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SUMMARIES FOR CARD INDEXES

Ion exchange in mixed solvents: Adsorption behaviour of uranium and thorium on strong-base anion-exchange resins from mineral acid-alcohol media: Separation methods for uranium and thorium: J. Korkisch and G. E. Janauer. *Talanta*, 1962, **9**, 957.

Summary—The present work summarises important data hitherto reported on the anion-exchange behaviour of uranium^{VI} and thorium^{IV} in mixed solvents, and the results of pertinent research work carried out in this laboratory. The purpose of this paper is to give a detailed description of the adsorption behaviour of these actinide elements on strong-base anion-exchange resins in mineral acid solutions containing aliphatic alcohols. Equilibrium studies show the distribution coefficients to vary greatly with the acid used, as is expected from the results earlier obtained in aqueous systems. In mixtures of a given mineral acid with different alcohols, the distribution coefficients depend on the alcohol percentage, as well as on the acidity of the solutions, and on the dielectric constants and chain lengths of the alcohols employed. The results of these investigations can be applied to the separation of thorium and uranium from each other and from practically all other cations and anions. Two of the separation methods developed have already found general application for the assay of uranium and thorium in materials of greatly varying composition. Finally, the general theoretical aspects of anion exchange in mixed solvents are discussed, and the results obtained for uranium and thorium are interpreted accordingly.

Analytical applications of Xylenol Orange—VI: A spectrophotometric study of the niobium-Xylenol Orange complex: K. L. Cheng and B. L. Goydish, *Talanta*, 1962, **9**, 987.

Summary—The red niobium-Xylenol Orange complex has been studied spectrophotometrically. It offers a sensitive and selective reaction for the determination of traces of niobium. The coloured complex formed at pH 2·4 to 2·8 by heating in the presence of tartrate has a molar absorptivity of 16,000 and a formation constant of 5×10^6 under the conditions studied. Most metals, including tantalum, vanadium and tungsten, do not interfere when zinc-EDTA complex and tartrate are used as masking agents. Nitrite, oxalate, pyrophosphate, and phosphate interfere. Fluoride can be demasked by addition of beryllium. Platinum gives a dark purple colour which also interferes.

The reactivity of chromium and titanium with pyrrolidinedithiocarbamate: H. Malissa und H. Kotzian, *Talanta*, 1962, **9**, 997.

Summary—The dependence of the reactivity with pyrrolidinedithiocarbamate of titanium on pH and the presence of other ions, and of chromium^{III} on the state of binding of the chromium^{III} ion and on pH have been investigated. The results of this investigation provide an explanation of the hitherto very variable accounts of the reactivity of titanium and chromium with disubstituted dithiocarbamates.

Thermogravimetry of some uranium^{VI} 8-hydroxyquinolates: JON BORDNER and LOUIS GORDON, *Talanta*, 1962, **9**, 1003.

Summary—The thermogravimetric behaviour of

$$UO_2(C_9H_6NO)_2.C_9H_6NOH \quad \text{and} \quad [UO_2(C_9H_6NO)_2]_2.C_9H_6NOH$$

prepared by precipitation from homogeneous solution with 8-acetoxyquinoline has been found to closely resemble that of

$$UO_2(C_9H_6NO)_2.C_9H_6NOH$$

prepared by direct precipitation of uranium^{VI} with 8-hydroxyquinoline.

New redox systems—V: Oxidation of uranium^{IV} with iron^{III} in 1,10-phenanthroline solutions: Indirect colorimetric determination of uranium: FRANTIŠEK VYDRA and RUDOLF PŘIBIL, *Talanta*, 1962, **9**, 1009.

Summary—The oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline has been studied both potentiometrically and colorimetrically. Suitable conditions for the indirect colorimetric determination of uranium via ferroïn have been found.

An investigation of reagents for niobium and tantalum—I: G. ACKERMANN und S. KOCH. *Talanta*, 1962, **9**, 1015.

Summary—On examination of a wide range of hydroxylic organic compounds it has been found that two hydroxyl groups in the *ortho* position to each other in an aromatic system act as a functional analytical group for niobium and tantalum. *peri*-Dihydroxynaphthalene derivatives react similarly. After a systematic examination, tribromopyrogallol is proposed as a new selective and sensitive reagent for niobium.

Determination of metals in metal chelate compounds: YUICHI TSUCHITANI, YUKO TOMITA, and KEIHEI UENO, *Talanta*, 1962, **9**, 1023.

Summary—A rapid and convenient method of determining the metal content of metal chelate compounds is reported. The sample is decomposed with mixed acids in an open tube, and the freed metal ion is titrated with EDTA. Of the mixed acids investigated, a 3:1 mixture of nitric acid (62%) and perchloric acid (60%) is found to be effective in most cases.

Extraction and determination of iron as the bathophenanthroline complex in high-purity niobium, tantalum, molybdenum and tungsten metals: Elsie M. Penner and W. R. Inman, *Talanta*, 1962, **9**, 1027.

Summary—A spectrophotometric method for determining iron in the range 0·001–0·125% in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of iron to the bivalent state with ascorbic acid and hydroxylamine hydrochloride, the red complex formed between iron^{II} and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) is extracted into *n*-amyl alcohol and the absorbance of the resulting extract is determined at 536 mμ. Interference from copper is eliminated with thiourea. Cobalt, cadmium, nickel, manganese and zinc also interfere but the amounts of each of these impurities present in the four high-purity metals described are so low that their interference effects are negligible in the proposed method. Highly reproducible and precise results can be obtained with careful control of the pH during reduction and extraction.

Precipitation from mixed solvents—I: Aluminium 8-hydroxyquinolate: Lester C. Howick and Jerry L. Jones, *Talanta*, 1962, **9**, 1037

Summary—The precipitation of aluminium 8-hydroxyquinolate from a buffered acetone–water system has been effected by the volatilisation of the acetone. The use of this procedure results in a precipitate with physical characteristics superior to that obtained in the conventional manner and allows more efficient separation from interfering cations. Separations of 10-mg quantities of aluminium from an equal amount of cadmium as well as separations of 25-mg quantities of aluminium from at least 420 mg of magnesium and twice that amount of calcium can easily be accomplished. These results compare favourably with those obtained by hydrolysis of 8-acetoxyquinoline. A procedure is described for the quantitative determination of 2–10 mg of aluminium.

Application of the radioactive ionisation detector to the determination of permanent gases by gas chromatography, and some uses in studies of chemical kinetics: A. K. Galwey, *Talanta*, 1962, **9**, 1043.

Summary—It has been found possible to determine volumes of hydrogen, methane, and carbon dioxide within the range 0·1–1·0 ml at S.T.P. and carbon monoxide and nitrogen within the range 0·1–0·4 ml at S.T.P. with an accuracy of around 5% in a gas chromatograph using the radioactive ionisation detector, provided that the detector temperature and the rate of carrier gas flow through the column are maintained between stated limits. Results of experiments on the sensitivity of the instrument to oxygen, sulphur dioxide, ethane, propane and n-pentane are also reported. Particular attention has been directed towards selecting the most suitable parameter of the response peaks for use in quantitative analysis.

Some particular applications of the argon chromatograph in studies of chemical kinetics involving permanent gases are described, and a method for the removal of corrosive gases from mixtures to be analysed is discussed.

Contributions to the basic problems of complexometry—X:* Determination of nickel and cobalt in the presence of iron, copper and some other metals: Rudolf Přibil and Vladimír Veselý. *Talanta*, 1962, **9**, 1053.

Summary—A complexometric determination of nickel and cobalt in the same solution has been devised. It is based on the determination of the sum of nickel and cobalt by back-titration of added excess EDTA in a strongly alkaline medium with calcium chloride using Fluorexon (Calcein) as indicator. After oxidation of cobalt with hydrogen peroxide to form the cobalt^{III}-EDTA complex and screening of nickel by potassium cyanide, the liberated EDTA corresponding to the amount of nickel present is titrated with further calcium chloride. High concentrations of iron and aluminium are screened with triethanolamine. Copper and other heavy metals are screened with thioglycollic acid.

The fractional combustion of organic materials: E. Pell and H. Malissa, *Talanta*, 1962, **9**, 1056.

Summary—A new application of the relative-conductimetric method for the determination of carbon and sulphur is described. The method consists of a slow programmed combustion, and trapping of the different fractions. Thus it is possible to analyse the various fractions of the organic material for their carbon and sulphur content.

Copper^{II} catalysis of 8-acetoxyquinoline hydrolysis: C. R. Wasmuth and Henry Freiser, *Talanta*, 1962, **9**, 1059.

Summary—The hydrolysis of 8-acetoxyquinoline in dilute acid solution has been found to be subject to copper^{II} catalysis. The catalysed reaction is first order in 8-acetoxyquinoline (as the free base), first order in copper ion, and first order in hydroxide ion. It is proposed that a copper chelate is a reaction intermediate in the hydrolysis.

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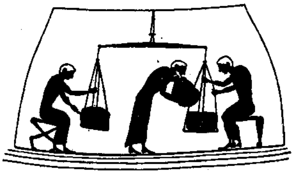

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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Short Communications

Letters to the Editor

Talanta, 1962, Vol. 9, pp. 957 to 985. Pergamon Press Ltd. Printed in Northern Ireland

ION EXCHANGE IN MIXED SOLVENTS

ADSORPTION BEHAVIOUR OF URANIUM AND THORIUM ON STRONG-BASE ANION-EXCHANGE RESINS FROM MINERAL ACID–ALCOHOL MEDIA

SEPARATION METHODS FOR URANIUM AND THORIUM

J. Korkisch and G. E. Janauer
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(*Received* 1 *January* 1962. *Revised* 5 *April* 1962. *Accepted* 5 *May* 1962)

Summary—The present work summarises important data hitherto reported on the anion-exchange behaviour of uranium^{VI} and thorium^{IV} in mixed solvents, and the results of pertinent research work carried out in this laboratory. The purpose of this paper is to give a detailed description of the adsorption behaviour of these actinide elements on strong-base anion-exchange resins in mineral acid solutions containing aliphatic alcohols. Equilibrium studies show the distribution coefficients to vary greatly with the acid used, as is expected from the results earlier obtained in aqueous systems. In mixtures of a given mineral acid with different alcohols, the distribution coefficients depend on the alcohol percentage, as well as on the acidity of the solutions, and on the dielectric constants and chain lengths of the alcohols employed. The results of these investigations can be applied to the separation of thorium and uranium from each other and from practically all other cations and anions. Two of the separation methods developed have already found general application for the assay of uranium and thorium in materials of greatly varying composition. Finally, the general theoretical aspects of anion exchange in mixed solvents are discussed, and the results obtained for uranium and thorium are interpreted accordingly.

1. INTRODUCTION

The anion-exchange properties of uranium^{VI} and thorium^{IV} in aqueous mineral acid solutions in the presence of a strong-base anion exchanger have been a subject of extensive investigations by many authors. Kraus and collaborators,[1–5] who can be regarded as pioneers in this field, have presented the first comprehensive studies on the distribution of nearly all elements, including thorium and uranium, between strong-base anion exchangers and mineral acids, especially hydrochloric acid. Their work has been confirmed and extended by Bunney, Ballou, Pascual and Foti[6] and others.[7–12] The adsorption of uranium and thorium on strongly basic resins from nitric acid solutions has been studied in detail by Buchanan and Faris,[13] Carswell,[14] Danon[15–16] and Ying-Mao Chen *et al.*[17] and others.[18–19] Jenkins and Richardson[20] as well as Saito and Sekine[21] proved the anionic character of uranium and thorium in nitrate and sulphate solutions.

Based on all these results numerous useful separation methods for uranium have been developed in hydrochloric,[3,22–27] nitric[14–16,28–30] and sulphuric[4,31–53] acid media, and are being extensively applied in the analysis of ores, rocks and various other materials. In addition, other strong and weak acids and complexing agents for uranium, such as hydrochloric-hydrofluoric-acid mixtures,[4,54] phosphoric acid,[55–57] carbonate,[58] acetate,[59–61] and ascorbinate[62–64] have been examined and found to be applicable for the isolation and separation of uranium. The anion-exchange properties of thorium, on the other hand, have found but little application and the methods developed are restricted mainly to ascorbic acid,[63–64] EDTA-solutions,[65–68] nitric[13,19] and sulphuric[69] acid solutions of this element.

