useful anion-exchange chromatographic method for the separation of scandium in ammonium sulfate media was developed previously[18], and was tested in the present work in the radiochemical procedure for scandium. Under the conditions indicated in the above radiochemical procedure, Y(III), rare earths, Be(II), Ga(III), Ge(IV), Al(III), Mn(II), Cu(II), Ni(II), Co(II), Zn(II), Mg(II), V(IV), Cd(II) and alkali metals passed through the column, while U(VI), Th(IV), Zr(IV), Mo(VI), Nb(V) and Ta(V) were retained strongly on the column. Indium and iron(III), when present in large quantities, tended to contaminate the eluted scandium; interference from iron was conveniently removed by precipitating scandium hydroxide in the presence of thioglycolic acid before starting the column separation of scandium. If γ-spectrometry is not carried out, an interference will arise from the induced activity, ^{192}Ir (74.5 d); however, this interference is not serious in most cases, because the elemental abundance of iridium is so low in natural materials except for those rich in platinum group metals, such as iron meteorites.

Because of the simplicity of the radiochemical procedure, the present method gave a good overall chemical yield, averaging 85%. Usually about 7 h were required for the whole procedure, compared to the 20 h required in the radiochemistry of previous work. The γ-ray spectra of the scandium activities from samples processed by the earlier and the present method were identical with that of ^{46}Sc of the reference standard. Fig. 1 shows a representative γ-ray spectrum of ^{46}Sc isolated from the rock standard W-1 along with that of the reference standard. No extraneous γ-activities were found in either spectra.
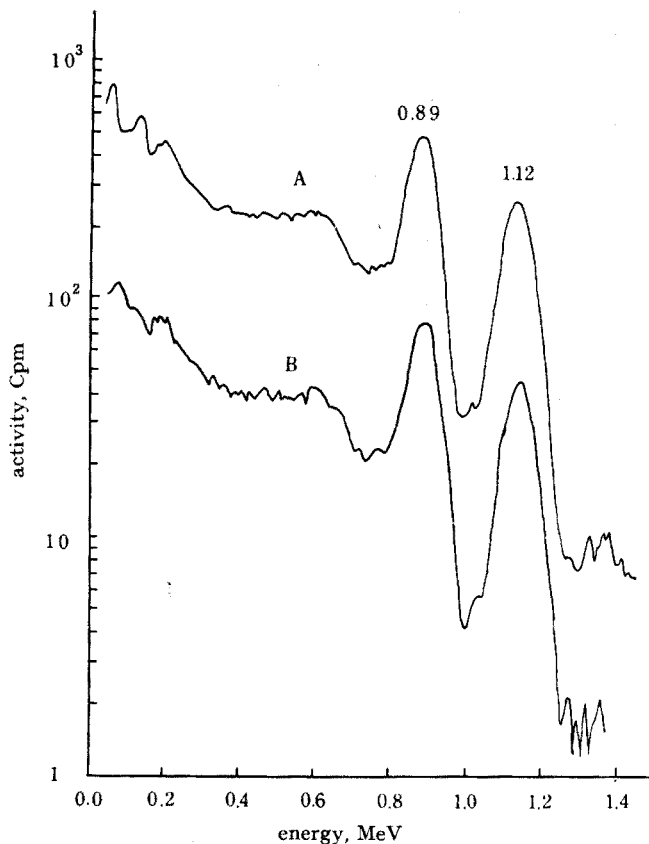
Fig. 1. Gamma-ray spectrum of 46Sc separated from standard rock G-1. (A) 46Sc isolated from G-1; (B) 46Sc induced in irradiated scandium comparative standard.

Interfering nuclear reactions

A list of possible interfering nuclear reactions was given by KEMP AND SMALES[3].

(I) 46Sc and a series of other radioactive scandium isotopes produced by the (n,p) reaction. There are 5 radioactive scandium isotopes formed by the action of fast reactions on titanium by the (n,p) reaction:

46Ti(n,p)46Sc(β^- 0.36, γ 0.89, 1.12 MeV, 85 d)
47Ti(n,p)47Sc(β^- 0.44, 0.60; γ 0.16 MeV, 3.4 d)
48Ti(n,p)48Sc(β^- 0.64, γ 1.32, 1.04, 0.99, 44 h)
49Ti(n,p)49Sc(β^- 2.0, no γ's, 57 min)
50Ti(n,p)50Sc(β^- 3.5, γ 1.6, 1.2, 1.7 min)
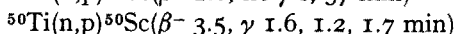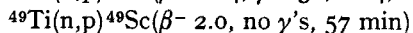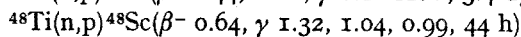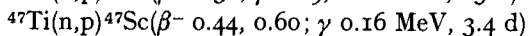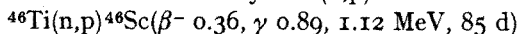
If these reactions are significant and if the activity is finally determined by total γ-counting, as in the present study, the error introduced becomes serious. Of the above isotopes, 49Sc and 50Sc decay away within 12 h of the end of irradiation. The γ-peaks of 48Sc overlap the peaks of 46Sc so that it is difficult to distinguish them,

but ^{48}Sc decays away almost to a negligible level within 3 weeks, whilst the γ-spectrum of ^{46}Sc remains without any serious reduction in activity. Regarding ^{47}Sc, it is easy to distinguish between ^{46}Sc and ^{47}Sc on a multichannel γ-ray analyzer. Because of the greater difference in half-lives of ^{46}Sc and ^{47}Sc it is also possible to allow the ^{47}Sc to decay away to a negligible level with some loss in the activity of ^{46}Sc. This simple procedure eliminates the use of the rather expensive gamma analyzer. The extent of interference from the ^{46}Sc formed by the (n,p) reaction on titanium had to be experimentally determined. Accordingly, *ca.* 100-mg portions of 99.9% pure titanium metal sponge were weighed into polyethylene ampoules (4 mm internal diameter) and sealed. Then one ampoule and reference standard were each wrapped with cadmium foil, 2 mm thick, and placed side by side in an aluminum capsule (25 mm internal diameter); finely powdered metallic boron was added to fill the space between the wall of the capsule and the wrapped ampoules. Another pair of ampoules containing titanium sponge and scandium reference standard, respectively, were prepared in a similar way but without cadmium foil and boron. Two capsules thus prepared were irradiated for 30 h in the same irradiation position as that for practical samples at the same power level. The radiochemical procedure for separating the radionuclides of scandium is given in the Appendix. The scandium fractions thus obtained were examined on the 100-channel analyzer at intervals over a few weeks. After 3 weeks the ^{48}Sc peak was not observable; the peaks distinguishable were those of ^{46}Sc and ^{47}Sc. The ^{46}Sc activity ratio between scandium reference standards with and without the cadmium–boron cut-off was found to be 117, while the same ratio calculated for ^{46}Sc induced in titanium was almost equal to unity. Therefore, the possibility of ^{46}Sc being produced from a scandium impurity in the titanium sponge could be disregarded. The maximum error which would be introduced by the (n,p) reaction on titanium is estimated to be of the order of 2.7 p.p.m., which is somewhat higher than the value of 1.6 p.p.m., reported by KEMP AND SMALES[3]. With regard to the titanium values for G-1 and W-1, the values for scandium contributed from the ^{46}Ti(n,p)^{46}Sc were found to be 0.002 p.p.m. and 0.009 p.p.m., respectively. These correction values do not affect the final results for G-1 and W-1 at any significant level. The ^{47}Sc peak (0.16 MeV) appeared distinctly in the γ-spectrum of the scandium fraction isolated from the irradiated titanium; although its contribution to the final estimation of scandium was not attempted, it seems unlikely that its effect is more significant than that of the ^{46}Sc formed by the fast reaction. There was no problem in the present work because the total γ-counting of the scandium activity was normally done after more than 4 weeks from the end of irradiation.

    (II) $^{51}V(n,\alpha)^{48}Sc$ *and* $^{50}V(n,\alpha)^{47}Sc$. There were no available data on the fission-neutron cross-sections for these reactions, so that their contribution was determined experimentally. Ammonium vanadate (170 mg) was irradiated as before and processed to obtain a pure scandium fraction by an ion-exchange method reported previously[20]. The scandium fraction showed no sign of the ^{47}Sc and ^{48}Sc peaks.

    (III) ^{47}Sc *and* ^{49}Sc *formed as the daughters of* ^{47}Ca *and* ^{49}Ca. The two reactions ^{46}Ca(n,γ)^{47}Ca and ^{48}Ca(n,γ)^{49}Ca followed by β-decay produce 2 scandium isotopes, ^{47}Sc and ^{49}Sc, respectively. Because of the extremely low abundance of ^{46}Ca (0.0032%) and of its relatively low isotopic activation cross-section (0.36 barns), the contribution of ^{47}Sc thus produced does not become serious. Indeed, there were no signs of

the ^{47}Sc peak in the scandium fraction isolated from two irradiated standard rocks 4 weeks after the end of irradiation.

APPENDIX

Procedure for the separation of scandium from irradiated titanium

Cool the irradiated titanium metal sponge for 30 min. Place it into a polyethylene centrifugal tube containing 5 mg of scandium carrier. Add 1 ml of hydrofluoric acid and then a few drops of nitric acid. When violent reaction ceases, add 5 mg of lanthanum and 20 ml of water. Warm on a steam bath. Centrifuge. Dissolve the precipitate in a mixture of 1 ml of saturated boric acid solution and 2–3 drops of hydrogen peroxide. Add ammonium hydroxide to precipitate scandium and lanthanum hydroxide and centrifuge. Dissolve the hydroxide in 1 ml of sulfuric acid and evaporate to dryness. Take up the residue in 5 ml of 0.07 M ammonium sulfate–0.025 M sulfuric acid solution. Load the solution on to the top of an anion-exchange column (1 cm i.d. and 5 cm long), containing Dowex 1-X8 (100–200 mesh, sulfate form). Remove foreign activities from the column by eluting with 35 ml of the above acid ammonium sulfate solution. Then elute scandium with 20 ml of 4 M hydrochloric acid. Add 10 ml of 2% oxine solution to the eluate and add ammonium hydroxide to precipitate scandium oxinate. Weigh. Dissolve the precipitate in hydrochloric acid and count. Treat the reference standard in a similar, but simpler way.

SUMMARY

A neutron activation method is proposed for the determination of trace quantities of scandium, down to submicrogram level, in rocks, ores and meteorites. The sample and standard are irradiated intermittently for a total of 30 h, at a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec; the radiochemical separation consists essentially of a one-step anion exchange. The induced γ-activity of ^{46}Sc, 85 days, isolated from the sample is measured and compared with that of a standard. The chemical yield averages 85% and there is a considerable saving of time in the radiochemical work. Results are quoted for the scandium contents of 2 standard rocks, cassiterite and several stony meteorites. Details of conflicting nuclear reactions are also given.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est proposée pour le dosage de traces de scandium dans les roches, minerais et météorites. L'échantillon et l'étalon sont irradiés de façon intermittente pendant 30 heures, avec un flux de neutrons de $5 \cdot 10^{11}$ n/cm²/sec. L'activité γ induite de ^{46}Sc, 85 jours, est mesurée et comparée avec celle de l'étalon. Le rendement chimique est en moyenne de 85%; le gain de temps est considérable.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren Scandium bis hinab zum Submikrogrammbereich in Gesteinen, Erzen und Meteoriten mit der Neutronen-

aktivierungsanalyse vorgeschlagen. Die Probe und ein Standard werden bei einem Neutronenfluss von $5 \cdot 10^{11}$ n/cm^2/sec intermittierend insgesamt 30 Std. lang bestrahlt. Die radiochemische Trennung besteht im wesentlichen aus einem einstufigen Anionenaustausch. Die erzeugte γ-Aktivität des ^{46}Sc, 85 Tage, wird, nachdem sie von der Probe getrennt ist, gemessen und mit dem Standard verglichen. Die chemische Ausbeute beträgt im Mittel 85%, bei einem beträchtlichen Zeitgewinn der radiochemischen Arbeiten. Es wurden Scandiumgehalte von einigen Proben wie Standardgesteinen und Meteoriten angegeben. Störende Kernreaktionen werden diskutiert.

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THE ABSORPTIOMETRIC DETERMINATION OF MOLYBDENUM AS MOLYBDENUM(V) THIOCYANATE IN STEEL

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Few methods for the determination of an element have been subjected to so many studies as the photometric thiocyanate method for molybdenum. Several of these studies[1-4,8] have been quite extensive and systematic; an excellent summary can be found in the text book of SANDELL[9]. The many studies indicate that the conditions of the method are inherently critical, and also that other methods of determination are not very satisfactory. In a recent study of HIBBITS AND WILLIAMS[8], the nature of the method was indicated by the statement that "the developed method is accurate to within $\pm$ 4%". This accuracy, if applicable to contents of, say, 1–2% in steel, is definitely unsatisfactory.

In our steel analytical laboratory, a modified procedure has been in use for several years, which is very similar to that described by B.I.S.R.A.[10]. The method in this form, however, is sensitive to interferences from copper, as well as from colored ions. It gives reasonably good short-term precision (relative standard deviation 1–2% within one series of samples), but the long-term precision is not nearly so good, and a change of analysts results in much too large deviations: 2–5% at a level of 0.5–1%. The color of molybdenum thiocyanate in the aqueous phase is, however, very stable.

A method with better stability and accuracy was highly desirable in order to be able to check high-speed methods (optical and X-ray spectrometry). A comparison of the published thiocyanate methods for molybdenum, together with some preliminary experiments, was therefore made to determine whether this method would be worth investigating in detail, in order to develop a method which would meet the following requirements:

range: 0.01 to 10% Mo in steel

precision: content   0.1%   1%   10%

　　　rel. st. dev. (n = 10)   3   1   0.5

interferences: no interferences $>$ 2 δ for Mo = 0.10% from the following elements up to the content indicated (only probable interference elements are listed)

Fe	V	W	Ti	Nb	Co	Cu	Cr	Ni	Mn
2000 mg	5	20	5	5	20	1	20	20	10 per cent

Comparison of the published methods and results of some preliminary experiments

　　Apart from the fact that a thiocyanate of molybdenum(V) is involved in the

color reaction, different opinions have been expressed concerning almost all other relevant details. The situation is summarized in Table I.

A study of the method should obviously include the effect of all these parameters, and also possible interactions. However, some practical limitations, together with some preliminary experiments, made the picture less confusing as indicated below.

TABLE I

THE EFFECT OF DIFFERENT PARAMETERS ON THE Mo-THIOCYANATE COLOR ACCORDING TO PUBLISHED METHODS

Parameter	References		
	No effect	Slight effect	Strong effect
HCl	8	3	1, 2
HClO$_4$, H$_2$SO$_4$	12	1, 11	8
NH$_4$SCN	(3), 11	1, 2, 11, 3	4, 8
SnCl$_2$		4, 2, 3	8
Fe		(2), 11	3, 4
Cu		2, 4, 8, 10	
Ti	10	2	

The effect of iron and copper. In the presence of iron and copper, molybdenum(VI) is not easily reduced to the trivalent state by tin(II) chloride. In their absence, the color of molybdenum(V) thiocyanate disappeared rapidly, when an excess of tin(II) was added, but could be redeveloped if some iron or copper was added. It is thus sufficient to know the concentration ranges of iron (copper) and tin(II) chloride within which the reduction to only molybdenum(V) is valid. Some preliminary experiments indicated that these limits were not too narrow.

The effects of thiocyanate and hydrochloric acid. A very large excess of thiocyanate tended to bleach the color, but the amount of thiocyanate was not very critical. Preliminary experiments gave evidence of a very strong effect of hydrochloric acid. Organic extracts containing 100 μg Mo and with an absorbance of 0.300 were discolored when shaken with an equal volume of 10 N hydrochloric acid. The recommended use of nitric acid[11] and perchloric acid[12] as stabilizers for the molybdenum(V) thiocyanate color is advantageous because these acids do not promote the reduction of Mo(V) to Mo (III).

Use of organic extractant. Through the use of organic extractant, the interferences of copper and colored ions such as Cr(III) and Ni(II), could be eliminated and probably the concentration of interfering anions controlled more effectively than in the aqueous phase.

Based on these considerations, an initial method was outlined as described below.

Preliminary method

Into a 250-ml separatory funnel, place 100 μg Mo and add 2 ml of concentrated phosphoric acid, 25 ml of 1:1 sulfuric acid, 20 mg of iron and 0.6 g of potassium thio-

cyanate. After shaking, add 10 ml of water containing 1 g of $SnCl_2 \cdot 2H_2O$ and 1 ml of hydrochloric acid and shake again. Adjust the volume to 100 ml, add 50.0 ml of amyl acetate and shake for 30 sec. Discard the aqueous phase and wash the organic phase with 50 ml of wash solution containing 2 g of potassium thiocyanate, 0.5 g of tin(II) chloride dihydrate and 11 ml of concentrated hydrochloric acid. Discard the aqueous phase and filter the extract through a dry filter paper into the cell. Measure the absorbance at 470 mμ.

Effect of variables

Effect of iron. According to PERRIN[2] "for 4 μg Mo, at least 0.5–1 mg Fe is necessary, and up to 10–30 mg causes no further change". CUNNINGHAM AND HAMNER[13] had up to 200 mg Fe present, whereas HIBBITS AND WILLIAMS[8] found no interference from 500 mg and 10 mg was always added. In the procedure of CROUT-HAMEL AND JOHNSON[4] more than 2 mg Fe interfered.

When the preliminary method was used, it was found that the stability and reproducibility (absorbance 0.378–0.380) were good in the presence of 2–200 mg of iron. As much as 500 mg did not interfere if the initial addition of tin(II) chloride was 3 g and the wash solution contained 1 g of tin(II) chloride. The extra quantities of tin(II) did not affect the absorbance readings even when only 20 mg of iron was present.

Effect of hydrochloric acid. According to PERRIN[2], the amount of hydrochloric acid is critical and "must be controlled to at least $\pm$ 1 ml of 4 ml added if the error is not to exceed 3%". HURD[1] also stated that the amount of hydrochloric acid is critical. B.I.S.R.A.[10] and HAYWOOD AND WOOD[12] did not add hydrochloric acid and HIBBITS AND WILLIAMS[8], who used about 1.5 N solution, stated, that its amount had "no significant effect on the results".

Table II contains the results obtained with various amounts of hydrochloric acid according to the preliminary method, but with omission of sulfuric acid. Interesting conclusions could be drawn from these results as regards the reduction of iron and molybdenum, but for use as a method for the determination of molybdenum, the system was far too critical. Hydrochloric acid was not used in any further studies.

TABLE II

THE EFFECT OF HYDROCHLORIC ACID

HCl (d = 1.19) added (ml)	Added as	Normality of HCl after dilution	Absorbance 470 mμ			Remarks
			After 0 min	After 1 h	After 20 h	
6	Undil.	0.7	(0.379)	(0.379)	(0.373)[a]	Iron not reduced
8	Undil.	1.0	0.235	0.232	0.232	Extraction after 15 min
12.5	Undil.	1.5	0.379	0.384	0.376	Extraction immediately
12.5	Undil	1.5	0.175	0.182	0.182	Extraction after 1 min
12.5	Dil. 1 + 1	1.5	0.379	0.378	0.376	Extraction after 1 min
12.5	Dil. 1 + 4	1.5	0.384	0.381	0.379	Extraction immediately
25	Undil.	3.0	0.373	0.375	0.370	Extraction immediately
37.5	Undil.	4.5	0.322	0.325	0.323	Extraction immediately
50	Undil.	6.0	Almost colorless			Extraction immediately

[a] These absorbances include the color of unreduced iron thiocyanate.

Effect of perchloric acid. HAYWOOD AND WOOD[12] state, that "perchloric acid is a stabilizing medium for the ferric thiocyanate and so also for molybdenum thiocyanate". However, perchloric acid is not used in any method to which reference is made, other than the B.I.S.R.A. method[10].

Table III gives the results obtained with varying amounts of perchloric acid according to the preliminary method. Compared with corresponding determinations in sulfuric acid media, the results with the higher concentrations of perchloric acid tended to be low. Moreover, the reproducibility was not good enough. Separate experiments showed that with larger amounts of tin(II) chloride, correct results could be obtained even with the higher concentrations of perchloric acid; but, obviously, perchloric acid can not generally be recommended, because of its oxidizing power.

TABLE III

THE EFFECT OF PERCHLORIC ACID

$HClO_4$ added (ml)	Normality at development of the color	Normality after dilution to volume	Absorbance 470 mμ		
			After 0 min	After 2–3 h	After 20 h
6	2.2	0.7	0.377	0.377	0.367
9	3.2	1.0	0.378	0.378	0.373
13	3.9	1.5	0.380	0.381	0.378
13[a]	3.9	1.5	0.385	0.382	0.378
26	5.8	3.0	0.358	0.365	0.358
26[a]	5.8	3.0	0.350	0.355	0.353
39	7.1	4.5	0.369	0.377	0.370
39[a]	7.1	4.5	0.378	0.375	0.370
52	7.7	6.0	0.315	0.338	0.345
65	8.4	7.5	Almost no color		

[a] Determination carried out later to test reproducibility.

TABLE IV

THE EFFECT OF SULFURIC ACID

H_2SO_4 (1 + 1) added (ml)	Resulting normality of H_2SO_4[a]	Absorbance at 470 mμ										
		Time between development and extraction										
		0 min			10 min			30 min			60 min		
		Time after separation of organic phase											
		0 min	1 h	20 h	0 min	1 h	20 h	0 min	1 h	20 h	0 min	1 h	20 h
8	1.3	(0.376)	(0.379)	(0.378)	0.338	0.337	0.335	0.302	0.300	0.298			
19	3.0	(0.380)	(0.380)		0.371	0.371		0.368	0.370				
22	3.5	0.380	0.381	0.381	0.380	0.379	0.378	0.379	0.379	0.376	0.378	0.380	0.378
25	4.0	0.382	0.383	0.382	0.379	0.378	0.379	0.378	0.379	0.379	0.379	0.379	0.378
38	6.0	0.380	0.380		0.380	0.380		0.378	0.378		0.378	0.379	
44	7.0	0.378	0.381	0.378	0.379	0.380	0.380	0.379	0.379	0.381	0.378	0.379	0.379
50	8.0	0.352	0.360	0.360	0.352	0.357	0.358						

[a] The solution was always diluted to constant volume before adding the reagents: Fe, KSCN and SnCl₂. Values in brackets indicate that the iron(III) thiocyanate color is included.

Effect of sulfuric acid. Little mention is made of sulfuric acid in published studies. HIBBITS AND WILLIAMS[8] stated that its concentration is critical. The influence of sulfuric acid was investigated in somewhat greater detail than the other acids; the variation of the time between the development of the color and the extraction was also studied. The results are given in Table IV. Obviously the reduction was too slow at acidities below 3 *N*. Above 7 *N*, low results were obtained, possibly because of a sulfate complex of molybdenum. However, the range between 3.5 and 7 *N* sulfuric acid was considered big enough for the determination and the stability and reproducibility were good.

Effect of thiocyanate. Almost all authors point out that the amount is not critical but that excessive amounts bleach the color. In the aqueous phase 0.5–3% thiocyanate (0.075–0.45 *N*) is generally used. Obviously the amount of thiocyanate in the organic phase depends not only on its concentration in the sample solution but also on the thiocyanate concentration of the wash solution, and thus both concentrations were varied.

The results (Table V) indicated that concentrations below 0.05 *N* in the aqueous phase tended to give low results which, however, could be somewhat improved by high concentrations of thiocyanate in the wash solution. Concentrations in excess of 0.20 *N* in the aqueous phase definitely gave low results, which could only be very slightly improved by having little or no thiocyanate in the wash solution. The thiocyanate concentration in the wash solution was less critical, though more than 0.5 *N*

TABLE V

THE EFFECT OF THIOCYANATE

Normality of aqueous phase (N)	Normality of wash solution (N)	Absorbance after			Normality of aqueous phase (N)	Normality of wash solution (N)	Absorbance after		
		0 min	1 h	20 h			0 min	1 h	20 h
0.01	1.00	0.310	0.314	0.313	0.13	0.50	0.378	0.380	0.382
0.01	0.50	0.316	0.320	0.320	0.13	0.25	0.384	0.387	0.388
0.01	0.25	0.332	0.332	0.330	0.13	0.075	0.385	0.391	0.387
0.01	0.075	0.285	0.285		0.13	—	0.384	0.392	0.387
0.05	1.00	0.375	0.369	0.371	0.21	1.00	0.372	0.372	0.378
0.05	0.50	0.382	0.375	0.381	0.21	0.50	0.381	0.375	0.372
0.05	0.25	0.386	0.382	0.382	0.21	0.25	0.384	0.379	0.379
0.05	0.075	0.385	0.376	0.379	0.21	0.075	0.384	0.383	0.382
0.05	—a	0.355	0.367	0.367	0.21	—	0.385	0.385	0.384
0.065	0.50	0.383	0.381	0.381	0.30	0.50	0.353	0.359	0.357
0.065	0.25	0.384	0.384	0.384	0.30	0.25	0.349	0.356	0.355
0.065	0.075	0.383	0.384	0.384	0.30	0.075	0.315	0.326	0.335
0.065	—	0.341	0.375	0.379	0.30	—	0.372	0.375	0.375
0.08	1.00	0.375	0.370	0.374	0.50	1.00	0.319	0.315	
0.08	0.50	0.383	0.383	0.380	0.50	0.50	0.236	0.255	
0.08	0.25	0.390	0.386	0.384	0.50	0.25	0.220	0.245	
0.08	0.10	0.387	0.387	0.382	0.50	0.075	0.205	0.235	
0.08	0.05	0.386	0.384	0.383					
0.08	—	0.385	0.380	0.380					

—a = No thiocyanate added to the wash solution.

gave low results. Thus the permitted limits of the thiocyanate concentrations in the solution to be extracted and in the wash solution were 0.05–0.15 N and 0.10–0.35 N respectively. These figures are, of course, dependent on the amounts of iron, molybdenum and other ions forming thiocyanates, but no effect was found for amounts of 0.5–500 mg Fe and 0.5–300 μg Mo.

Effect of tin(II) chloride. According to the generally accepted explanation of the reaction mechanisms involved, the color intensity should depend on the amount

TABLE VI

THE EFFECT OF THE CONCENTRATION OF TIN(II) CHLORIDE

Normality of $SnCl_2$ (N)		Normality of HCl (N)		Absorbance 470 mμ after		
In aqueous phase	In wash soln.	In aqueous phase	In wash soln.	10 min	1 h	20 h
0.10	0.00	0.025	2.00	0.335	0.308	0.218
0.10	0.10	0.025	2.02	0.390	0.393	0.392
0.10	0.20	0.025	2.05	0.385	0.391	0.388
0.10	0.40	0.025	2.10	0.382	0.386	0.383
0.10	0.60	0.025	2.15	0.346	0.378	0.377
0.10	0.80	0.025	2.20	0.336	0.358	0.377
0.10	0.00	0.10	2.00	0.370	0.346	0.193
0.10	0.10	0.10	2.02	0.395	0.393	0.393
0.10	0.20	0.10	2.05	0.390	0.388	0.389
0.10	0.40	0.10	2.10	0.383	0.384	0.384
0.10	0.60	0.10	2.15	0.348	0.368	0.383
0.10	0.80	0.10	2.20	0.343	0.363	0.380
0.15	0.00	0.0375	2.00	0.396	0.401	0.391
0.15	0.10	0.0375	2.02	0.396	0.401	0.389
0.15	0.20	0.0375	2.05	0.396	0.399	0.385
0.15	0.40	0.0375	2.10	0.388	0.394	0.382
0.15	0.60	0.0375	2.15	0.382	0.392	0.381
0.20	0.00	0.05	2.00	0.396	0.396	0.387
0.20	0.10	0.05	2.02	0.397	0.397	0.388
0.20	0.20	0.05	2.05	0.395	0.393	0.383
0.20	0.40	0.05	2.10	0.389	0.397	0.388
0.20	0.60	0.05	2.15	0.360	0.389	0.384
0.20	0.80	0.05	2.20	0.346	0.375	0.380
0.25	0.00	0.0675	2.00	0.394	0.400	0.395
0.25	0.10	0.0675	2.02	0.392	0.399	0.395
0.25	0.20	0.0675	2.05	0.394	0.401	0.395
0.25	0.40	0.0675	2.10	0.385	0.393	0.385
0.25	0.60	0.0675	2.15	0.360	0.384	0.382
0.30	0.00	0.075	2.00	0.388	0.394	0.389
0.30	0.10	0.075	2.02	0.392	0.395	0.396
0.30	0.20	0.075	2.05	0.396	0.390	0.400
0.30	0.40	0.075	2.10	0.377	0.384	0.387
0.30	0.60	0.075	2.15	0.355	0.383	0.385
0.40	0.00	0.10	2.00	0.390	0.394	0.384
0.40	0.10	0.10	2.02	0.390	0.394	0.384
0.40	0.20	0.10	2.05	0.389	0.391	0.383
0.40	0.40	0.10	2.10	0.377	0.387	0.381
0.40	0.60	0.10	2.15	0.347	0.365	0.378
0.40	0.80	0.10	2.20	0.338	0.365	0.379

of the reductant; if insufficient tin(II) is added Mo(VI) is not completely reduced to Mo(V), and if too much is added, the reduction continues to form Mo(III), in which case the Mo(V)-thiocyanate color fades. Most authors[1–3] point out that the excess of tin(II) is not very critical, but that the amount of acid added with tin(II) chloride is important. The effects of varying both the tin(II) and the hydrochloric acid concentrations are shown in Table VI (the procedure on p. 22–23 was used). Although the results obtained confirmed earlier results[1–3] they still indicated that if the best precision is to be attained, the concentration of tin(II) chloride is quite critical.

Interactions between molybdenum, sulfuric acid, tin(II) chloride, thiocyanate and iron. It was considered advisable to study possible interactions between reagents only within certain limits of the reagents used. The levels were chosen arbitrarily to correspond to twice as great variations as could be expected in practical determinations. The results of these tests, which were carried out according to the procedure given on p. 22–23 in other respects (but with only 25 ml of amyl acetate) are given in Table VII.

Although significant interactions can be traced from these results, the probability of obtaining errors larger than 1%, due to interactions in practical determinations, is very slight, considering that such great variations of reagent concentrations would be excluded and that the standing time would be much more constant.

TABLE VII

INTERACTIONS BETWEEN REAGENTS AT DIFFERENT LEVELS

Level[a] of					Recovery, absorb. measured after			Remarks
Mo	H_2SO_4	Fe	KCNS	$SnCl_2$	0 min	1 h	4 h	
L	M	M	M	M	0.156	0.157	0.158	Values used as
L	M	M	M	M	0.158	0.158	0.157	reference for
H	M	M	M	M	0.779	0.780	0.780	calculation of
H	M	M	M	M	0.781	0.780	0.781	recovery
L	L	H	H	H	100.0	101.3	98.2	
H	L	H	H	H	99.3	98.6	99.8	
L	M	H	H	L	98.8	99.4	98.8	
H	M	H	H	L	99.2	98.7	99.0	
L	M	L	L	H	99.4	100.0	99.4	
H	M	L	L	H	101.0	101.0	102.3	
L	H	L	H	L	97.0	95.5	95.5	Values calculated as
H	H	L	H	L	99.5	99.0	100.0	percentage of the
L	H	H	L	L	101.3	100.6	100.0	above absorbance
H	H	H	L	L	100.2	100.2	101.8	values
L	L	H	L	L	99.4	98.8	98.2	
H	L	H	L	L	100.2	100.2	101.5	
L	L	L	M	M	99.4	97.5	97.0	
H	L	L	M	M	100.0	100.5	101.5	
L	L	L	L	L	100.0	100.5	100.0	
H	L	L	L	L	100.6	100.8	102.1	
L	H	H	H	H	100.6	99.4	100.0	
H	H	H	H	H	99.3	99.5	99.8	

[a] The concentrations of reagents were as follows:

	Mo	H_2SO_4	Fe	KSCN	$SnCl_2$
L = Low level	20 μg	4 N	5 mg	0.07 N	0.10 N
M = Medium level	50 μg	5 N	20 mg	0.10 N	0.20 N
H = High level	100 μg	7 N	200 mg	0.15 N	0.30 N

EXPERIMENTAL

The following procedure was accepted for the determination of molybdenum in contents of 0.01–10% in all steels. For convenience, the modification required for tungsten-containing steels is included.

Reagents and apparatus

Tin(II) chloride. Stock solution 10 N. Dissolve 225 g of $SnCl_2 \cdot 2H_2O$ in 50 ml of concentrated hydrochloric acid and dilute to 200 ml with water. Add 1–5 g of tin. Prepare a 2 N solution daily by dilution with boiled water.

Wash solution. Stock solution 0.5 N $SnCl_2$. Dissolve 56 g of $SnCl_2 \cdot 2H_2O$ in 1000 ml of concentrated hydrochloric acid. Prepare the wash mixture immediately before use from 10 ml of 0.5 N $SnCl_2$, 5 ml of 1 N KSCN and 35 ml of water.

Amyl acetate. Reagent grade is not necessary, but a quality which is colorless as well as free from oxidants, is essential.

Separatory funnels. 250 ml, marked at 80 ml and preferably with teflon stop-cocks (to avoid grease).

Thermostat device, which allows handling of the solutions involved at a convenient temperature (20–25°) controlled to ± 0.5°.

Procedure

Depending on the expected content of Mo, weigh out 1000–100 mg ($\Delta < 0.1\%$) (see Table VIII), and dissolve in 10 ml of sulfuric acid (d = 1.84), 5 ml of phosphoric acid (d = 1.68) and 50 ml of water. Oxidize iron(II) with a few drops of nitric acid (d = 1.42). Dissolve high-alloy steels in hydrochloric and nitric acids and evaporate to remove these acids with the same amounts of sulfuric and phosphoric acid as mentioned above. Expel silicic acid with a few drops of hydrofluoric acid.

TABLE VIII

OPTIMUM SIZE OF SAMPLES, ALIQUOTS ETC. ACCORDING TO THE AMOUNT OF Mo EXPECTED

Mo % expected	Sample weight (mg)	Citric acid (g)[a]	Diluted to (ml)	Aliquot (ml)	Fe added (mg)
0.01–0.10	1000	10	100	20, 10	—
0.10–0.50	500	5	200	20, 10	—
0.50–2.0	200	5	500	20, 10	20
1.0–5.0	100	5	500	20, 10	20
5.0–10.0	100	10	1000	15, 10	20

[a] Only if W present.

Dilute the solution to volume (Table VIII) with water, at a temperature of 25° ± 0.5°. In the presence of tungsten, add citric acid before dilution. Transfer a suitable aliquot (Table VIII) to a 250-ml separatory funnel, add 25 ml of 1:1 sulfuric acid and adjust the volume to 80 ml. Mix well, add 10 ml of 1 N potassium thiocyanate, shake, add 10 ml of 2 N tin(II) chloride and mix again. (This solution is

5 N H_2SO_4, 0.10 N KSCN and 0.20 N $SnCl_2$.) Add 25.0 ml of amyl acetate at 25° and shake for 30 sec. Remove the aqueous phase, and wash the organic phase with 50 ml of solution containing 10 ml of HCl, 10 ml of 0.5 N $SnCl_2$ and 5 ml of 1 N KSCN.

Filter the organic phase through an iron-free filter paper into a dry volumetric flask, at a temperature of 25°. Measure the absorbance of the solution with a Beckman DU spectrophotometer at 470 mμ in a 1-cm cell against amyl acetate as reference.

Note

It is necessary to avoid contamination of iron(III) greater than that which can be eliminated by the tin(II) chloride in the organic phase. Avoiding excessive oxidation from strong oxidants is also essential. The freshness of the tin(II) solutions is important.

RESULTS AND DISCUSSION

The effect of various elements on the color development

The effect of ions present in solutions obtained from steel samples was investigated by adding varying amounts of the ions to the separatory funnel, together with 50 μg of molybdenum after which molybdenum was determined as described above

TABLE IX

THE EFFECT OF INTERFERING IONS

(50 μg Mo present; 20 mg Fe added)

W (mg)	Rec. (%)	Co (mg)	Rec. (%)	V (mg)	Rec. (%)	Ti (mg)	Rec. (%)	Nb (mg)	Rec. (%)
0	100.3	0	100.0	0	99.5	0	100.0	0	100.0
5	100.0	10	100.5	2.5	99.5	1	99.8	1	100.5
10	100.8	20	100.0	5	100.0	2.5	100.0	2	100.5
20	100.0	40	100.3	7.5	100.3	5	99.8	3.5	101.0
40	99.5	80	100.0	10	101.0	10	99.5	5	102.0
60	99.0	100	100.3	15	102.0	—	—	10	103.8

Cu (mg)	Rec. (%)	Cr (mg)	Rec. (%)	Ni (mg)	Rec. (%)	Mn (mg)	Rec. (%)
0	99.5	20	100.0	20	100.5	5	100.5
1	100.3	40	100.3	40	100.3	15	100.5
2	99.8	100	100.3	60	100.0	30	100.3
3	100.5	—	—	80	100.3	—	—
—	—	—	—	100	101.0	—	—
—	—	—	—	—	—	—	—

(Table IX). In the case of a color interference, the observed interference is better expressed as the absolute percentage error caused by 1% of the interfering element in the original sample. As can be seen from Table X, the interferences from the ions tested can be considered negligible in the analysis of steel.

In the analysis of some steels containing tungsten, surprisingly low results were obtained. This error was evident only when solutions of samples were diluted to large volumes, and thus some kind of cohydrolysis of molybdenum and tungsten was suggested. The low results could be remedied by adding citric acid which had no effect on molybdenum alone. With extremely high concentrations of tungsten + vanadium, a slight positive interference was also indicated; the error corresponding to 1% V (with excess W) was only 0.001% Mo.

Precision

From previous measurements with the Beckman DU spectrophotometer (1958 model) used, it was known that if a solution with a stable color ($CoSO_4$) was measured repeatedly at the wavelength in question (525 mμ) and at the absorbance level of 0.4–0.5 units, a relative standard deviation of the order of 0.10–0.15% could be expected.

The reproducibility of the color development includes variations in the color and volume measurements, and in the chemical reactions involved, but not variations in the dissolution of the sample or in the homogeneity of the sample, as only aliquots of one solution taken with one pipet are compared. These tests were carried out as described on p. 28 and the results are given in Table XI (I).

TABLE X

THE ABSOLUTE PERCENTAGE ERROR CAUSED BY 1% OF THE INTERFERING ELEMENT

Co	V	Ti	Nb	Cu	Cr	Ni	Mn
<0.00000	0.00005	<0.0000	0.0002[a]	0.0001	<0.00000	<0.0000	<0.0000

[a] Would correspond to 0.02% Mo in the Nb metal used (Specpure Matthey Niobium) which is not probable.

The short-term reproducibility of the entire procedure was determined by repeated analyses of three samples, with different amounts of the sample in one series of measurements; the results are given in Table XI (II).

The long-term reproducibility of the entire procedure is of decisive importance to the practical analyst. This reproducibility includes variations due to different volumetric vessels and newly prepared reagents, in addition to the variations listed above but not a change of analysts. The results of analyses over a 1-month period are shown in Table XII.

Accuracy (recovery)

As in all procedures of this type, obtaining the correct level of results depends on (a) the value of the blank, (b) the purity of the molybdenum used for establishing the curve (factor), and (c) differences in the conditions for preparation of the analytical curve and for analysis of unknown samples, *i.e.* interferences. Since the effects of

TABLE XI

RELATIVE STANDARD DEVIATION OF THE DETERMINATION OF Mo ($n = 10$)

Mo determined in	Sample[a]				
	BC5L	BC6H	BC11H	NBS153A	JK2A
S.D. for aliquots of the same solution (I)	0.09	0.22	0.11	—	—
S.D. for different weights of the same sample (II)	0.32	0.36	0.30	0.44	0.43
Sample amount taken (g)	0.490–0.500	0.191–0.201	0.202–0.209	0.191–0.198	0.487–0.529
Aliquot taken (ml)	10/200	10/500	10/500	10/1000	25/100
Absorbance	0.363–0.369	0.413–0.437	0.387–0.404	0.644–0.667	0.354–0.413

[a] Composition of the samples.
BC5L: 0.19 Mo, 0.3 C, 0.3 Si, 0.6 Mn, 0.02 P, 0.02 S, 1.5 Cr, 1.3 Ni, 0.04 V + W, 0.06 Cu.
BC6H: 1.40 Mo, 0.4 C, 1.1 Si, 0.5 Mn, 0.02 P, 0.008 S, 5.4 Cr, 0.2 Ni, 1.1 V, 0.07 Cu, 0.02 Co.
BC11H: 1.22 Mo, 0.8 C, 0.4 Si, 0.2 Mn, 0.02 P, 0.005 S, 4.5 Cr, 0.18 Ni, 1.4 V, 0.06 Cu, 16.8 W, 2.3 Co.
NBS153A: 8.85 Mo, 0.8 C, 0.2 Si, 0.2 Mn, 0.02 P, 0.007 S, 3.7 Cr, 0.2 Ni, 2 V, 1.7 W, 0.09 Cu, 8.5 Co.
JK2A: Carbon steel.

TABLE XII

LONG-TERM REPRODUCIBILITY OF Mo DETERMINATIONS

Sample no.	BC5L[a]	BC6H	JK8B	Pure Mo solution
Mean (%)	0.191	1.398	2.674	50 μg
Absolute standard deviation	0.00084%	0.0039%	0.010%	0.12 μg
Relative standard deviation (%)	0.44	0.28	0.37	0.24
No. of determinations	8	18	9	54

[a] Sample composition: see Table XI. JK8B is a 18Cr10Ni-steel.

all the known variable interferences were discussed on p. 23–27 and 29, only (a) and (b) are discussed here.

Molybdenum does not generally occur as an impurity in reagents; no special difficulty was experienced from this source, except that iron from some sources was found to contain a few thousandths of a percent of molybdenum and iron of the highest purity must therefore be used. The solution to be measured must not be colored by other substances absorbing at the wavelength used for Mo-thiocyanate; colorless amyl acetate must be used, although it is used as a reference. As pointed out on p. 29, iron contamination after the extraction must be avoided. When due consideration was given to these factors, the blank values were always less than 0.002 absorbance units.

With samples of high-purity molybdenum metal of different origin*, absorbance values conforming to each other and lying on a straight line between the absorbance values of 0.000 and 1.00 all within the precision claimed before were obtained; thus the calibration factor between the absorbance and the amount of molybdenum

* Johnson Matthey Specpure Molybdenum and Light Co, Mo 3N.

TABLE XIII

DETERMINATIONS OF MO IN STANDARD SAMPLES

Sample no.	Composition of the sample (%)	Certificate values (%)			Values obtained (%)	
		Lowest	Highest	Mean	Mean	Individual values
JK2B	0.2 C, 0.3 Si, 0.5 Mn, 0.03 Cr, 0.07 Ni, 0.16 Cu	0.038	0.045	0.042	0.040	0.040 0.0399 0.040 0.0399
JK7A	0.35 C, 0.2 Si, 1.15 Cr, 3.3 Ni, 0.05 Cu	0.24	0.256	0.25	0.255	0.255 0.255 0.254 0.257
NBS8i	0.08 C, 0.02 Si, 0.51 Mn, 0.02 Cu	0.002	0.005	0.003	0.0027	0.0026 0.0027 0.0026 0.0028
NBS19f	0.19 C, 0.2 Si, 0.5 Mn, 0.05 Cr, 0.32 Ni, 0.15 Cu	0.056	0.060	0.058	0.058	0.058 0.059 0.058 0.058
NBS36a	0.12 C, 0.3 Si, 0.4 Mn, 2.4 Cr, 0.24 Ni, 0.11 Cu	0.91	0.930	0.920	0.917	0.917 0.918 0.913 0.919
NBS100b	0.4 C, 0.2 Si, 1.9 Mn, 0.06 Cr, 0.03 Ni, 0.06 Cu	0.229	0.243	0.237	0.239	0.237 0.239 0.238 0.240
BCS251/1	0.4 Si, 1.5 Mn, 0.5 Cr, 1.2 Ni, 0.65 V, 0.55 Cu	1.46	1.55	1.51	1.56	1.556 1.565 1.562 1.562
BCS252/1	0.3 Si, 0.3 Mn, 0.4 Cr, 2.2 Ni, 0.23 V, 0.20 Cu	1.02	1.11	1.05	1.11	1.111 1.108 1.104 1.112
BCS258/1	0.9 Si, 0.4 Mn, 1.3 Cr, 0.55 Ni, 0.35 V, 0.15 Cu	0.81	0.84	0.83	0.835	0.832 0.839 0.830 0.839
JK8A	0.05 C, 0.6 Si, 1.1 Mn, 17.5 Cr, 11.0 Ni, 0.12 Cu	2.40	2.48	2.45	2.42	2.421 2.426 2.410 2.417
JK8B	0.04 C, 0.6 Si, 1.2 Mn, 17.8 Cr, 11.2 Ni, 0.03 V, 0.03 Ti, 0.17 Cu	2.66	2.74	2.68	2.67	2.668 2.668 2.672 2.666
NBS101e	0.05 C, 0.4 Si, 1.8 Mn, 18.0 Cr, 9.5 Ni, 0.36 Cu, 0.04 V, 0.18 Co	0.42	0.43	0.426	0.430	0.430 0.431 0.430 0.428

Sample no.	Composition of the sample (%)	Certificate values (%)			Values obtained (%)	
		Lowest	Highest	Mean	Mean	Individual values
NBS133a	0.12 C, 0.4 Si, 1.0 Mn, 12.9 Cr, 0.24 Ni, 0.12 Cu	0.288	0.30	0.294	0.293	0.290 0.296 / 0.292 0.295
NBS160a	0.06 C, 0.6 Si, 1.6 Mn, 18.7 Cr, 14.1 Ni, 0.17 Cu, 0.05 V, 0.07 Co	2.77	2.88	2.83	2.84	2.857 2.842 / 2.830 2.845
BCS246	0.06 C, (18.8 Cr, 12.1 Ni), 0.22 W, 0.13 Cu, 0.82 Nb + Ta	2.83	2.93	2.89	2.91	2.900 2.906 / 2.925 2.920
JK12	0.81 C, 0.3 Si, 0.2 Mn, 5.1 Cr, 18.5 W, 5.0 Co, 1.1 V, 0.1 Cu	0.43	0.57	0.51	0.558	0.554 0.565 / 0.552 0.559
NBS50c	0.72 C, 0.3 Si, 0.3 Mn, 4.1 Cr, 0.07 Ni, 1.16 V, 18.4 W, 0.08 Cu	0.073	0.10	0.082	0.081	0.081 0.082 / 0.081 0.081
NBS132a	0.83 C, 0.2 Si, 0.3 Mn, 4.2 Cr, 0.14 Ni, 1.9 V, 6.2 W, 0.12 Cu	4.46	4.57	4.51	4.51	4.534 4.508 / 4.498 4.502
NBS134a	0.81 C, 0.3 Si, 0.2 Mn, 3.7 Cr, 0.09 Ni, 1.2 V, 2.0 W, 0.10 Cu	8.29	8.39	8.35	8.36	8.365 8.36 / 8.360 8.35
NBS153a	0.90 C, 0.3 Si, 0.2 Mn, 3.7 Cr, 0.17 Ni, 2.1 V, 1.8 W, 0.09 Cu, 8.5 Co	8.82	8.91	8.85	8.82	8.810 8.815 / 8.810 8.857
NBS167	0.38 C, 0.4 Si, 1.6 Mn, 20.0 Cr, 20.6 Ni, 0.01 V, 0.03 Cu, 42.9 Co, 4.5 W, 3.15 Nb, 2.1 Fe			3.90	3.86	3.872 3.863 / 3.863 3.855
BCS220	0.86 C, 0.3 Si, 0.3 Mn, 4.6 Cr, 0.15 Ni, 0.67 Co, 0.14 Cu, 1.3 V, 6.7 W	4.10	4.42	4.17	4.19	4.205 4.192 / 4.174 4.190
BCS241/1	0.85 C, 0.3 Si, 0.3 Mn, 5.0 Cr, 0.07 Ni, 5.7 Co, 0.10 Cu, 1.6 V, 19.6 W	0.51	0.52	0.52	0.540	0.541 0.545 / 0.531 0.540

was considered to have an error of less than 0.2%. This statement is based on 40 measurements with different amounts of molybdenum. In the method described and with the particular instrument used, the equation was μg Mo (/25 ml amyl acetate) = 1.285 × absorbance (1 cm, 470 mμ, 25°).

In order to obtain an idea of the practical utility of the method developed, several standard samples were analyzed (Table XIII).

The determinations described show that even in the Mo-thiocyanate system, a precision close to the limit set by the precision of all volumetric work, and also absorptiometric measurements, can be obtained. This is considered to depend mostly on the elimination of certain sources of error, which impair many methods involving basically the same chemical system. The exclusion of hydrochloric acid and, to a smaller extent, of perchloric acid from the aqueous phase, is essential. One of the special advantages is that tungsten is not reduced in the absence of hydrochloric acid, and does not interfere. The inclusion of hydrochloric acid in the wash solution might be then considered controversial. In fact, hydrochloric acid cannot promote any tungsten interference, and chloride ions must be present as a carrier to ensure the presence of tin(II) in the organic phase, which eliminates any atmospheric oxidation and also prevents iron contamination. The most critical point of the method is considered to be the interaction of chloride ion and tin(II) in the molybdenum reduction. The extraction of molybdenum into the organic phase was always observed to be rapid and complete. A spectrographic check of the aqueous phase after the extraction revealed no molybdenum (less than 0.002% with 1% in sample).

From the point of view of interferences, the method is considered to be very satisfactory. The observed interferences (Nb, V) are of no significance in practical steel analysis. Considering that the number of colored thiocyanates is large, the selectivity of the method is good. However, platinum metals and rhenium were not investigated.

The overall stability and accuracy of the method appear to be satisfactory as regards the critical nature of the reaction mechanism involved. It must be stressed that the reagents must be fresh and always added in exactly the same amounts, if the best long-term precision is to be obtained. For contents higher than, say, 2% Mo in steels, a method of better accuracy would be desirable if the values were to be used for analyzing samples of standards.

SUMMARY

The absorptiometric thiocyanate method for molybdenum has been thoroughly studied with regard to the role of the following reagents: HCl, H_2SO_4, $HClO_4$, KSCN, $SnCl_2$ and Fe. A method is described, which allows the determination of 0.01–10% Mo in steel with a relative standard deviation of less than 0.5%. The only interferences (slight) are Nb and the combination V and W. The method gives better than 99.8% recoveries. Results for the determination of molybdenum in standard samples are presented.

RÉSUMÉ

L'auteur a effectué une étude sur le dosage absorptiométrique du molybdène, au thiocyanate. L'influence de: HCl, H₂SO₄, HClO₄, KSCN, SnCl₂ et Fe a été examinée. Le procédé décrit permet le dosage du molybdène dans l'acier (0.01 à 10% Mo), avec une déviation standard relative inférieure à 0.5%. Seuls Nb, V + W gênent. Des résultats sont donnés.

ZUSAMMENFASSUNG

Die absorptiometrische Thiocyanatmethode zur Bestimmung des Molybdäns wurde ausführlich untersucht, unter Berücksichtigung folgender Reagenzien: HCl, H₂SO₄, HClO₄, KSCN, SnCl₂ und Fe. Es wird eine Methode beschrieben, die die Bestimmung von 0.01 bis 10% Mo in Stahl mit einer relativen Standardabweichung von weniger als 0.5% erlaubt. In geringem Masse stört nur Nb und die Kombination von V und W. Die Methode ergibt Ausbeuten von mehr als 99.8%.

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THE DETERMINATION OF SELENIUM IN SEA WATER, SILICATES AND MARINE ORGANISMS

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The natural abundance of selenium relative to sulphur is very low; it is principally found concentrated in sulphide minerals, in which selenium atoms can replace sulphur atoms to a limited extent. The native element and a number of selenide minerals also occur in nature and appear to have been formed under conditions of low redox potential. Selenium(IV) is the thermodynamically most probable state of the element under normal aerobic conditions and a number of selenite minerals are known to occur. It is probable that selenium(IV) is set free during the weathering of rocks and that this is the form in which the element enters the sea and participates in the marine sedimentary cycle. As far as is known at present, selenium(VI) is only found naturally in the Chilean nitre beds; these have been formed under conditions of unusually high redox potential and contain other characteristic ions such as iodate and perchlorate.

The occurrence of the element in sea water was first recorded by GOLDSCHMIDT AND STROCK[1] who found 3.8 μg of selenium /l. This figure was confirmed by WATTENBERG[2] and by ISHIBASHI et al.[3]. In each of these procedures, selenium was concentrated by coprecipitation with iron(III) hydroxide, separated from iron by distillation with hydrobromic acid, and determined colorimetrically either as selenium[1,2] or with thiourea[3]. BYERS et al.[4] were unable to detect selenium in ocean waters but found 0.25 μg/l in the waters of Puget Sound. More recently, in a world-wide survey, SCHUTZ AND TUREKIAN[5,6] found only 0.05–0.12 (av. 0.08) μg/l in 28 samples of surface and deep ocean waters using a neutron activation procedure.

Although many analyses have been made for selenium in sulphide minerals and soils, very few determinations in silicate and carbonate rocks seem to have been carried out since the pioneer work of GOLDSCHMIDT AND STROCK[1]. In consequence there does not seem to have been any systematic study of methods for the determination of selenium in these materials. The double-arc spectrographic method for selenium[7] is not sufficiently sensitive for the determination of the element in most rocks.

Many species of plants are able to concentrate selenium from the soil, and the very high toxicity of the element (as little as 10 p.p.m. in feeding stuffs can lead to chronic poisoning in man and animals) has led to a considerable amount of work being carried out on methods for its estimation in soils[4,8] and bio-materials[9-12]. Recently, the recognition that trace amounts of selenium are essential for animal life[13,14] has

necessitated the development of techniques for the determination of less than 1 p.p.m. of the element in plant and animal tissues[13,15].

Much of the difficulty associated with the determination of traces of selenium in geological and biological materials is caused by the volatility of the element. This may cause very severe losses when samples are brought into solution, or when organic matter is destroyed. Compensation can be made for such losses by using isotope dilution (with selenium-75) to determine the overall chemical yield of the analytical process[16].

For the destruction of organic matter prior to selenium analysis, techniques using oxygen flasks[15,17] or wet digestion with, for example, mixtures of nitric and sulphuric acids[10], nitric and perchloric acids[11,13,14,18] or sulphuric and perchloric acids in presence of molybdate[12] have been described.

A study of the marine geochemistry and biogeochemistry of selenium is in progress in these laboratories and it was therefore necessary to develop techniques for its determination in sea water, marine sediments and marine organisms. Since the concentration of selenium in the materials to be examined was always low, it was thought desirable to use coprecipitation to concentrate it and to separate it from the major components prior to photometric determination. Isotope dilution methods, using selenium-75 (as selenite), were used for developing the analytical methods, and their use for correction of the overall yields of the multistage analytical process for losses is to be recommended.

Coprecipitation of selenium from sea water

In order to enable a coprecipitant for selenium to be selected, tests were made in which tracer amounts of selenium-75 as Se^{6+} and Se^{4+} were added to membrane-filtered sea water and the hydrous oxides of a number of elements were precipitated in the water by addition of the chloride of the element followed by adjustment of the pH to 8.0. The precipitates were allowed to settle for 2 days, separated by centrifugation and dissolved in dilute hydrochloric acid for counting of the selenium-75 coprecipitated. The results of these experiments (Table I) indicated that iron(III) hydroxide was an effective coprecipitating agent for selenium(IV). None of the coprecipitating agents carried down appreciable amounts of selenium(VI).

TABLE I

PERCENTAGE COPRECIPITATION OF SELENIUM FROM SEA WATER BY THE HYDROUS OXIDES OF A NUMBER OF ELEMENTS

Element	Weight of element used (mg/l)	Percentage of selenium coprecipitated	
		Se^{4+}	Se^{6+}
Aluminium	20	31.2	0
Iron(III)	20	82.5	2.5
Indium	30	19.6	0.4
Gallium	30	17.4	0.9
Zinc	20	27.0	0.8
Manganese[a]	11	2.5	0.1

[a] Hydrous manganese dioxide precipitated by treatment of water sample with permanganate and ethanol.

Since iron(III) hydroxide appeared to be the most efficient coprecipitating agent for selenium, experiments were made to determine the effect of pH on the coprecipitation of selenite with this compound. Aliquots (2 l) of filtered sea water were equilibrated with *ca.* 0.2 μC of selenium-75 (Se^{4+}) and their pH values were adjusted to a series of values lying in the range 3–9 by addition of dilute hydrochloric acid or ammonium hydroxide. Iron(III) chloride solution (equivalent to 40 mg Fe^{3+}) was added with vigorous stirring, and the pH values of the solutions were again adjusted to the selected values. The solutions were allowed to stand for 2 days after which the precipitated hydroxide was separated by centrifugation, dissolved in hydrochloric acid and the coprecipitation of selenium was measured by comparing the activity of this solution with that of the amount of selenium-75 originally added. The results of these experiments (Fig. 1) indicate that in the pH range 3–6.5 selenium was carried with *ca.* 95% efficiency. At pH values above 6.5 the efficiency of coprecipitation fell considerably. In all further work a pH of 4–6 was used for the precipitation.
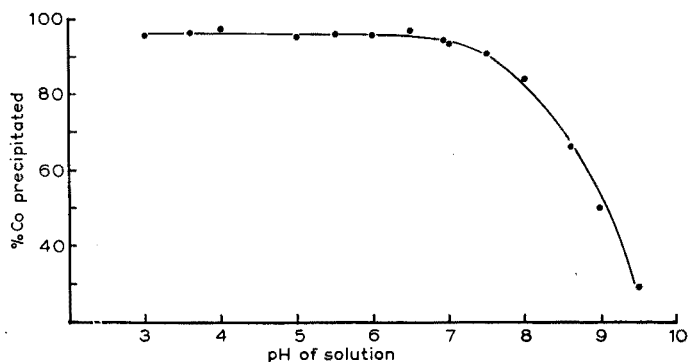
Fig. 1. Percentage coprecipitation of Se(IV) from sea water with ferric hydroxide as a function of pH.

In an attempt to increase the recovery of selenium, the effect of varying the amount of iron(III) used for the precipitation was studied. The experimental method used was similar to that described above, but the final pH of the sample was adjusted to 5, and the amount of iron added was varied between 40 and 120 mg. It was found that the recovery of selenium did not depend, within this range, on the amount of iron used, and was constant at 95.2 $\pm$ 0.6%.

Experiments were then carried out in which the addition of the coprecipitant was made in two or, in one case, three stages, with 2–3 h between successive additions. It was observed that two additions of 40 mg of iron(III) carried down 97.0 $\pm$ 0.8% of the selenium present in 2 l of sea water. A similar recovery of selenium (97.1 $\pm$ 0.5%) was obtained from a 5-l sample using two successive additions of 60 mg of iron(III). The use of a third coprecipitation did not appreciably increase the recovery of selenium. In view of the comparatively low concentrations of selenium present in sea water, all subsequent work was carried out using 5-l samples and coprecipitating by adding two successive 60-mg portions of iron(III).

Separation of iron from selenium by ion exchange

Before the photometric determination of selenium with diaminobenzidine, it is necessary to remove the iron used as coprecipitant and certain other trace elements coprecipitated from sea water by iron(III) hydroxide. Iron and most of these trace elements would occur in the form of cations when the precipitated iron(III) hydroxide is dissolved in dilute nitric acid, whereas the selenium would be in an anionic form; it was therefore thought that the separation would be most satisfactorily achieved by ion exchange.

Experiments were carried out in which 10-ml aliquots of solutions containing selenium-75 as selenite or selenate and 80 mg of iron(III) were passed through columns of Zeo-Karb 225 cation-exchange resin (see p. 000); the columns were washed with distilled water and the washings were assayed radiometrically. It was found that selenate, the salt of a strong acid, passed through the columns quantitatively in a total volume of 60 ml of water, whereas only *ca.* 20% of the selenite, the salt of a rather weak acid, was recovered in this volume. This behaviour is in line with the well-known fact that weak acids such as phosphoric acid are adsorbed onto cation-exchange resins, probably by van der Waals' forces[19]. They can be removed from the resin by washing with large volumes of water or more readily by washing with dilute mineral acid.

Accordingly, 25-ml aliquots of nitric acid of various normalities ranging from 0.01 to 0.5 N each containing *ca.* 2 μC of selenium-75 as selenite and 160 mg of iron(III) were passed through ion-exchange columns which were then washed with acid of the corresponding strength. The radioactivity of the washings was assayed. It was found that the removal of selenium was >99% complete when 225 ml of 0.10–0.5 N acid had passed through the column; under these conditions iron was quantitatively retained. The washing of selenium from the column required progressively more and more acid as the normality of the latter fell, until, at 0.01 N, several litres were needed to remove 99% of it (Fig. 2).

Selenium becomes considerably diluted during the ion-exchange separation, and the volume of the solution must be reduced before the photometric determination.
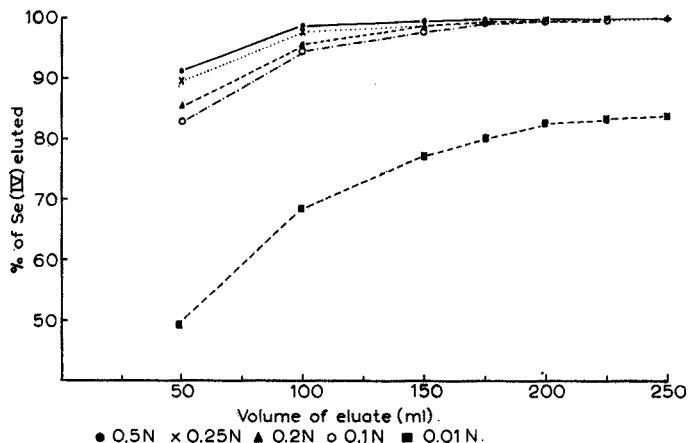

Fig. 2. Elution of Se(IV) from column of Zeo-Karb 225 with nitric acid of various strengths.

The photometric determination of selenium with diaminobenzidine requires an almost neutral solution. Since selenium tends to be rather volatile, particularly from solutions containing chloride, selenium-75 was used to determine which mineral acid solutions could be evaporated without loss of selenium. When 250 ml of 0.2 N acid solutions were evaporated to 10 ml on the water bath, no selenium was lost with sulphuric and nitric acids but *ca.* 10% was lost with hydrochloric acid. When the evaporation was continued to dryness on a hot plate at the minimum temperature necessary, losses of 82%, 27% and 73% with hydrochloric, nitric and sulphuric acids respectively were found. It was found, however, that if 1 ml of 2 N sodium hydroxide solution were added to a 0.2 N nitric acid solution of selenium before evaporation to dryness no selenium was lost, even in the presence of up to *ca.* 70 mg of chloride. This technique was used to prevent loss of selenium during the evaporation of the eluate from the ion-exchange columns and yielded an almost neutral residue.

The overall recovery of selenium from sea water through the coprecipitation, ion-exchange and evaporation stages, as assessed by the isotope dilution method averaged 94%.