In contrast to the systematic work done on ion exchange in pure aqueous acidic systems, few efforts have been made to cover the vast field of organic solvents systematically in respect of their influence on the anion-exchange behaviour of elements in different mineral acid solutions. Fritz and Pietrzyk[70] determined the distribution coefficients of many metal ions, including thorium and uranium, between the strong-base anion exchanger Dowex 1 and mixtures of methanol, ethanol and isopropanol, with varying contents of hydrochloric acid of different normalities. A number of successful column separations of metal ion mixtures were developed by these authors. Beside the authors cited by Fritz and Pietrzyk,[70] Katzin and Gebert,[71] Davies and Owen,[72] Tuck and Welch,[73] Iguchi,[74,75] Burstall *et al*[76], Berg and Truemper,[77] Kojima[78,79] and Yoshino and Kurimura[80] there are a few more who have published on the subject of anion exchange in non-aqueous and mixed solvents. Recently Janauer and Korkisch[81] have studied the anion-exchange behaviour of vanadium in hydrochloric acid solutions of the aliphatic alcohols; and a method for the separation of vanadium and nickel from iron and copper was developed. This separation method proved to be suitable for the determination of vanadium and nickel in ashes of oil products.[82] Samuelson and Sjöström[83] used 60% ethanol as an eluent for the alkali metals from a column of Dowex 2 loaded with EDTA. When separation of transition elements was desired (Samuelson, Sjöström and Forsblom[84]) the elution of the alkali metals was performed with 50% ethanol, the column containing acetate or oxalate or citrate instead of EDTA. Edge[85,86] studied the anion-exchange behaviour of yttrium, neodymium and lanthanum in dilute nitric and hydrochloric acid solutions containing ethanol, and found that these three rare earth elements could not be resolved by any of the ethanol-hydrochloric acid eluent systems employed. Elution with $0{\cdot}8N$ nitric acid-80% ethanol or $1{\cdot}6N$ nitric acid-80% ethanol appeared to be suitable for preparing "light" and "heavy" concentrates from mixtures of rare earth elements. Katzin and Sullivan[87] have invented a process utilising the strongly basic exchangers Dowex 1 and 2 for the separation of inorganic salts from their solutions in oxygen-containing organic solvents mixed with hydrochloric or nitric acid. The main object of this process is the separation of uranium^{VI} and/or plutonium^{IV} from organic solutions and/or uranium from thorium. Among other solvents, acetone and hexone were used. Very interesting results have also been obtained by the study of cation exchange in acetone-mineral acid mixtures, as, for instance, by Kember *et al.*,[88] who developed a useful method for the separation of copper and nickel using acetone containing 4% hydrochloric acid and 10% water as the eluent. Other cation-exchange methods in non-aqueous and mixed solvents have been reviewed by Bonner.[89]

From a close survey of all the literature available on anion exchange in non-aqueous or mixed solvents it appears that information on the exchange behaviour of uranium and thorium in such media is still scanty,[70,87]* and no class of organic solvents has as yet been systematically investigated.

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* The methods for the isolation of uranium and thorium described by Korkisch *et al*[99,100] (see also page 959) have been the first in which ion exchange in mixed solvents was applied to separate these two radioelements from a number of foreign elements.

For this reason, a long-term research programme was initiated at this Institution which has, since 1960, been continued in close co-operation with the International Atomic Energy Agency and the U.S. Atomic Energy Commission.[90,91] Part of this research was devoted to a systematic investigation of the aliphatic alcohols* with regard to their influence on the adsorption of uranium and thorium from mixtures with mineral acids on strongly basic anion-exchange resins of the quaternary amine type. The systems hydrochloric acid-ROH, nitric acid-ROH and sulphuric acid-ROH were completely covered,[90–98] and the condensed results and a number of the most important applications[64,96,97,99–103] based on these findings are presented in this paper, and compared with relevant results published by other research teams.

2. EXPERIMENTAL PART

I. *Reagents*

(a) *Ion-exchange resins:* The most usual was the strongly basic anion exchanger Dowex 1, ×8 (100–200 mesh, occasionally also 50–100 mesh chloride form).[90–98]

For the experiments in nitric and sulphuric acid solutions, the resin was transformed into the nitrate or sulphate form. After preparation of the sulphate form, prolonged washing is necessary, since free sulphuric acid adheres very strongly to the resin.[104] The air-dried form of the nitrate or the sulphate form of this resin was employed. In a few cases the strongly basic anion exchanger Amberlite IRA-400 (50–100 mesh, chloride form) was also used.

(b) *Standard solutions of uranium and thorium:* Hydrochloric, nitric, and sulphuric acid solutions of uranyl and thorium chlorides, nitrates, and sulphates of exactly known acidity and uranium[105] and thorium[106] content were employed.[90–98]

(c) *Solvents:* The aliphatic alcohols employed (methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol and a mixture of the amyl alcohols) were reagent-grade solvents.[90–98] All hydrochloric, nitric, and sulphuric acid solutions needed were prepared from their reagent-grade concentrated acids.

(d) *Solutions of other elements:* Standard solutions of a great number of elements were prepared from their reagent-grade salts. They were mainly employed for checking the possibilities of separating these elements from uranium and thorium. Their standardisation and quantitative determination has been described earlier.[64,81,96,99–103]

(e) *Dyestuff solutions:* 0·1% aqueous solution of thoronol.[106] The preparation of Solochromate Fast Red solutions and those of other dyestuffs of the Solochrome class which have also been used for spectrophotometric determination of uranium and thorium has already been described elsewhere.[107]

(f) *Other reagents:* Ascorbic acid; pure product (Wiener Heilmittelwerke). Hydrofluoric acid; 38–40% reagent grade. Perhydrol; 30% hydrogen peroxide, reagent grade.

II. *Apparatus*

(a) *Ion-exchange columns:* The column operations were carried out in columns of the same type and dimensions as described earlier.[29,59,62,90–98]

(b) *Spectrophotometer:* For the spectrophotometric determination of thorium and greater amounts of uranium the Beckman model B and DU spectrophotometers were employed. The measurements were carried out at wavelengths of 545 mμ (thorium-thoronol[106]) and 490 mμ (thorium or uranium-Solochromate Fast Red[107]) using 1-cm cells and a blue-sensitive phototube.

(c) *Polarographs:* For the quantitative determination of uranium by means of the catalytic nitrate wave, the polarographs Sargent, model XII and Metrohm-Polarecord type E,261 R were employed. The exact conditions of measurements and the evaluation of the polarograms has been described earlier.[59,60,61]

(d) *Fluorimeter:* Very small amounts of uranium were determined fluorimetrically using a procedure described by Schönfeld, El Garhy, Friedmann and Veselsky.[108] The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

III. *Determination of distribution coefficients*

The distribution coefficient for uranium or thorium is defined by the following equation:

$$\text{Distribution coefficient} = \mathrm{K_d} = \frac{\mu\text{g of uranium or thorium/g of resin}}{\mu\text{g of uranium or thorium/ml of solution}},$$

---

* Other solvents as instance ethers and ketones, are being investigated in the course of these studies.

and was determined employing the batch equilibrium method (batch method).[90–98] In the case of higher alcohols like n-butanol, isobutanol and amyl alcohol, which are partly miscible with water, the distribution coefficients can only be determined at very high percentages of these alcohols; that is, if the ratio of aqueous phase to alcoholic phase is 1:10 or lower. This ratio, however, can be 1:5 or above if hydrochloric acid-alcohol mixtures are employed, because the miscibility in such media is much higher than in nitric- or sulphuric acid mixtures.

All measurements of the distribution coefficients were performed disregarding any changes from mixing in preparing the acid-alcohol mixtures.

IV. *Determination of exchange capacities (Effect of concentration on the distribution coefficients)*

The capacity of the resin for uranium or thorium under certain experimental conditions was determined by measuring the distribution coefficients at different steadily increasing uranium or thorium concentrations under identical conditions. The maximal exchange capacity thus obtained corresponds to complete saturation of the resin with the uranium or thorium complex in question. The results of these measurements are given on page 972 (Section 3). The chloride, nitrate, and sulphate capacity of the resin was found to be 3·4 ± 0·05 mg equiv./g of air dried resin.

V. *Column operations*

The column operations pertaining to the individual separation methods (see Tables I–III) were performed in the manner described earlier[90–98].

VI. *Quantitative determination of uranium and thorium*

(*a*) *Determination of uranium:* The quantitative determination of uranium in the eluates or filtrates (after removal of the resin by filtration) was performed polarographically, as has earlier been described.[59,90–98] This method allows the exact determination of 0·1–20 μg of uranium in 10 ml of solution. For the determination of higher amounts of uranium a spectrophotometric method using Solochromate Fast Red[107] was used. Amounts of uranium below 0·1 μg were determined fluorimetrically.[108]

(*b*) *Determination of thorium:* For the quantitative determination of thorium, thoronol was employed as the photometric reagent.[95,97,99]

3. RESULTS

I. *Effect of Alcohol Concentration on the Adsorption of Uranium and Thorium*

1. *In hydrochloric acid-alcohol mixtures*

The results are shown in Figs. 1a and 1b.

Discussion

Fig. 1*a*: From the curves it is seen that uranium adsorption increases with the alcohol concentration and also with the chain length of the alcohols (see also Fig. 4). The increase is more marked at higher alcohol concentrations. As will be shown later, there is also a relationship between the increase of the distribution coefficients and dielectric constants of the alcohols used (see Fig. 5). In order to simplify the recording of the results, the individual values of the distribution coefficients obtained in amyl alcohol mixtures are not shown as a curve but only as single points and for the same reason, the results obtained in isopropanol and isobutanol are recorded in Table I. From these results it may be seen that the uranium adsorption from such mixtures is lower than that from media containing the corresponding n-alcohols (compare values from Table I with Fig. 1a).

Fig. 1*b:* This figure shows that the distribution coefficients for thorium also increase with increasing concentration and chain length of the alcohols employed (compare with Fig. 4). The effect of the chain length of the alcohols is, however, only noticeable with the short chain alcohols, *i.e.*, methanol and ethanol, in comparison with

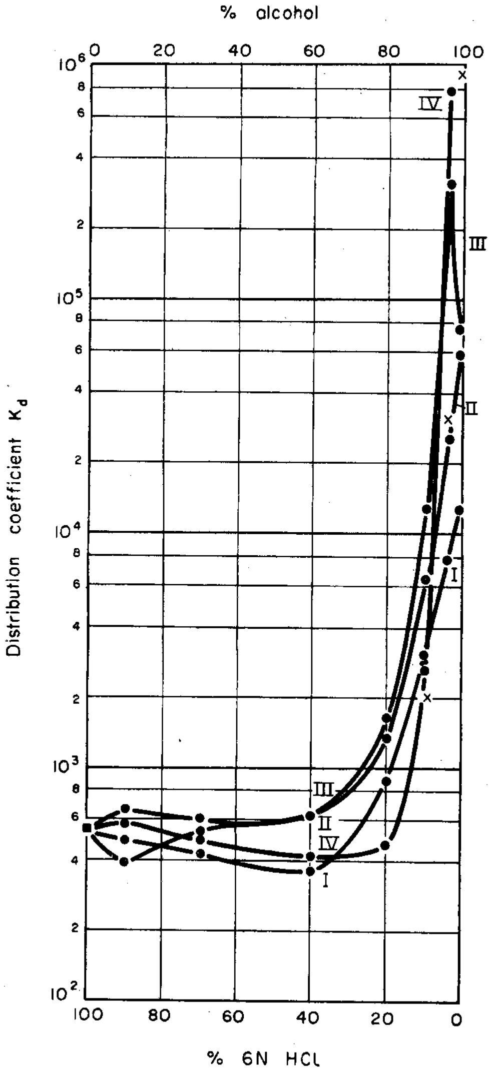

FIG. 1a.—Effect of alcohol concentration on the adsorption of uranium on Dowex 1 from hydrochloric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol; ×—Amyl alcohol; ■—Kraus and Nelson[2] (Dowex 1)