Photometric determination of selenium

The colour reaction between selenium(IV) and 3,3′-diaminobenzidine, which leads to the formation of yellow piazselenol, was first observed by HOSTE AND GILLIS[20], and was later adapted for a photometric determination by CHENG[21], who formed the yellow compound in a medium containing E.D.T.A. as a masking agent and extracted it with toluene before photometry. Although several photometric[22] and fluorimetric[15,17,18,23] procedures have been described which have greater sensitivity than CHENG's method, they are generally less reproducible and much less specific. It was therefore decided to use this technique for the determination of selenium isolated from sea water, silicates and bio-materials. Since a high sensitivity was required, CHENG's procedure was slightly modified by carrying out the extraction of the piazselenol with 5 ml of toluene instead of 10 ml. With the photometric technique described below, Beer's law was obeyed up to at least 5 μg of selenium and the sensitivity[24] was 0.06 $\mu g/cm^2$. The coefficients of variation were 2.4% and 1.8% with 1 and 2 μg of selenium respectively.

Although diaminobenzidine is an almost specific reagent for selenium, oxidizing agents, such as iron(III), chromate and vanadate, interfere by oxidizing the reagent; reducing agents, such as tin(II) and arsenic(III) interfere by reducing selenium to the element.

In the present method, almost all of the cations coprecipitated by iron(III) hydroxide from sea water are likely to be removed by the cation exchanger. Nevertheless, the possible interference of a number of these elements in the photometric process was investigated. It was found that no interference was experienced with at least 5 times the quantity of uranium, iron, nickel, copper, cobalt and manganese present in 5 l of sea water.

Vanadium, molybdenum and arsenic are all known to be coprecipitated by iron(III) hydroxide and are likely to occur in the final analysis solution since they are not taken up by the cation-exchange resin from a 0.2 N nitric acid solution. However, tests showed that at least 100 times the quantity of these elements present in 5 l of sea water would not cause interference in the photometric method.

Determination of selenium in silicate rocks and sediments

In opening up silicate rocks and sediments there is a considerable risk of loss of selenium by volatilization. Several methods of opening up silicates were investigated using a chloride-free siliceous deep sea sediment ('red clay') which had been impregnated with radioactive selenite (^{75}Se) in order to check the recovery.

Fusion of the sediment with either sodium hydroxide at 600° or with sodium carbonate at *ca.* 950° did not cause loss of selenium, but the element became oxidized to the hexa-positive state and was not therefore coprecipitated with iron(III) hydroxide. In addition, the silicic acid gel formed on acidification of the solid from the fusion made the use of processes involving alkali fusion difficult and their investigation was discontinued.

Since it had been established that evaporation of nitric acid solutions of selenite ion could be conducted without loss, experiments were carried out to determine whether evaporation with a mixture of nitric and hydrofluoric acids could be used for the decomposition of silicates without loss of selenium. Portions of the marine sediment (1 g) were weighed into a platinum crucible, spiked with selenium-75 and digested overnight on a water bath with 25 ml of a 1 : 1 mixture of nitric and hydrofluoric acids. On the following morning, the liquid was evaporated to dryness. Fluoride was removed from the residue by evaporating to dryness three times with 10 ml of concentrated nitric acid under an infrared heater. The residue was transferred to a beaker and taken up in 20 ml of 4 N hydrochloric acid. After boiling gently to complete the dissolution of the solid, and to reduce any selenate to selenite, the solution was diluted to 50 ml and a suitable aliquot was taken for counting of the selenium-75 activity remaining. It was found that 100% of the activity originally added was present in this solution. The aliquot taken for counting was returned to the main bulk of the solution. The solution was then diluted to *ca.* 2 l with water and neutralized to a pH of *ca.* 5 with sodium hydroxide. Sodium chloride (30 g) was added in order to assist in the subsequent precipitation of iron(III) hydroxide which was produced by the addition of iron(III) chloride solution (60 mg Fe). After the precipitate had settled, it was separated by centrifugation and dissolved in hydrochloric acid, and the solution was diluted to 25 ml. Counting of the selenium-75 activity of a suitable aliquot of this solution showed that the recovery of selenium was 94.7 ± 0.17%; similar to that found with sea water.

The small amounts of selenium normally present in silicate rocks may occur either in the silicate lattice, or as selenide in the associated sulphide minerals. It seemed probable that the acid digestion process would liberate the former as selenite, but it was not certain that it would convert selenide to selenite. However, experiments using berzelianite (Cu_2Se) showed that the digestion did in fact convert selenide quantitatively to selenite. It is thus evident that digestion with a mixture of nitric and hydrofluoric acid followed by coprecipitation with iron(III) hydroxide provides a convenient method for the recovery of selenium from silicates before its photometric determination.

The practical details of the proposed method are given in the experimental section below. The recovery of selenium varies somewhat from one type of silicate to another and it is therefore advisable to use isotope dilution (with selenium-75) to estimate the chemical yield of the analytical process, and to correct the determined amount of selenium for losses.

Determination of selenium in organic materials

For the destruction of organic matter before the determination of selenium in biological materials, the acid digestion process described by CUMMINS *et al.*[12] appeared to offer a number of advantages. In this method, the sample is heated with a mixture of sulphuric and perchloric acids containing 2% (w/v) of sodium molybdate. When this method of digestion was tested with 1-g samples of finely chopped *Pelvetia canaliculata* spiked with selenium-75 it was found that the organic matter could be readily destroyed without loss of selenium. In addition, the selenite was not oxidized to selenate and could therefore be recovered in *ca.* 98% yield by coprecipitation with iron(III) hydroxide. The concentration of molybdate used in the digestion is not critical and it was found to be advantageous to reduce it to about a third of that used by Cummins *et al.*, since less molybdic acid is then left as an insoluble residue after completion of the digestion.

Digestions of 1-g samples of the same algae in the presence of known amounts of chloride ion showed that up to 250 mg of chloride could be present without leading to appreciable loss of selenium.

EXPERIMENTAL

Determination of selenium in sea water, silicates and bio-materials

An Optica CF4 spectrophotometer adapted for 4-cm micro-cells was used for all measurements. For counting of γ-activity of solutions, an EKCO scintillation counter Type N664A with NaI(Tl) well crystal coupled to an EKCO scaler Type N530F was used.

Reagents

Digestion mixture. Dissolve 0.4 g of ammonium molybdate in 15 ml of water; add with cooling 15 ml of concentrated sulphuric acid and 20 ml of 60% (w/w) perchloric acid.

Diaminobenzidine reagent. Dissolve 0.12 g of 3,3'-diaminobenzidine hydrochloride in 25 ml of water. This reagent should be prepared freshly as required.

E.D.T.A. solution. Dissolve 37.2 g of the disodium salt of ethylenediaminetetraacetic acid in water and dilute to 1 l.

Standard selenium solution. Dissolve 1.000 g of selenium shot ('Specpure' grade) in *ca.* 5 ml of concentrated nitric acid and dilute to 1 l with water. Use this standard solution, which contains 1 mg Se^{4+}/ml, for the preparation of the working standard solution.

Selenium-75 solution. Tracer-free, containing *ca.* 0.07 μC ^{75}Se/ml as selenite.

Ion-exchange column

Fill an ion-exchange column (diameter 1.5 cm) with a 10-cm length of the hydrogen form of Zeo-Karb 225 resin (8% cross-linked, 52–100 mesh). After use, the ion-exchange resin may be regenerated by washing with 2 N hydrochloric acid until free from iron and then washing with water until practically free from acid.

Determination of selenium in sea water

Filter the water sample through a membrane filter (pore size 0.5 μ), and

add to 5 l of it, with vigorous stirring, 3 ml of iron(III) chloride solution (20 mg Fe/ml). Allow the solution to stand for 30 min, and if its pH is higher than 6.5, add sufficient 2 N hydrochloric acid to bring the pH into the range 5–6. After about 2 h, when the precipitate has begun to settle, add a further 3 ml of iron(III) chloride solution. After this addition, the pH of the solution is normally reduced to 3–4, which is too low for reliable coprecipitation of selenium. Add 2 N ammonium hydroxide cautiously to bring the pH within the range 4–6.

After about 48 h, when the precipitate has settled, carefully syphon off the supernatant liquid, and separate the precipitate by centrifugation. Wash the precipitate 4 times with 30-ml aliquots of 0.5% (w/v) ammonium nitrate solution, centrifuging and decanting after each wash. Without delay, dissolve the precipitate in 1 ml of concentrated nitric acid, warming on the water bath to facilitate solution. Dilute the solution with water until its acidity is *ca.* 0.2 N, and pass it through the ion-exchange column. Desorb selenium from the column with 270 ml of 0.2 N nitric acid. Combine these washings with the original percolate, add 1 ml of 2 N sodium hydroxide and evaporate to dryness on the water bath.

Dissolve the residue in 5–10 ml of water, add 2–3 drops of bromothymol blue indicator and add 1–2 drops of 2 N ammonium hydroxide to neutralize any free nitric acid (until the indicator turns blue). Add 2 ml of 2.5 M formic acid and 5 ml of E.D.T.A. solution and dilute to about 23 ml with water. Measure the pH of the solution and adjust it to 2–3 if necessary by addition of 2 N nitric acid or ammonium hydroxide. Add 2 ml of diaminobenzidine reagent, and after 30 min, add 7 N ammonium hydroxide dropwise until the colour of the indicator just changes to greenish-blue. Using a pH meter, check that the pH of the solution is 6–7, and if not, add dilute acid or alkali, as appropriate, to bring the pH into this range.

Transfer the solution to a 50-ml separatory funnel, add 5 ml of toluene and shake the funnel mechanically for 3 min. Run off the lower layer and centrifuge the organic phase for a few minutes to remove any drops of water. Measure the optical density of the extract in a 4-cm micro-cell at 420 mμ against pure toluene. Since the iron(III) chloride reagent normally contains no detectable selenium, prepare the reagent blank by evaporating 300 ml of 0.2 N nitric acid to dryness in the water bath after adding 1 ml of 2 N sodium hydroxide. Dissolve the residue in 5–10 ml of water and continue as described in the previous paragraph. Calibrate the method by adding aliquots of the standard selenium solution (2 μg Se) to 300 ml of 0.2 N nitric acid and continuing as described for the reagent blank. The overall recovery of selenium from sea water was found to be 94.5 ± 1.5% and the determined concentration of selenium should therefore be multiplied by 1.05 in order to correct for losses occurring during the concentration and separation processes. Preferably the chemical yield of the whole process should be determined by equilibrating the sea water sample at the commencement of the analysis with carrier-free selenite-^{75}Se and counting the γ-activity of the solution of the residue left after evaporation of the 0.2 N nitric acid eluate.

Determination of selenium in silicates

Wash marine sediments and other samples containing appreciable amounts of chloride with water until free from chloride. Weigh 1.0–2.0 g of the dried sample (ground to pass an 80-mesh sieve) into a platinum dish and add about 0.2 μC of

carrier-free ^{75}Se as selenite. Add 20 ml of 40% (w/w) hydrofluoric acid and 20 ml of concentrated nitric acid and heat the covered dish on the water bath overnight. Then remove the lid from the dish and evaporate the liquid almost to dryness on the water bath. Add a further 20 ml of hydrofluoric acid and 20 ml of nitric acid and, after stirring, repeat the evaporation. Evaporate to dryness 3 times with concentrated nitric acid to remove fluoride.

Add 25 ml of 4 N hydrochloric acid to the residue and boil gently for 2 min in order to dissolve it and to reduce to selenite any selenate which might have been formed. Cool, and centrifuge to remove any undissolved material; wash the latter twice with *ca.* 10 ml of water and combine the washings with the supernatant liquid. Digest the residue again with 2 ml of concentrated nitric acid and 2 ml of hydrofluoric acid, and evaporate to dryness. Evaporate to dryness twice with 5-ml aliquots of nitric acid. Add 2–3 ml of 4 N hydrochloric acid and warm. Centrifuge the solution and discard any residue which may remain, after washing it twice with small volumes of 4 N hydrochloric acid. Combine the solution and washings with the main hydrochloric acid solution.

Transfer the combined hydrochloric acid solutions to a 5-l conical flask and dilute to *ca.* 2.5 l with water. Adjust the pH of the solution to *ca.* 3.5–4 with sodium hydroxide, but avoid raising the pH above 4. Dilute the solution to *ca.* 5 l and add 60 g of sodium chloride to assist the coagulation of the iron(III) hydroxide precipitate. Add, with shaking, 3 ml of iron(III) chloride solution (20 mg Fe^{3+}/ml) and adjust the pH to 4.5–5.0 with dilute ammonium hydroxide. After 2 h, add a further 3 ml of iron(III) chloride solution and restore the pH to 4.5–5.0.

Allow the solution to stand for 2 days. Syphon off the supernatant liquid, separate the precipitate by centrifugation and wash it with 0.5% ammonium nitrate as described for sea water. Dissolve it by warming with 1 ml of concentrated nitric acid, adding in addition 0.1 ml of concentrated hydrochloric acid if the precipitate is difficult to dissolve. If there is any insoluble material present remove it by centrifugation and redigest it with 0.2 ml of concentrated nitric acid. Combine the nitric acid extracts, add sufficient water to reduce the acidity to 0.2 N, and pass the solution through the ion-exchange column filled with Zeo-Karb 225 resin (hydrogen form). Elute with 350 ml of 0.2 N nitric acid. Combine the percolate and eluate, add 1 ml of 2 N sodium hydroxide and evaporate to dryness on the water bath. Dissolve the residue in water and dilute to 25 ml. Count the ^{75}Se activity of a suitable aliquot of this solution with a scintillation counter. Calculate the chemical yield of the separation process by comparing the activity of this solution with that of the corresponding volume of the ^{75}Se solution added initially.

Place the aliquot taken for counting in a 50-ml beaker and add to it the remainder of the selenium concentrate. Evaporate to *ca.* 15 ml on the water bath and carry out the photometric determination as described above for sea water.

Ideally the blank determination should be carried out as described above but with the omission of the sample. However, the A.R. grade chemicals normally appear to contain negligible amounts of selenium. It has been found satisfactory to evaporate 400 ml of 0.2 N nitric acid with 1 ml of 2 N sodium hydroxide to dryness on the water bath, to dissolve the residue in water, and to use the solution for the photometric determination. For calibration purposes, prepare a similar blank, add to it 2 μg of selenium, and carry out the photometric procedure.

Determination of selenium in marine organisms

Weigh *ca.* 1–2 g of the washed, finely chopped sample into a 25-ml Kjeldahl flask, and add 10 ml of the digestion mixture and *ca.* 0.2 μC of carrier-free selenium-75 solution. Heat the flask carefully over a small flame until all the organic matter has been destroyed and the digest has turned colourless. Pour into *ca.* 20 ml of water and centrifuge to remove the white precipitate of molybdic acid; wash the precipitate twice with 5-ml aliquots of 2 *N* sulphuric acid and then discard it since it is free from selenium. Combine the solution and washings and dilute to 1 l with water. Add 15 g of sodium chloride and 1 ml of iron(III) chloride solution (20 mg Fe^{3+}). Neutralize the solution with 4 *N* sodium hydroxide solution to a pH of 4–6. After about 2 h, add a further 1 ml of iron(III) chloride solution and restore the pH to 4–6. Allow the precipitate of iron(III) hydroxide to coagulate and separate it by centrifugation. Wash it three times with 25 ml of 0.5% (w/v) ammonium nitrate solution. Dissolve by warming on the water bath with 1 ml of concentrated nitric acid, and dilute to *ca.* 20 ml with water. A small amount of lemon-yellow solid (phosphomolybdic acid?) may remain and should be separated by centrifugation and discarded after washing with a small volume of *N* nitric acid. Combine the washings with the main bulk of the solution, dilute to *ca.* 0.2 *N* acidity and pass the resultant solution through the ion-exchange column. Continue the analysis as described for sea water. A small amount of yellow insoluble solid (phosphomolybdic acid?) may remain after dissolution of the residue from evaporation of the eluate; it contains no selenium and may be discarded after washing with 2–3 ml of *N* nitric acid. Before the photometric determination, the chemical yield of the analytical process should be assessed by γ-counting a suitable aliquot of the solution. The determined amount of selenium can then be corrected for losses occurring during the analysis.

Determine the reagent blank for the method in the same manner, but omitting the sample. Laboratory grade sulphuric acid often contains appreciable amounts of selenium and it is therefore important to use exactly the same volumes of digestion mixture for the blank and determinations. Calibrate the method by carrying a reagent blank spiked with 2 μg of selenium through the whole process.

RESULTS

Sea water

The reproducibility of the method was tested by carrying out replicate analyses (5) on 4.5-l aliquots of two surface sea water samples. One (Cl = 19.0⁰/₀₀) from the English Channel, gave 0.50 ± 0.02 μg Se/l; the other (Cl = 18.7⁰/₀₀) from the Irish Sea showed the presence of 0.34 ± 0.01 μg Se/l. These results have been corrected (using the isotope dilution method) for losses occurring during the analytical process.

The accuracy of the method was tested by analysing selenium-free sea water samples (freed from selenium by iron(III) hydroxide coprecipitation) which had been spiked with known amounts of selenium. The chemical yield of the process was checked using isotope dilution. The corrected results, which are shown in Table II, indicate that the analytical process had a satisfactory accuracy.

Although thermodynamic considerations suggested that dissolved selenium would occur in sea water almost entirely as Se(IV), it was thought advisable to check

TABLE II

RECOVERY OF SELENIUM FROM 'SELENIUM-FREE' SEA WATER TO WHICH INCREMENTS OF SELENIUM
HAD BEEN ADDED

Volume of water (l)	Selenium added (µg)	Selenium found (uncorrected) (µg)	Selenium-75 recovery (%)	Selenium found (corrected) (µg)
2	0	0.00	No isotope added 0.00	
2	1	0.92	93.5	0.98
2	2	1.84	92.5	1.99
2	2	1.90	94.2	2.02
2	2	1.83	93.7	1.96
2	3	2.72	90.2	3.04
2	3	2.84	93.8	3.03
2	3	2.88	94.2	3.06
2	5	4.93	96.5	5.11
2	5	4.79	95.0	5.04
2	5	4.71	94.0	5.02
5	3	2.74	92.4	2.97
5	4	3.74	93.0	4.02
5	4	3.83	94.0	4.07
5	4	3.65	92.6	3.95

whether Se(VI) was present. For this purpose, Se(IV) was stripped from 3.5 l of sea water by coprecipitating it with iron(III) hydroxide (this treatment was shown to remove only *ca.* 2% of Se(VI) added to sea water). The stripped water was treated with carrier-free selenate-^{75}Se and after the addition of 4 g of hydrazine sulphate it was rendered *ca.* 3 N with hydrochloric acid. A solution of 4 mg of 'Specpure' tellurium in nitric acid was added as a carrier for selenium. The solution was saturated with sulphur dioxide and heated to boiling. After standing overnight, the precipitated tellurium was collected on a glass-fibre filter and washed with water. The filter was heated with 2 ml of concentrated nitric acid and then washed well with water. The resultant solution was neutralized with 7 N ammonium hydroxide, evaporated to small volume and diluted to 25 ml. The recovery of selenium was found by γ-counting of an aliquot of the solution to be 90 $\pm$ 2%. The photometric determination of selenium was carried out on the solution using diaminobenzidine as described above. An analogous blank determination was carried out on distilled water. It was found that, within the precision of the method (0.01 μg Se/l), Se(VI) was absent from sea water. The validity of the procedure was tested by a similar experiment which was carried out on 3.5 l of stripped sea water spiked with 2 μg of Se(VI) and gave a recovery of 1.91 μg of selenium (corrected).

Silicates

Replicate analyses (8) were carried out on a red clay sample [collected at 34° 11'N, 55° 32'W (R.R.S. Discovery II, Station No. 3498)]. These gave an average selenium content (corrected by the isotope dilution method) of 1.6 $\pm$ 0.2 μg/g. As

a check on the precision of the method 1-g portions of the same sediment were spiked with known amounts of selenium (2 and 3 μg) and then analysed; satisfactory recoveries of selenium were obtained [3.8 and 4.7 μg respectively (corrected)]. The U.S. Geological Survey standard granite G1 was analysed and found to contain 2.5 $\pm$ 0.1 μg Se/g; selenium does not appear to have been determined previously in this sample.

Marine plants

Replicate analyses (8) were also carried out on an air-dried, washed sample of *Pelvetia canaliculata* and showed the presence of 0.84 $\pm$ 0.08 μg Se/g. Analyses carried out on the specimen spiked with 2 and 4 μg Se/g showed 2.91 and 4.80 μg Se/g, in satisfactory agreement with the amount of selenium thought to be present.

Storage of sea water samples

Since a considerable time may elapse between the collection of water samples and their analysis, experiments were carried out to determine whether selenite is adsorbed by glass or polyethylene containers. Aliquots (1 l) of filtered sea water (0.5 μ membrane filter), both autoclaved and unsterilized, were equilibrated with *ca.* 8 μC of selenium-75 (Se^{4+}) and placed in sterilized 1-l bottles of glass and high-density polyethylene. The bottles were stored in the dark at *ca.* 20° and the γ-activity of the sea water which they contained was measured at intervals over a period of several weeks. This activity, corrected for the loss of activity occurring through radioactive decay of the selenium-75 (half-life 120 days) was compared with the activity originally added. It was found that over a period of 10 weeks there was no appreciable loss of selenium from the sea water samples.

SUMMARY

Spectrophotometric procedures are described for the determination of selenium in sea water, silicates (especially marine sediments) and marine organisms. Co-precipitation with iron(III) hydroxide at pH 4–6 is used to concentrate selenium and to separate it from many of the commoner elements. Separation from iron and other cations is achieved by ion exchange. Selenium is determined photometrically with diaminobenzidine. Isotope dilution with selenium-75 is used to correct results for the small losses occurring during the analysis. Silicates can be decomposed without loss of selenium by means of a mixture of hydrofluoric and nitric acids. The method of CUMMINS *et al.*, with sulphuric and perchloric acids in presence of molybdate ion, is highly satisfactory for the decomposition of bio-materials. For sea water, which contains *ca.* 0.4–0.5 μg Se/l, a standard deviation of 0.03 μg/l was obtained. A silicate sediment and a sea weed containing *ca.* 1.5 μg Se/g and 0.8 μg Se/g respectively gave coefficients of variation of 8.0% and 4.7%. The U.S. Geological Survey standard granite G1 was found to contain 2.5 $\pm$ 0.1 μg Se/g.

RÉSUMÉ

Des méthodes spectrophotométriques sont décrites pour le dosage du sélénium dans l'eau de mer, les silicates (spécialement les sédiments marins) et les organismes

marins. On effectue une coprécipitation avec hydroxyde de fer pour concentrer le sélénium et le séparer d'avec d'autres éléments. Le sélénium est ensuite séparé du fer et d'autres cations au moyen d'un échangeur d'ions; il est enfin dosé par photométrie au moyen de la diaminobenzidine. Une dilution isotopique avec sélénium-75 est utilisée pour corriger les résultats, en raison de faibles pertes se produisant au cours de l'analyse. Les silicates sont désagrégés au moyen d'un mélange acide fluorhydrique/acide nitrique. Le procédé à l'acide sulfurique/acide perchlorique, en présence de molybdate, convient très bien pour la décomposition des matières biologiques.

ZUSAMMENFASSUNG

Es werden spektralphotometrische Verfahren zur Bestimmung von Selen im Seewasser, in Silikaten (besonders Meeressedimente) und in Meeresorganismen beschrieben. Zur Anreicherung wird das Selen mit Eisen(III)-Hydroxid beim pH-Wert 4–6 mitgefällt und dadurch von einer Anzahl von Elementen abgetrennt. Die Abtrennung vom Eisen und anderen Kationen geschieht durch einen Ionenaustauscher. Das Selen wird photometrisch mit Diaminobenzidin bestimmt. Mit Hilfe der Isotopenverdünnung (mit Selen-75) werden kleine, während der Analyse auftretende Verluste, korrigiert.

Silikate können ohne Verlust des Selens mittels einer Mischung aus Fluss- und Salpetersäure zersetzt werden. Die Methoden von CUMMINS et al. mit Schwefel und Perchlorsäure in Gegenwart von Molybdationen ist für die Zersetzung biologischen Materials sehr zufriedenstellend.

Für Seewasser, das ca. 0.4–0.5 μg Se/l enthält, wurde eine Standardabweichung von 0.03 μg/l erhalten. Silikatsedimente und Seepflanzen die ca. 1.5 μg Se/g bzw. 0.8 μg Se/g enthielten, ergaben Variationskoeffizienten von 8.0% und 4.7%. Im Standardgranit G1 wurde 2.5 ± 0.1 μg Se/g gefunden.

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PHOTOMETRIC TITRATIONS WITH INDICATORS

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The theory of photometric titrations has been discussed by a number of authors. GODDU AND HUME[1] presented a survey of the various types of titration curves. Theoretical papers on titrations using indicators have been published, for instance, by RINGBOM AND SUNDMAN[2], by FORTUIN, KARSTEN AND KIES[3], by RINGBOM AND WÄNNINEN[4], by FLASCHKA AND KHALAFALLAH[5], by REILLEY AND SCHMID[6], and by KOTRLY[7]. The field is reviewed in the monograph by HEADRIDGE[8] and in a chapter by UNDERWOOD[9] in *Advances in Analytical Chemistry and Instrumentation*.

In his monograph on complexation in analytical chemistry, RINGBOM[10] divides photometric titrations using indicators into 3 classes depending on the forms of the curves obtained by plotting absorbance (extinction) as a function of added volume of titrant.

(*a*) Break-point curves of type *a* in Fig. 1 arising when the colour change occurs considerably before the equivalence point, *i.e.*, in compleximetric titrations, when $pM_{trans} < pM_{eq}$ where M denotes a metal ion. The indicator is in this case a 'low sensitivity' indicator.

(*b*) Symmetrically rounded curves of type *b* in Fig. 1, arising when the transition point of the indicator coincides with the equivalence point ($pM_{trans} = pM_{eq}$). The indicator is in this case a 'medium sensitivity' indicator.

(*c*) Break-point curves of type *c* in Fig. 1 arising when the colour change occurs considerably after the equivalence point ($pM_{trans} > pM_{eq}$). The indicator is in this case a 'high sensitivity' indicator.

It may be noted that the terms 'low, high, and medium sensitivity' are relative, not absolute, *i.e.*, one and the same indicator may function as a low sensitivity indicator in one titration but as a high sensitivity indicator in another titration with another complexing agent.

In the following paragraphs the theory of photometric compleximetric titrations will be treated, but the results can be applied also to acid–base titrations.

Most of the papers in the literature deal with titrations which involve low sensitivity indicators, which are advantageous from the point of view that at the break-point practically all the indicator is in its free form, *i.e.*, not bound to any metal. Hence no indicator correction is needed even when extremely dilute solutions are titrated. On the other hand, if a high sensitivity indicator is used, all the indicator is bound to the metal ion at the break-point. Consequently, if a 1 : 1 metal–indicator compound, MI, is formed, a volume of titrant equivalent to the total concentration

of the indicator, C_{ind}, must be added to the volume consumed. Finally, if a symmetrically rounded curve arises, the inflection point will coincide with the transition point and $[I]=[MI]$. Half of the indicator will be bound to the metal, and thus a correction equal to the volume of titrant equivalent to $\frac{1}{2}C_{ind}$ should be added to the result.
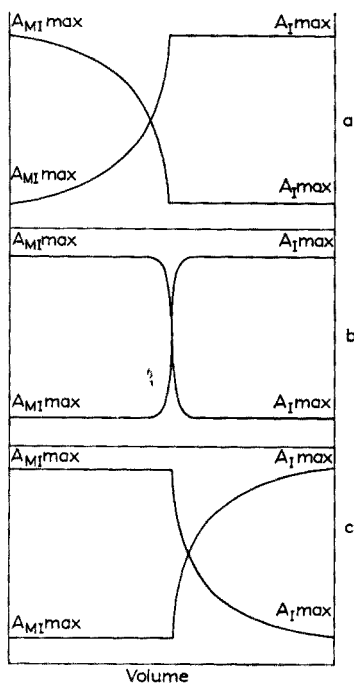

Fig. 1. Absorbance curves obtained in photometric titrations using indicators of low sensitivity (*a*), medium sensitivity (*b*), and high sensitivity (*c*).

These 3 types of titration curves are readily treated theoretically. In practice, however, titration curves of an intermediate type which are asymmetrical and rounded often result. Some authors[11] consider that the inflection point of such an absorbance curve (or the inflection point of a transmittance curve) coincides with the equivalence point; in other words, the curves are treated in the same way as potentiometric titration curves obtained when a binary product is formed. BRUCKENSTEIN AND GRACIAS[12] calculate $\Delta pM/\Delta V$ (V=volume of titrant) from the change of the absorbance, $\Delta A/\Delta V$. In this way it is possible to determine the point where the value of $\Delta pM/\Delta V$ is a maximum, *i.e.*, the equivalence point.

RINGBOM AND SUNDMAN[2] derived the following expression for the relationship between ΔpM (or ΔpH) and the change in transmittance, ΔT:

$$\frac{\Delta pM}{\Delta T} = -\,0.188/\Delta T(1-\alpha) \tag{1}$$

or

$$\frac{\Delta pM}{\Delta T} = \frac{0.188}{AT} \frac{(1 + [M]K_{MI})}{[M]K_{MI}} \tag{2}$$

where α is the fraction of the indicator present as the coloured ion I. It is assumed that only the indicator anion, I, absorbs light. If the metal complex also absorbs light, the absorbance A has to be replaced by $(A - A_{MI}^{max})$.

As every chemist has some idea about the sensitivity of his instrument —usually expressed as ΔT—eqns. (1) and (2) allow him to estimate the accuracy of his pM (or pH) measurements at various absorbances.

The absorbance at the equivalence point is given[4,10] by the equation

$$A_{eq} = (A_I^{max} + A_{MI}^{max} [M]_{eq} K_{MI})/(1 + [M]_{eq} K_{MI}) \tag{3}$$

where A_I^{max} and A_{MI}^{max} are the limiting absorbance values.

Little attention was paid to the significance of the inflection points of asymmetrical curves obtained in photometric titrations until STILL[13] recently showed that, if the absorbance is plotted as a function of added volume of titrant, the following expression is valid at the inflection point:

$$([MI]/[I])_{infl} = ((1-\alpha)/\alpha)_{infl} = (C_M K_{MI}^2/K_{MY})^{\frac{1}{2}} \tag{4}$$

C_M is the total concentration of metal; MY is the complex formed in the titration. Since

$$[MI]/[I] = [M]K_{MI} \tag{5}$$

it follows that

$$[M]_{infl} = (C_M/K_{MY}K_{MI})^{\frac{1}{2}} \tag{6}$$

It should be noted that the concentration of the indicator C_{ind} does not appear in this expression.

Equation (6) can be combined with the following expressions giving the concentrations of the metal ion at the transition point and at the equivalence point:

$$[M]_{trans} = 1/K_{MI} \tag{7}$$

$$[M]_{eq} \approx (C_M/K_{MY})^{\frac{1}{2}} \tag{8}$$

Equation (8) assumes that $[MY] \gg [MI]$ at the equivalence point, i.e., that the amount of metal bound to the indicator can be neglected. When titrating extremely dilute solutions, $[M]_{eq}$ is calculated from eqn. (8) but then an indicator correction has to be applied which will be discussed later in this paper. If Y, I, and M are involved in side reactions, conditional constants have to be used. (Y and I react mainly with hydrogen ion, M mainly with hydroxide ion or with buffer components. For details about the concept of conditional constants, see the monograph by RINGBOM[10].)

Equations (6), (7) and (8) give

$$[M]_{infl}^3 = [M]_{trans}[M]_{eq}^2 \tag{9}$$

or, if logarithms are taken,

$$3 pM_{infl} = pM_{trans} + 2 pM_{eq} \tag{10}$$

This equation reveals that a surprisingly simple mathematical relationship applies between these 3 fundamental quantities in photometric titrations. The inflection point and the equivalence point coincide only when the absorbance curve is fully symmetrical; in fact, all 3 points will coincide. A closer study of the above equations shows further that

(a) with a low sensitivity indicator the inflection point occurs *before* the equivalence point,

(b) with a medium sensitivity indicator the inflection point occurs *at* the equivalence point;

(c) with a high sensitivity indicator the inflection point occurs *after* the equivalence point.

An error will theoretically arise in all titrations when the inflection point is taken as the equivalence point except when the absorbance curve is perfectly symmetrical. The magnitude of this error can be conveniently calculated from $\Delta pM = pM_{infl} - pM_{eq}$. This quantity can be derived from eqns. (6) and (8) which give

$$\frac{[M]_{eq}}{[M]_{infl}} = (C_M K_{MI}^2/K_{MY})^{\frac{1}{3}} \tag{11}$$

Hence

$$\Delta pM = \tfrac{1}{6} \log (C_M K_{MI}^2/K_{MY}) \tag{12}$$

The following relationship is also valid

$$\Delta pM = pM_{infl} - pM_{eq} = \tfrac{1}{3}(pM_{trans} - pM_{eq}) \tag{13}$$

The error can be easily evaluated from a diagram in which the percentage error is shown as a function of stability constant for different values of $pM = pM_{infl} - pM_{eq}$, and for various concentrations of the metal in the titrated solution (see reference 10, p. 80). The abscissa, $\log K_{MY}/C_M$, is known and ΔpM can be calculated from eqn. (12). The diagram is based on the equation:

$$\text{Error} = (10^{\Delta pM} - 10^{-\Delta pM})/(C_M K_{MY})^{\frac{1}{2}} \tag{14}$$

When extremely dilute solutions ($<$ about 10^{-4} M) are titrated, it often happens that the indicator is present in a concentration that does not greatly differ from the total concentration of the metal in the sample solution, and the necessity of applying an indicator correction must then be considered. In the beginning of this article it was pointed out that no correction is needed when a low sensitivity indicator is used whereas the use of a high sensitivity indicator requires the application of an indicator correction equal to the volume of titrant equivalent to C_{ind}. For symmetrically rounded absorbance curves the correction is the volume of titrant equivalent to $\tfrac{1}{2}C_{ind}$.

If the absorbance curve is asymmetrical, the evaluation of the indicator correction requires a knowledge of [MI] at the end-point of the titration. Generally, the value of [MI] at any absorbance value A can be calculated, if the limiting absorbance values A_I^{max} and A_{MI}^{max} are known, from the equation

$$[MI] = C_{ind}(A_I^{max}-A)/(A_I^{max}-A_{MI}^{max}) \tag{15}$$

The value of $[MI]_{infl}$ can be found by inserting for A in eqn. (15) the absorbance at the inflection point.

In many connections it is practical to operate with the percentage change of an indicator, as, for instance, SCHWARZENBACH[14] has done in his monograph on compleximetric titrations. The calculation of this percentage change at the inflection point can be based on eqn. (4) which gives the relationship between the stability constants and the concentrations of the forms of the indicator. The percentage colour change depends on the direction in which the titration is performed and can be computed also from the absorbance values, either from the equation

$$100\ [I]/([MI] + [I]) = 100\ [I]/C_{ind} = 100\ (A - A_{MI}^{max})/(A_I^{max} - A_{MI}^{max}) \qquad (16)$$

or from

$$100\ [MI]/([MI] + [I]) = 100\ [MI]/C_{ind} = 100\ (A_I^{max} - A)/(A_I^{max} - A_{MI}^{max}) \qquad (17)$$

If side reactions occur, primed concentrations and conditional constants must be used. In most cases it is necessary to replace [I] by [I'] which is equal to the sum of concentrations of all protonated indicator species:

$$[I'] = [I] + [HI] + [H_2I] + - - - - + [H_nI] \qquad (18)$$

Figure 2 illustrates the error arising when the inflection point is taken as end-point. The abscissa, $\log C_M K_{MI}^2/K_{MY}$ includes the three factors that (in addition to the absorbance coefficients) determine the course of a photometric titration curve. ΔpM defined by eqn. (12) is the left ordinate. The percentage colour changes at the inflection point and at the equivalence point are also plotted in this figure on the ordinates to the right as functions of the same logarithmic quantity. If the
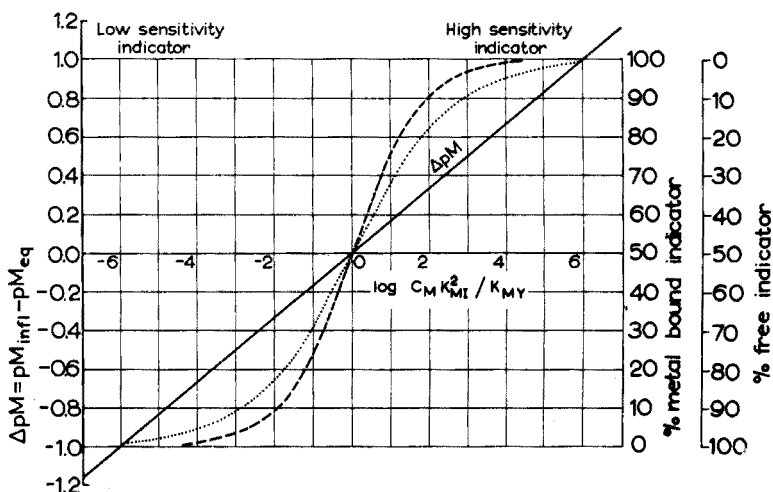
Fig. 2. $\Delta pM = pM_{infl} - pM_{eq}$ and percentage colour changes at the inflection point $(\ldots\ldots\ldots)$ and at the equivalence point $(- - - - -)$ as functions of $\log C_M K_{MI}^2/K_{MY}$.

inflection point is detected and the percentage colour change at this point is measured, Fig. 2 gives the corresponding ΔpM value; the titration error can then be estimated from the diagram described previously (reference 10, p. 80).

REILLEY AND SCHMID[6], in their presentation of the theory of photometric titrations, used the concepts Δ_1 and Δ_2 defined by

$$\Delta_1 = \log K_{MI} + \log C_M \tag{19}$$

and

$$\Delta_2 = \log K_{MY} - \log K_{MI} \tag{20}$$

(Conditional constants should be used by inserting appropriate α coefficients.) The relationship between our quantity ΔpM and the Δ values of REILLEY AND SCHMID is given by

$$\Delta_1 - \Delta_2 = \log \frac{C_M K_{MI}^2}{K_{MY}} = 6\,\Delta pM \tag{21}$$

Hence $\Delta_1 - \Delta_2$ is the abscissa of Fig. 2.

A negative value of the abscissa means a low sensitivity indicator, a positive value a high sensitivity indicator.

It may be noted that the titration error can be determined from the inflection point by means of Fig. 2 and the diagram given previously[10] even if K_{MI} is not known. This means that the indicator constant K_{MI} can be estimated from the percentage colour change at the inflection point by means of Fig. 2. However, a necessary condition is that the indicator and the metal ion combine to form only one species, MI.

The following example illustrates the use of Fig. 2. Let a metal ion in 10^{-3} M concentration be titrated with a complexing agent that forms a complex MY with the metal whose stability constant equals 10^9 in the presence of an indicator that forms a complex MI with the stability constant $K_{MI} = 10^5$. $C_{ind} \approx 10^{-6}$. Thus $pM_{trans} = 5$ and $pM_{eq} = 6$ according to eqns. (7) and (8). As pM_{trans} is considerably lower in value than pM_{eq}, an asymmetrically rounded low sensitivity curve will be obtained. The abscissa of Fig. 2 thus equals -2. Figure 2 shows that the percentage colour change is about 82% at the inflection point and 91% at the equivalence point. $\Delta pM = -0.33$, and according to the previously published diagram[10] an error of -0.2% will arise if the inflection point is considered as the equivalence point. The indicator concentration is so low that no indicator correction is needed (error below 0.02%).

If pM_{trans} were taken as the equivalence point, ΔpM would be -1, which corresponds to an error of about -1%.

If the solution given in the above example were ten times more dilute, i.e., if $C_M = 10^{-4}$, the error would be larger. The abscissa value of -3 would correspond to a colour change of 92% at the inflection point and a colour change of 97% at the equivalence point. ΔpM would be -0.5 and the corresponding error -0.9%. The indicator would bind some of the metal, and an additional error of -0.1% would result. The total error would be equal to -1%.

When $\log C_M K_{MI}^2/K_{MY}$ is below -3 or above $+3$, more than 90% of the indicator will be in the form of I or MI, respectively, at the inflection point. The

absorbance curve will not deviate greatly from a break-point curve, and a break-point can be obtained by graphic extrapolation. A value of the abscissa of ± 3 corresponds to a ΔpM value of ± 0.5. A consequence of this is that when a pronounced break-point does *not* occur, pM_{infl} and pM_{eq} will differ by *less* than half a pM unit.

When the value of K_{MY} is low, the slope of the absorbance curve will be rather small, and accurate detection of the inflection point may be difficult.

It is obvious that when the absorbance curve is considerably rounded on both sides of the inflection point, a graphically extrapolated break-point does not represent an exact equivalence point. If very dilute solutions are titrated, this method (which is frequently suggested in the literature) may lead to a large error (*cf.* reference 10, p. 132).

If other compounds than $1 : 1$ complexes are formed—say MY_n or MI_n — the equations will be more involved. These cases will not be treated in this paper.

The influence of various side reactions can easily be estimated by inserting the appropriate conditional constants.

All the curves considered in the preceding paragraphs were absorbance curves in which the absorbance was plotted *vs.* the volume of titrant. However, very few instruments are able to indicate directly a logarithmic quantity like the absorbance; most instruments measure the photocurrent which is (at least approximately) directly proportional to the transmittance. If the photocurrent is recorded, a photometric titration implies the plotting of the transmittance or—if balanced instruments are used—the absorptance (defined as $1 - T$) but *not* the absorbance. Consequently, the question arises where the 3 fundamental points, pM_{trans}, pM_{eq}, and $pM_{infl(T)}$, are located on this curve.

The transmittance corresponding to the transition point, pM_{trans}, is not in the middle of the curve but at a point obtained from the expression

$$- \log T_{trans} = \log \frac{1}{T_{trans}} = \tfrac{1}{2}(A_I^{max} - A_{MI}^{max}) \tag{22}$$

when the limiting absorbance values of the titration, A_I^{max} and A_{MI}^{max}, are known.

The transmittance at the equivalence point can be calculated from eqn. (3) which gives the absorbance at the equivalence point.

The inflection point of a transmittance curve is not easily interpreted. Theoretically, it does *not* coincide with the inflection point of an absorbance curve since, as can easily be found by differentiating the Lambert–Beer law expression, the relationship between the change of transmittance and the change of absorbance is

$$dT/dA = -2.3T \tag{23}$$

It was shown above that the inflection point of an absorbance curve where dA/dV attains its maximum value does not depend on the indicator concentration as long as $C_M \gg C_{ind}$. The expression for dT/dV

$$dT/dV = -2.3 \, T \, dA/dV \tag{24}$$

contains as a factor the transmittance of the solution. Consequently, the inflection point of the transmittance curve, where dT/dV attains its maximum value, will vary with the concentration of the indicator.

An insight into the change of the transmittance during the titration can be obtained from the previously given eqn. (1) or from eqn. (2). However, it may suffice to point out that it is mostly advantageous to operate with only weakly coloured solutions, using a low concentration of the indicator, which is, as a rule, possible when modern instruments of high sensitivity are used. At high transmittance values the absorptance $(1-T)$ is approximately proportional to the absorbance. This fact is immediately realized by a glance at eqn. (24): at large transmittance values, T does not change its order of magnitude, and hence dT/dV is approximately proportional to dA/dV. It follows that at low indicator concentrations the difference between the volume of the titrant added up to the inflection point of the absorbance curve and the volume added up to the inflection point of the transmittance curve cannot be great. When in a titration the colour of the solution increases, T_{infl} will appear just a little before A_{infl}. On the other hand, if A_{infl} is very large, *i.e.*, when the indicator concentration is high or when long cells are used, the difference between the two inflection points may be considerable.

The above treatment of photometric titrations is related to complexation reactions. If the same approach is applied to photometric acid–base titrations, M and pM in the given expressions will be replaced by H and pH, respectively. Thus, eqn. (10) will take the form

$$3 \text{ pH}_{infl} = \text{pH}_{trans} + 2 \text{ pH}_{eq} \tag{25}$$

In acid–base titrations the percentage colour change and the titration error at the inflection point can also be found by means of Fig. 2 and the previously described diagram[10].

SUMMARY

Various types of photometric titration curves are discussed. If a metal M is titrated compleximetrically using a metal indicator and the absorbance is plotted *vs.* the titrant consumed, the inflection point appears at a pM value defined by the equation

$$3 \text{ p}M_{infl} = \text{p}M_{trans} + 2 \text{ p}M_{eq}$$

This expression is valid when M combines in a 1 : 1 ratio with the complexing agent and the indicator and when the indicator concentration is small compared to the total metal concentration.

The difference between the pM values at the inflection and equivalence points can be calculated from the equation

$$\Delta \text{p}M = \text{p}M_{infl} - \text{p}M_{eq} = \tfrac{1}{3}(\text{p}M_{trans} - \text{p}M_{eq}) = \tfrac{1}{6}\log(C_M K^2_{MI}/K_{MY})$$

If the inflection point is taken as the equivalence point, the error arising can be calculated from $\Delta \text{p}M$, or more simply, read from a diagram.

If transmittance, instead of absorbance, is plotted as a function of the titrant volume, the inflection point depends on the added amount of indicator. However, at high transmittance values, *i.e.*, at low indicator concentrations, the inflection point of a transmittance curve occurs practically at the same volume of added titrant as the inflection point of an absorbance curve. Rules are given for applying an indicator correction for the amount of metal bound to the indicator at the end-point.

The derived equations and discussions can also be applied to acid–base titrations.

RÉSUMÉ

Les auteurs ont examiné divers types de courbes de titrage photométrique: soit par mesure de l'exctinction, soit par mesure de la transmission, en fonction du volume de réactif de titrage. Des équations exprimant la rélation entre le point d'inflexion, le point de virage de l'indicateur et le point d'équivalence sont discutées. En mesurant la transmission, le point d'inflexion varie avec la quantité d'indicateur ajoutée. Cependant pour de fortes valeurs de transmission et de faibles concentrations d'indicateur, le point d'inflexion d'une courbe de transmission correspond à celui d'une courbe d'absorption, pour un même volume de réactif. On introduit une correction de la quantité de métal lié à l'indicateur, au point final. Les équations dérivées et discussions peuvent également s'appliquer aux titrages acide–base.

ZUSAMMENFASSUNG

Es werden verschiedene Typen photometrischer Titrationskurven diskutiert. Trägt man bei der komplexometrischen Titration eines Metalls unter Anwendung eines Metallindikators die Extinktion gegen die ml des zugegebenen Titrationsmittels auf, so lässt sich eine Gleichung für den Wendepunkt aufstellen unter den Voraussetzungen, dass das Metall sowohl mit dem Komplexbildner als auch mit dem Indikator im Verhältnis 1 : 1 reagiert und dass die Indikatorkonzentration klein gegen die gesamte Metallkonzentration ist. Ferner kann aus einer weiteren Gleichung die Differenz zwischen dem Wende- und dem Äquivalenzpunkt berechnet werden. Misst man statt der Extinktion die Lichtdurchlässigkeit, dann ist die Lage des Wendepunktes von der Menge des Indikators abhängig. Jedoch ist diese Abweichung bei hohen Durchlässigkeiten und kleinen Indikatorkonzentrationen praktisch vernachlässigbar. Für eine Indikatorkorrektur werden Regeln angegeben. Die abgeleiteten Gleichungen und die Diskussionen können auch auf Säure–Basen-Titrationen angewandt werden.

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A COMPARISON OF THREE ABSORPTIOMETRIC METHODS FOR THE DETERMINATION OF COPPER IN BIOLOGICAL MATERIALS

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With the introduction of more selective organic reagents for traces of copper, such as the oxalyldihydrazones[1-4] and the derivatives of 1,10-phenanthroline[5,6], the development of quicker absorptiometric methods for the analysis of biological materials became possible. Since comparatively little work has been carried out on the chemical background of these methods it is important that their performance should be compared carefully with that of the well established methods but so far little information on this point has appeared in the literature. This paper describes an investigation which was carried out to assess the performance of two of these methods, involving 2,9-dimethyl-1,10-phenanthroline and bis-cyclohexanone-oxalyl-dihydrazone respectively, in comparison with a dithizone method which had been in regular use for a number of years. The experiments were designed to detect systematic errors as well as to give estimates of the precision of each method, the pattern followed being similar to that adopted for a comparison of methods for magnesium described previously[7].

EXPERIMENTAL

Strict precautions were taken to prevent contamination of the samples by adventitious traces of copper at all stages of the analysis. These and the methods used to purify reagents have already been described[8,9].

Dithizone. The method used was described in a previous paper[9]. Copper was removed from zinc and other interfering metals by adjusting the pH of the sample solution to about 4.5 and extracting with dithizone in carbon tetrachloride. It was then transferred to an aqueous phase by shaking the extracts with a permanganate solution, from which it was re-extracted with dithizone under standard conditions and determined absorptiometrically with the Hilger Spekker instrument, using a procedure which avoids the difficulties associated with the instability of dithizone in solution. Iodide was added before the final extraction to prevent interference from mercury, silver and bismuth. The standard curve was linear for amounts of copper up to 1.7 μg and passed through the origin (Table I). Over this range 1 μg of copper produced a change in absorbancy of 0.223.

2,9-Dimethyl-1,10-phenanthroline (neocuproine). The procedure studied was

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TABLE I

CHARACTERISTICS OF STANDARD CURVES

(The values shown are expressed as μg Cu)

Method	Slope	S.E. of fit	Intercept ± S.D.[a]
Dithizone	4.48	±0.022	0.011±0.011[b]
Neocuproine	12.06	±0.12	0.076 ±0.029[c]
BCOD	30.80	±0.33	0.897±0.088[d]

[a] The statistical significance of the intercept is indicated thus: [b] not significant ($P = >0.05$); [c] very significant ($P = 0.01–0.001$); [d] highly significant ($P = <0.001$).

derived from those published by other authors[10–13] and from the results of our own experiments, and was as follows.

To an aliquot of the sample solution was added 2 ml of citrate solution*, 2 ml of 15% (w/v) hydroxylamine hydrochloride, 1 ml of a 0.1% solution of neocuproine in ethanol, and copper-free glass-distilled water to bring the total volume to about 25 ml. This solution had a pH of about 6.3 and was extracted with 2 ml of chloroform by shaking for 3 min with a mechanical shaker (220–230 c/min). The absorbancy of this extract was measured with a Spekker absorptiometer using a tungsten filament lamp, Kodak No. 1 violet filters and 2-cm micro-cells. This procedure gave a linear standard curve for amounts of copper up to 6 μg and over this range 1 μg of copper gave an absorbancy of 0.083.

In developing this method it was found that the extraction of copper was complete after shaking for 2 min. A time of 3 min was adopted to allow a margin of safety. The pH–extraction curve was also determined (Fig. 1) and showed that complete extraction was achieved at a pH of about 4.2 and was not appreciably reduced when the pH was raised to 9.2. Within this pH range it was not affected by halving or doubling the concentration of citrate used in the above procedure.

Bis-cyclohexanone-oxalyldihydrazone (BCOD). The method investigated was similar to those used by other authors[2,13–15]. An aliquot of the sample solution was placed in a 25-ml standard flask and 2 ml of citrate solution (prepared as for the
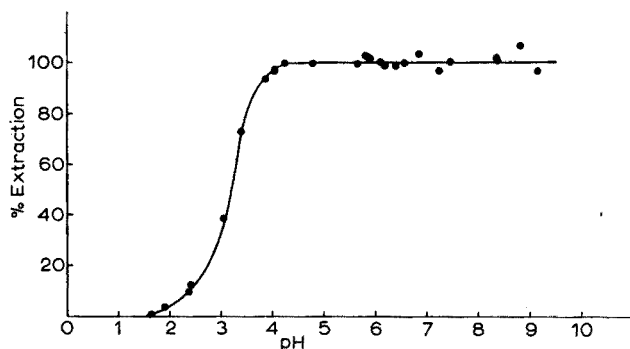

Fig. 1. Extraction of the copper–neocuproine complex with chloroform.

*50% (w/v) citric acid monohydrate containing sufficient ammonia to make it alkaline to neutral red.

neocuproine method) and 1 ml of 0.5% BCOD in 50% ethanol were added. After making the volume up to 25 ml with copper-free water and mixing thoroughly, the solution was allowed to stand for 1 h to allow the colour to develop to its maximum intensity. Its absorbancy was measured with a Spekker instrument using Ilford No. 607 orange filters and 4-cm cells. The pH of this solution was about 9.0.

The standardisation data are shown in Table I from which it can be seen that the curve intercepted the axis. This was found to be due to a difference between the optical characteristics of the cells. The linear portion of the curve extended as far as 40 μg copper and over this range 1 μg produced a change in absorbancy of 0.032.

Design of experiments

The performance tests were carried out on specimens of liver obtained from sheep. This tissue was chosen in preference to others since it was likely to contain larger amounts of elements which might interfere with the copper estimations. For the first series of experiments the entire ventral lobes were removed from the livers of 4 animals, cut into slices and freeze-dried. They were then dried further in an electric oven at 100–105° and powdered in a Hillman coffee mill, care being taken to mix the powder as thoroughly as possible.

Samples weighing about 0.5 g were taken, ashed with a mixture of nitric, perchloric and sulphuric acids and brought into solution with citrate and ammonia as described previously[9]. Three or four different aliquots of these solutions were taken and analysed by each of the 3 methods described above, the size of the aliquots being chosen so that the amounts of copper they contained were well distributed over the linear portions of the standard curves. The entire procedure was repeated with fresh samples 4 or 5 times depending on the amount of liver powder available. In this way each method gave a table of results which was suitable for statistical examination by the analysis of variance procedure to determine whether the volume of sample solution taken for analysis had any influence on the results, thereby providing a test for the presence of systematic errors.

In order to explore differences observed between the results given by the dithizone and neocuproine methods, 30 additional specimens of liver with a much wider range of copper content were analysed by these methods, single analyses being carried out in each case. The copper content of the aliquot of the sample solution taken for analysis was near the middle of the linear portion of the standard curve.

RESULTS

Table II summarises, in the form of mean values and standard deviations, the results obtained for the 4 specimens of liver with the 3 methods. It can be seen that on the whole the agreement was poor. The mean values obtained with the neocuproine and BCOD methods all differed significantly from those given by the dithizone method. These differences were not, however, consistent in direction. Three of the neocuproine values were higher than the dithizone values by 4.4 to 21.1% while the other result was 6.7% lower. Two of the BCOD values were higher than the corresponding dithizone values (4.1 and 1.5%) and the other two showed larger negative differences (7.6 and 13.3%). On the other hand the differences between the neocuproine and BCOD values were consistent in direction, the latter being lower by 5.0

TABLE II

SUMMARY OF RESULTS OF REPLICATE ANALYSES

(The figures shown are mean values ± standard deviations and are expressed as p.p.m. Cu in dry liver)

Liver no.	Dithizone	Neocuproine[a]	BCOD[a]
I	250 ± 13.7	261 ± 14.3[b]	231 ± 7.9[c]
13	480 ± 15.1	448 ± 20.6[c]	416 ± 14.1[c]
14	270 ± 14.5	305 ± 20.0[c]	282 ± 10.6[b]
15	263 ± 19.5	318 ± 23.8[c]	302 ± 7.5[c]

[a] The statistical significance of the differences between these and the dithizone mean values is indicated thus: [b] significant ($P = 0.05-0.01$); [c] highly significant ($P = <0.001$).

TABLE III

ANALYSIS OF VARIANCE OF RESULTS

Source of variance	Sum of squares	Degrees of freedom	Variance	F[a]
Dithizone method				
Specimens	540,738	3	180,246	706 [d]
Amounts	176	2	88.0	0.34[b]
Interaction	2,451	6	408.5	1.60[b]
Residual (samples)	12,251	48	255.2	—
Total	555,616	59	—	—
Neocuproine method				
Specimens	318,160	2	159,080	490 [d]
Amounts	1,938	3	646.0	1.99[b]
Interaction	2,839	6	473.2	1.46[b]
Residual (samples)	11,679	36	324.4	—
Total	334,616	47	—	—
BCOD method				
Specimens	24,146	2	12,073	211 [d]
Amounts	748	2	374.0	6.53[c]
Interaction	65	4	16.3	0.28[b]
Residual (samples)	1,031	18	57.3	—
Total	25,990	26	—	—

[a] The statistical significance of the F-ratio is indicated as described in the footnote to Table I.

to 11.5%. The variances of these results showed a more regular pattern, the order of decreasing magnitude being neocuproine, dithizone and BCOD.

When these results were subjected to an analysis of variance (Table III) a significant influence of aliquot size was found only in those given by the BCOD method but this was not consistent over the whole range of aliquots taken. The results for livers Nos. 13 and 2 obtained with this method and the neocuproine method respectively were not included in this analysis since their variances were significantly greater than those of the results for the other specimens.

Further information on the difference between the results given by the dithizone and neocuproine methods is given in Table IV which compares the values obtained for a series of 30 liver specimens with widely different copper contents and the 4 specimens discussed above. The differences between the pairs of results are shown in Fig. 2 which indicates a change from a random difference to a positive one

TABLE IV

COMPARISON OF RESULTS OBTAINED WITH DITHIZONE AND NEOCUPROINE METHODS

(The values shown are expressed as p.p.m. Cu in dry liver)

Liver no.	Method		Difference	
	Dithizone	Neocuproine	p.p.m.	%
31	7.27	11.0	+3.73	+51.3
28	7.51	10.6	+3.09	+41.1
30	7.87	9.36	+2.51	+31.9
29	11.0	28.4	+17.4	+158.2
11	11.6	11.5	−0.1	−0.9
19	11.7	1.44	−10.3	−88.0
12	12.5	1.93	−10.6	−84.8
9	12.7	13.5	+0.8	+6.3
22	13.1	20.2	+7.1	+54.2
8	15.4	18.5	+3.1	+20.1
20	16.8	0.46	−16.3	−97.0
5	20.2	21.8	+1.6	+7.9
21	20.8	29.1	+8.3	+39.9
34	23.7	12.6	−11.1	−46.8
4	34.9	39.8	+4.9	+14.0
6	36.4	42.4	+6.0	+16.5
3	38.7	37.9	−0.8	−2.1
10	44.4	37.5	−6.9	−15.5
2	44.4	50.0	+5.6	+12.6
7	49.7	46.3	−3.4	−6.8
25	77.9	65.8	−12.1	−15.5
Mean difference ± standard deviation =				+4.6 ± 12.2%
24	106	107	+1.0	+0.9
32	129	169	+40.0	+31.0
27	141	129	−12.0	−8.5
23	146	230	+84.0	+57.5
26	186	262	+76.0	+40.9
17	211	215	+4.0	+1.9
18	226	380	+154.0	+68.1
1	250	261	+11.0	+4.4
15	263	318	+55.6	+21.1
16	269	330	+61.0	+22.7
14	270	305	+35.0	+13.0
13	480	448	−32.0	−6.7
33	579	824	+245.0	+42.3
Mean difference ± standard deviation =				+22.2 ± 6.8%

when the copper content of the liver exceeded 100 p.p.m. dry weight. This trend was confirmed by carrying out 't' tests on the differences in the two sections of Table IV. For the livers containing less than 100 p.p.m. copper the mean difference is + 4.6%, which is not statistically significant, while the corresponding value for the remaining specimens is + 22.2% which is highly significant ($P = <0.001$).

DISCUSSION

Few direct comparisons of the performance of methods for the determination of copper in biological materials have been reported and none has been as detailed

Fig. 2. Comparison of results obtained for specimens of liver with dithizone and neocuproine methods.

as those described above. An important feature of these experiments is that they were designed to detect systematic errors as well as to give an estimate of the precision. The results obtained with the BCOD method showed an error of this kind but it was not consistent with sample size. No such error was detected in the results given by the other two methods.

On the other hand, the BCOD results had the smallest scatter with a co-efficient of variation ranging from 2.5 to 3.8%. The corresponding values for the dithizone and neocuproine results were 3.1–7.4% and 4.6–7.5% respectively. However, a different pattern was shown by the standardisation errors (Table I). When the standard error of fit was expressed as a percentage of the slope, values of 0.5, 1.0 and 1.1% were obtained for the dithizone, neocuproine and BCOD methods respectively, indicating that the scatter of the points about the dithizone curve was about half that associated with the other two.

Significant differences were shown by the mean values obtained with these 3 methods for the 4 specimens of liver but only those given by the neocuproine and BCOD methods showed a consistent relationship, the latter being lower in each case by 5.0–11.5%. A difference in this direction is also evident in the results published by RUSSELL AND HART[16] for 7 samples of gelatin. These authors made no comment on this discrepancy which varied from 3.7 to 100% (mean 51%) or on the fact that the results given by the BCOD method were also generally lower than those obtained by methods based on 2,2-diquinolyl, zinc dibenzyldithiocarbamate or polarography.

The relationship between the results given by the neocuproine and dithizone methods was explored more extensively by analysing 30 additional specimens of liver with a wide range of copper content. It was found that when the copper content was less than 100 p.p.m. dry weight (according to the dithizone method) the differences, although large, were distributed roughly equally about zero and the average difference was not statistically significant. However, as the copper content increased the results began to diverge significantly and over the range 100 to 500 p.p.m. the neocuproine values were on the average 22.2% higher (Table IV, Fig. 2). It is interesting to note that 100 p.p.m. marks roughly the lower limit of the normal range for sheep. A systematic error is obviously present in the results given by one of the

methods and since it was not detected in the tests described above it must vary in proportion to the sample size. If the neocuproine method is at fault the interfering factor must be some element or substance which gives a coloured complex with the reagent and accumulates with copper in the liver. Elements such as zinc which form colourless complexes[17] would, therefore, be excluded from consideration. The alternative explanation postulates a factor which inhibits the reaction of copper with dithizone, but in view of the fact that a preliminary extraction of copper was made and this was carried out to completion this explanation is much less plausible.

In the absence of reference standards for biological materials the decision as to which method gives the most accurate results must be based on a comparison of performance. If the results obtained with two or more methods agree closely and these methods are free from systematic errors then there is justification for taking the mean result as the best estimate of the true value, particularly if the methods have a radically different basis. Unfortunately, this did not occur in the experiments discussed above and the choice of the best method must be based on other criteria. The BCOD method is the first to be eliminated from consideration since a systematic error was detected in its results. In any case it is much less sensitive than the other two methods and for this reason would be unsatisfactory for many purposes.

So far as the neocuproine and dithizone methods are concerned it was noted above that the difference between the two sets of results was more likely to be due to interference in the former method than in the latter. The dithizone method also has distinct advantages in precision and sensitivity, the latter being about 3 times that of the neocuproine method (Table I). Confidence in a method also depends on the extent to which its chemical background has been studied and here again the dithizone method is more satisfactory. The use of neocuproine as a copper reagent was investigated recently[18] but the results have not yet been published in detail. However, it was concluded that more experience and information are needed before this reagent can be recommended in preference to others.

We are indebted to Miss JUNE TELFORD for technical assistance.

SUMMARY

Absorptiometric methods for traces of copper based on dithizone, 2,9-dimethyl-1,10-phenanthroline (neocuproine) and bis-cyclohexanone-oxalyldihydrazone (BCOD) were compared by carrying out replicate analyses on specimens of liver; the amount of sample taken was varied so as to provide a means of detecting systematic errors. Agreement between the results by the different methods was poor, the neocuproine method giving higher and more variable results than the other two. A systematic error, inconsistent with the sample size, was detected in the BCOD method. The dithizone method showed no systematic error and possessed better precision and sensitivity.