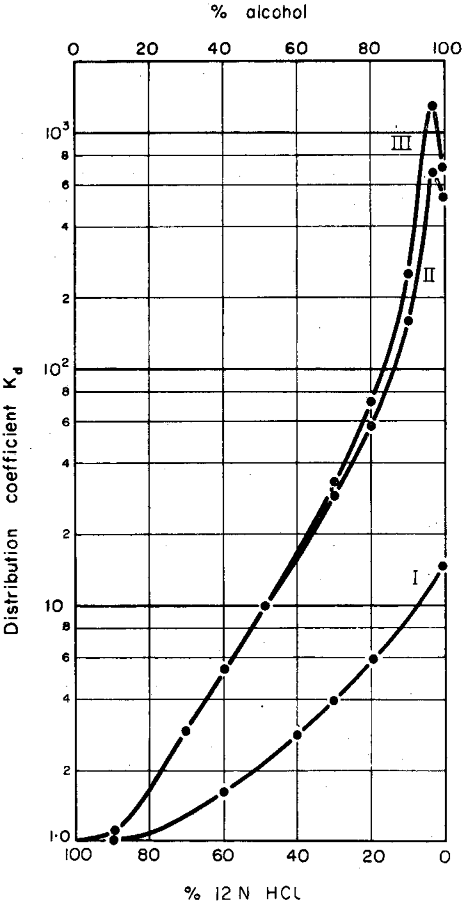

FIG. 1b.—Effect of alcohol concentration on the adsorption of thorium on Amberlite IRA 400 from hydrochloric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol, Isopropanol, n-Butanol and Amyl alcohol

TABLE I. URANIUM ADSORPTION FROM ISOPROPANOL AND ISOBUTANOL-HYDROCHLORIC ACID MIXTURES

Alcohol, %	K_d in isopropanol-HCl	K_d in isobutanol-HCl
99	$2·5 \times 10^5$	$2·2 \times 10^5$
96	$4·2 \times 10^5$	$1·5 \times 10^5$
90	$1·35 \times 10^5$	$4·14 \times 10^3$
80	$9·98 \times 10^3$	$1·64 \times 10^3$
60	$1·12 \times 10^3$	$5·8 \times 10^2$
30	$7·8 \times 10^2$	$4·8 \times 10^2$
10	$5·6 \times 10^2$	$4·8 \times 10^2$

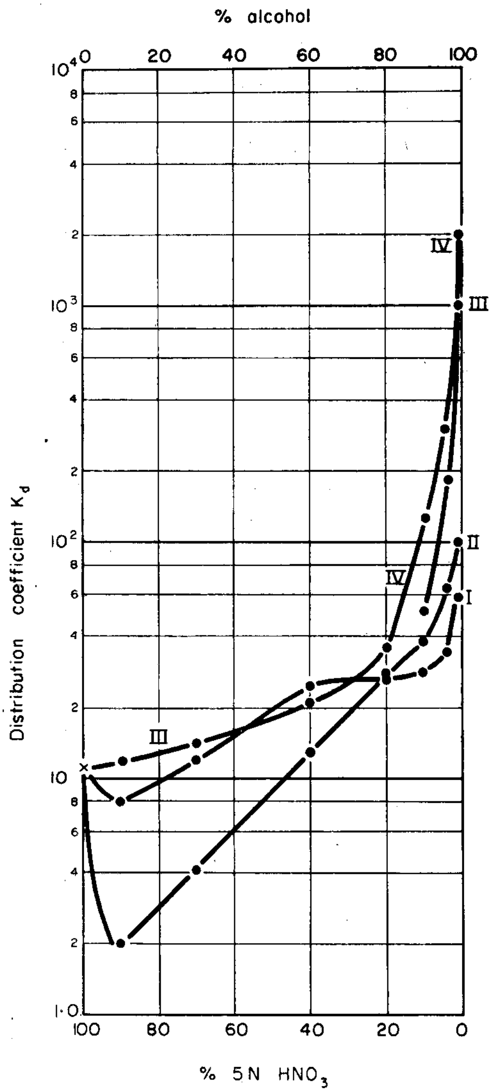

FIG. 2a.—Effect of alcohol concentration of the adsorption of uranium on Dowex 1 from nitric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol, Isobutanol, Amyl alcohol, ×—Buchanan and Faris[13] (Dowex 2)

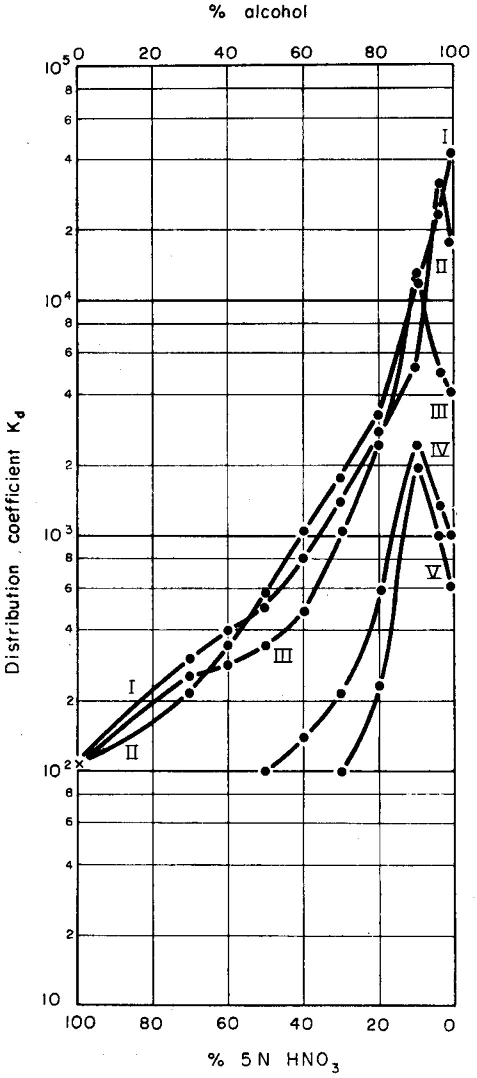

FIG. 2b.—Effect of alcohol concentration on the adsorption of thorium on Dowex 1 from nitric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol; V—Amyl alcohol; ×—Buchanan and Faris[13] ((Dowex 2)

the longer chain alcohols propanol, butanol and amyl alcohol, in the mixtures of which identical distribution coefficients were obtained (see also Fig. 4).

In conclusion, it may be said that uranium and thorium can be adsorbed from mixtures of the longer-chain alcohols at high percentages of these alcohols, although the distribution coefficients differ considerably. However, the absolute values of the distribution coefficients in those systems are still high enough to ensure quantitative adsorption of both elements. Thus the simultaneous adsorption of uranium and thorium can be accomplished in such media, although it is impossible in pure aqueous hydrochloric acid solutions, as shown by Kraus and collaborators.[1-5]

2. *In nitric acid-alcohol mixtures*

The results of these investigations are given in Figs. 2a and 2b.

Discussion

Fig. 2a: From this figure it is evident that the adsorption of the uranyl nitrate complex is strongest from butanol and amyl alcohol media, and weakest from methanol medium; and this effect is also accentuated with increasing alcohol concentration. In addition, the distribution coefficient increases with increasing chain length (see also Fig. 4), but the regularity is interrupted at lower percentages of alcohol in the mixtures, a result which might possibly be caused by partial esterification.

Fig. 2b: The results recorded in these curves make it apparent that reverse conditions are encountered with thorium from those with uranium under identical experimental conditions. The thorium nitrate complex is most strongly adsorbed from methanol, and is only weakly adsorbed from amyl alcohol medium. The adsorption of thorium decreases with increasing chain length of the alcohols (see also Fig. 4). Secondary alcohols like isopropanol and isobutanol show the same behaviour as the corresponding straight-chain alcohols.

3. *In sulphuric acid-alcohol mixtures*

The results of these experiments are recorded in Fig. 3a and 3b.

Discussion

Fig. 3a: It is seen that the distribution coefficient of uranium in sulphuric acid–alcohol mixtures also rises with increasing alcohol concentration, but not with increasing chain length (see also Fig. 4). Very high values for the distribution coefficients are reached at high alcohol concentrations, independent of the chain length of the alcohols used.

Fig. 3b: The distribution coefficient of thorium shows the same behaviour as that of uranium *i.e.*, it also rises with increasing alcohol concentration independent of the alcohol chain length (see Fig. 4). The curve in Fig. 3b therefore shows the adsorption coefficients for thorium in all the alcohols investigated.

II. *Effect of Chain Length and Dielectric Constant of Alcohols on the Distribution Coefficients of Uranium and Thorium*

1. *Effect of chain length*

To illustrate the effect of the chain length of the alcohols on the distribution coefficients of uranium and thorium, the distribution coefficients were plotted against the number of carbon atoms (see Fig. 4). (For every curve the experimental conditions such as over-all acidity and alcohol concentration were kept constant).

As can be seen from curves I and II of this figure, the increase of chain length produces a steep increase of the distribution coefficients of uranium and thorium in hydrochloric acid-alcohol media, as has earlier been observed[81] with vanadium^{IV} and vanadium^{V}. In nitric acid-alcohol media, uranium also shows an increase of K_d

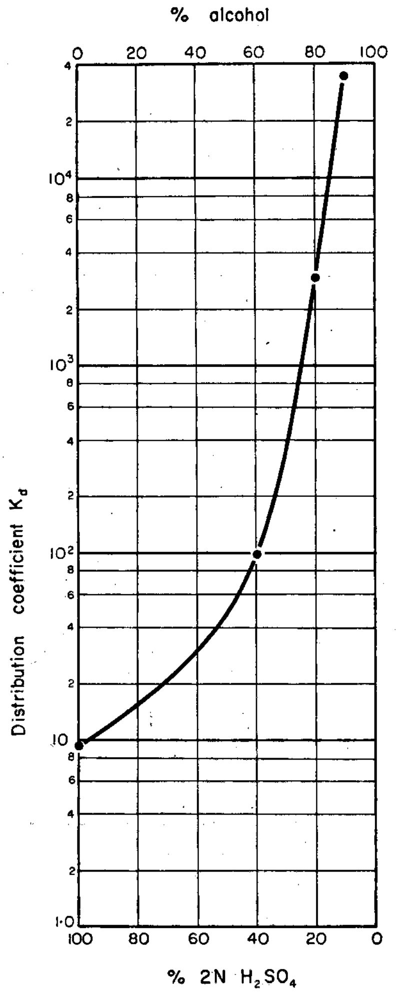

FIG. 3a.—Effect of alcohol concentration on the adsorption of uranium on Dowex 1 from sulphuric acid-alcohol mixtures

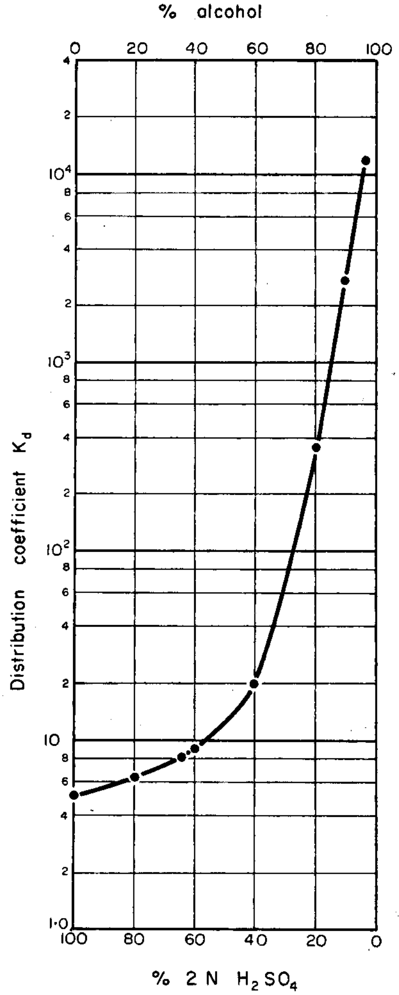

FIG. 3b.—Effect of alcohol concentration on the absorption of thorium on Dowex 1 from sulphuric acid-alcohol mixtures

while the distribution coefficient of thorium falls off rather rapidly with increasing number of carbon atoms. In sulphuric acid-alcohol mixtures no effect of chain length whatsoever was found. As the change of K_d caused by the increase of carbon atoms from 4 to 5 is rather small in nitric and hydrochloric acid media, we have neglected the fact that amyl alcohol is not a pure n-alcohol, but a mixture of some isomers.