RÉSUMÉ

Les auteurs ont effectué une étude de comparaison de méthodes absorptiométriques de dosages de traces de cuivre dans des substances biologiques, utilisant

E. J. BUTLER, D. H. S. FORBES

comme réactifs la dithizone, la 2,9-diméthyl-1,10-phénanthroline (néocuproïne) et la bis-cyclohexanone-oxalyldihydrazone (BCOD). La méthode à la dithizone ne présente pas d'erreur systématique; elle offre une précision et une sensibilité supérieures à celles obtenues avec les deux autres réactifs.

ZUSAMMENFASSUNG

Absorptiometrische Methoden für die Bestimmung von Spuren Kupfer, die auf Dithizon, 2,9-Dimethyl-1,10-phenanthrolin (Neocuproin) und Bis-cyclohexanon-oxalyldihydrazon (BCOD) beruhen, wurden am Beispiel von Leberproben verglichen. Die Menge der Probe wurde variiert, um systematische Fehler zu vermeiden. Die Übereinstimmung zwischen den Ergebnissen der verschiedenen Methoden war schlecht. Die Neocuproin-Methode ergab höhere und schwankendere Ergebnisse als die anderen zwei. Ein systematischer Fehler, der unabhängig von der Probengrösse war, wurde bei der BCOD-Methode nachgewiesen. Die Dithizonmethode zeigte keine systematischen Fehler und besass eine bessere Genauigkeit und Empfindlichkeit.

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COMPLEX FORMATION OF COPPER(II) WITH TRIETHYLENETETRAMINE-HEXAACETIC ACID

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During recent years many polyaminocarboxylic acids have been used as masking agents and titrimetric reagents for various metals. Recently a new chelating agent, triethylenetetraminehexaacetic acid (TTHA), has been recommended as a titrant in compleximetric titrations[1]. This acid is a very interesting substance, because binuclear complexes of the type Me_2TTHA are formed with certain metals. The polarographic behaviour of some of these complexes has been investigated by CONRADI AND KOPANICA[2]. They claim that the Cu_2TTHA complex is reversibly reduced at the dropping mercury electrode and that no mononuclear copper complex is formed even in the presence of excess complexing agent.

Preliminary experiments performed in this laboratory indicated that both a mononuclear and a binuclear copper complex can exist in TTHA solutions and that the composition of the complex formed is dependent on the concentration of TTHA. The present work was carried out in order to determine the composition and the stability of the various copper–TTHA complexes.

EXPERIMENTAL

Materials

Triethylenetetraminehexaacetic acid (TTHA) was obtained from Geigy Chemical Co., Basel, Switzerland. The commercial product was recrystallized once from a minimum amount of hot water and dried in vacuum over calcium chloride. Analysis of the purified product showed that it was sufficiently pure. (Found: C 43.5%, H 6.1%, N 11.2%; calculated for $C_{18}H_{30}N_4O_{12}$: C 43.7%, H 6.1%, N 11.3%.) A 0.05 M stock solution was prepared by dissolving 24.724 g of TTHA in 130 ml of 1 M sodium hydroxide and diluting to 1 l with distilled water. The molarity was checked by titration against dipyridozincthiocyanate[3]. A $2 \cdot 10^{-3}$ M solution, which was used for potentiometric titrations, was prepared by dissolving 0.4962 g TTHA in distilled water and diluting to 500 ml. The molarity of this solution was checked by potentiometric titration with standard sodium hydroxide. The titrations were performed in presence and in absence of excess magnesium and gave end-points at 6 and 4 equivalents of base added, respectively.

Standard copper(II) solution was prepared by dissolving copper(II) nitrate in distilled water; the solution was standardized with EDTA.

Standard sodium hydroxide was prepared by dissolving reagent-grade sodium hydroxide in carbon dioxide-free water and standardized by potentiometric titration against sulphamic acid. The titration curves showed that the standard solution was practically carbonate-free.

Dodecylamine perchlorate and sodium dodecyl sulphate were used as surface-active agents. Solutions of these substances were prepared as described previously[4].

The remaining chemicals were of reagent-grade quality and were used without further purification.

Apparatus

Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). All experiments were performed with the electrodes and electrolysis cell described previously[5]. A Zeiss spectrophotometer PMQ II with 4.000-cm glass cells was used for the determination of optical densities. The pH of all solutions was measured with a Beckman Zeromatic pH meter using glass and calomel electrodes.

RESULTS AND DISCUSSION

Polarography

Polarograms of copper(II) in the presence of *excess* TTHA exhibited a single well-defined wave when recorded from neutral or acidic medium. The reversibility of the electrode reaction was tested by plotting $\log i/(i_d - i)$ *vs.* the applied potential. The plots yielded straight lines at all pH values in the range 4–9 (0.2 M acetate or phosphate buffers) and the slopes (−0.032 to −0.036) indicated a slightly irreversible 2-electron reduction of copper to the amalgam.

The half-wave potential shifted to more negative values with increasing TTHA concentration and plots of the values of $E_{\frac{1}{2}}$ *vs.* the corresponding values of $\log C_x$ resulted in a straight line. The slope of the line (−0.030 V/log unit) indicated that only one ligand was coordinated in the complex.

The effect of pH on the copper–TTHA wave was tested by recording polarograms of 10^{-4} M copper and 10^{-2} M TTHA in acetate and phosphate buffers of various pH values. The half-wave potential was shifted to more negative values with increasing pH of the supporting electrolyte. At pH values below 5 the shift was 0.07 V/pH unit and in the pH range 5–9 the shift was 0.04 V/pH unit.

When the pH was increased above 9, the wave was broken into two parts and a new irreversible wave appeared at more negative potentials. A further increase in pH of the supporting electrolyte resulted in an increase of the second wave at the expense of the first one, the limiting current of the total wave remaining constant. The splitting of the wave is probably the result of an inhibited electrode reaction caused by the reduction product as previously reported for the copper–DTPA complex[5].

Polarograms recorded from solutions with TTHA and *excess copper* exhibit 3 waves. Preliminary experiments indicated that the waves were well separated when the pH of the supporting electrolyte was 7.1 and the following experiments were performed at this pH value. Polarograms of various mixtures of copper and TTHA were recorded and the half-wave potentials and limiting currents of the waves determined. A few typical polarograms are shown in Fig. 1.

The half-wave potential of copper in phosphate buffer with pH 7.1 was −0.07 V

vs. S.C.E. The diffusion current of this wave decreased upon addition of TTHA to the supporting electrolyte and 2 new waves with equal height appeared at more negative potentials. When the molar ratio of copper to TTHA was 2 : 1, only the two new waves with half-wave potentials −0.21 and −0.33 V *vs.* S.C.E. respectively, were observed on the polarogram (Fig. 1 B). A further increase in TTHA concentration resulted in an increase in the height of the second of these waves at the expense of the first one. When the ratio of copper to TTHA was 1 : 1, only the second wave ($E_{\frac{1}{2}} =$ −0.326 V *vs.* S.C.E.) appeared on the polarogram.

Polarograms of the same mixtures were also recorded in the presence of surface-active substances. The experiments were performed as previously described for the copper–DTPA complexes[6] and indicated that the first wave (Curve A in Fig. 1) is due to reduction of uncomplexed copper and that the double waves are due to reduction of negatively charged complexes.

The effect of the drop time on the two waves was investigated by recording polarograms at various heights of the mercury column. The height of both waves increased with the height of mercury and the value $i_d/\sqrt{h}$, where h is the height of the column after correction for the "back pressure", was constant, indicating that the electrode reactions were diffusion-controlled. The reversibility of the two waves was tested by plotting the curves of $\log i/(i_d−i)$ *vs.* the potential. The points yield straight lines and the slopes indicated a nearly reversible 2-electron reduction of copper to the amalgam for both waves. The slight irreversibility was probably due to the lack of excess complexing agent in the solution.

The effect of pH on the double wave was investigated by recording polarograms of 2 : 1 mixtures of copper and TTHA using acetate and phosphate buffers as sup-
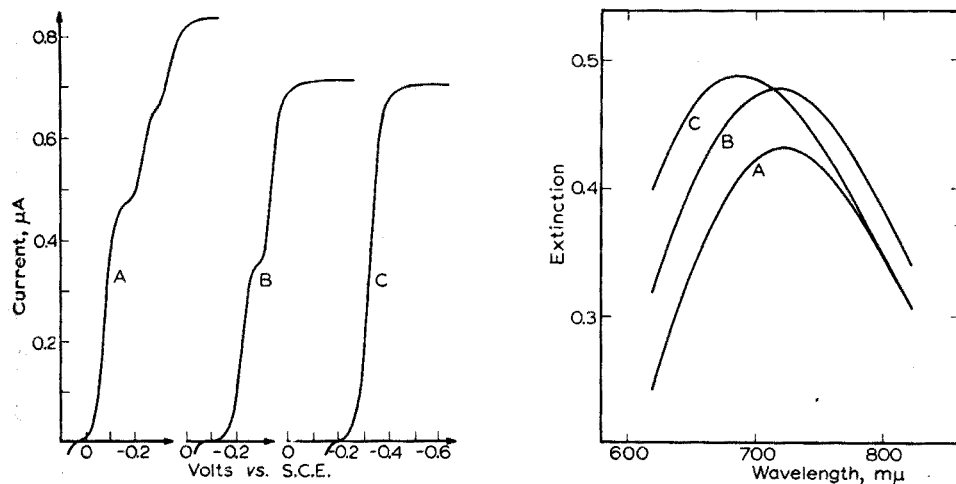
Fig. 1. Polarograms of 10^{-4} M copper(II) in phosphate buffer with pH 7.1 and various amounts of TTHA present. Curve A = $2.5 \cdot 10^{-5}$, curve B = $5 \cdot 10^{-5}$ and curve C = 10^{-4} M TTHA.

Fig. 2. Absorption curves of $1.6 \cdot 10^{-3}$ M copper(II) in the presence of TTHA: Curve A = $0.8 \cdot 10^{-3}$ M TTHA (pH 4.6), curve B = $4 \cdot 10^{-3}$ M TTHA (pH 4.6) and curve C = $4 \cdot 10^{-3}$ M TTHA (pH 9.4). Extinctions measured against distilled water.

porting electrolytes. The half-wave potential of the first wave was constant, independent of pH, whereas the second wave shifted linearly to more negative values with increasing pH of the electrolyte. At a given pH value the half-wave potential of the second wave was exactly the same as that of the single wave obtained from 1 : 1 mixtures.

The above results indicate that the polarographic behaviour of copper in the presence of TTHA is very similar to that of the copper–DTPA complexes previously investigated[5,6]. In the presence of excess copper a binuclear copper–TTHA complex is formed, and upon addition of more complexing agent, this complex is rapidly converted to a more stable mononuclear complex. The binuclear complex is reduced in two steps at the dropping mercury electrode. The first step is probably due to the reduction of one of the copper atoms to the amalgam, and the second step to a 2-electron reduction of copper in the mononuclear complex formed during the electrolysis.

Spectrophotometric measurements

In order to verify the existence of both mono- and binuclear copper–TTHA complexes, absorption curves of two copper–TTHA mixtures were recorded at several pH values in the range 4.6 to 9.4. The concentration of copper(II) was $1.6 \cdot 10^{-3}$ M in both series and that of TTHA $0.8 \cdot 10^{-3}$ M and $4.0 \cdot 10^{-3}$ M, respectively. A few absorption curves are shown in Fig. 2.
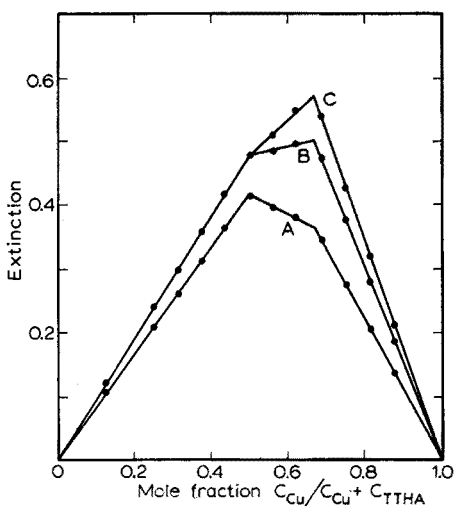
Fig. 3. Continuous variation curves for the system copper(II)–TTHA at pH 8.87. Constant sum of concentrations $C = C_{Cu} + C_{TTHA} = 3.2 \cdot 10^{-3}$ M. Extinctions measured against distilled water at: 630 mμ (curve A), 670 mμ (curve B) and 720 mμ (curve C).
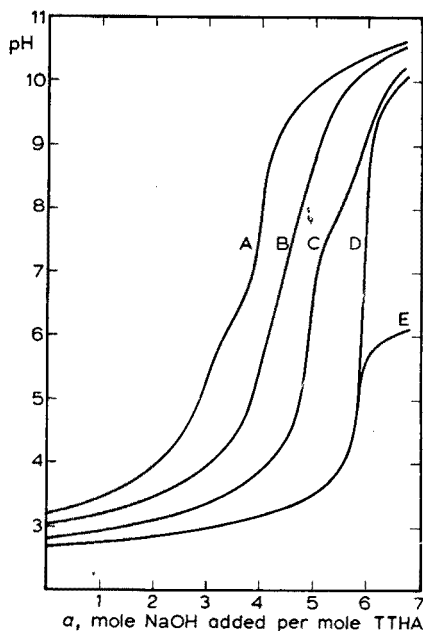
Fig. 4. Potentiometric titration curves of $5 \cdot 10^{-4} M$ TTHA in absence and in presence of various amounts of copper(II). Copper–TTHA ratio: curve A = 0 : 1, B = 0.5 : 1, C = 1 : 1, D = 2 : 1 and E = 10 : 1.

All the absorption curves with metal/ligand ratio 2 : 1 were identical. The absorption maximum was 721 mμ, independent of the pH of the solution. The absorption maximum of the mixture with a copper–TTHA ratio of 1 : 2.5, however, shifted to shorter wavelengths with increasing pH. At a given pH value, identical absorption curves were obtained from 1 : 1 and 1 : 2.5 mixtures of copper and TTHA.

The composition of the complexes was determined by the method of continuous variation[7]. Copper(II) nitrate and TTHA were mixed in various ratios in 0.01 M borax buffer of pH 8.87 containing 0.1 M potassium nitrate. The sum of the concentrations of copper and TTHA was initially constant (3.2 · 10⁻³ M) in all solutions. The extinctions were measured against distilled water at the wavelengths 720, 670 and 630 mμ. A precipitate of copper(II) hydroxide was formed in solutions with a copper–TTHA ratio greater than 2 : 1 and was filtered off before the measurements. The results are plotted in Fig. 3 and indicate that two complexes with metal–ligand ratios of 2 : 1 and 1 : 1, respectively, were formed in copper–TTHA solutions.

The binuclear complex had an absorption maximum at 721 mμ and a molar extinction coefficient 135, both of which were independent of pH. The absorption maximum of the mononuclear complex shifted from 717 to 685 mμ in the pH range 4.6 to 9.4 and the molar extinction coefficient increased from 74 to 76.3 in the same pH range.

Potentiometric titrations

Potentiometric pH-titrations of TTHA in the absence and presence of copper-(II) were performed, using carbonate-free 0.04763 N sodium hydroxide as titrant. The titration curves of the acid and of mixtures with copper/TTHA ratios 0.5 : 1, 1 : 1, 2 : 1 and 10 : 1 are plotted in Fig. 4. The initial volume of the solutions (80 ml), the TTHA concentration (5 · 10⁻⁴ M) and the ionic strength (0.1 M potassium nitrate) were kept constant in all titrations.

The titration curve of the acid in absence of copper (Curve A in Fig. 4) exhibits a slight inflexion at an a value of 3 and a well-defined inflexion at $a = 4$, where a denotes the number of mole of alkali added per mole of the acid. This curve is in accordance with earlier data[8]. The titration curve (D) of the solution containing two moles copper per mole ligand, shows only a single steep inflexion at $a = 6$ and a buffer region at low pH values, corresponding to a one-step neutralization of a strong acid. The titration curve of the solution with a large excess of copper (Curve E) coincides with that of the 2 : 1 mixture up to an a value of 6. Further addition of sodium hydroxide to this solution resulted in the formation of copper(II) hydroxide, indicating that not more than two copper atoms can be coordinated to one TTHA molecule. The titration curve (C) of equimolar concentrations of copper(II) and TTHA, exhibits two inflexions at $a = 5$ and $a = 6$, indicating a reaction taking place in two steps. The titration curve (B) of the 0.5 : 1 mixture of copper(II) and TTHA was plotted in order to determine the stability constants of the complexes.

It is evident from these experiments that a binuclear complex is formed in solutions with a copper–TTHA ratio equal to or greater than 2 : 1, according to the reaction:

$$2 \, Cu^{2+} + H_6A \rightleftharpoons Cu_2A^{2-} + 6 \, H^+$$
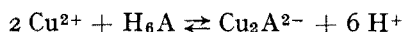
where H_6A denotes TTHA. In solutions with equimolar concentrations of copper(II)

and TTHA, however, a mononuclear hydrogen complex is formed which is neutralized when the pH is increased above 8:

$$Cu^{2+} + H_6A \rightleftarrows CuHA^{3-} + 5 H^+$$

$$CuHA^{3-} \rightleftarrows CuA^{4-} + H^+$$
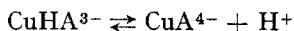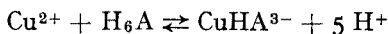
Calculation of the stability constants

As stated above, the reduction of the copper–TTHA complexes at the dropping mercury electrode was slightly irreversible. The stability constants of the complexes were therefore calculated from the potentiometric titration curves by the method of SCHWARZENBACH[9] and UHLIG[10]. In the calculation the species: Cu_2A^{2-}, CuA^{4-}, $CuHA^{3-}$, CuH_2A^{2-} and the anions of the free ligand, had to be considered. The corresponding equilibrium constants of the complexes were defined:

1. $\beta_{M_2A} = [M_2A]/[M]^2[A]$

2. $K_{MHA}^{M} = [MHA]/[M][HA]$

3. $k_{MA}^{H} = [MA][H]/[MHA]$

4. $k_{MHA}^{H} = [MHA][H]/[MH_2A]$

5. $K_1 = [MA]/[M][A]$

6. $K_2 = [M_2A]/[M][MA]$

where M denotes copper(II) and the charge signs are omitted.

The dissociation constants of the ligand were defined:

7. $k_i = [H_{6-i}A][H]/[H_{7-i}A]$

It follows that

8. $K_1 = K_{MHA}^{M} \cdot k_{MA}^{H}/k_6$ and $K_2 = \beta_{M_2A}/K_1$

and the system is completely defined by the equations:

9. $C_M = [M] + \gamma[MHA] + 2[M_2A]$

10. $C_A = \alpha[H_2A] + \gamma[MHA] + [M_2A]$

11. $C_A \cdot g = \beta[H_2A] + \delta[MHA]$

where C_M and C_A are the total concentrations of copper and of TTHA, respectively, and g the average number of moles of protons bounded per mole ligand[9]. The coefficients are defined by the equations:

12. $\alpha = \dfrac{[H]^4}{k_1k_2k_3k_4} + \dfrac{[H]^3}{k_2k_3k_4} + \dfrac{[H]^2}{k_3k_4} + \dfrac{[H]}{k_4} + 1 + \dfrac{k_5}{[H]} + \dfrac{k_5k_6}{[H]^2}$

13. $\beta = 6\dfrac{[H]^4}{k_1k_2k_3k_4} + 5\dfrac{[H]^3}{k_2k_3k_4} + 4\dfrac{[H]^2}{k_3k_4} + 3\dfrac{[H]}{k_4} + 2 + \dfrac{k_5}{[H]}$

$$14. \; \gamma = \frac{[H]}{k^{H}_{MHA}} + 1 + \frac{k^{H}_{MA}}{[H]}$$

$$15. \; \delta = 2 \frac{[H]}{k^{H}_{MHA}} + 1$$

The coefficients α and β were calculated as a function of pH using the dissociation constants determined by FROST[11].

Preliminary calculations showed that the constant β_{M_2A} could not be obtained from the titration curve of the 2 : 1 mixture (Fig. 4, curve D), because the buffer region occurred at too low pH values. Further calculations showed that the M_2A complex had to be considered also in copper–TTHA mixtures with ratios 1 : 1 and 1 : 2. Hence, the titration curves of 1 : 1 and 1 : 2 mixtures in the pH region 4.0 to 5.0 were used for the calculation of K^{M}_{MHA} and β_{M_2A}. As an approximation the value of pk^{H}_{MHA} was chosen to be 3.0. Later calculations showed that it could not be much higher and that smaller values of this constant did not affect the result appreciably.

After these approximations had been made the equations 9–11 contained 4 unknown concentrations ($[M_2A]$, $[MHA]$, $[M]$ and $[H_2A]$) which could be calculated by a method of successive approximations. A value of β_{M_2A} was predicted, the expression

$$16. \; [M_2A] = \beta_{M_2A} k_5 k_6 [M]^2 [H_2A]/[H]^2$$

was substituted in eqns. 9 and 10, and the values of $[M]$, $[H_2A]$ and $[MHA]$ were calculated for several experimental points on curves B and C in Fig. 4. An equation of the third degree in $[M]$ was obtained and solved graphically and the constant

$$K^{M}_{MHA} = \frac{[MHA]}{[M] \, [H_2A]} \cdot \frac{[H]}{k_5}$$

calculated. The latter expression was then substituted for $[MHA]$ in eqns. 9–11. New values of $[M]$, $[H_2A]$ and $[M_2A]$ were calculated from points on curve C (Fig. 4) and a new and more correct value of β_{M_2A} was obtained. This procedure was repeated until constant values of $\log \beta_{M_2A}$ and $\log K^{M}_{MHA}$ were obtained. The result is given in Table I together with the successive stability constants K_1 and K_2 which were calculated from eqn. 8. Finally the dissociation constant of the weak acid $CuHA^{3-}$, pK^{H}_{MA}, was calculated from the titration curve C (Fig. 4), in the pH region 7.8–8.8. This constant is also reported in Table I.

The stability constants of the copper–diethylenetriaminepentaacetic acid

TABLE I

EQUILIBRIUM CONSTANTS OF COPPER(II) COMPLEXES WITH DTPA AND TTHA

	$\log K^{M}_{MHA}$	$\log \beta_{M_2A}$	pK^{H}_{MA}	pK^{H}_{MHA}	$\log K_1$	$\log K_2$
DTPA (ref. 12)	15.5		4.81	3.04	21.1	6.79
TTHA	12.6	24.5	8.06		15.4	9.1

(DTPA) complexes were determined by CHABEREK et al.[12]; these constants are also included in Table I and indicate that the mononuclear DTPA complex is more stable, and that the binuclear DTPA complex is less stable than the corresponding TTHA complexes.

According to PŘIBIL AND VESELÝ[1] the binuclear copper–TTHA complex is sufficiently stable to be used for compleximetric titrations. Thus, if TTHA is added to a copper(II) solution and the excess TTHA is backtitrated with lead(II) using xylenol orange as an indicator, the end-point corresponds to the formation of the binuclear copper–TTHA complex. If, however, EDTA or DTPA is used as chelating agent, mononuclear copper complexes are formed at the end-point. PŘIBIL AND VESELÝ utilized the different composition of EDTA and TTHA complexes for the titration of two-component mixtures. The formation of the binuclear copper–TTHA complex in these titrations was confirmed by the present work. It is, however, evident that a mononuclear copper complex is formed in the presence of excess TTHA. The binuclear copper complex is therefore assumed to be formed *during* the backtitration with lead(II), according to the equation:

$$2\ CuA^{4-} + 2\ Pb^{2+} \rightleftarrows Cu_2A^{2-} + Pb_2A^{2-}$$
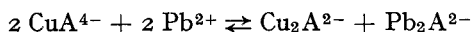
where H_6A denotes TTHA. The end-point in the compleximetric titration is very sharp, indicating that this reaction shifts very quickly to the right. A similar reaction does not occur with the copper–DTPA complex, probably because of the very great difference in the stability of the mono- and the binuclear DTPA complexes (K_1 and K_2 in Table I).

SUMMARY

The interaction between copper(II) and triethylenetetraminehexaacetic acid (TTHA) was investigated by polarographic, spectrophotometric and potentiometric methods. The existence of chelates with the formulae CuH–TTHA, Cu–TTHA and Cu_2-TTHA was shown. The polarographic behaviour and absorption curves of the chelates are described and the equilibrium constants defining the formation of the various species, are reported.

RÉSUMÉ

Les auteurs ont examiné la réaction du cuivre(II) avec l'acide triéthylènetétraminehexacétique (TTHA), par polarographie, spectrophotométrie et potentiométrie, montrant l'existence des chélates CuH–TTHA, Cu–TTHA et Cu_2-TTHA. Le comportement polarographique et les courbes d'absorption des chélates sont décrits; les constantes d'équilibre sont données.

ZUSAMMENFASSUNG

Das Zusammenwirken von Kupfer(II) mit Triäthylentetraminhexaessigsäure

(TTHA) wurde mittels polarographischer, spektralphotometrischer und potentio-metrischer Methoden untersucht. Es wurde die Existenz der Chelate mit den Formeln CuH–TTHA, Cu–TTHA und Cu$_2$-TTHA nachgewiesen. Das polarographische Verhalten und die Absorptionskurven der Chelate werden beschrieben. Über die Gleichgewichtskonstanten, die die Bildung der verschiedenen Spezies erklären, wird berichtet.

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EFFECT OF COBALT-60 GAMMA RADIATION ON THE DETERMINATION OF URANIUM(VI) IN PHOSPHORIC ACID SOLUTIONS OF URANIUM(IV) OXIDE*

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Uranium(IV) oxide (UO_2), either alone or together with a variety of other materials (*e.g.*, ZrO_2 and ThO_2), is used widely as a nuclear fuel. In the solid state, uranium readily forms mixed oxides; the physical properties of a nuclear fuel that contains UO_2 vary with the composition of the oxide. Therefore it is often necessary to determine the stoichiometry or the uranium(VI) content of UO_2 before and after its use as a nuclear fuel. Methods exist for the determination of uranium(IV) and uranium(VI) in UO_2 and for the subsequent determination of the UO_2 stoichiometry[1–11]. The method that preserves the oxidation state of uranium in nonradioactive samples[2] involves dissolution of UO_2 in phosphoric acid followed by analysis for uranium(VI). If the sample is radioactive, the oxidation state of the uranium may change during the dissolution and analysis.

Little has been reported on the radiation chemistry of uranium solutions. The effect of radiation on materials is commonly expressed as radiolytic yield, G, which is defined as the number of radicals, molecules, molecule-equivalents, or ions produced per 100 eV of absorbed ionizing radiation. BOYLE *et al.*[12] found that uranium(IV) is oxidized to uranium(VI) when irradiated with mixed α-, β-, and γ-radiation and fission fragments. HAISSINSKY AND DUFLO[13,14] report that the radiolytic yield of uranium(VI) from deoxygenated solutions of uranium(IV) that were irradiated with X-rays and γ-rays increases toward a G value of 2.1 molecule-equivalents/100 eV with increase in the concentration of uranium(IV). They report that G is much higher ($G = 20$) in the presence of oxygen and depends on radiation intensity in the manner expected for a chain reaction. FIRSOV AND ERSHLER[15,16] also studied the radiolytic oxidation of uranium(IV) both in the presence and in the absence of oxygen at 25° and at higher temperatures up to 310°. Oxygen causes $G_{U(VI)}$ to increase with increase in uranium(IV) concentration from about 2.0 to 16.0 $\pm$ 0.1 molecule-equivalents/100 eV. They report that in the absence of oxygen $G_{U(VI)}$ increases with an increase in uranium(IV) concentration from about 1.5 to nearly 5.0 molecule-equivalents/100 eV in the concentration range 5–110 mg-equivalents/l of uranium(IV). At higher concentrations, $G_{U(VI)}$ decreases. They attribute this decrease to the reduction of uranium(IV) by H radicals. At a uranium(IV) concentration of 110 mg-equivalents/l,

an increase in the temperature of the solution to 310° under vacuum conditions results in an increase in $G_{U(VI)}$ to 8.7 molecule-equivalents/100 eV. FIRSOV AND ERSHLER attribute this increase to oxidation of uranium(IV) by H radicals at the high temperature; their results indicate that this oxidation is slow at 25°. It has been demonstrated[17] that H radicals can react as oxidizing or as reducing agents in aqueous solutions. All the above-mentioned studies were carried out in aqueous solutions of sulfuric acid.

No studies on the effects of γ-radiation on the determination of the oxidation states of uranium in UO_2 have been reported. Results of the study of the effects of γ-radiation on the determination of uranium(VI) in UO_2 are described herein. The method for dissolving the UO_2 and analysis for uranium(VI) described by KUBOTA[2] was selected for use in following the radiolytic production of uranium(VI) in phosphoric acid solutions of UO_2. In this method, reactor-grade uranium(IV) oxide (99+% UO_2) is dissolved in 85–87% phosphoric acid; the solution is then analyzed polarographically for uranium(VI). The method has the advantage that the oxidation state of the uranium does not change during the dissolution of the UO_2.

EXPERIMENTAL

Apparatus

Radiation source. A nominal 2900-curie ^{60}Co γ-radiation source was used to make all the irradiations[18].

Spectrophotometer. A Cary Model 11 recording spectrophotometer was used to measure the radiolytic oxidation of iron(II) to iron(III) in determining the γ-radiation dose rate of the ^{60}Co source (see *Procedure*).

Polarograph. An ORNL Model Q-1160[19] polarograph, in conjunction with a dropping-mercury electrode and a saturated calomel electrode (S.C.E.) as the reference electrode, was used. Electrical contact between the electrodes was made through a salt bridge that was a saturated solution of potassium nitrate.

Reagents

All the chemicals and reagents were reagent grade.

Dosimeter solution. A ferrous sulfate dosimeter solution of the kind described by HOCHANADEL[20] was used to determine the γ-radiation dose rate of the ^{60}Co · source. The solution was 0.002 M in iron(II) ammonium sulfate, 0.001 M in sodium chloride, and 0.4 M in sulfuric acid.

Uranium(IV) oxide solutions. Reactor-grade uranium(IV) oxide (99+% UO_2, −100 to +325 mesh), obtained from the Metallurgy Division of the Oak Ridge National Laboratory was dissolved in concentrated phosphoric acid (14.8 M) by KUBOTA's procedure[2]. Solutions that contained 0.92 ($3.86 \cdot 10^{-3}$ M) and 4.60 mg of uranium per ml ($1.93 \cdot 10^{-2}$ M) were prepared by dissolving the necessary amount of UO_2. These solutions are herein referred to as solutions of low and high concentration of uranium(IV), respectively. Previously determined values for the stoichiometry of the particular UO_2 sample were used to calculate the initial amounts of UO_2 required for the experiments. Under the conditions used, about 16 h was required to dissolve 1 g of UO_2 in 200 ml of 85–87% (14.8 M) phosphoric acid.

Perchloric acid solution. The 0.2 M perchloric acid solution used to dilute the

phosphoric acid solution of UO_2 for polarographic analysis was deoxygenated by passing nitrogen through the solution for at least 2 h.

Procedures

Calibration of ^{60}Co *source.* The dose rate of γ-radiation from the ^{60}Co source to 0.4 M sulfuric acid was determined by using the standard ferrous-sulfate-dosimetry technique[20]. This technique is based on the fact that ^{60}Co γ-radiolysis of iron(II) in 0.4 M H_2SO_4 produces 15.6 molecules of iron(III) per 100 eV of energy absorbed. The iron(III) concentration was measured with a Cary recording spectrophotometer at 3050 Å and 25°. Dose rate to the phosphoric acid solutions was calculated from the calibration data by assuming a direct proportionality between energy absorbed and electron density.

Irradiation of test solutions. The volume of test solution irradiated was 20 ml for both the low and high concentrations of uranium(IV). Air-saturated or argon-saturated solutions at 25° were irradiated in 50-ml flasks. Degassed solutions at 25° and argon-saturated solutions at 140° were irradiated in specially fabricated Pyrex tubes provided with a stopcock to facilitate their being evacuated. The space above the argon-saturated solutions that were irradiated at 140° was swept with argon during the irradiation. The space above the degassed solutions was evacuated except for the phosphoric acid vapor.

Polarographic analysis of irradiated test solutions. After the 20 ml of phosphoric acid solution of UO_2 was irradiated, 25 ml of deoxygenated 0.2 M perchloric acid was added to it. The volume was brought to 50 ml with deoxygenated distilled water. Portions of the well-mixed samples were transferred to a polarographic cell, and a stream of argon was passed through the solution for about 15 min to purge it of air absorbed during the transfer. The voltage was scanned from +0.1 to −0.6 V *vs.* S.C.E. The concentration of uranium(VI) was determined by means of a previously prepared calibration plot. Prior to the analysis of each set of solutions, the calibration plot was checked with a standard solution of uranium(VI). During the course of these experiments, the various points on the calibration plot could be reproduced with a deviation not greater than ± 3%.

RESULTS AND DISCUSSION

Studies by SATO *et al.*[21] and by HAISSINSKY[13,14] show that phosphoric acid is exceptionally stable to radiation. The effect of γ-radiation on a wide variety of aqueous solutions, including solutions of uranium(IV), has been documented[17,22]. Absorption of energy in water through radiolysis produces H and OH radicals. These radicals may react with each other to produce H_2, H_2O_2, or H_2O or they may react directly with the solute. The quantity of solute converted to an oxidized or reduced product depends, in part, on the type of radiation, the energy of the radiation, the susceptibility of the solute to oxidation or reduction, the presence or absence of oxygen in the system, and the pH of the solution.

For the radiolysis of deoxygenated solutions of uranium(IV) in sulfuric acid, HAISSINSKY[14] suggests the following reactions:

$$H_2O \xrightarrow{\gamma\text{-radiation}} H, OH \tag{1}$$

$$2H \rightarrow H_2 \tag{2}$$

$$UOH^{3+} + OH \rightarrow UO_2^+ + 2H^+ \tag{3}$$

$$UO_2^+ + OH + H^+ \rightarrow UO_2^{2+} + H_2O \tag{4}$$

$$UOH^{3+} + H_2O_2 + H^+ \rightarrow UO_2^{2+} + 2H_2O \tag{5}$$
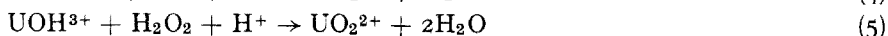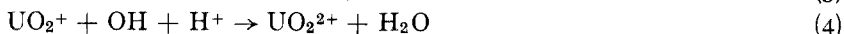
These equations are adaptable even if uranium(IV) exists as $U(SO_4)^{2+}$, $U(SO_4)_2$ or $U(SO_4)_3^{2-}$. The species UOH^{3+} was selected by HAISSINSKY for convenience. Both HAISSINSKY[14] and FIRSOV AND ERSHLER[15,16] present evidence which indicates that H does not react with uranium(IV) at room temperature. HAISSINSKY also proposes that, in sulfuric acid solutions, the following reactions occur in the presence of oxygen:

$$H_2O, O_2 \xrightarrow{\gamma\text{-radiation}} OH, HO_2 \tag{6}$$

$$UOH^{3+} + OH \rightarrow UO_2^+ + 2H^+ \tag{7}$$

$$UO_2^+ + O_2 \rightarrow UO_2^{2+} + O_2^- \tag{8}$$

$$(H^+ + O_2^- \rightarrow HO_2) \tag{9}$$

$$UOH^{3+} + HO_2 \rightarrow UO_2^{2+} + OH \tag{10}$$

$$UO_2^+ + OH \rightarrow UO_2^{2+} + H_2O \tag{11}$$

$$UOH^{3+} + H_2O_2 + H^+ \rightarrow UO_2^{2+} + 2 H_2O \tag{12}$$
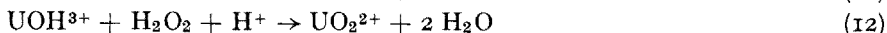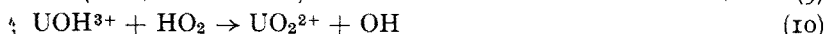
Equations (1) through (12) indicate that irradiation of an aqueous solution usually results in a net major chemical change in the solute species and in a net minor chemical change in the solvent. Thus, the solvent may be thought to act as an energy-transfer agent and to be relatively unchanged in the process.

In the present study, the phosphoric acid concentration was 14.8 M, and the water concentration was 13.1 M. The low concentration of uranium(IV) was $3.86 \cdot 10^{-3}$ M; the high was $1.93 \cdot 10^{-2} M$. The initial uranium(VI) concentrations were $1.25 \cdot 10^{-4}$ M and $2.42 \cdot 10^{-5}$ M, respectively. Since phosphoric acid changes only very little under irradiation, the energy it absorbs is probably dissipated as heat or is transferred to the water, which in turn dissociates to H and OH radicals.

The results of the present study are given in Fig. 1. Each point on this Fig. represents an average of 3 runs. The maximum deviation for all values given on Fig. 1 is $\pm 3\%$.

The results presented in Fig. 1 are consistent with those of HAISSINSKY and of FIRSOV AND ERSHLER in that $G_{U(VI)}$ increases with an increase in uranium(IV) concentration. This effect is presumably due to more efficient scavenging of H and OH at high uranium(IV) concentration than at the low concentration. A systematic study of the effects of uranium(IV) and uranium(VI) concentrations on $G_{U(VI)}$ was not made, because the work was limited to the conditions normally associated with the determination of uranium(VI) in uranium(IV) oxide. In view of the relatively low water content of the solutions used in this study, it is not surprising that the observed $G_{U(VI)}$ values are lower than those reported by HAISSINSKY and by FIRSOV AND ERSHLER for sulfuric acid solutions of uranium(IV). A much higher acid concentration (14.8 M phosphoric acid compared with 0.4 M sulfuric acid) was used in this study.
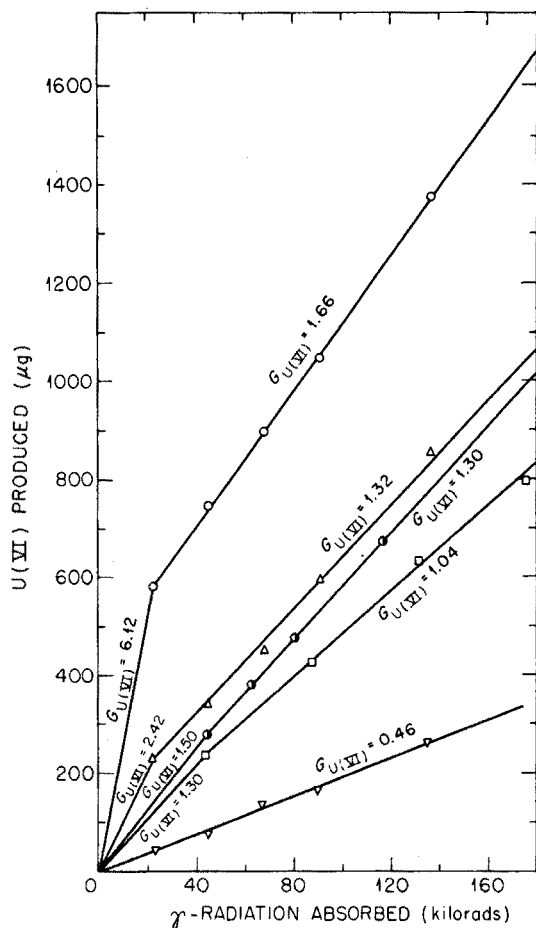
Fig. 1. Cobalt-60 γ-ray radiolytic yield of uranium(VI) in phosphoric acid solutions of uranium(IV) oxide.

Initial U(VI) concentration (mg/ml)	T (°)	Pretreatment
○ 4.60	25	Air-satd.
△ 4.60	25	Ar-satd.
◑ 4.60	25	Degassed
□ 4.60	140	Ar-satd.
▽ 0.92	25	Ar-satd.

Since phosphoric acid does not enter directly into the radiolytic reaction, it probably absorbs some energy that otherwise would be used to excite (or ionize) water and subsequently to produce more H and OH radicals at lower acid concentration. Unless the phosphoric acid transfers all its absorbed energy to the water, $G_{U(VI)}$ will decrease with increasing acid concentration.

The magnitude of $G_{U(VI)}$ also varies with the concentration of oxygen in the solution. As seen in Fig. 1, $G_{U(VI)}$ is largest for air-saturated solutions. Participation of H as an oxidizing agent through the reaction of H and O_2 to form HO_2 would account for this fact. At the high initial uranium(IV) concentration, the initial $G_{U(VI)}$ is always greater than the succeeding yield. That portion of each curve between the origin and the first experimental point probably does not present the true picture of the initial rate of change of $G_{U(VI)}$ with dose. Conceivably, the initial $G_{U(VI)}$ could be higher than that indicated and could then decrease until the oxygen initially present is depleted. The initial portion of these curves represents the overall yield during the period of irradiation when oxygen is being depleted. Because of experimental limitations, a study of this region was not attempted.

Of the solutions that contained the high concentration of uranium(IV), the argon-saturated solution irradiated at 140° gave the lowest radiolytic yield of uranium(VI). The high temperature and the helium sweep of the space above the solution during irradiation probably effects the rapid escape of dissolved hydrogen and oxygen and the decomposition of H_2O_2 formed by the combination of OH radicals, thus lowering the yield of uranium(VI).

Initially, $G_{U(VI)}$ of the degassed uranium(IV) solution is lower than that of the argon-saturated solution at 25°, but the succeeding yields are equal. The discrepancy between the initial $G_{U(VI)}$ values for these 2 solutions is probably due to the higher initial concentration of oxygen in the argon-saturated solution. The good agreement between the initial $G_{U(VI)}$ value of the argon-saturated solution at 140° and the degassed and argon-saturated solutions at 25° is probably fortuitous.

The initial and succeeding $G_{U(VI)}$ values for the solution having the low uranium(IV) concentration are equal. Possibly these values should be different, but their difference may be in the range of the experimental error of the technique.

The solutions of high uranium(IV) concentration were irradiated at dose rates of $1.90 \cdot 10^{14}$ eV/l/min (1.80 kilorads/min) to $4.63 \cdot 10^{14}$ eV/l/min (4.39 kilorads/min). No dose-rate effect was observed. The solutions of low uranium(IV) concentration were irradiated at a dose rate of $4.63 \cdot 10^{14}$ eV/l/min only.

TABLE I

EFFECT OF γ-RADIATION ON THE DETERMINATION OF THE STOICHIOMETRY OF URANIUM(IV) DIOXIDE

γ-Radiation dose (kilorads)	Increase in O/U ratio[a,b]				
	A	B	C	D	E
0	0	0	0	0	0
50	0.0095	0.0046	0.0038	0.0033	0.0059
100	0.0138	0.0079	0.0071	0.0060	0.0118
150	0.0180	0.0112	0.0105	0.0087	0.0178

[a] The theoretical O/U ratio is 2.00000.
[b] The solutions were as follows: (A) air-satd., 25°, initial concn. of U(IV) = 4.60 mg/ml; (B) argon-satd., 25°, initial concn. of U(IV) = 4.60 mg/ml; (C) degassed, 25°, initial concn. of U(IV) = 4.60 mg/ml; (D) argon-satd., 140°, initial concn. of U(IV) = 4.60 mg/ml; (E) argon-satd., 25°, initial concn. of U(IV) = 0.92 mg/ml.

Effect of ^{60}Co γ-radiation on the determination of stoichiometry of uranium(IV) oxide

An important use of the phosphoric acid dissolution and polarographic analysis of UO_2 is to determine the stoichiometry of the compound. The effect of ^{60}Co γ-radiation on the measurement of the O/U ratio of reactor-grade UO_2 is shown in Table I.

The practical values of the results of the present study are that they show that radiation does affect the results of analyses of UO_2 solutions, and that they point out conditions under which the radiation effects are minimum. If a solution of uranium(IV) is exposed to a reasonably well-defined dose of γ-radiation, the amount of uranium(VI) produced can be estimated by use of the data given herein. To reduce the radiolytic oxidation of uranium(IV) to uranium(VI) in aqueous solutions, oxygen must be excluded from the solutions and the uranium(IV) concentration must be kept as low as the method of analysis permits. An inert gas such as helium, argon, or nitrogen should be passed through the solvent during the dissolution of the UO_2.

SUMMARY

The effect of ^{60}Co γ-radiation on aerated and deaerated phosphoric acid solutions of uranium(IV) oxide (UO_2) was studied as a function of temperature, concentration of UO_2, and radiation dose rate. The effect was measured in terms of the radiolytic yield of uranium(VI), $G_{U(VI)}$. For solutions of high initial UO_2 concentration, $G_{U(VI)}$ is largest for the aerated solutions at 25°; it is lowest for the deaerated solutions at 140°. The $G_{U(VI)}$ is lower for the solution of low initial UO_2 concentration than for any of the solutions of high initial UO_2 concentration. At the high starting UO_2 concentration, the initial $G_{U(VI)}$ values are always higher than the succeeding values; this effect is attributed to the depletion of oxygen originally present in the solution. Gamma radiation causes an error in the determination of the stoichiometry of UO_2; the error is a function of the radiation dose. This error can be minimized by excluding oxygen from solutions of UO_2 and by keeping the initial UO_2 concentration as low as possible.

RÉSUMÉ

On a examiné l'influence de la radiation gamma du cobalt-60 sur le dosage de l'uranium(VI), dans des solutions phosphoriques d'oxyde d'uranium(IV). L'effet a été mesuré en fonction du rendement radiolytique de l'uranium(VI), $G_{U(VI)}$. La radiation gamma cause une erreur dans la détermination de la stoéchiométrie de UO_2, fonction de la dose de radiation. Cette erreur peut être réduite au minimum en chassant l'oxygène des solutions de UO_2 et en maintenant la concentration initiale de UO_2 aussi basse que possible.

ZUSAMMENFASSUNG

Der Einfluss der ^{60}Co-γ-Strahlung auf belüftete und entlüftete Phosphorsäure-lösungen von Uran-(IV)-Oxid (UO_2) wurde als Funktion der Temperatur, der Konzen-

tration des UO_2 und der Strahlendosis untersucht, und durch die radiolytische Ausbeute G des Uran(VI) gemessen. Für Lösungen mit anfangs hoher UO_2-Konzentration ist G für die belüfteten Lösungen bei 25° am grössten, für die entlüfteten Lösungen bei 140° am niedrigsten. Für Lösungen mit anfangs kleiner UO_2-Konzentration ist G niedriger als für irgendeine der Lösungen mit anfangs hoher UO_2-Konzentration. Bei anfangs hoher UO_2-Konzentration war das G zu Beginn immer höher als bei den folgenden Werten. Dieser Einfluss wird der Entfernung des Sauerstoffs, der ursprünglich in der Lösung anwesend war, zugeschrieben. Die Gammastrahlung verursacht in der Bestimmung der Stöchiometrie des UO_2 einen Fehler, der von der Strahlendosis abhängig ist. Dieser Fehler kann durch Ausschluss des Sauerstoffs und durch eine möglichst niedrige Anfangskonzentration an UO_2 verringert werden.

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SEPARATION OF AMINES BY LIGAND EXCHANGE

PART III. A COMPARISON OF DIFFERENT CATION EXCHANGERS

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"Ligand Exchange" is the exchange of ligands coordinated to metal ions that in turn are bound to a cation-exchanging material. Thus, amine molecules may be substituted for ammonia molecules in complex ions such as $Ni(NH_3)_6^{2+}$ while the metal ions remain bound to the exchanger[1]. Applications of ligand exchange to the elution chromatography of amine mixtures have been explored in a preliminary way by LATTERELL AND WALTON[2,3]. The technique has many possibilities, for the nature of the coordinating metal ion can be varied as well as the nature of the exchanger matrix. This report describes a comparison of 3 different types of exchanger, each loaded with nickel(II) ions. A limited number of amines was used and aqueous ammonia was the eluant. Most of this work was done with amines labelled with carbon-14, which makes it possible to use very small amounts of adsorbate and hence to evaluate relative distribution coefficients and theoretical-plate heights. We have also been experimenting with a flowing differential refractometer for monitoring column effluents, and some of the data here reported were obtained with this instrument.

EXPERIMENTAL

Materials

Four amines labelled with carbon-14 were used: ethanolamine and dimethylamine, obtained from the New England Nuclear Co., and diethanolamine and *n*-butylamine, obtained from Nuclear Research Chemicals, Inc. They were diluted with water and inactive amines to give *ca.* 0.01 M stock solutions with activities of about 1 μc/ml. Volumes of 0.1–0.2 ml were placed on the columns. The inactive amines (which included benzylamine) were purified by distillation.

Three sulfonated polystyrene resins (Dowex-50) were used, with nominal cross-linkings of 2%, 4% and 8%. The 8% cross-linked resin was 200–400 mesh, and the others 50–100 mesh. A carboxylated resin (Bio-Rex 70), which is a cross-linked polymethacrylic acid, was used in 50–100 mesh size, and so was a zirconium phosphate cation exchanger. All these exchangers were obtained from the Bio-Rad Corporation, Richmond, California.

Preliminary tests were also made with a macroreticular sulfonated polystyrene resin, Amberlite XE-219, kindly supplied by the Rohm and Haas Company. This was unsuitable for our purpose because the nickel ions (and also copper(II) ions)

were displaced too readily by the ammonium ions in the aqueous ammonia solutions used as eluants.

Columns and analyzers

The columns had 10–12 mm internal diameter and contained 10–15 ml of exchanger in bulk volume. Flow rates were generally 0.3–0.4 ml/min.

In most of the tests the effluents were collected by a Vanguard fraction collector, Model 1000. Carbon-14 activity was counted by liquid scintillation using a Packard Tri-Carb spectrometer. Benzylamine was determined by absorbance at 255 mμ.

The data for 8% cross-linked sulfonated polystyrene resin were obtained with a flowing differential refractometer made by Waters Associates, Inc. This is designed specifically for liquid chromatography. It allows continuous recording of the difference in refractive index between influent and effluent, and it is extraordinarily sensitive. We have so far been unable to use the full sensitivity owing to random fluctuations in refractive index.

Nickel determination

The nickel content of the various exchangers was found by preparing small columns of exchanger in the same way as the columns used for ligand exchange, measuring their bulk volume, then eluting the nickel with 2 N hydrochloric acid and determining it by EDTA titration. The effluents from the columns used in ligand exchange were also analyzed for nickel to estimate the leakage of nickel that occurred as aqueous ammonia was passed. This was done photometrically using the dimethylglyoxime method of CLAASSEN AND BASTINGS[4].
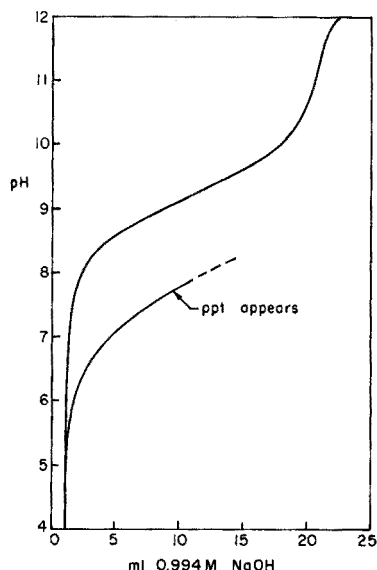
Fig. 1. Determination of formation constants for Ni(II) and diethanolamine. 100 ml 0.200 M diethanolammonium chloride plus slight excess HCl titrated as shown. Upper curve, solution is 0.80 M in KCl. Lower curve, solution is 0.50 M in KCl, 0.0980 M in NiCl$_2$.

Stability constant determination

To help interpret the data, attempts were made to determine the stabilities of the various nickel–amine complexes in aqueous solution by the glass-electrode titration method of CALVIN AND BJERRUM[5]. The complexes with dimethylamine and *n*-butylamine were so unstable by comparison with the protonated forms of these amines that nickel hydroxide precipitated almost immediately after the inflection point was reached in titrating mixtures of nickel(II), HL+ (L = ligand) and hydrochloric acid with sodium hydroxide. With diethanolamine, however, curves were obtained which allowed the first two stability constants to be determined (Fig. 1). The stability constants for the nickel(II)–ethanolamine association had been measured previously[6].

TABLE I

PEAK ELUTION VOLUMES

Exchanger and cross-linking	Ni content (mmol/ml)	Amine[a]	NH₃ concn. (M)	Elution volume[b]
Sulfonic, 2%	0.65	Dietol	0.22	3.6
			0.94	1.2
		Etol	0.44	8.9
			0.97	3.4
		Dimethyl	0.97	4.4
		Butyl	0.97	9.7
Sulfonic, 4%	0.87	Dietol	0.22	3.85
		Etol	0.88	3.60
		Dimethyl	0.88	4.32
		Butyl	0.88	10.6
Sulfonic, 8%	1.15	Dietol	1.20	0.96
		Etol	1.20	4.6
		Dimethyl	1.20	4.0
		Butyl	1.20	9.8
		Benzyl	1.95	9.0
Carboxylic	0.63	Dietol	0.70	1.51
		Etol	0.70	3.52
		Dimethyl	0.70	3.00
		Butyl	0.70	1.76
Zirconium phosphate	0.21	Dietol	0.94	4.00
		Etol	0.94	2.50
		Dimethyl	0.94	1.08
		Butyl	0.94	0.83
		Benzyl	2.48	0.50

[a] Dietol = diethanolamine; etol = ethanolamine; dimethyl = dimethylamine; butyl = *n*-butylamine; benzyl = benzylamine.
[b] Elution volumes are multiples of the bulk column volume, *i.e.* (volume passed to elute the peak)/(bulk column volume).

RESULTS AND DISCUSSION

A selection of the measured peak elution volumes are given in Table I. The elution volumes are expressed as multiples of the bulk column volume with no attempt made to allow for the void volume. It is hard to evaluate the effective void fraction of the columns, since dissolved uncomplexed amine penetrates the resin beads along with water and ammonia, but the minimum elution volumes obtained with very weakly bound amines and high ammonia concentrations suggest that the effective void fraction is 0.5–0.6, compared to 0.4 for uniform non-permeable spheres.

It is interesting to note that the order of elution of the 4 ^{14}C-labelled amines is different for different resins. Between low cross-linked sulfonated polystyrene and zirconium phosphate the order is exactly reversed. The stabilities of the nickel–amine complexes in water appear to have little to do with the elution order. The 2 amines for which reliable data are available have stability constants as follows: ethanolamine $K_1 = 950$ and $K_2 = 125$; diethanolamine $K_1 = 620$ and $K_2 = 45$. Ethanolamine should be held more strongly by the nickel-loaded exchangers than diethanolamine, and this is true for all exchangers except zirconium phosphate, but the ratio of the distribution constants varies from one exchanger to another and is considerably larger than the ratio of the K_1 values.

It seems that the affinity of the amines for the exchanger matrix is more
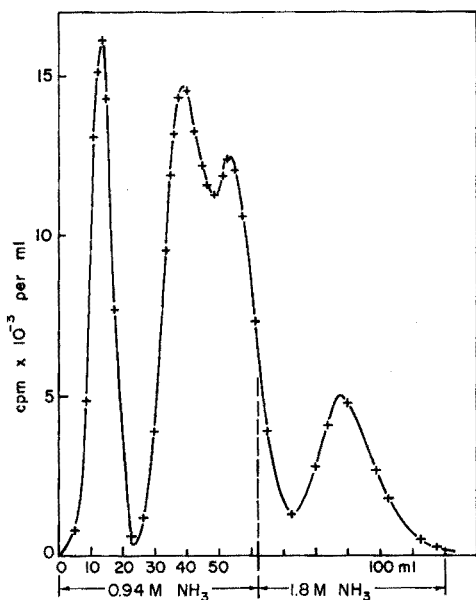
Fig. 2. Elution of amine mixture on Ni-sulfonic resin, 2% cross-linked, 50–100 mesh. Bulk column volume, 10.6 ml; diameter, 1.0 cm; flow rate, 0.3 ml/min. Order of elution: diethanolamine, ethanolamine, dimethylamine, butylamine.
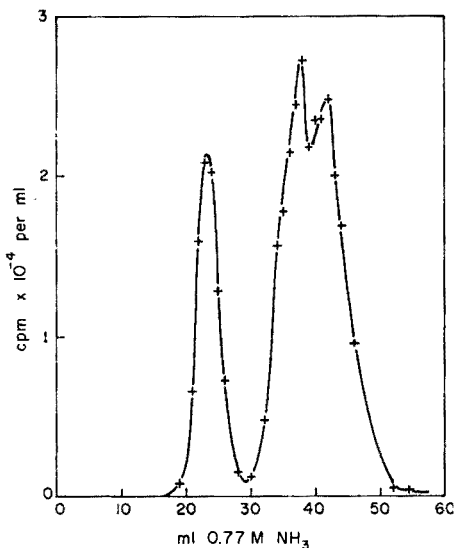
Fig. 3. Elution of amine mixture on Ni-carboxylic resin, 50–100 mesh. Bulk column volume, 14.0 ml; diameter, 1.0 cm; flow rate, 0.3 ml/min. Order of elution: butylamine, dimethylamine, ethanolamine.

important than their affinity for the nickel ions. This is very obvious with benzyl-amine, which is held strongly by a polystyrene-base resin but very weakly by zir-conium phosphate, and the same effect is noted with butylamine. This is held strong-ly by the polystyrene matrix but only weakly by the less carbonaceous, less "oleo-philic" matrix of the carboxylic resin, cross-linked polymethacrylic acid. Diethanol-amine is bound strongly by the extremely "hydrophilic" or polar matrix of zirconium phosphate. Whatever the reasons, the changes in selectivity orders between different exchangers are of obvious analytical interest. Elution curves for mixtures of amines on sulfonic and carboxylic resins are shown in Figs. 2 and 3.
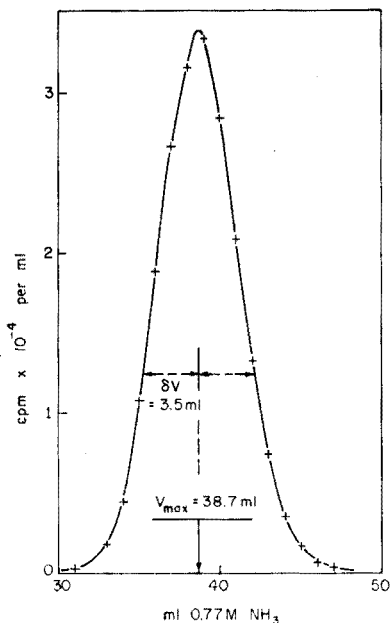
Fig. 4. Elution of dimethylamine on Ni-carboxylic resin, 50–100 mesh. Same column as in Fig. 3; flow rate, 0.3 ml/min.

Figure 4 shows the elution curve for a single amine on a column of carboxylic resin. It has almost ideal shape for a trace amount of adsorbate and permits evalua-tion of the number of theoretical plates in the column, using the relation[7]:

$$\frac{\delta V}{V_{max}} = \sqrt{\frac{2}{N}}$$

where N is the number of theoretical plates, δV is the half-width of the band at a concentration $1/2.718$ times the peak value, and V_{max} is the volume of eluant passed at the peak, corrected for the void column volume. Taking the void volume as one-half of the bulk volume, the theoretical-plate heights were calculated for different

TABLE II

THEORETICAL-PLATE HEIGHTS

Exchanger[a]	Amine	Elution volume (bulk column volumes)	Plate height (no.)
Sulfonic, 2%	Dimethyl	3.60	2.8
Carboxylic	Dimethyl	2.77	1.0
	Butyl	1.7	1.8
Zirconium phosphate	Dimethyl ·	3.2	5.5

[a] The first two exchangers were 50–100 mesh.

columns. The data are summarized in Table II; they show that the carboxylic resin gives the sharpest bands and hence the smallest plate heights, while zirconium phosphate gives the largest plate heights. The bands obtained with zirconium phosphate are, moreover, decidedly unsymmetrical. One concludes that the diffusion of these amines is fastest in the carboxylic resin (since the bead size was roughly the same as in the sulfonic resin) and slowest in the zirconium phosphate.

The concentrations of nickel and phosphate leached out of the exchangers by the ammonia solutions are shown in Table III. They are approximate only, and seem to get smaller as more of the nickel ions in the exchangers are replaced by ammonium ions.

TABLE III

NICKEL AND PHOSPHATE CONTENTS OF EFFLUENTS (moles/l)

Exchanger	Ammonia concn.	Ni concn.	PO_4^{3-} concn.
Sulfonic, 8%	1.1	$2.2 \cdot 10^{-4}$	—
Sulfonic, 4%	1.1	$1.2 \cdot 10^{-4}$	—
Carboxylic	0.7	$2 \cdot 10^{-4}$	—
Zr phosphate	0.9	$4 \cdot 10^{-5}$	$7 \cdot 10^{-6}$

SUMMARY

The elution behavior of 4 amines, ethanolamine, diethanolamine, dimethylamine and n-butylamine, was studied on 4 cation-exchange resins and zirconium phosphate, all loaded with nickel ions. Aqueous ammonia was used for elution. Different selectivity orders were found with exchangers of different types. The carboxylic cation-exchange resin gave the sharpest bands, but 2% cross-linked sulfonic resin gave the best separation of these amines.

RÉSUMÉ

L'élution de 4 amines (éthanolamine, diéthanolamine, diméthylamine et *n*-butylamine) a été examinée sur 4 résines échangeuses de cations et phosphate de zirconium, tous chargés d'ions nickel. L'ammoniaque a été utilisée pour l'élution. Les auteurs ont trouvé divers ordres de sélectivité avec les échangeurs de différents types. La résine carboxylique a donné les bandes les plus nettes; mais la résine sulfonique, à liaisons transversales (2%) a permis la meilleure séparation de ces amines.

ZUSAMMENFASSUNG

Das Elutionsverhalten von 4 Aminen, Äthanolamin, Diäthanolamin, Dimethylamin und *n*-Butylamin wurde an 4 Kationenaustauscherharzen und Zirkoniumphosphat untersucht, die mit Nickelionen beladen waren. Zur Elution wurde wässrige Ammoniaklösung benutzt. Die Austauscher zeigten verschiedene Selektivität. Das karbonsaure Kationenaustauscherharz ergab die schärfsten Banden, ein 2%iges vernetztes sulfonisches Harz ergab die beste Trennung der Amine.

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ANION–EXCHANGE BEHAVIOR OF RARE EARTHS, THORIUM, PROTACTINIUM AND URANIUM IN THIOCYANATE–CHLORIDE MEDIA

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The behavior of thorium, protactinium and uranium towards ion exchangers in mineral acid media is of particular interest since protactinium-233 is produced in irradiated thorium; it will become important to process protactinium in future reactors working on the thorium-232 and uranium-233 cycle. Many papers regarding the ion-exchange separation of rare earths–thorium, thorium–uranium, or rare earths–uranium have appeared recently. The anion-exchange behavior and chromatographic separation of rare earths, thorium, uranium, zirconium and scandium in sulfate media has been reported by HAMAGUCHI et al.[1]. The distribution coefficients of thorium, protactinium, uranium and other elements on an anion-exchange resin in sulfuric as well as in nitric and hydrochloric acids have been provided by BUNNEY et al.[2] and ICHIKAWA AND URUNO[3]. No results of separation are given. KORKISCH AND JANAUER[4] have summarized the extensive studies on the anion-exchange behavior of thorium and uranium in mixed solvents and the results of pertinent separation work done in their laboratory. The behavior of protactinium in the mixed solvents is not known. HULET et al.[5] have effected a group separation of the actinides from the lanthanides by anion exchange at an elevated temperature by column elution with lithium chloride solutions, 10 M or stronger. Hydrochloric acid seems to provide the most effective separation of thorium, protactinium and uranium with a strong base type resin[6]. However, thorium behaves like rare earths in this system so that their separation is difficult. In addition, removal of protactinium must be achieved at low hydrochloric acid concentration where hydrolysis of protactinium inevitably interferes unless hydrofluoric acid is substituted for hydrochloric acid[6]. The anion-exchange behavior of rare earths, thorium, protactinium and uranium in nitric acid has been separately investigated by several authors[2,3,7-14] and some results on their separation have been reported. Little is known about the possibility of achieving the actual column separation of protactinium in this system. HAMAGUCHI et al.[15] have described experiments on the anion exchange of scandium, rare earths and thorium from thiocyanate–chloride media. This work has been extended and detailed results are presented below on the ion exchange of protactinium and uranium from thiocyanate solution as well as chromatographic separation of rare earths, thorium, protactinium and uranium. A rapid and effective ion-exchange method for separating protactinium-233 from irradiated thorium is also presented.