2. *Effect of dielectric constant*

To show the effect of the dielectric constant (DC) of the alcohols and water on the adsorbability of uranium and thorium on strong-base anion exchangers from mineral acid-alcohol solutions, we have plotted the K_d values against $\frac{1 \times 10^2}{\text{D.C}}$ (20°) of the pure alcohols, neglecting the influence of the small water content [alcohol percentages were 99% or 90% (see Fig. 5) in the mixtures].

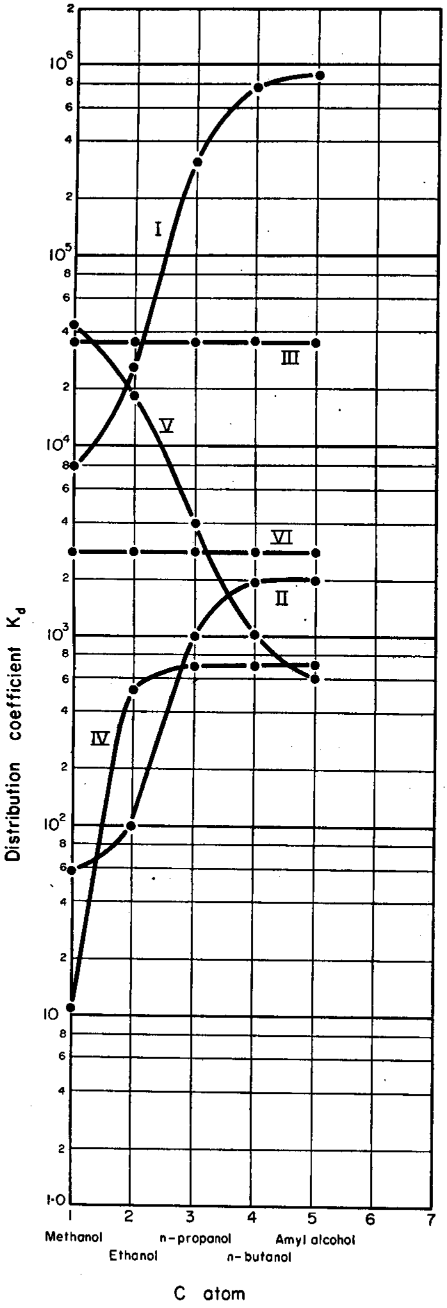

FIG. 4.—Effect of chain length
I—Uranium; 96% alcohol, 4% $6N$ HCl;
II—Uranium; 99% alcohol, 1% $5N$ HNO_3:
III—Uranium; 90% alcohol, 10% $2N$ H_2SO_4:
IV—Thorium; 99% alcohol, 1% $12N$ HCl:
V—Thorium; 99% alcohol, 1% $5N$ HNO_3:
VI—Thorium; 90% alcohol, 10% $2N$ H_2SO_4.

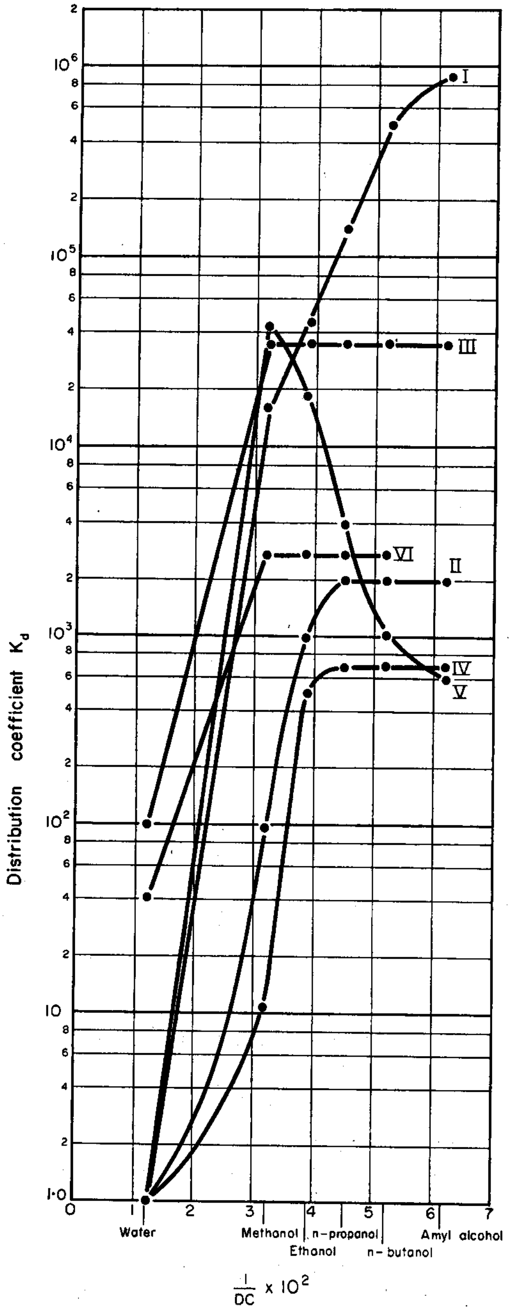

FIG. 5.—Effect of dielectric constant
I—Uranium; 99% alcohol or water, 1% $6N$HCl: II—Uranium; 99% alcohol or water, 1% $5N$ HNO_3: III—Uranium; 90% alcohol or water, 10% $2N$ H_2SO_4: IV—Thorium; 99% alcohol or water, 1% $12N$ HCl: V—Thorium; 99% alcohol or water, 1% $5N$ HNO_3: VI-Thorium; 99% alcohol or water, 1% $2N$ H_2SO_4.

Comparison with Fig. 4 shows a very similar relationship between both the effects of chain length and dielectric constant and the adsorption of uranium and thorium; that is, increasing adsorption with decreasing DC of both uranium and thorium in hydrochloric acid-alcohol media and for uranium in nitric acid-alcohol media. In sulphuric acid-alcohol mixtures, thorium and uranium adsorption is independent of the DC of the alcohols employed, but thorium adsorption in nitric acid-alcohol media decreases with decreasing DC. This effect of DC on adsorption was earlier observed by Sakaki and Kakihana[109] in equilibrium experiments with K, Na, and Li ions in ethanol-water and methanol-water solutions, using a strongly acidic cation exchanger. (See also Section 5.)

III. *Effect of Mineral Acid Concentration on the Adsorption of Uranium and Thorium*

In order to investigate the effect of acidity on uranium and thorium adsorption, the over-all acidity of solutions of identical alcohol concentrations was varied, and the values for the distribution coefficients found are recorded in Figs. 6a, 6b and 6c. The theoretical interpretation of the shapes of the various curves obtained will be given in Section 5.

Discussion

Fig. 6a: The results in hydrochloric acid-alcohol mixtures show that the distribution coefficient of uranium at a given alcohol concentration increases practically linearly with the over-all acidity of the solution. Curve X, showing the results obtained by Fritz and Pietrzyk[70] in 74% isopropanol and 26% hydrochloric acid-mixture, deviates somewhat from this linearity. As can be seen from Fig. 1a, the distribution coefficient rises also at constant acidity with increasing alcohol content of the solutions. In pure aqueous hydrochloric acid solutions, the uranium adsorption is very low, but increases greatly, as earlier observed by Kraus and collaborators,[1–5] at higher hydrochloric acid concentrations. Distribution coefficients measured by Bunney *et al.*[6] under identical conditions, using the exchanger Dowex 2, ×8, are somewhat lower at low acidities, but reach, at an over-all normality of 2·4*N* hydrochloric acid, values which are practically identical with those found by Kraus and collaborators.[1–5] It is therefore possible to adsorb uranium at relatively small over-all acidities from hydrochloric acid-alcohol media on strongly basic anion-exchange resins. Based on this fact, two methods for the adsorption and separation of uranium have been developed, by means of which uranium can be isolated and separated in 80% ethanol or 80% methanol-hydrochloric acid mixtures of 0·8*N* or 1·2*N* over-all acidity. It can further be seen from this figure (curve XII) that the distribution coefficient for thorium in 96% isopropanol + 4% hydrochloric acid shows no variation with the over-all acidity. At very low acid concentrations, the K_d decreases rapidly because of the hydrolysis of thorium tetrachloride. An effect resulting from acidity was also found by Fritz and Pietrzyk[70] in mixtures of 74% isopropanol + 26% hydrochloric acid and 65% isopropanol + 35% hydrochloric acid (see curves IV and IX). The K_d values found for thorium by these authors at such alcohol concentrations are in agreement with the values found by Korkisch and Tera[96] (see Fig. 1b). A considerable divergence exists between results for the K_d values of thorium found by Fritz and Pietrzyk[70] in ethanol-hydrochloric acid and the values found by Korkisch and Tera[96] in these media. Korkisch d Tera[96] oanbtained, for instance, in 96% ethanol, a distribution coefficient

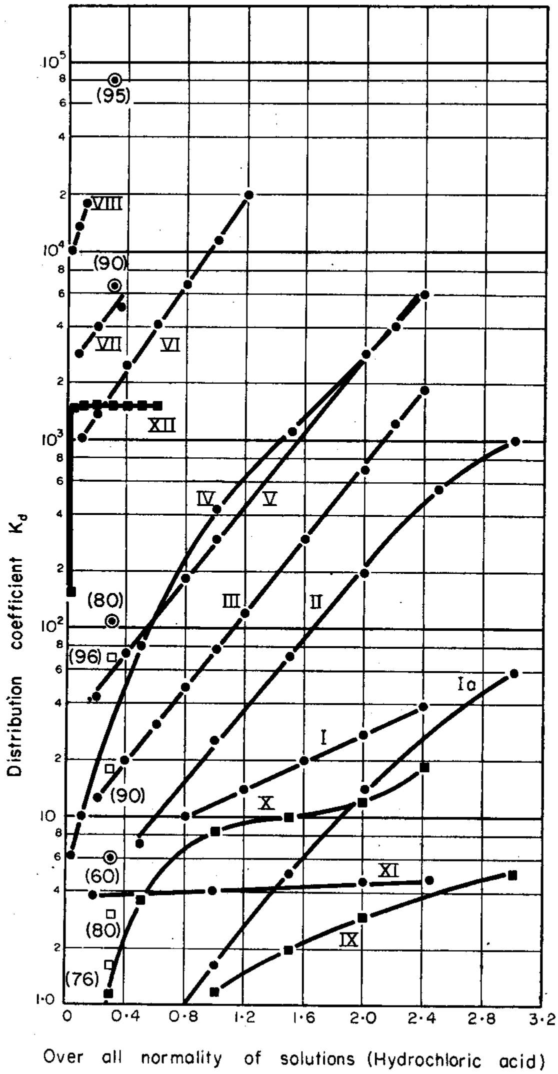

FIG. 6a.—Effect of hydrochloric acid concentration on the adsorption of uranium and thorium

I—Uranium; 100% HCl (Kraus and Nelson)[2]: Ia—Uranium; 100% HCl (Bunney *et al.*)[6]: II—Uranium; 55% isopropanol, 45% HCl (Fritz and Pietrzyk)[70]: III—Uranium; 60% ethanol, 40% HCl; IV—Uranium; 74% isopropanol, 26% HCl (Fritz and Pietrzyk)[70]: V—Uranium, 80% ethanol, 20% HCl: VI—Uranium; 90% methanol, 10% HCl: VII—Uranium; 94% methanol, 6% HCl: VIII—Uranium; 99% methanol 1% HCl: IX—Thorium; 65% isopropanol, 35% HCl (Fritz and Pietrzyk)[70]; X—Thorium; 74% isopropanol, 26% HCl (Fritz and Pietrzyk)[70]: XI—Thorium; 80% ethanol, 20% HCl: XII—Thorium; 96% isopropanol, 4% HCl (Amberlite IRA 400): ×—Thorium; 55% isopropanol, 45% HCl (Fritz and Pietrzyk)[70]: ○—Uranium in ethanol (% Ethanol) (Fritz and Pietrzyk)[70]; □—Thorium in ethanol (% ethanol) (Fritz and Pietrzyk)[70] for thorium of 700 (compare with Fig. 1b), while the value found by Fritz and Pietrzyk[70] is only 70. This divergence may be explained by the high amounts of thorium used by the latter authors for their batch experiments. From Fig. 7b it may also be seen that there is a very pronounced effect of thorium concentration on the distribution coefficient of thorium when the amount of thorium adsorbed on the resin exceeds 10 mg/g of resin.

As the distribution coefficients of thorium and uranium at high alcohol concentrations reach very high values, simultaneous adsorption of both elements is possible, if longer-chain alcohols like propanol and butanol are employed, but not if methanol is used (see Fig. 1b).