EXPERIMENTAL

Apparatus and reagents

Stock solution of metals. An appropriate amount of each rare earth(III) oxide, 99.9% purity, was dissolved in a minimum amount of 6 M hydrochloric acid and evaporated to dryness. The residue was taken up in a definite volume of 0.5 M hydrochloric acid to give a solution which contained 1–5 mg of each rare earth metal per ml of the solution. Thorium(IV) nitrate and uranyl acetate were converted to chlorides by treating several times with hydrochloric acid to give the final stock solutions which contained 3 mg U and 2 mg Th per ml of 0.5 M hydrochloric acid, respectively. Carrier-free protactinium-233 was produced by irradiating approximately 50 mg of thorium(IV) nitrate tetrahydrate for 6 h in a TRIGA-II type reactor at a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec. Protactinium-233 thus produced was separated and purified from the matrix by a diisobutylketone extraction method[16]. A final solution of the protactinium(V) in 8 M hydrochloric acid–0.1 M hydrofluoric acid, was stored for further use. Before use an aliquot of the stock solution was evaporated to dryness along with a few drops of perchloric acid. The residue was treated with a small amount of hydrochloric acid, evaporated to dryness, and finally taken up in a thiocyanate solution of the desired concentration. All other chemicals were of analytical grade unless otherwise mentioned.

Determination of metal ions. Rare earths(III) and thorium(IV) were determined by the titration with 0.001 M EDTA using xylenol orange as indicator at pH 5 and 3, respectively. Uranium(VI) was colorimetrically determined with hydrogen peroxide as colorimetric reagent after ammonium thiocyanate had been destroyed with nitric acid. The radioactivity of ^{233}Pa (half-life 27.4 days, 0.313 MeV) was measured by a conventional standard well-type scintillation counter.

Ion-exchange column

Ion-exchange resin. Dowex 1-X8, thiocyanate form, 100–200 mesh, was purified as described in the previous paper[17]; 4.60 g of the dried resin was slurried with water and poured into a conventional ion-exchange column, i.d. 1.0 cm, pulled to a tip and plugged with a glass wool at the outlet. The resulting bed was about 10 cm long. Another much smaller column, 0.5 cm i.d., and bed height 3 cm long, was used for separating ^{233}Pa from irradiated thorium(IV) nitrate.

Procedure

Evaporate the sample solution containing rare earths(III), thorium(IV), protactinium(V) and uranium(VI) to near dryness, and take up the residue in approximately 10 ml of 1.5 M ammonium thiocyanate–0.5 M hydrochloric acid solution. Load the solution slowly on to the top of the column and remove the rare earths(III) by eluting with 80 ml of the same acid thiocyanate solution at a flow rate of 0.3–0.5 ml per min. Then elute thorium(IV) with 20 ml of 8 M hydrochloric acid; protactinium(V) and uranium(VI) remain adsorbed on the column. Remove protactinium-(V) by eluting with 20 ml of 8 M hydrochloric acid–0.001 M hydrofluoric acid mixture and subsequently uranium(VI) with 80 ml of 1 M perchloric acid solution. Determine each metal ion in the corresponding fraction as described above.

If either protactinium(V) or uranium(VI) is absent, the procedure is simpler: elute protactinium(V) with 100 ml of 2 M sulfuric acid–2 M ammonium sulfate solution after the consecutive separation of rare earths(III) and thorium(IV) as described above. More than 90% of protactinium(V) is usually recovered from the column in an early 50-ml fraction of the eluant. Elution of uranium(VI) is effected quantitatively by 150 ml of 1 M perchloric acid after the removal of rare earths(III) and thorium(IV).

CARRIER-FREE SEPARATION OF [233]Pa FROM NEUTRON IRRADIATED THORIUM(IV) NITRATE

Convert the irradiated thorium(IV) salt to a chloride form by treating with small portions of hydrochloric acid. Take up the residue in 4 ml of 0.2 M ammonium thiocyanate–0.5 M hydrochloric acid and load the solution on to the top of the small
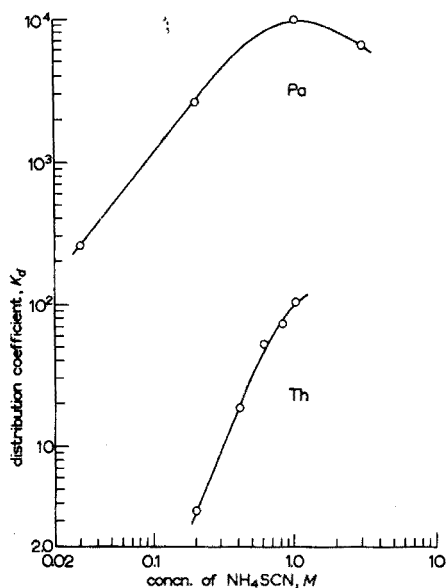
Fig. 1. A plot of the distribution coefficients of Pa(V) and Th(IV) on Dowex 1-X8 $vs.$ the concentration of ammonium thiocyanate; the concentration of hydrochloric acid was kept constant at 0.5 M.

column. Remove thorium(IV) by eluting with 20 ml of the same acid thiocyanate solution at a flow rate of 0.3 ml per min. Elute protactinium(V) with about 40 ml of 2 M sulfuric acid–2 M ammonium sulfate solution at the same flow rate.

RESULTS AND DISCUSSION

A batch equilibrium study showed that the weight distribution coefficient of uranium(VI) was largest, running to *ca.* 10^4, over the concentration range 0.1–3 M ammonium thiocyanate in 0.5 M hydrochloric acid, whereas yttrium(III) and rare earths(III) showed only slight adsorption from the same solution. The distribution coefficient values for protactinium(V) as a function of the concentration of ammonium thiocyanate are given in Fig. 1 along with those for thorium(IV) which are reproduced from previous work[15] for comparison. The K_d values were determined as described before[17]. From Fig. 1 we may expect a good separation of rare earths(III), thorium-(IV) and protactinium(V) or uranium(VI) in this system. Because thorium(IV) attains ion-exchange equilibrium slowly in the thiocyanate–chloride media, its adsorption is best conducted from a > 1 M thiocyanate solution in 0.5 M hydrochloric acid. The thiocyanate system provides a great advantage in handling protactinium(V) which forms a strong anionic complex with thiocyanate. In media other
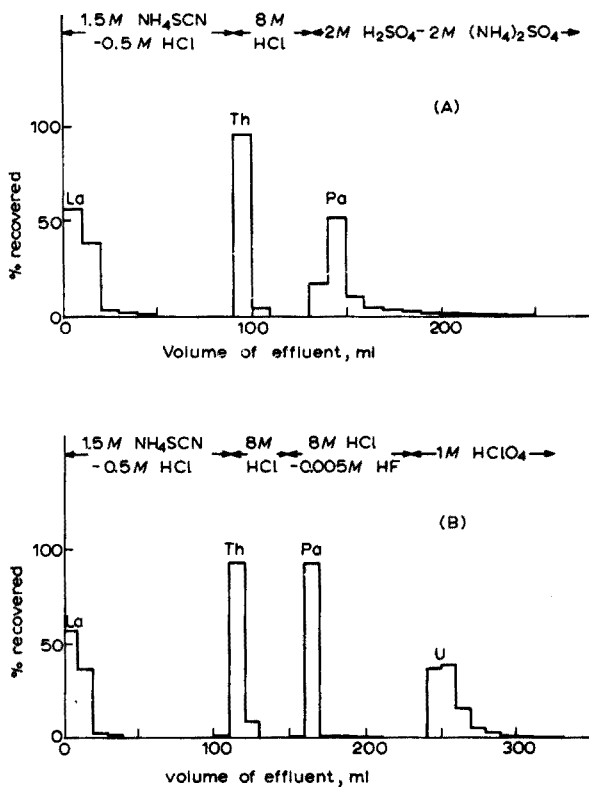
Fig. 2. Elution profile curves. (A) Separation of La(III), Th(IV) and Pa(V). La(III) 4.44 mg added, 4.42 mg found. Th(IV) 4.92 mg added, 5.10 mg found. Pa(V) 96,200 counts/min activity added, 98.6% recovered. (B) Separation of La(III), Th(IV), Pa(V) and U(VI). La(III) 22.2 mg added, 22.0 mg found. Th(IV) 4.92 mg added, 4.97 mg found. U(VI) 22.4 mg added, 22.1 mg found. Pa(V) 62,100 counts/min activity added, 102% recovered.

than sulfuric and hydrofluoric acids, protactinium(V) tends to be seriously hydrolyz-ed, so that a considerable loss of protactinium(V) occurs through hydrolytic adsorp-tion on the surface of a container. The thorium adsorbed on the resin from the thio-cyanate system can be desorbed simply by washing the column with hydrochloric acid. The choice of the concentration of hydrochloric acid is rather arbitrary. The higher the concentration of hydrochloric acid, the smaller the volume required to complete the elution.

In Fig. 2 typical elution profile curves are given for La(III)–Th(IV)–Pa(V) and La(III)–Th(IV)–Pa(V)–U(VI) mixtures. Where only the separation of rare earths(III) and thorium(IV) is concerned, a shorter column and lower concentration of ammonium thiocyanate suffice; adsorption on a 6.5-cm column from 1 M thio-cyanate–0.5 M hydrochloric acid solution and elution with the same solution permits the clear separation of thorium(IV) from large quantities of rare earths(III) and yttrium(III). In Table I results are given on the quantitative separation of thorium-(IV) from rare earths(III) and uranium(VI). Lanthanum(III), samarium(III) and lute-tium(III) were selected as representatives of the rare earths. The thiocyanate elution system has the distinctive feature that the actinide elements are strongly adsorbed

TABLE I

SEPARATION RESULTS

Th (mg)			Foreign metal (mg)		
Added	Found			Added	Found
1.64	1.68	Y(III)		4.68	4.72
	1.58	Y(III)		4.68	4.73[a]
	1.61	La(III)		4.44	4.41
	1.63	La(III)		4.44	4.56[a]
	1.65	La(III)		88.8	88.3
	1.61	Sm(III)		4.04	4.02
	1.68	Lu(III)		1.70	1.68
3.28	3.25	{La(III)		22.2	21.8
		{U(VI)		22.4	21.9
3.28	3.32	{Sm(III)		16.2	16.1
		{U(VI)		22.4	23.2

[a] Taken up on the column from 1 M NH₄SCN–0.5 M HCl solution. A shorter column, 6.5 cm long, employed.

on the resin, while the lanthanides are not. Thus the present method has a great advantage for group separation of the actinides and the lanthanides as well as for the intraactinide separation. It can also be conveniently applied to the preparation of carrier-free [233]Pa from neutron-irradiated thorium salts. When the concentration of ammonium thiocyanate is decreased to 0.2 M (the concentration of hydrochloric acid being kept constant at 0.5 M), the thorium(IV) actually passes through the column, while protactinium(V) still shows strong adsorption on the resin. This

behavior of thorium(IV) and protactinium(V) allows the use of a much smaller column (less than 0.5 g of resin) for their separation. Removal of protactinium(V) strongly retained on the column can be easily conducted by elution with 2 M sulfuric acid–2 M ammonium sulfate. About 80% of protactinium(V) is removed rapidly by an early 10-ml fraction of the eluant. The protactinium(V) shows some tailing, but the strong complexing action of sulfuric acid prevents the hydrolysis of protactinium(V) completely so that a quantitative overall recovery can be obtained. In this case rare earths(III) behave like thorium(IV) and therefore the method provides an excellent carrier-free preparation of protactinium free of rare earths and thorium.

SUMMARY

The anion exchange of rare earths(III), thorium(IV), protactinium(V) and uranium(VI) from thiocyanate–chloride media was investigated. The equilibrium distribution study showed that the rare earths(III) and yttrium(III) were not significantly adsorbed on a basic anion-exchange resin, while thorium(IV), protactinium(V) and uranium(VI) were strongly adsorbed. Adsorption from the thiocyanate–chloride solutions is in the order, U(VI) > Pa(V) > Th(IV). The separation of rare earths(III) or yttrium(III), thorium(IV), protactinium(V) and uranium(VI) was successfully accomplished by column elution in thiocyanate–chloride media. A rapid and effective ion-exchange method for separating protactinium-233 from irradiated thorium-(IV) is also presented.

RÉSUMÉ

Les auteurs ont examiné le comportement des terres rares, thorium(IV), protactinium(V) et uranium(VI) sur échangeur d'anions, en milieu thiocyanate-chlorure. L'adsorption des terres rares et de l'yttrium est insignifiante sur résine basique d'échange d'anions, tandis que celle du thorium(IV), du protactinium(V) et de l'uranium(VI) est forte. L'ordre d'adsorption est le suivant: U(VI) > Pa(V) > Th-(IV). La séparation terres rares ou yttrium(III), thorium(IV), protactinium(V) et uranium(VI) a été effectuée avec succès par élution sur colonne, en milieu thiocyanate-chlorure. On propose également une méthode rapide pour la séparation du protactinium-233 d'avec le thorium(IV) irradié.

ZUSAMMENFASSUNG

Der Anionenaustausch Seltener Erden, Thorium(IV), Protactinium(V) und Uran(VI) aus Thiocyanat–salzsaurer Lösung wurde untersucht. Die Untersuchung der Gleichgewichtsverteilung zeigte, dass die Seltenen Erden und das Yttrium an basischen Ionenaustauscherharzen nicht wesentlich, während das Thorium(IV), Protactinium(V) und Uran(VI) stark absorbiert werden. Die Absorption geschieht in der Reihenfolge U(VI) > Pa(V) > Th(IV). Die Trennung der Seltenen Erden oder des Yttriums, Thoriums, Protactiniums und Uran wurde erfolgreich ausgeführt. Eine schnelle und wirksame Ionenaustauschermethode zur Trennung von Protactinium-233 von bestrahltem Thorium(IV) wird ebenfalls angegeben.

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THERMODILATOMETRIC ANALYSIS: SOME CHEMICAL APPLICATIONS

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The dilatometry of solids is an old thermal technique. However, most of studies with this technique have been in the area of metallurgy, ceramics, coal, and glass industries. More recently, the technique has been applied to rubber and polymeric materials[1-7]. Studies of interest in inorganic chemistry include, among others, the following compounds: calcium hydroxide[8], alkali metal halides[9,10], sulfur[11,12], ammonium nitrate[11,12], ammonium halides[13] and sodium nitrate[14]. Generally speaking, any compound which has a *solid–solid* phase transition at either lower or elevated temperatures will undergo a volume change as well. Hence, the compound will show a pronounced change in the dilatometric curve at the temperature of the phase change. Since the dilatometric curve of a substance can be determined readily, the technique can be used to detect previously unknown phase transitions. If a compound undergoes a thermal decomposition reaction in which one or more of the products is volatile, marked deviations in the dilatometric curve will also be observed. Thus, from the above discussion, it is seen that dilatometry can be applied in a general manner to many chemical systems, much like other thermal methods. The application of dilatometry, or more precisely, thermodilatometric analysis, to several new chemical systems is given here, as well as an inexpensive automatic recording dilatometer.

EXPERIMENTAL

Dilatometer

The automatic dilatometer is illustrated in Figs. 1 and 2.

The furnace consisted of an aluminum cylinder, 40 mm × 70 mm. After wrapping the cylinder with several layers of asbestos paper, enough Nichrome heater wire was wound on it to give a total resistance of about 20 ohms. The heating element was then wrapped with several additional layers of 4-mm thick asbestos insulation. Holes were bored in the cylinder to accept a 5-mm diameter Pyrex glass sample tube and a 3-mm diameter two-holed ceramic insulator tube for the Chromel–Alumel thermocouple. The push rod consisted of a 3 mm × 90 mm ceramic rod, to one end of which was attached the LVDT (linear variable differential transformer) armature. The other end of the push rod rested on the surface of the sample contained in a 5 mm × 90 mm sample tube. The LVDT, Type 6208-A, obtained from Automatic Timing and Controls, Inc., King of Prussia, Pa., was held by a movable sliding
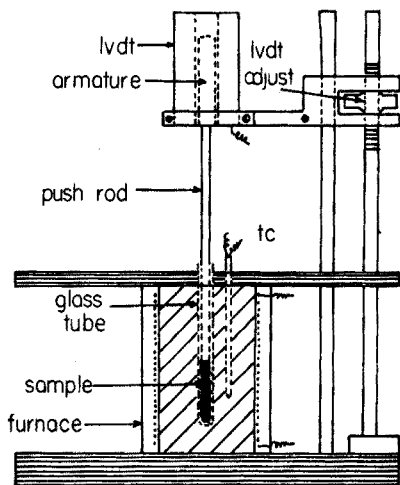
Fig. 1. Schematic diagram of dilatometer.
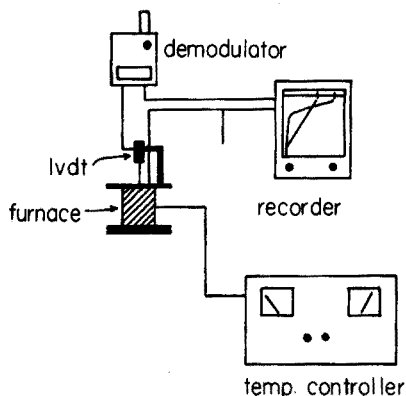
Fig. 2. Schematic diagram of complete dilatometric apparatus.

carriage. Hence, it was possible to adjust the position of the LVDT around the push-rod core.

The output voltage from the LVDT was converted to a DC voltage by the demodulator, Type 6101-CK, also obtained from Automatic Timing and Controls, Inc. The demodulator furnished the 12-V AC exciting voltage for the LVDT. Using this excitation voltage, a movement of ±0.001 in. of the LVDT core gave an output DC voltage of ±1.11 mV. The output of the LVDT was recorded on one channel of a two-channel Type G-22 Varian potentiometric strip-chart recorder. The furnace temperature, as detected by the thermocouple in the furnace block, was recorded on the other channel. For the LVDT channel, full scale corresponded to 5 mV, hence a change of approximately 0.005 in. could be recorded. Full scale on the temperature channel was either 250° or 500°.

The furnace temperature programmer was the same as previously described[15]. A heating rate of about 3°/min was employed.

Compounds

The compounds studied were the same as used previously; they included: $Co(py)_2Cl_2$[16]; KCH_3SO_4 and $KC_2H_5SO_4$[17]; $KAsF_6$, from Ozark-Mahoning Company, Tulsa, Oklahoma; $BaCl_2 \cdot 2H_2O$, reagent grade quality; and acetanilide, from the A. H. Thomas Company, Philadelphia, Pa., a melting point standard.

RESULTS AND DISCUSSION

The dilatometric curves of the compounds are given in Figs. 3 and 4.

To illustrate *solid–solid* phase transitions, $KAsF_6$, KCH_3SO_4, $KC_2H_5SO_4$, and $Co(py)_2Cl_2$ were studied by thermodilatometric analysis (TDA). A decomposition reaction, the dehydration of $BaCl_2 \cdot 2H_2O$, and a fusion reaction, the melting of acetanilide, were also examined by this technique.
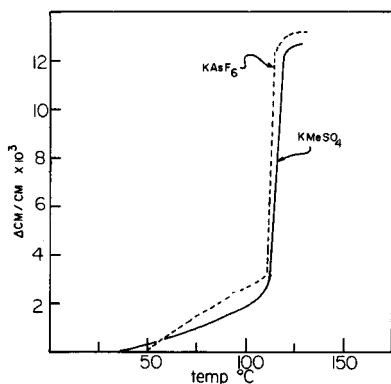
Fig. 3. TDA curves of some representative compounds.
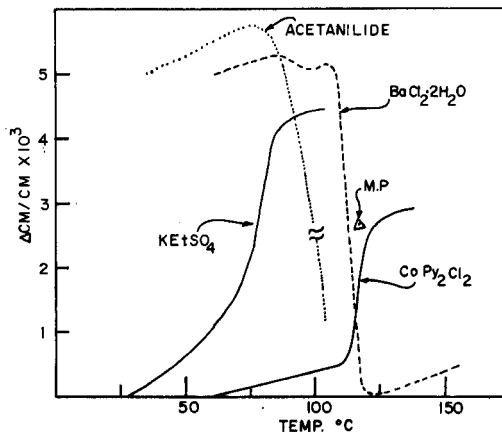
Fig. 4. TDA curves of some representative compounds.

Two compounds, KCH_3SO_4 and $KAsF_6$, exhibited very pronounced TDA changes at the solid phase transition. For KCH_3SO_4, the transition was from the monoclinic α-form to the monoclinic β-form[17]. From the DTA curve, the transition temperature was about 110°; in the TDA curve, the most rapid change took place from 110–117°, in good agreement with the DTA temperatures.

The crystal structure change for the $KAsF_6$ transition has not been determined as yet[18] but the transition temperature is similar to that for KCH_3SO_4, namely, from 110–115°.

The TDA curve for $KC_2H_5SO_4$ contained a rather large base-line change prior to the phase change. The most rapid change took place over the temperature range of 75–85°. This is somewhat lower than the 87° previously reported[17] for the $\alpha \rightarrow \beta$ transition, both forms of which are monoclinic.

The phase transition for $Co(py)_2Cl_2$ is the result of the change from octahedral (α-form) to tetrahedral (β-form) coordination for the cobalt(II) ion. As seen from the TDA curve, the transition began at about 110° and was completed by 125°. This is in agreement with the results found by other thermal methods such as DTA and dynamic reflectance spectroscopy[16].

To illustrate the application of TDA to a decomposition reaction, the TDA curve for the dehydration of $BaCl_2 \cdot 2H_2O$ is illustrated here. In the case of this compound, the TDA curve indicated a volume decrease rather than a volume increase as was observed with the previous compounds. The first volume decrease began at about 90°, followed by a more pronounced decrease beginning at about 105°. The dehydration reaction was completed by 120°. Following the dehydration reaction, the TDA curve increased due to the thermal expansion of the anhydrous barium chloride.

The fusion of acetanilide was also observed by TDA. The curve showed that the volume of the sample began to decrease starting at 75°, far below the reported melting point of 114–116°. This behavior was anticipated because of the sintering and softening of the compound and the weight of the push rod and armature assembly

on the sample. It appears very unlikely that TDA can be used to determine the precise melting points of organic compounds.

The applications of TDA illustrated here are only a small number of the many that may be investigated by this technique. The technique may be coupled with other thermal techniques or crystallographic methods to better solve chemical problems.

SUMMARY

Some applications of thermodilatometric analysis are discussed. The technique may be used for the determination of *solid—solid* phase transitions and decomposition reactions. An inexpensive recording dilatometer is described.

RÉSUMÉ

On décrit quelques applications d'analyse thermodilatométrique. Cette technique peut être utilisée pour la détermination de transitions de phase solide—solide et réactions de décomposition. Un dilatomètre enregistreur peu coûteux est décrit.

ZUSAMMENFASSUNG

Es werden einige Anwendungen der thermodilatometrischen Analyse diskutiert. Die Technik kann zur Bestimmung von Phasenübergängen zwischen Feststoffen und von Zersetzungsreaktionen benutzt werden. Ein billiges registrierendes Dilatometer wird beschrieben.

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THERMOGRAVIMETRIC CHARACTERISTICS OF SOME SALTS OF VIOLURIC ACID AND 1,3-DIMETHYLVIOLURIC ACID

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The thermogravimetric characteristics of violuric acid (5-isonitrosobarbituric) and 1,3-dimethylvioluric acid (1,3-dimethyl-5-isonitrosobarbituric acid) (DMVA) have been described previously[1]. The sodium and potassium salts of violuric and 1,3-dimethylvioluric acids have been prepared as solids by methods previously described[3]; their thermogravimetric characteristics in air and helium atmospheres are described in the present paper.

EXPERIMENTAL

Reagents

    Potassium dimethylviolurate (KDMV) was prepared by mixing a methanolic solution of potassium methoxide in excess with a methanolic solution of DMVA. The bright blue precipitate was collected on a filter and was washed 3 times with absolute methanol. This procedure of filtration and washing was used in the preparation of each of the salts.

    Monopotassium violurate (KV) was prepared by adding a solution of violuric acid (VA) in 95% ethanol to a filtered 95% ethanolic solution of potassium hydroxide until the solution just became acid. A blue precipitate formed.

    Dipotassium violurate (K$_2$V) was prepared by the addition of alcoholic potassium hydroxide to an alcoholic VA solution until the solution became basic. The solution color changed from blue to red and the precipitate formed was red.

    Sodium dimethylviolurate (NaDMV), monosodium violurate (NaV), and disodium violurate (Na$_2$V) were prepared by similar procedures except that sodium ethoxide in absolute ethanol was used as the sodium solution.

    The violuric acid used for these preparations was purchased from Eastman Kodak Company. It was recrystallized from aqueous ethanol, m.p. 222–224° (dec.).

    The dimethylvioluric acid was synthesized from caffeine by the method of BILTZ[2]. It was recrystallized from aqueous ethanol and had a melting point of 141–141.5°.

Apparatus

    An ADAMEL recording thermobalance (Chevenard system) was used for the thermolyses in air and a Stanton thermobalance for the decompositions in helium.

Procedure

The thermolytic reactions in air were run with samples varying in weight from 46.0 to 122.2 mg, as recorded on the various figures. No. 000 porcelain crucibles of 6 ml capacity were used as the sample containers. The rate of heating was 65°/h in a non-circulating air atmosphere.

The thermolytic reactions in helium were obtained with samples varying in weight from 280 to 500 mg, also indicated on the figures. The sample container in this case was a vitreosil low-form crucible of approximately 3 ml capacity. The rate of heating was 10°F/min $\simeq$ 5.5°/min and the rate of helium flow was 310 ml/min.

RESULTS

The curves for the weight loss during the thermolyses of potassium violurate and sodium violurate in air are shown in Fig. 1. Both salts were air-dried on the filter, desiccated over calcium chloride, and then pyrolysed.

KV lost weight corresponding to 1.5 molecules of water between 70 and 120° to form the anhydrous salt which was stable to 200°. Above this temperature, decomposition was fast with a slight inflection at a weight corresponding to K_2CO_3 and with the residue at 1050° having the weight of K_2O.
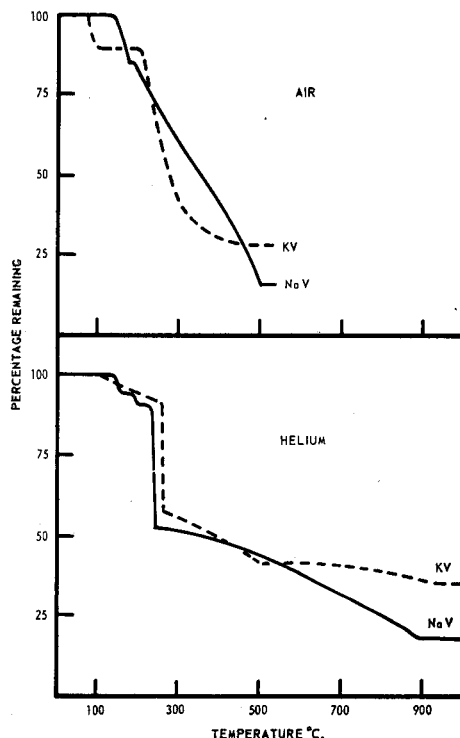
Fig. 1. Thermolysis curves. KV, monopotassium violurate in air, 49.8 mg; NaV, monosodium violurate in air, 122.2 mg; KV, monopotassium violurate in helium, 132 mg; NaV, monosodium violurate in helium, 293 mg.

The corresponding NaV began to lose weight only above 120°. After a loss equal to 1.5 molecules of water, it yielded the anhydrous compound that was stable from 170 to 180°. A nearly linear decomposition followed to 500° when a horizontal break in the curve occurred yielding a residue of 15.5% by weight indicating a composition of Na$_2$O.

The curves for the thermolyses of dipotassium violurate and disodium violurate are shown in Fig. 2.
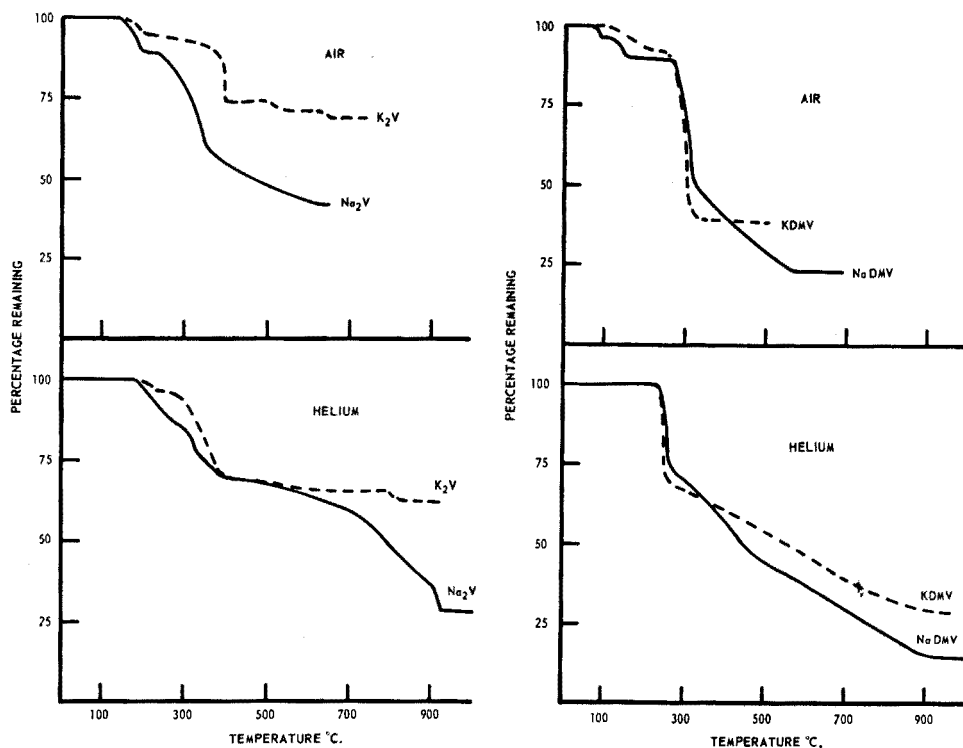
Fig. 2. Thermolysis curves. K$_2$V, dipotassium violurate in air, 46.0 mg; Na$_2$V, disodium violurate in air, 63.0 mg; K$_2$V, dipotassium violurate in helium, 500 mg; Na$_2$V, disodium violurate in helium, 500 mg.

Fig. 3. Thermolysis curves. KDMV, potassium 1,3-dimethylviolurate in air, 79.9 mg; NaDMV, sodium 1,3-dimethylviolurate in air, 63.7 mg; KDMV, potassium 1,3-dimethylviolurate in helium, 500 mg; NaDMV, sodium 1,3-dimethylviolurate in helium, 170 mg.

K$_2$V formed a hydrate that lost weight slowly from 100 to 170° and then rapidly to 190°. The loss in weight corresponded to one molecule of water. The anhydrous compound, which formed at 190°, was not stable and lost weight slowly to 380° then rapidly to 400°. A stable intermediary was formed in the range 400–490°. Further stepwise decomposition occurred to 740° where the weight of the residue was 62.2%, apparently mostly K$_2$CO$_3$. The X-ray pattern of this residue was similar to the K$_2$CO$_3$ pattern (Table I).

Na$_2$V lost weight in air between 150 and 190°, corresponding to slightly more than one molecule of water, and then decomposed rapidly. A break occurred in the curve at 350°. At 604°, the end of the determination, the residue weight was 42% of the original, which is less than the 48% required for Na$_2$CO$_3$, indicating some decomposition to Na$_2$O.

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF THE RESIDUE OF THE THERMOLYSIS OF DIPOTASSIUM VIOLURATE AT 740° [a]

Residue pattern		K$_2$CO$_3$ pattern		Residue pattern		K$_2$CO$_3$ pattern	
d	I/I$_0$	d	I/I$_0$	d	I/I$_0$	d	I/I$_0$
6.9	08	7.0	02	2.10	25	2.09	14
		5.5	02	1.99	08	2.00	10
4.9	08			1.86	08	1.85	08
3.38	26	3.39	06	1.77	05	1.77	03
2.96	46	2.97	16	1.71	05	1.70	03
2.81	100			1.69	05		
		2.80	100			1.67	02
2.78	94			1.61	05	1.61	03
2.61	85	2.61	32	1.55	02	1.55	02
2.38	31	2.37	16	1.41	03	1.41	05
2.31	23	2.31	08	1.36	03	1.35	02
2.19	08	2.18	06	1.31	03	1.31	02

[a] All the experimental d values were within ± 0.01.

The thermolysis curves of potassium dimethylviolurate and sodium dimethylviolurate are shown in Fig. 3.

KDMV also formed a monohydrate that was stable to 100°. A slow dehydration followed to 200° yielding the anhydrous compound stable from 200 to 250°. A fast decomposition occurred between 250° and 315°, followed by a slow decomposition from 315° to the end of the run at 420°. The percentage weight of the residue at 420° was approaching the percentage weight of K$_2$CO$_3$, but the decomposition was not complete at that temperature.

NaDMV lost weight in two steps at low temperatures. The first loss occurred from 70° to 85° and corresponded to 0.5 molecule of water. The second occurred between 115° and 145° and corresponded to one molecule of water. The anhydrous compound was quite stable to 270°, then an abrupt loss in weight occurred to 320°. From 320° to 570° there was a slow loss in weight. The percentage weight remaining corresponded to Na$_2$CO$_3$.

The thermogravimetric analyses of these salts were repeated in helium after drying at 110° for 24 h. In most cases the color of the salts changed markedly upon drying. For example, the colors of the hydrated salts were various shades of red and violet whereas the dehydrated salts were blue, pink and lavender. NaV alone showed little or no change, remaining a red-purple color. KV changed from red-blue to a pastel blue. K$_2$V and Na$_2$V were red; the first changed to pale pink, the latter to pale purple. KDMV was red-violet and changed to purple. NaDMV was red and changed

to lavender. With the exception of NaV and K_2V, crystals that were dehydrated changed from a red hue to a blue coloration.

The curves for the weight loss during the thermolysis of KV and NaV in helium are shown in Fig. 1.

KV showed no weight loss to 100°. At that temperature it began a slow 7% loss that ended abruptly at about 265° with a very rapid, almost explosive, weight loss with 57% of the original weight remaining. A slow weight loss occurred to about 930° leaving a final residue of constant weight equivalent to 36.5% of the original sample. This experiment was repeated with essentially the same results except the first loss was rapid but not explosive; the final weight was 34.5%. The amount required for the original material to go to K_2CO_3 is 35.4%.

NaV showed no decomposition to 135° at which point it lost about 10% in weight in two steps to 227°. At this temperature a very rapid decomposition occurred leaving a residue of 52%. Even though this decomposition was extremely rapid, there was no evidence of material loss through eruption from the crucible. After the vigorous reaction at 227°, a slow decomposition ensued with constancy of weight at 900°. A residue of 18.9% was left which indicated formation of Na_2O.

The pyrolysis of K_2V in helium is recorded in Fig. 2. There was an explosive decomposition at 209° when the material had been air-dried at room temperature before analysis. When it had been dried 24 h at 105°, a very rapid and vigorous decomposition occurred at 290° with some loss of material from the crucible. However, upon further drying over P_2O_5 in a desiccator the decomposition reaction occurred more slowly. At 390° the material had lost 30% by weight. It then remained relatively stable to 500° when it slowly lost weight to 616°, the weight then remaining constant at 65.7% of the original. Air was passed into the furnace at 780° whereupon the residue changed to 62.2% of the original. The residue required for conversion to K_2CO_3 is 59.2% by weight of the original.

The reactions of Na_2V in helium are illustrated in Fig. 2. Less than a 1% loss was registered to 195°, at which point gradual step-wise losses occurred to 950°. The residue assumed a constant weight at this temperature. With the exception of a nearly horizontal plateau at about 70% in the temperature range 450–550°, the weight loss was continuous at a moderate rate. The final weight per cent was 27.2% which is slightly less than the 30.8% required for the formation of Na_2O. If the weight loss at 200° was due to solvent not removed by oven-drying or if a small amount of the material was lost by sublimation, then the residue would be less than that required.

The reactions of KDMV in helium are illustrated in Fig. 3. The material underwent an explosive weight loss at about 230° that was violent enough to eject material from the crucible. A correction factor was applied to the weight recordings after the explosion. On this basis 29.0% of the original weight remained as residue. The formation of K_2O required 21.1% while the formation of K_2CO_3 required 31.0%.

The reactions of NaDMV are also shown in Fig. 3. The material behaved very similarly to KDMV in that an extremely rapid decomposition occurred at about 250°. However, decomposition was not explosive enough to throw sample from the crucible. Decomposition giving a linear weight loss occurred from 280° to about 420°. This was followed by a slow decomposition to about 900° where the residue had a constant weight. The per cent by weight of residue remaining was 15.0%. The formation of Na_2O required 14.6% by weight of residue.

DISCUSSION

The sodium and potassium salts of both violuric acid and 1,3-dimethylvioluric acid contain solvents of crystallization. The color of the violuric and dimethylvioluric salts depended on the solvation of the solid. The anhydrous salts decomposed in air below 270° in all cases; in helium they decomposed vigorously in the temperature range 210–265° except for Na_2V which decomposed much more slowly.

Judged on a weight basis alone the salts tended to decompose in air to a constant weight corresponding to a carbonate composition, with the exception of NaV and KV. The potassium salts tended to stabilize at a weight that was equivalent to K_2CO_3 in the range 400–700°. However, when KV was heated to 1100°, the residue weight corresponded approximately to K_2O.

The same samples tended to decompose to different constant weight percentages in inert atmospheres. The sodium salts yielded residues that had weights corresponding to Na_2O. However, the potassium salts decomposed to constant weights corresponding to K_2CO_3 in the temperature range 940–960°.

The above results also show that in the case of 1,3-dimethylvioluric acid, the sodium and potassium salts were formed in 1:1 ratios. The violuric acids formed two salts in stoichiometric quantities with monovalent metals. The ratios were 1:1 and 2:1, metal to acid respectively.

SUMMARY

The thermolysis curves of the various salts of violuric acid and 1,3-dimethylvioluric acid with sodium and potassium are described. These salts form hydrates in all cases. 1,3-Dimethylvioluric acid forms 1:1 salts with sodium or potassium; violuric acid may form either 1:1 or 1:2 salts with these metals.

RÉSUMÉ

Les auteurs décrivent les courbes de thermolyse des sels de sodium et de potassium de l'acide violurique et de l'acide diméthyl-1,3-violurique. L'acide violurique forme deux sels avec les métaux alcalins (mono- et di-). Dans chaque cas, ces sels forment des hydrates (1–1.5 H_2O). L'acide diméthyl-1,3-violurique forme des sels dans le rapport 1:1 avec le sodium et le potassium; l'acide violurique forme des sels dans le rapport 1:1 ou 1:2 avec le sodium et le potassium.

ZUSAMMENFASSUNG

Es werden die Thermolysekurven verschiedener Salze der Violursäure und der 1,3-Dimethylviolursäure mit Natrium und Kalium beschrieben. Die Salze bilden in allen Fällen Hydrate. 1,3-Dimethylviolursäure bildet 1:1-Salze mit Natrium oder Kalium; Violursäure bildet entweder 1:1- oder 1:2-Salze mit diesen Metallen.

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QUANTITATIVE ANALYSIS OF SOLID MIXTURES BY DIFFUSE REFLECTANCE MEASUREMENTS

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The factors affecting the diffuse reflectance spectrum of an absorbing substance diluted 10^3- to 10^5-fold with a non-absorbing standard have been investigated by KORTÜM and co-workers in a series of papers, the main results of which have been recently summarized[1]. It has been shown that when certain variables such as grainsize are kept constant the KUBELKA–MUNK function, $(1 - R)^2/2R$ (R = diffuse reflectance relative to the pure standard), is proportional to the mole fraction of absorbing substance provided that the absorbing substance, which is adsorbed on the standard, does not form a complete monomolecular layer; as a result the KUBELKA–MUNK function is proportional to the mole fraction only when the value of the latter is less than 10^{-3}. The results have been applied to the determination of concentration by diffuse reflectance in evaluating paper chromatograms[2], as well as to solid mixtures. FISCHER AND VRÁTNÝ found[3] that the plot of the logarithm percentage weight of iron(III) oxide in magnesium carbonate against (100 − % reflectance) was linear in the range 20–60% reflectance; these authors state that mixtures containing more than one coloured component are quite complex and that no analytically useful means of interpreting the reflectance readings was found. In a similar study, LERMOND AND ROGERS investigated[4] the possibility of using reflectance measurements for the analysis of solid mixtures, their measurements being made mainly on mixtures of iron(III) oxide and barium sulphate; linear relationships were usually obtained by plotting $\log C$ vs. $(1 - R)^2/2R$ or by plotting $(R - R_m)$ vs. $C^{\frac{1}{2}}$ or $(C/1 - C)^{\frac{1}{2}}$ where C is the concentration, R is the reflectance and R_m is the reflectance of the sample having the highest concentration of absorbing component in the series; because of the dependence of reflectance on particle size, the most reliable measurements were expected to result with samples having the same particle size distribution. The object of the present work was to investigate the effect of experimental variables on the reflectance of a wider variety of mechanical (rather than adsorbate–adsorbent) mixtures in order to develop a general method for the analysis of two-component mixtures and to extend reflectance analysis to three-component mixtures.

EXPERIMENTAL

A Unicam SP 500 spectrophotometer fitted with a standard diffuse reflectance attachment was used to measure reflectances in the range 270–1000 mμ. Solids

absorbing in this region were lead monoxide, which has an absorption maximum, as measured by diffuse reflectance, at 515 mμ, silver iodide, absorption maximum 425 mμ, and zinc oxide, absorption maximum 368 mμ; as solids not absorbing in this region magnesium oxide and silicic acid were used. Mixtures were prepared by mechanical shaking of components passing 200 B.S., or finer, mesh; the compositions of all mixtures are expressed as percentages by weight. Matt sample surfaces were prepared by arranging the sample in a heap in the sample-holder of the reflectance attachment and using a rubber bung to remove excess material and to level the surface, taking care not to compress the sample in the holder. All reflectances were measured relative to the non-absorbing material in the particular mixture which was taken as 100% reflectance. Percentage reflectance has been shown to be dependent on particle size[5]. It was found, however, that the expected variation of reflectance with degree of grinding could be eliminated by hand-grinding of the mixtures in an agate mortar for about 15 min; grinding for longer periods resulted in no further change in reflectance. This is illustrated in Table I for a mixture of silver iodide and magnesium oxide containing

TABLE I

EFFECT OF PROLONGED GRINDING ON REFLECTANCE OF A SILVER IODIDE–MAGNESIUM OXIDE MIXTURE

Total grinding time (min)	0	2	5	8	10	12	14	16	20	30
% reflectance at 425 mμ	69.5	49.8	30.9	27.0	23.6	21.7	23.5	22.9	23.2	23.4

9.0% silver iodide originally passing 300 mesh. During this work and work to be described elsewhere, reflectances were measured for several different compositions of each of 20 different mixtures; in every case grinding for not longer than 15 min resulted in a limiting value of reflectance. The reference substance was always ground for the same length of time as the test material so that its packing characteristics would be similar.

The effect of unavoidable variations in surface preparation on the measured reflectance of a given mixture was investigated. It was found that variations in the standard surface affected the reflectance of the test sample equally at all wavelengths. Hence the effect of such variations was reduced for all substances with a non-absorbing region in the range 270–1000 mμ by expressing reflectances in an absorbing region relative to the reflectance in the region of no absorption. For 3.0% zinc oxide–magnesium oxide mixtures, the standard deviation of the reflectance measured as described was 2.4%. To reduce the effect of variations in the preparation of the sample surface, the reflectance of a given sample was always measured usually for 4, and never for less than 3, separately prepared surfaces and the mean value used.

RESULTS

The variation of reflectance, at the wavelength of maximum absorption, with concentration of the absorbing component was investigated for 5 two-component

mixtures. As shown in Fig. 1, for all the mixtures investigated a linear relationship was obtained by plotting $\log A/R$ (R = percentage reflectance; $A = 100 - R$) against $\log W$ (W is the percentage by weight of the absorbing component). The slope of the line was, within experimental error, independent of the particular mixture and
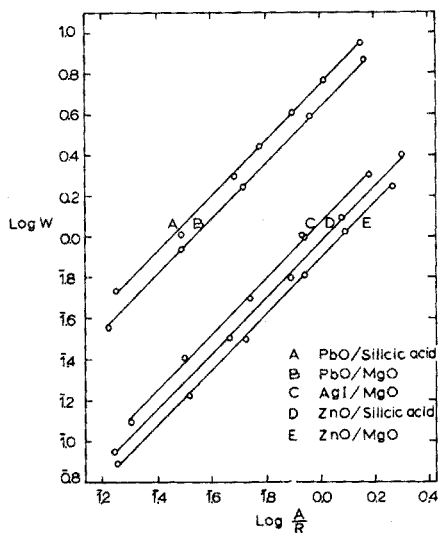

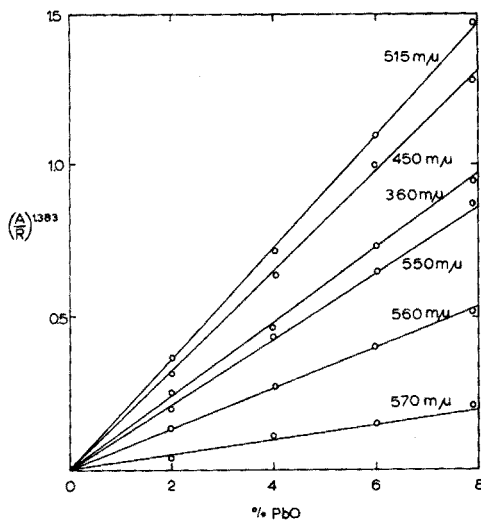Fig. 1. Plot of $\log (A/R)$ vs. $\log W$ for some two-component mixtures at the wavelength of maximum absorption.

Fig. 2. Plot of $(A/R)^{1.383}$ vs. W for lead monoxide–silicic acid mixtures at a number of wavelengths.

the mean value of the slope was 1.383 so that the results may be represented by the equation $W = K (A/R)^{1.383}$ where the value of K depends on the particular mixture. This equation holds when the measured reflectance is in the range 30–70%; outside this range a small error in reflectance results in a comparatively large error in $(A/R)^{1.383}$ so that the validity of the equation cannot be assessed. Of the 20 investigated mixtures containing different components, only zinc oxide–aluminium oxide mixtures did not conform to the equation; the results for these mixtures are given below. The quantity $(A/R)^{1.383}$ is subsequently termed the "absorption function".

It was found that the linear relationship between the absorption function and concentration held at all wavelengths and not only at the wavelength of maximum absorption. Figure 2 shows the results for 4 different concentrations of lead monoxide in silicic acid at a number of wavelengths.

These results were applied to the quantitative analysis of two-component mixtures by preparing a calibration plot of absorption function vs. concentration for the particular mixture and interpolating the measured absorption function of the sample of unknown concentration. The results for a number of independently prepared zinc oxide–magnesium oxide mixtures are shown in Table II. The standard deviation from the actual concentration was 6.4%.

TABLE II

RESULTS OF ANALYSIS OF ZINC OXIDE–MAGNESIUM OXIDE MIXTURES

% ZnO	Actual	0.14	0.59	0.70	0.73	0.81	1.12	1.18
	Found	0.13	0.56	0.70	0.77	0.83	1.23	1.11

TABLE III

EFFECT OF THERMAL TREATMENT OF COPPER(II) OXIDE ON ABSORPTION FUNCTION FOR 3.6% COPPER(II) OXIDE–MAGNESIUM OXIDE MIXTURES

Preheating temperature (°)	$(A/R)^{1.383}$	
	650 mμ	750 mμ
650	7.00	4.20
850	3.40	2.02
950	0.61	0.75
1000	0.36	0.42

Analysis by diffuse reflectance is applicable to poorly crystallized materials, which could not be determined by X-ray powder diffraction, as well as to materials of larger crystallite size. For example, it was found that there were no lines in the powder diffraction photograph of aluminium molybdate but this substance could be determined in mixtures with molybdenum trioxide and magnesium oxide by diffuse reflectance measurements.

For some substances the reflectance proved to be dependent on the previous history of the particular sample. For example, the effect of pre-heating copper(II) oxide to various temperatures for 24 h on the value of the absorption function at two wavelengths is shown in Table III.

The following deviations from the behaviour described above were observed for zinc oxide–aluminium oxide mixtures: (1) mixtures ground to a limiting reflectance absorbed less strongly than mixtures of larger particle size; (2) the variation of absorption with concentration did not conform to the equation $W = K (A/R)^{1.383}$ but was in accord with the KUBELKA–MUNK function as shown in Fig. 3; (3) in mixtures with a variety of non-absorbing substances zinc oxide began to absorb between 410 and 425 mμ but in zinc oxide–aluminium oxide mixtures there was a bathochromic shift to 450 mμ. This behaviour corresponds to that observed in mixtures where one component is adsorbed on the other[1] and suggests that the zinc oxide is adsorbed on the aluminium oxide. Thus in general the proposed analytical method may not apply when there is physical interaction between the components of the mixture.

For a three-component mixture, the region of no absorption is in general followed at shorter wavelengths by a region in which only one component absorbs and this region is followed by a region in which both the first and a second component absorb; determination of the second component by reflectance measurements in this region requires that the absorptions of the two components be additive. To test for additivity, the reflectance spectra of 3 lead monoxide–zinc oxide–silicic acid mixtures of different concentrations were measured and for each mixture, at all wavelengths the

absorption function was found to be additive, as illustrated for one of the mixtures in Fig. 4.

The validity of the analytical method for three-component mixtures was investigated by measurements on lead monoxide–zinc oxide–silicic acid mixtures. Calibration curves were first prepared for lead monoxide–silicic acid mixtures at
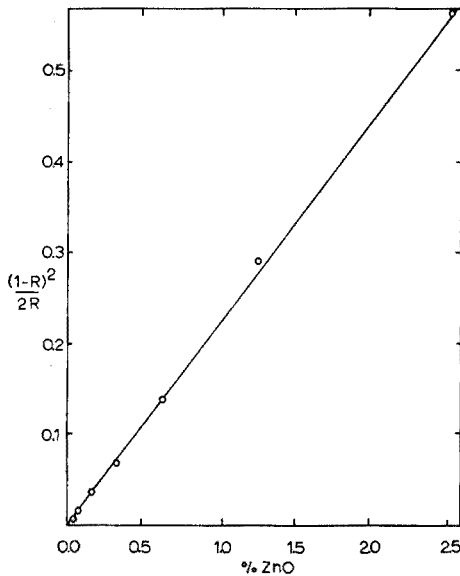
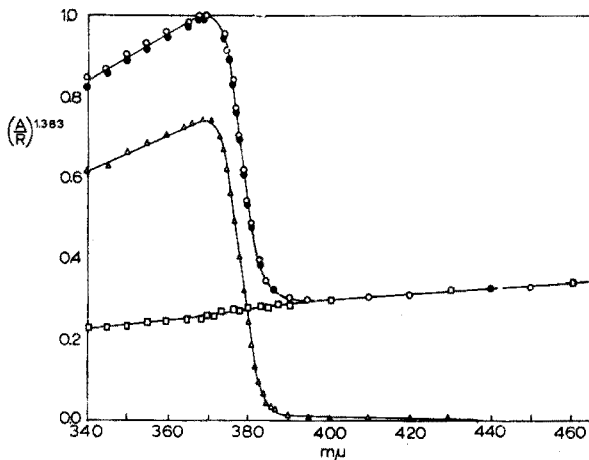Fig. 3. KUBELKA–MUNK plot for zinc oxide–aluminium oxide mixtures at 368 mμ.

Fig. 4. Additivity of absorption function for zinc oxide–lead monoxide–silicic acid mixture. □ spectrum of 2.02% PbO–silicic acid; △ spectrum of 0.64% ZnO–silicic acid; ○ sum of spectra of 2.02% PbO–silicic acid and 0.64% zinc oxide–silicic acid; ● observed spectrum of 2.02% PbO–0.64% ZnO–silicic acid.

515 mμ and for zinc oxide–silicic acid mixtures at 368 mμ. Also the ratio of the ab-sorption function at 368 mμ to that at 515 mμ was determined from measurements on several lead monoxide–silicic acid mixtures; the mean value was 0.689. To analyse a lead monoxide–zinc oxide–silicic acid mixture, the absorption function was determin-ed at 515 mμ, whence the percentage of lead monoxide was derived, and at 368 mμ; in the latter value, allowance was made for the absorption due to lead monoxide by subtracting 0.689 times the value of the absorption function at 515 mμ thus giving the value of the absorption function at 368 mμ due to zinc oxide alone. The results obtained are shown in Table IV. The standard deviation from the actual percentage was 6.6% for zinc oxide and 5.2% for the lead monoxide.

TABLE IV

RESULTS OF ANALYSIS OF LEAD MONOXIDE–ZINC OXIDE–SILICIC ACID MIXTURES

Mixture	% PbO		% ZnO	
	Actual	Found	Actual	Found
1	6.98	7.15	3.05	3.26
2	5.93	5.69	2.60	2.62
3	4.95	5.22	2.16	2.29
4	3.94	4.08	1.72	1.87
5	2.90	2.82	1.27	1.28
6	1.91	1.99	0.83	0.86
7	7.65	8.24	1.54	1.71
8	3.86	4.10	1.48	1.58
9	3.20	2.98	1.51	1.49
10	2.02	2.11	1.49	1.62
11	0.98	1.01	1.49	1.55
12	0.54	0.56	1.45	1.53

CONCLUSIONS

Advantages of the method described are the accuracy obtainable in the anal-ysis of two- and three-component mixtures and its applicability to poorly crystallized materials. Since reflectance may depend on the previous history of the particular sample the method is most useful in applications where the calibration curves can be prepared from the same samples as are present in the mixture to be analysed. The method would be less useful in the analysis of an unknown mixture; in such a case the components present might be identified by infrared spectroscopy or by X-ray powder diffraction and the mixture then analysed by diffuse reflectance measure-ments, but the results would be of varying reliability, because of difficulties in prepar-ing calibration curves.

SUMMARY

The factors affecting the reflectance of an absorbing substance mixed with material not absorbing at the wavelength of measurement were investigated and it was found that the effect of particle size could be eliminated by prolonged grinding. It is shown that the percentage by weight of the absorbing substance is directly proportional to the quantity $(A/R)^{1.383}$ ($R =$ percentage reflectance; $A = 100 - R$) and that this quantity is additive for 2 absorbing substances. A method is developed for the accurate determination of low concentrations of one and two absorbing substances mixed with non-absorbing material. The method is applicable to poorly crystallized substances which give no characteristic X-ray powder diffraction patterns as well as to crystalline solids. The reflectance of some substances is shown to be dependent on the previous history of the particular sample. The method is not applicable if there is physical interaction between the components of the mixture.

RÉSUMÉ

Les auteurs ont examiné les facteurs influençant le pouvoir réflecteur de substances absorbantes, mélangées à des produits non-absorbants, à la longueur d'onde de la mesure. Une méthode est développée pour le dosage précis de faibles concentrations d'une ou de deux substances absorbantes, mélangées à des corps non-absorbants. Ce procédé peut être appliqué aussi bien à des substances mal cristallisées qu'à des solides cristallins.

ZUSAMMENFASSUNG

Es wurden die Faktoren untersucht, die die Reflektion einer absorbierenden Substanz beeinflussen, die mit Material gemischt ist, das bei der Messwellenlänge nicht absorbiert. Es zeigte sich, dass der Einfluss der Teilchengrösse durch verlängertes Mahlen eliminiert werden kann; ferner, dass der prozentuale Gewichtsanteil der absorbierenden Substanz direkt proportional ist der Grösse $(A/R)^{1.383}$ ($R =$ prozentuale Reflektion; $A = 100 - R$), und dass diese Grösse für zwei absorbierende Substanzen additiv ist. Es wird eine Methode entwickelt für die genaue Bestimmung niedriger Konzentrationen von einer oder zweier absorbierender Substanzen, die mit nicht absorbierendem Material gemischt sind. Die Methode is anwendbar sowohl für schlecht kristallisierende Substanzen, die keine charakteristischen Röntgenbeugungsaufnahmen zeigen, als auch für gut kristallisierende Festkörper. An einigen Substanzen wird gezeigt, dass die Reflektion von ihrer Vorgeschichte abhängig ist. Die Methode ist nicht anwendbar, wenn die Komponenten der Mischung sich physikalisch beeinflussen.

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SHORT COMMUNICATION

Über die Anwendung des Ringofens in der Dünnschichtchromatographie

Das Grundprinzip der Ringofentechnik[1], nämlich die Überführung der löslichen Anteile eines Tüpfelfleckes in einen Tüpfelring, lässt sich auch zur Ausführung von Nachweisreaktionen und semiquantitativen Bestimmungen in der Dünnschichtchromatographie anwenden. Für den Nachweis und die Bestimmung anorganischer Verbindungen, sowie zur Erfassung radioaktiver Substanzen auf autoradiographischem Weg[2,3] sind besonders die aus bindemittelfreien, selbsthaftenden Zellulosepulvern hergestellten Schichten von Interesse, die bei einem Flächengewicht von 1–3 mg/cm^2 eine sehr homogene Struktur und gute Saugeigenschaften aufweisen. Die Umwandlung der Tüpfelflecke kann sowohl direkt, als auch nach der chromatographischen Auftrennung in der Weise erfolgen, dass ein Ringofen auf die horizontal mit der Schicht nach oben liegenden Platte so aufgesetzt wird, dass der jeweilige Fleck möglichst genau im Zentrum der Bohrung des Ofens zu liegen kommt. Durch Aufbringen eines geeigneten Lösungsmittels mit einer Kapillarpipette wird der lösliche Anteil des Tüpfelfleckes in bekannter Weise zum Ring gewaschen und dort als scharf begrenzter Tüpfelring konzentriert. Je nach der Grösse des Ausgangs-Tüpfelfleckes ergibt sich dabei infolge des kleineren Flächeninhaltes des Tüpfelrings (< 20 mm^2) eine Steigerung der Flächendichte der Probe und eine dadurch bedingte erhöhte Nachweisempfindlichkeit. So können zum Beispiel weniger als 5 ng Nickel mit Diacetyldioxim, 2 ng Eisen als Berlinerblau oder 5 ng Kobalt als Kobaltsulfid einwandfrei nachgewiesen werden. Die im Zellulosepulver enthaltenen anorganischen Verunreinigungen lassen sich durch Auswaschen der Dünnschicht mit verd. Salzsäure oder einem anderen, der jeweiligen Aufgabenstellung angepassten Lösungsmittel leicht entfernen.

Zur autoradiographischen Bestimmung radioaktiver Substanzen wird in analoger Weise verfahren. Die im Tüpfelring enthaltene Probe wird in bekannter Weise durch Auflegen von Röntgenfilm autoradiographiert und kann durch visuelle oder instrumentelle Schwärzungsmessung ausgewertet werden. Bei dieser autoradiographischen Methode sind die ausgezeichnete Homogenität und das geringe Flächengewicht von besonderem Vorteil. Bei punktweiser Messung der Schwärzung eines Autoradiogrammes aus einem Tüpfelring auf Filterpapier Schleicher und Schüll 5892 (Weissband) ergab sich z.B. eine Standardabweichung von $+22.3/-19.2$ Rel.-% (logarithmische Normalverteilung). Ein in ähnlicher Weise hergestelltes Dünnschichtautoradiogramm liefert eine Standardabweichung der Schwärzung von $+8.1/-8.0$ Rel.-%. Für den Vertrauensbereich der Mittelwerte aus 16 Messungen an einem Ring wurden im 95%-Bereich $+11.1/-10.0$ gegenüber $+4.6/-4.4$ Rel.-% und im 99.9%-Bereich $+22.7/-18.5$ gegenüber $+9.0/-7.3$ Rel.-% errechnet.

Das Flächengewicht der in der Ringofentechnik vielfach verwendeten Filter- und Chromatographiepapiersorten liegt zwischen 8.0 und 13.0 mg/cm^2, das der Zellulose-Dünnschicht zwischen 1 und 3 mg/cm^2. Durch diese bedeutende Verringerung des Flächengewichtes werden auch sehr schwache Strahler wie z.B. Kohlenstoff-14 der

autoradiographischen semiquantitativen Bestimmung besser zugänglich, worüber demnächst ausführlicher berichtet werden soll.

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1 H. WEISZ, *Microanalysis by the Ring Oven Technique*, Pergamon, Oxford, 1961.
2 H. WEISZ UND L. J. OTTENDORFER, *Mikrochim. Acta*, (1961) 191; (1962) 752.
3 H. WEISZ UND D. KLOCKOW, *Anal. Chim. Acta*, 28 (1963) 467.

BOOK REVIEW

Comprehensive Analytical Chemistry. Vol. IIA. Electrical Methods, Edited by C. L. WILSON AND D. W. WILSON with the assistance of C. R. N. STROUTS, Elsevier Publishing Company, Amsterdam, 1964, xvi + 268 pp., price 60 s.

This book is a further part of WILSON AND WILSON's *Comprehensive work on analytical chemistry*. It is the first of five parts of Volume II which, when complete, will cover electrical methods, physical methods and physical separation methods. It contains an introductory chapter by A. J. LINDSEY, followed by Chapters on Electro-deposition (A. J. LINDSEY), Potentiometric Titrations (D. G. DAVIS), Conducto-metric Titrations (D. G. DAVIS) and High Frequency (Impedimetric) Titrations (T. S. BURKHALTER).

The introductory chapter is an excellent example of conciseness, providing a general introduction to the subject and selected references to more fundamental works, together with notes on units, symbols and sign conventions. It also contains a very useful classification of electrochemical methods of analysis.

All the chapters contain a short section on essential theory, followed by sections dealing with apparatus and technique, and applications. The general balance within, and between chapters is good, the sections on applications are useful and the value of the book as a work of reference is enhanced by the inclusion of over 700 references. The chapter on potentiometric titrations is by far the longest, as might be expected in view of the very widespread application of these methods. That on electrodeposition contains useful sections on internal electrolysis and electrographic methods, which might serve to stimulate their wider application.

The book is well produced and errors are few. It will be useful to the practising analyst whether he specialises in electrochemistry or not. It is also recommended to workers in other fields and to students. The index is poor, but this fault should be corrected when the general index appears in Volume V, at a time which is probably far in the future.

G. F. REYNOLDS (Loughborough)

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