It is noteworthy that thorium is adsorbed at all, since all investigations hitherto carried out in pure aqueous hydrochloric acid solutions have shown that thorium, because of its low tendency to form negatively charged chloride complexes, is not adsorbed on anion-exchange resins of the quaternary amine type, even from concentrated hydrochloric acid.[1,2] Quadrivalent uranium, however, is relatively well adsorbed from hydrochloric acid of higher normality on such resins.[1,2] This is astonishing, because thorium, as a rule, shows a very similar behaviour to quadrivalent uranium, and is known also, like uranium^{IV}, to form a comparable first chloride complex $ThCl^{3+}$ of similar stability.[110]

Fig. 6b: In nitric acid-alcohol solutions the adsorption of uranium is much less than in hydrochloric acid mixtures (in aqueous nitric acid solutions the conditions are till more unfavourable, as has been shown by Carswell[14] (see curve VII).

The distribution coefficients of uranium only reach values high enough for analytical purposes in solutions of high percentages of the longer-chained alcohols. This fact can be used for the simultaneous adsorption of uranium and thorium (see Section 4, Table III). Thorium, however, is much more strongly adsorbed from nitric acid solutions containing high percentages of methanol or ethanol than from hydrochloric acid-alcohol solutions (compare with Fig. 6a). Ready separation from uranium and other elements is therefore possible (see Section 4, Table II). In solutions of corresponding composition, the distribution coefficients of uranium are a linear function of the over-all normality (see curves IV, V and VI). At a lower alcohol concentration the uranium and thorium adsorption shows a linear increase, with increasing over-all normality slowly reaching a saturation value for uranium; and maxima for thorium which are followed by a decrease of the distribution coefficients with rising acidity. No maximum is reached for thorium, however, in 40% ethanol or in 40% methanol. As can further be seen from this figure no effect of the over-all acidity of the solution on the distribution coefficient of thorium was found only in solutions of very high methanol content. (A theoretical explanation for this phenomenon will be given in Section 5.)

From $0{\cdot}6N$ to $0{\cdot}005N$ (over-all normality) no hydrolysis of thorium nitrate occurred. Only when an over-all normality of $0{\cdot}0025N$ nitric acid was reached could partial hydrolysis of thorium nitrate be observed; this is another proof of the considerably higher stability of the negatively charged thorium complex in comparison with the corresponding chloride complex—thorium chloride is already hydrolysed when a hydrochloric acid normality of $0{\cdot}04N$ is reached.

Fig. 6c: It is seen that the highest distribution coefficients for uranium are reached in these sulphuric acid-alcohol media. As the distribution coefficient of uranium is independent of DC and chain-length of the alcohols used (see also Figs. 4 and 5), curve IV was obtained by measuring the adsorption in 90% methanol + 10% sulphuric acid only. As comparison with curve III shows, the distribution coefficients in 80% and 90% alcohol differ only at over-all normalities of less than 0·2*N*. Comparing curves III and IV with the curves obtained by Kraus and Nelson[2] (curve I) and Bunney *et al.*[6] (curve Ia) for the effect of acidity in pure aqueous solutions, it is seen that at equal over-all normalities the distribution coefficients of uranium in alcohol solutions exceed the corresponding values obtained in pure aqueous-sulphuric acid solutions by about three orders of magnitude. The same can be said for thorium, as is shown in curves IIa (Bunney *et al.*[6]) and II (Janauer and Korkisch[98]) in comparison with curve VI. The

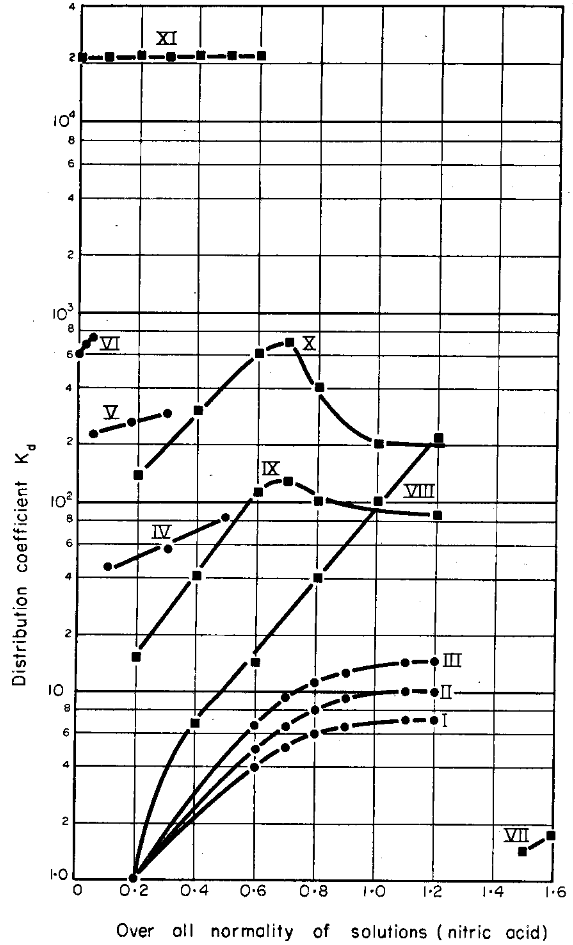

FIG. 6b.—Effect of nitric acid concentration on the adsorption of uranium and thorium I—Uranium; 40% ethanol, 60% HNO_3 (Korkisch *et al.*)[92]: II—Uranium; 60% ethanol, 40% HNO_3 (Korkisch *et al.*)[92]: III—Uranium; 80% ethanol, 20% HNO_3 (Korkisch *et al.*)[92]: IV—Uranium; 90% propanol, 10% HNO_3 (Korkisch and Tera)[103]: V—Uranium; 96% propanol, 4% HNO_3 (Korkisch and Tera)[103]: VI—Uranium; 99% propanol, 1% HNO_3 (Korkisch and Tera)[103]: VII—Thorium; 100% HNO_3 (Carswell)[14]: VIII—Thorium; 40% ethanol, 60% HNO_3 (Antal *et al.*)[95]: IX—Thorium; 60% ethanol, 40% HNO_3 (Antal *et al.*)[95]: X—Thorium; 80% ethanol, 20% HNO_3 (Antal *et al.*)[95]: XI—Thorium; 90% methanol, 4% HNO_3 (Tera *et al.*)[97].

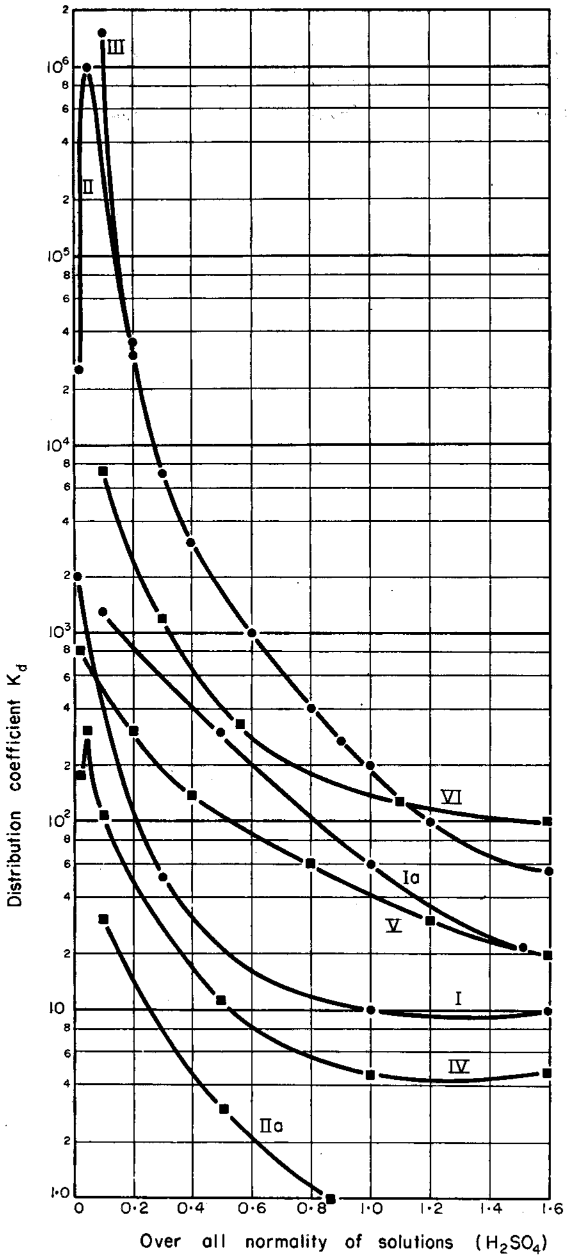

FIG. 6c.—Effect of sulphuric acid concentration on the adsorption of uranium and thorium

I—Uranium; 100% H_2SO_4, Dowex—1 (Kraus and Nelson)[2]: II—Thorium; 100% H_2SO_4 (Janauer and Korkisch)[98]: III—Uranium; 80% ethanol, 20% H_2SO_4 (Korkisch *et al.*)[92]: IV—Uranium; 90% methanol, 10% H_2SO_4 (Janauer and Korkisch)[98]: V—Thorium; 80% ethanol, 20% H_2SO_4 (Antal *et al.*)[95]: VI—Thorium; 90% methanol, 10% H_2SO_4 (Janauer and Korkisch)[98]: Ia—Uranium; 100% H_2SO_4, Dowex 2 (Bunney *et al.*)[6]: IIa—Thorium; 100% H_2SO_4, Dowex 2 (Bunney *et al.*).[6]

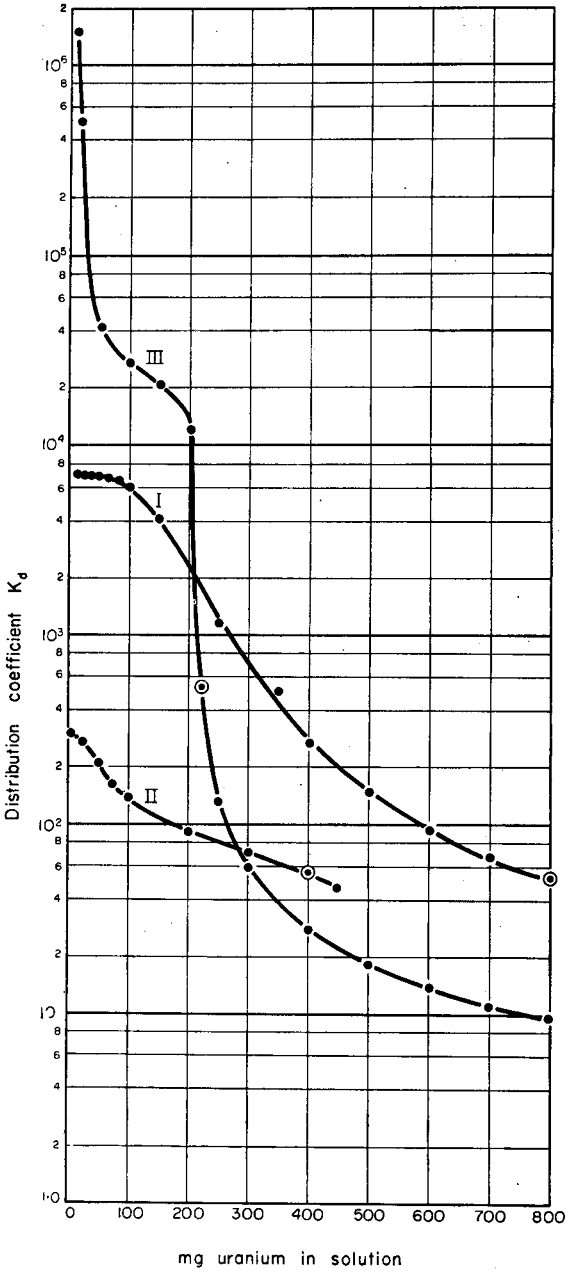

FIG. 7a.—Effect of concentration on the distribution coefficient of uranium I—Uranium; 90% ethanol, 10% 6N HCl (50 ml solution): II—Uranium; 96% n-propanol, 4% 5N HNO_3 (50 ml solution): III—Uranium; 90% n-propanol 10% 1N H_2SO_4 (25 ml solution): ⊙ Kd-values used for calculating the exchange capacities.

sudden decrease of the distribution coefficients of uranium and thorium below an over-all normality of 0·05N sulphuric acid (see curves II and III) is caused by the formation of neutral complexes of a higher order, which is equivalent to hydrolysis.

In conclusion, it can be said that on the basis of these results the simultaneous adsorption of uranium and thorium is feasible; it is, however, only applicable to technical processes[111] and is not to be recommended for analytical operations.

IV. *Effect of Concentration on the Distribution Coefficients of Uranium and Thorium Determination of Exchange Capacities*

The results of these investigations are shown in Figs. 7a and 7b.

Discussion

Fig. 7a: As may be seen from curve I, the distribution coefficient for uranium in 90% ethanol + 10% 6N hydrochloric acid shows no variations up to a concentration of

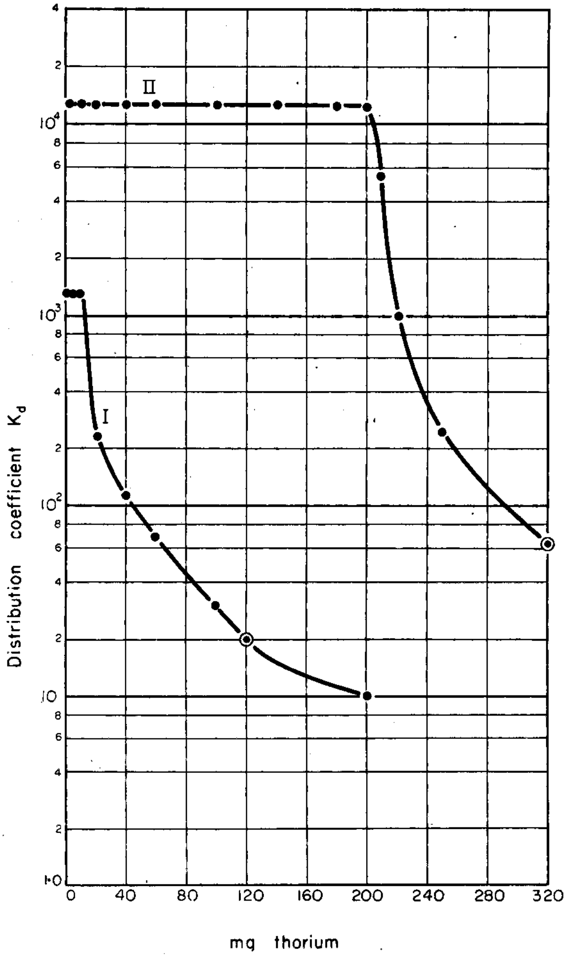

Fig. 7b.—Effect of concentration on the distribution coefficient of thorium I—Thorium; 96% isopropanol, 4% 12N HCl (25 ml solution) Amberlite IRA 400): II—Thorium; 90% methanol, 10% 5N HNO_3 (25 ml solution): ○ Kd-values used for calculating the exchange capacities.

50 mg of uranium. A steep descent is, however, observed at higher uranium concentrations, reaching a value of 35 when 1,000 mg of uranium are present in the solution. (The maximum exchange capacity of 412·5 mg of uranium/g of dry resin is reached when 800 mg or more of uranium are present in solution.)

From curve II for uranium in nitric acid, it is evident that the distribution coefficient remains constant only within a small range of concentrations. At a uranium concentration of 400 mg, the maximum capacity of the resin (212·5 mg of uranium/g of dry resin) is reached. In sulphuric acid-alcohol media a two-step curve was obtained (curve III), indicating the possible presence of two different uranyl sulphate complexes (see Section 5). The maximum capacity is reached in practice when 220 mg of uranium are present in solution. A value of 210 mg of uranium/g of dry resin was obtained.

Fig. 7b: The distribution coefficients of thorium in hydrochloric acid and nitric acid-alcohol solutions are shown as a function of the concentration of the solution. As may be seen from curve I (96% isopropanol + 4% 12*N* hydrochloric acid) the distribution coefficient for thorium remains constant up to 10 mg of the element, and falls off rather rapidly at higher concentrations. The capacity of the resin was found to be 58 mg of thorium/g of dry resin.

In nitric acid solutions the distribution coefficient does not vary over a fairly wide concentration range (curve II). However, when the thorium concentration exceeds 200 mg the K_d decreases rapidly at first and then somewhat more slowly. The exchange capacity of the resin was found to be 230 mg/g of dry resin for concentrations exceeding 320 mg of thorium/25 ml of solution.

As thorium sulphate is only sparingly soluble in sulphuric acid-alcohol solutions of high alcohol content ($2{\cdot}3 \times 10^{-5}$ moles of thorium are soluble in 1 liter of a mixture containing 90% methanol + 10% 2*N* sulphuric acid) no K_d-concentration plot was set up. The encircled points on the curves in Figs. 7a and 7b represent the uranium (thorium) concentrations where the maximum exchange capacities are reached. These points are thus equivalent to the beginning of the horizontal part of the adsorption isotherms corresponding to the K_d-concentration curves shown.

5. ION EXCHANGE SEPARATIONS IN MIXED SOLVENTS

Based on the experimental results given in Section 3 it was possible to develop seven isolation and separation methods for uranium and/or thorium in mixed alcohol-mineral acid solutions. The procedures briefly presented in the following three tables have already been described in detail elsewhere.[64,96,99–103]

Discussion

All the methods shown in Tables II–IV have in common the fact that separations of other elements from uranium or thorium in the corresponding media are the more difficult the higher the distribution coefficients of uranium and thorium under these conditions, since the adsorbability of the other elements increases too. On the other hand, high distribution coefficients allow the adsorption of large amounts of uranium or thorium. For micro-analytical purposes Methods (1) and (4) are suitable, where the distribution coefficients of uranium and thorium are not too high, but are nevertheless adequate.

As has been stated [Method (1)], a separation of uranium from tervalent iron is only possible if the sorption solution contains a reducing agent to transform tervalent iron

TABLE II.—METHODS FOR THE SEPARATION OF URANIUM AND THORIUM IN HYDROCHLORIC ACID-ALCOHOL MEDIA

Method	Composition of sorption solution	Anion-exchange resin	Elements separated from U and/or Th	Remarks
(1) Separation of uranium from thorium and other elements in hydrochloric acid-ethanol solution[100]	80% ethanol, 20% 4*N* HCl + ascorbic acid K_d for U = 200	Dowex-1 (Cl^- form)	Alkali metals, alkali earth metals, Mn^{II}, Al, Fe^{II}, Th, V^V, Zn, Sn, Cu, Co, Ni, Cr, Ti, Zr, rare earth elements, fluoride, sulphate, nitrate, phosphate, *etc.*[100]	Adsorbed on the resin are U, W, Mo, Bi and Pb. During the elution with 0·1*N* HCl saturated with diethyl ether, only U is eluted. To prevent the adsorption of Fe^{III} ascorbic acid has to be added to the sorption solution. This ion-exchange method can be employed for the assay of microgram amounts of U in practically all naturally occurring materials, as for instance silicate rocks, marine sediments[112,113] *etc.*
(2) Separation of U from Th and other elements in hydrochloric acid-methanol solution[101]	80% methanol, 20% 6*N* HCl + ascorbic acid K_d for U = 867	Dowex 1 (Cl^- form)	As above under (1)	U, Bi and Pb are adsorbed on the resin in the presence of ascorbic acid, or if present in higher amounts than 1 mg/100 ml each, Co, Ni and Cu are also adsorbed. The elution of U is performed with 1*N* HCl. This method can be used for the separation of microgram or milligram amounts of U from microgram or milligram amounts of other elements.
(3) Adsorption of Th from hydrochloric acid-isopropanol solution[96]	96% isopropanol, 4% 12*N* hydrochloric acid K_d for Th = 1,400	Dowex 1 or Amberlite IRA-400 (Cl^- form)	Alkali metals, alkali earth metals and some other elements not forming negatively charged chloride complexes.	This method can be used for the adsorption of microgram and milligram amounts of Th and in a modified form [see Table IV, method (6)] for the simultaneous adsorption of Th and U, with successive separation of these two elements.

TABLE III.—METHODS FOR THE SEPARATION OF Th IN NITRIC ACID-ALCOHOL MEDIA

Method	Composition of sorption solution	Anion-exchange resin	Elements separated from Th	Remarks
(4) Adsorption of Th from nitric acid-ethanol solution[99]	80% ethanol, 20% 3·5*N* nitric acid K_d for Th = 700 K_d for U = 9	Dowex 1 (nitrate form)	U, Ti, Zr, Fe, Al alkali-metals, nitrate, *etc.*[99]	Only Th is adsorbed on the resin. The elution of Th is performed with 0·1*N* nitric acid saturated with diethyl ether. Interference only in presence of high amounts of fluoride or phosphate. This method enables the determination of micrograms of Th in silicate rocks, marine sediments and other materials.[99,112,113]
(5) Separation of Th from U and other elements in nitric-acid-methanol solution[64]	90% methanol, 10% 5*N* nitric acid K_d for Th = 12,475 K_d for U = 33	Dowex 1 (nitrate form)	Fe^{III}, Co, Ni, Cu, Ag, Mg, Ca, Sn, Zn, Cd, Al, Y, Ti, Zr, Hf, V^{V}, Cr^{III}, Mo^{VI}, Mn^{II}, UO_2^{2+}, alkali metals, phosphate, chloride, sulphate and nitrate	Th, Ba, Pb, Bi, La Ce and other rare earth elements are adsorbed on the resin. The elution is performed with 1*N* nitric acid. Interference only caused by the co-adsorbed elements, if they are present in amounts exceeding 10 mg each. This procedure can be used for the quantitative separation of microgram and milligram amounts of Th. Pu^{IV} should under these conditions show a rather similar behaviour to Th[115,116]

to the bivalent form [see Methods (1) and (2)]. Among the reducing agents investigated, ascorbic acid turned out to be the most suitable, as it causes no interference in the column operations. Moreover, reduction of uranium^{VI} to uranium^{IV} does not take place under the conditions employed. The reducing effect of ascorbic acid on tervalent iron increases with decreasing concentrations of hydrochloric acid and alcohol (because of increasing complex formation of the tervalent iron ion with increasing hydrochloric acid and alcohol concentration). Because of this, the reduction of iron in Method (1) is more complete than it is in Method (2), where higher amounts of ascorbic acid must be used. A separation of thorium and iron cannot be affected in hydrochloric acid mixtures, since the necessary high alcohol concentrations inhibit the

TABLE IV. METHODS FOR THE SIMULTANEOUS ISOLATION AND SUBSEQUENT SEPARATION OF URANIUM AND THORIUM

Method	Composition of sorption solution	Eluants	Anion-exchange resin	Elements separated	Remarks
(6) Adsorption of U, Th, and Bi from nitric acid-propanol solution and separation of U, Th and Bi[102]	96% n-propanol, 4% 5*N* nitric acid K_d for U = 300 K_d for Th = 5,000 K_d for Bi = 4,000	For U: 80% methanol, 20% 5*N* nitric acid For Th: 80% methanol, 20% 6*N* hydrochloric acid For Bi: 1*N* nitric acid	Dowex 1 (nitrate form)	U, Th, Bi	This method is applicable for the separation of microgram and milligram amounts of U, Th and Bi. The determination of Bi was carried out using the well known bismuth iodide method.[114]
(7) Adsorption of Th and U from hydrochloric acid-butanol solution and separation of these elements from each other in hydrochloric acid-methanol solution[103]	90% n-butanol, 10% 6*N* hydrochloric acid K_d for Th = 250 K_d for U = 2,600	For Th: 90% methanol, 10% 6*N* hydrochloric acid For U: 1*N* hydrochloric acid.	Dowex 1 (nitrate form)	U, Th	This technique can be employed for the separation of microgram amounts of U and Th.

reduction of iron by ascorbic acid. In nitric acid solutions the separation of iron from thorium is very effective. Separation of uranium from thorium can be performed with practically all the above cited methods.

For simultaneous adsorption of uranium and thorium, Methods (6) and (7) can be employed successfully, utilising mixtures of very high alcohol content of higher aliphatic alcohols (90–96%) because otherwise the distribution coefficients for uranium would not be sufficiently high.

The precision of the individual methods described above for the various separations is, because of the completely quantitative adsorption or separation of uranium and/or thorium in practice, given by the precision of the polarographic, spectrophotometric or fluorimetric methods used for the final determination of these radioelements.

5. GENERAL THEORETICAL ASPECTS OF ION EXCHANGE IN MIXED SOLVENTS AND DISCUSSION OF RESULTS

Ion exchange in mixed and non-aqueous solutions is far less understood than ion exchange in pure aqueous systems; theoretical treatment is difficult because of the lack of sufficient data on the behaviour of electrolytes in mixed media. It is, however, a well known fact that the replacement of part of the aqueous phase by an organic solvent often enhances the ion-exchange absorbabilities of inorganic ions. In addition, the equilibrium quotient or selectivity coefficient for a given pair of ions is often higher when these ions are dissolved in a mixed or non-aqueous solvent, than when they are dissolved in water.[89,117,118]

The replacement of water by a non-aqueous solvent in an ion-exchange system can be expected to influence,[104] both in the solution and in the resin phase:

(*a*) Solvent uptake and swelling of the resin

(*b*) Dissociation
(*c*) Solvation
(*d*) Complex formation
(*e*) Ionic and molecular interaction.

These factors must be regarded as a coherent complex of mutually related variables.

Solvent uptake and swelling is primarily caused by the solvation tendency of all ions inside the resin phase, together with the electrostatic repulsion between the exchange sites of the matrix; or generally speaking, by osmotic and electrostatic forces acting against the tension of the resin matrix. Experiments have in many cases shown a relationship between solvent uptake and polarity of the solvent; the more polar the solvent the greater, usually, is the amount of solvent taken up, and hence the greater is the swelling of the resin, while solvents of low polarity are as a rule taken up to a less extent and produce less swelling.[72,117,119–124] For a mixture of water with an organic solvent, *e.g.*, acetone, in contact with an ion-exchange resin, it follows that water will be concentrated in the resinous phase[72,88,125] while the solution will be richer in the organic solvent. Thus the distribution of an ion between its solution and the ion-exchange resin in a mixed system cannot be regarded merely as an ion-exchange equilibrium but at the same time also as a partition between two liquid phases of different composition. The "selective solvent uptake" by a resin becomes more accentuated with decreasing water content of the mixed solvent and increasing cross linkage of the polystyrene matrix.[122,126,127]

That the ion-exchange resins swell less in solvents of smaller dielectric constant (DC) can be readily explained by Bjerrum's theory[128] of ion-pair formation. As ionic interaction increases with decreasing DC of the solvent, dissociation is repressed, and ion-pairs or even -triplets[129] can be formed, with the result that the effective number of osmotic-active exchange ions will diminish. Less swelling of a resin, like increased cross-linkage, causes an increase of selectivity coefficients.[117] Resin swelling is, however, not only influenced by the effect of polarity of the solvent on the ionic interaction, but also by the loading[122,123,126,127] of the resin, and by polar interactions as well as by dispersion interactions[130] between the solvent molecules and the resin. Solvent-uptake and swelling increase with increased similarity between the structure of the solvent molecules and the functional and structural groups of the matrix. The swelling of strong-base anion exchangers of the quaternary amine type in alcohols may be taken as a typical example of these effects, since the functional groups of these exchangers show a very high affinity for alcohols; this can compensate the contrary influence of the (compared with water) lower polarity of these solvents. Some authors[119,120] claim that resins of this type swell even more in methanol or ethanol than in water, while others[122,123] find that water, in comparison with alcohols, is still preferentially sorbed by such resins (but to a much less extent than by cation exchangers of the sulphonic acid type.)

Solvation and complex formation play a most important role in ion-exchange equilibria in mixed solvents. The substitution of increasing amounts of water by an organic solvent leads to stepwise dehydration[80] of the hydrated ions, to a progressive increase of ionic interaction, and hence to association in the mixed solution. It has been shown that the stability of negatively charged complexes,[1–21,131] *e.g.*, chlorocomplexes of cations in solution, can be markedly enhanced by the introduction of organic solvents.[70,80,81,92–98] This makes possible the adsorption of cationic elements which are only weakly, or almost not at all, adsorbed from pure aqueous solution as anionic complexes on anion-exchange resins. On the other hand, organic solvents can also serve to bring about selective elution, by complex formation with the ion to be removed from the resin.[76,88] In such a way selectivity coefficients can be greatly increased. The high adsorbabilities which are sometimes encountered in mixed-solvent ion-exchange systems can be explained by neutral adsorption.[71,87,119] Dissociation of the electrolyte is repressed by the low-DC solvent and the hydrophilic electrolyte is "extracted" as the "entire salt"[87] into the resin phase, where water is concentrated as mentioned above. On the other hand, neutral adsorption will also be promoted by the uptake of solvents of low DC into the resin.

High concentration and low DC will both intensify ionic interaction and pair formation. The ionic activities in the resin are correspondingly diminished, and consequently the interface potential (Donnan-potential) will be considerably reduced.[104] A decrease of the interface potential means that strong electrolytes, which are otherwise kept out (ion-exclusion), can enter the resin.

Several other factors, such as, for instance, the influence of ionic radii (solvated and unsolvated), ionic charge, ionic strength, the pH of the solution, which influence ion-exchange equilibria in mixed solvents, have not been discussed in the crude qualitative treatment given above; these must be taken into account if a particular system is to be investigated quantitatively. Severe limitations are, however, imposed in many cases by the lack of sufficient data on the behaviour of electrolytes in such systems.

Despite this complexity, an attempt has been made to approach the problem simply from the viewpoint of the DC of the solvent,[93,109,122,123,132] which seems to be justified to some extent because of the effect of the polarity of the solvent on resin swelling and on dissociation and complex formation, as already discussed. On the other hand, there are exceptions[117–120] to the parallelism between resin swelling and the DC of the solvent (caused for instance by interactions between resin and solvent molecules), and it is as yet impossible to calculate the DC within the resin phase.[104] Although apparently general quantitative information cannot be derived from the macroscopic DC of a solvent, it still seems possible to make qualitative predictions in some cases. Experiments with cation exchangers[89,132] have shown that in mixtures of some solvents of low DC with water the selectivity coefficients increase with increasing content of organic solvent; this can be taken as the effect of decreasing the DC of the solutions. Selectivity coefficients of various exchangers have been observed to increase in solvent mixtures where the organic solvent was replaced by a solvent with a similar type of molecular structure, but having a lower DC.[109,117,118] In our experiments (Section 3, Part II, 1 and 2) we have found that the effect of DC and chain length on the adsorption of uranium^{VI} and thorium^{IV} from ROH-mineral acid systems on strong-base anion exchangers is, in three cases out of six (uranium in HCl- and HNO_3-ROH and thorium in HCl-ROH), the expected effect (rise of K_d with decreasing DC); while in two cases no effect of DC was observed (uranium and thorium in H_2SO_4-ROH) and in one case there was actually a reverse effect, *i.e.*, a decrease of K_d with growing DC and chain length of the alcohols was found (thorium in HNO_3-ROH, see Fig. 5). For this last no theoretical explanation can be offered. Yet in all mixtures of a given alcohol, the adsorption increased with increasing percentage of the alcohol (and decreasing DC) in the solution; and in any mixture containing any alcohol the adsorption was higher than if this alcohol was replaced by water. It may be mentioned here that a study of the adsorption behaviour of vanadium^{IV} and vanadium^{V} in hydrochloric acid-alcohol solutions, which was earlier described,[81] showed almost the same relationship between alcohol chain length (and also DC) and K_d as uranium^{VI} and thorium^{IV} under corresponding conditions. So far it seems that where the effect of the DC of the solvent on the adsorption of ions from acid-solvent mixtures on strong-base anion exchangers is concerned, with a few exceptions only systems containing the same mineral acid in the same concentration, and solvents of a very similar molecular structure (homologous alcohols, ketones, ethers, *etc.*), can be compared.

Thermodynamically there are three mechanisms of adsorption possible[133] for anion exchange on strong-base anion exchangers:

Mechanism I: Strong anionic complexes are formed in solution, and these are regularly exchanged with the counter-ions of the exchanger.

1. *Complex formation:*

$$A^{n+} + bB^{m-} \rightleftharpoons (AB_b)^{(m-n)-}$$

2. *Anion exchange:*

$$(AB_b)^{(m-n)-} + \overline{(m-n)\cdot[(R_s^+)(C^-)]} \rightleftharpoons \overline{[(R_s^+)_{(m-n)}(AB_b]^{(m-n)-}} + (m-n)C^-$$

Mechanism II: Because of insufficient stability of the charged complex in the liquid phase, the formation of the neutral complex is favoured; this diffuses into the resin, where it is bound by the counter-ions as a complex with several ligands.[71,134,135]

1. *Complex formation:*

$$mA^{n+} + nB^{m-} \rightleftharpoons A_mB_n$$

2. *Adsorption:*

$$A_mB_n + \overline{x[(R_s^+)(C^-)]} \rightleftharpoons \overline{[(R_s^+)_x(A_mB_n)(C^-)_x]}$$

Mechanism III. The cations which exist in solution can only enter the resin if the counter-ions have at least one exchangeable proton:

1. *Proton exchange:*

$$n(CH)^{m-} + A^{n+} \rightleftharpoons (C_nA)^{m-} + nH^+$$

2. *Anion exchange:*

$$(C_nA)^{m-} + \overline{[(R_s^+)m(CH)^{m-}]} \rightleftharpoons \overline{[(R_s^+)_m(C_nA)^{m-}]} + (CH)^{m-}$$

A^{n+} = cation of charge n+
B^{m-} = anion of charge m−
b = number of anions to form the anionic complex $(AB_b)^{(m-n)-}$ in solution with a negative charge of (m − n)−
R_s^+ = bound cation (resin phase)
C = counter-ion
x = number of ligands
$(CH)^{m-}$ = complex anion of charge m−, containing an exchangeable H [*e.g.*, $(SO_3H)^-$)]. Components covered by a bar are in the resin phase.

The existence of negatively charged uranyl and thorium complexes[1–21,133–137] has earlier been established (except for thorium in hydrochloric acid medium.) It is believed, however, that at higher alcohol concentrations, especially with the higher alcohols, ion-exchange adsorption has neutral adsorption increasingly superimposed on it, as has been postulated by Katzin and Sullivan[87] for the adsorption of uranyl chloride and uranyl nitrate from oxygen-containing organic solvents on strong-base anion-exchange resins, and by Tera and Korkisch for their adsorption from hydrochloric acid-[93] and nitric acid[94]-alcohol systems on such resins.

To establish the formulae of the complexes in the systems where highest adsorption occurred, the exchange capacities of Dowex 1 for uranium and thorium (see Section 3, part IV) have been determined by constructing the corresponding adsorption isotherms. In this paper the variation of the distribution coefficient with increasing concentration (see Figs. 7a and 7b) is emphasised, in order to make the analytical applicabilities more obvious. The encircled points in these figures (pp. 971–2) are equivalent to the beginning of the horizontal part of the corresponding adsorption isotherms, where the resin is already saturated with the ion in question. The exchange capacity can be calculated there, or for other points on the curve, using the simple relationship:

$$\text{mg of uranium or thorium/g of resin} = \frac{K_d \times W}{V_s + K_d}$$

W = mg of uranium or thorium in solution before the addition of the resin
V_s = volume of the solution.

The maximal amount of uranium or thorium taken up by the resin (= exchange capacity = C_e) was used for calculating the number of negative charges of the complexes in the resin phase, by means of the formula:

$$n = \frac{3{\cdot}4 \times A}{C_e}$$

A = atomic weight of adsorbed element (uranium or thorium)
3.4 = capacity of the resin (chloride, nitrate or sulphate; see Section 2, part IV) in mg equiv./g of dry resin
n = number of negative charges in the complex
C_e = exchange capacity of the resin for uranium or thorium in mg/g of dry resin under the conditions selected.

The values found for n were as follows:

UO_2^{2+} in 90% ethanol + 10% 6*N* HCl	2
UO_2^{2+} in 96% n-propanol + 4% 5*N* HNO_3	4
UO_2^{2+} in 90% n-propanol + 10% 1*N* H_2SO_4	4
Th^{4+} in 90% isopropanol + 4% 12*N* HCl	13·6
Th^{4+} in 90% methanol + 10% 5*N* HNO_3	3·4

(Neither the adsorption isotherm nor a K_d-concentration plot were set up for thorium sulphate in H_2SO_4-alcohol medium because of its low solubility in this system.)

The negatively charged uranyl complexes calculated from the above values correspond to the formulae:

$$(UO_2(Cl)_4)^{2-} \quad (UO_2(NO_3)_6)^{4-} \quad \text{and} \quad (UO_2(SO_4)_3)^{4-}.$$

For thorium in hydrochloric and nitric acid-alcohol media no stoicheiometric formulae could be derived.

To support the above postulates concerning the adsorption mechanism of uranyl and thorium (combination of mechanisms I and II) we shall discuss in detail the adsorption of uranyl chloride from hydrochloric acid alcohol mixture on Dowex 1, and then the other systems more briefly. Mechanism I is known to take place in aqueous hydrochloric acid solutions as shown by Kraus and collaborators[1–5] and can be written:

1. $UO_2Cl_2 + 2\,Cl^- \rightleftharpoons UO_2(Cl)_4)^{2-}$

2. $(UO_2(Cl)_4)^{2-} + \overline{2(R_s{}^+Cl^-)} \rightleftharpoons \overline{((R_s{}^+)_2(UO_2)(Cl_4{}^{2-})} + 2\,Cl^-$

From equation 1 it is evident that increasing concentration of chloride ions should favour complex formation and hence adsorption. Since the increase of hydrochloric acid concentration also strongly increases the adsorption of uranyl chloride from hydrochloric acid-alcohol mixtures (see Fig. 6a, Section 3), mechanism I appears to be valid in such systems. If it is considered that there is a direct addition of uranyl chloride to the resin, mechanism II can be represented:

$$UO_2Cl_2 + 2\,\overline{(R_s{}^+Cl^-)} \rightleftharpoons \overline{((R_s{}^+)_2(UO_2\,(Cl)_4{}^{2-})}$$

This mechanism is supported by the fact that equilibrium is attained almost immediately in hydrochloric acid-alcohol mixtures with a high percentage of alcohol; this can be observed visually by the rapid loss of colour of the solution after addition of the anion exchanger.[71] Measurements show that 5 min after the resin is brought into contact with the uranium-containing solution (90% ethanol + 10% 6*N* hydrochloric acid) more than 90% of the exchange capacity is reached.

Since the diffusion rate is a function of the radius of the solvated ion in question, and since a neutral complex will be much less solvated than a charged one, mechanism II seems also to apply here. Further, it was observed that UO_2Cl_2 was also considerably adsorbed from mixtures containing water and alcohols in the absence of hydrochloric acid,[93] supporting the assumption that mechanisms I and II occur simultaneously. The existence of only one negatively charged chloro complex of uranium is obvious from Fig. 6a, since the slope,

$$\mathrm{tg}\alpha = \frac{\text{charge of complex}}{\text{charge of complexing anion}} = \frac{d \log K_d}{d \log \text{normality of acid}},^{133}$$

of the K_d acidity curves shows practically no deviation from linearity. Since the adsorption of thorium from hydrochloric acid-alcohol mixtures of low alcohol content (see Fig. 6a, curves X, XI and XII) increases with increasing hydrochloric acid concentration, mechanism I seems to be partly responsible for the adsorption. At a very high alcohol concentration, however (see Fig. 6a, curve XIII), K_d does not vary with acidity; this can be taken as evidence for mechanism II, indicating that only neutral adsorption occurs under these conditions. Further evidence comes from the fact that no stoicheiometric amount of thorium is taken up by the resin (see above, page 980).

For the adsorption of uranium nitrate in nitric acid-alcohol mixtures, mechanism I seems to apply; this can be concluded from the increase of K_d with acidity (see Fig. 6b, curves 1–VI), although it diminishes at acidities higher than 0·7*N*, so that the K_d reaches a saturation value. At high alcohol concentration mechanism II will prevail. From the linearity of curves IV–VI it follows that only one negatively charged uranium complex is present, the composition of which (for the formula see above was calculated for a 96% n-propanol-4% nitric acid mixture.

The adsorption of thorium nitrate from nitric acid-alcohol solutions shows an increase of neutral adsorption with increasing alcohol concentration (compare curves VIII–XI, Fig. 6b). Mechanism I accounts for the linear increase of the distribution coefficient with increasing acidity in 40% alcohol (curve VIII). The maxima in curves IX and X correspond to the maximal molality of the neutral complex in solution, as has been pointed out by Antal,[133] who proved that the increase of K_d with the acidity at low nitric acid concentrations (left hand side of the maxima) is the result of mechanism I, whereas the increase of K_d with decreasing acidity at higher nitric acid concentration (right hand side of the maxima) is caused by mechanism II (increasing neutral adsorption). At very high alcohol percentage in the mixture (curve XI), no effect of acidity on the distribution coefficient was observed, suggesting that only neutral adsorption (mechanism II) takes place. Since even in 90% methanol + 10% 5*N* nitric acid mixture more than the theoretical amount of thorium nitrate is adsorbed on the resin, this can be taken as definite proof of the existence of neutral adsorption. Under these conditions, 3·96 mg equiv of thorium or 230 mg were taken up by the resin, which has a real capacity of only 3·4 mg equiv of thorium/g (see Section 2 and Fig. 7b, Section 3), so that no stoicheiometric formula for a thorium nitrate complex could be established.

Since mechanism II has already been confirmed for the adsorption of uranyl sulphate in pure aqueous sulphuric acid solution by Arden and Wood,[134] the introduction of alcohol should be expected to enhance neutral adsorption further. That this is really the case may be deduced from the fact that the distribution coefficients in such media are extremely high at high alcohol concentrations and very low acidity. (See Fig. 6c). The uranyl trisulphato complex corresponding to the formula derived from our results (see above, page 970) is in accordance with that obtained by Arden and Wood[134] in aqueous sulphuric acid. As the first "step" in curve III (Fig. 7a) seemed to imply the existence of a higher charged sulphato complex, n was calculated for the middle of the step (135 mg uranium originally in soln, $K_d \simeq 22{,}000$) and found to be $\sim$6. This is another proof of the existence of the complex $[(UO_2)(SO_4)_4]^{6-}$, which was also postulated by the above mentioned authors.[134] Neither of these highly charged negative complexes is, however, believed to exist in measurable amounts in solution. The investigations of Antal,[133] who has postulated the existence of several thorium sulphate complexes, including neutral complexes such as $[Th(SO_4)_2]^\circ$ and $(ThOSO_4)^\circ$, in the resin phase, as well as the results of our own experiments (see Fig. 6c), suggest that thorium is also adsorbed from sulphuric acid-alcohol mixtures in the same way as uranium (mechanism II).

In conclusion, it might be said that much more research will have to be conducted in the field of the anion exchange of uranium and thorium in mixed and non-aqueous solvents, before we will have gained complete understanding of the subject; but current investigations are likely to lead to the development of useful new analytical methods in the near future.

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Zusammenfassung—In der vorliegenden Arbeit werden die bis jetzt veroeffentlichten Resultate hinsichtlich des Anionaustauschverhaltens von Uranium (VI) und Thorium (IV) in Loesungsmittelgemischen zusammengefasst und das Adsorptionsverhalten dieser beiden Radioelemente am stark basischen Anionenaustauscher Dowex 1 in Mischungen bestehend aus Salz-, Salpeter-oder Schwefelsaeure und aliphatischen Alkoholen genau beschrieben. Die Verteilungskoeffizienten bei verschiedenen Saeurenormalitaeten, Alkoholkonzentrationen, Uran- und Thoriumkonzentrationen sowie bei den unterschiedlichen Kettenlaengen und Dielektrizitaetskonstanten der angewendeten Alkohole werden angegeben. Ausserdem werden einige auf Grund dieser Resultate entwickelten Trennungsverfahren des Urans bezw. Thoriums voneinander oder von anderen Elementen beschrieben. Abschliessend werden theoretische Betrachtungen ueber die Art, wie diese beiden Elemente adsorbiert werden, angestellt.

Résumé—Cet article résume les résultats importants obtenus jusqu'à présent sur le comportement de l'uranium (VI) et du thorium (IV) sur résine échangeur d'anions dans des mélanges de solvants, ainsi que les résultats de travaux de recherches effectuées au laboratoire. Les auteurs se proposent de donner une description détaillée du comportement de ces actinides sur des résines échangeurs d'anions fortement basiques dans des solutions d'acide minéral contenant des alcools aliphatiques. Les études d'équilibre ont montré que les coefficients de partage varient beaucoup avec l'acide utilisé comme le montrent les résultats récents obtenus dans les systèmes aqueux. Dans les mélanges d'un acide minéral donné avec différents alcools, les coefficients de partage dépendent du pourcentage d'alcool, de l'acidité des solutions, des constantes diélectriques et des longueurs de chaîne des alcools utilisés. Les résultats de ces recherches peuvent être appliqués à la séparation du thorium et de l'uranium, d'une part l'un de l'autre, d'autre part pratiquement de tous les cations et les anions. Deux des méthodes de séparation mises au point ont déja été appliquées au dosage de l'uranium et du thorium dans des produits de composition très variée. Finalement les aspects théoretiques généraux de l'échange anionique dans des mélanges de solvants sont discutés et les résultats obtenus pour l'uranium et le thorium sont interprétés par conséquence.

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ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—VI*

A SPECTROPHOTOMETRIC STUDY OF THE NIOBIUM-XYLENOL ORANGE COMPLEX

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Summary—The red niobium-Xylenol Orange complex has been studied spectrophotometrically. It offers a sensitive and selective reaction for the determination of traces of niobium. The coloured complex formed at pH 2·4 to 2·8 by heating in the presence of tartrate has a molar absorptivity of 16,000 and a formation constant of 5×10^6 under the conditions studied. Most metals, including tantalum, vanadium and tungsten, do not interfere when zinc-EDTA complex and tartrate are used as masking agents. Nitrite, oxalate, pyrophosphate, and phosphate interfere. Fluoride can be demasked by addition of beryllium. Platinum gives a dark purple colour which also interferes.

XYLENOL Orange forms a red coloured complex with niobium in a weakly acidic medium.[1] The coloured complex is stable and can be used as a basis for the determination of traces of niobium. The recent excellent review by Elwell and Wood[2] makes it apparent that new, sensitive, and selective methods for niobium are desirable. This paper reports a new, sensitive and selective photometric method for niobium, including the conditions for the colour development of the complex, its composition, its formation constant, and masking effects. It is interesting to point out that tantalum does not undergo any colour reaction with Xylenol Orange and that the interference of titanium, vanadium, molybdenum, and many other metals may be eliminated by zinc-EDTA and tartrate. It seems that Xylenol Orange offers one of the most sensitive and highly selective reactions for niobium (see Table I).

TABLE I.—SENSITIVITY OF SOME COMMON PHOTOMETRIC METHODS FOR NIOBIUM

Method	μg of Nb per cm^2 log $I_0/I = 0{\cdot}001$
Thiocyanate (ethyl ether extraction)	0·0029 (385 mμ)
Thiocyanate (60% v/v acetone)	0·0024 (383 mμ)
Xylenol Orange	0·0058 (535 mμ)
Oxine (chloroform extraction)	0·009 (345 mμ)
Tiron	0·01 (281 mμ)
Hydrochloric acid (12M)	0·01 (281 mμ)
Hydrogen peroxide	0·11 (365 mμ)

EXPERIMENTAL

Apparatus and reagents

Standard niobium solution: A 0·01M stock solution was prepared by fusing 0·1329 g of pure niobium pentoxide with 3 g of potassium pyrosulphate in a platinum crucible, dissolving the melt with 4 ml of concentrated sulphuric acid and 6 ml of water, and making to 100 ml with sulphuric acid and

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* Part V: *Talanta*, 1960, **5**, 254.

water after cooling. The solution contained 40 ml of concentrated sulphuric acid in 100 ml. Alternatively, the melt may be dissolved in 50 ml of water containing 10 mmoles of tartaric acid and diluted to 100 ml with water. Appropriate standard niobium solutions, such as $5 \times 10^{-4}M$, were prepared from the stock solution.

1·0M Tartaric acid

0·1M Zinc-EDTA complex solution: Prepared from pure zinc-ethylenediaminetetra-acetate complex or by mixing appropriate amounts of zinc and the disodium salt of EDTA in water. This solution should contain no significant amounts of free EDTA.

Other apparatus and reagents are the same as those reported previously.[1]

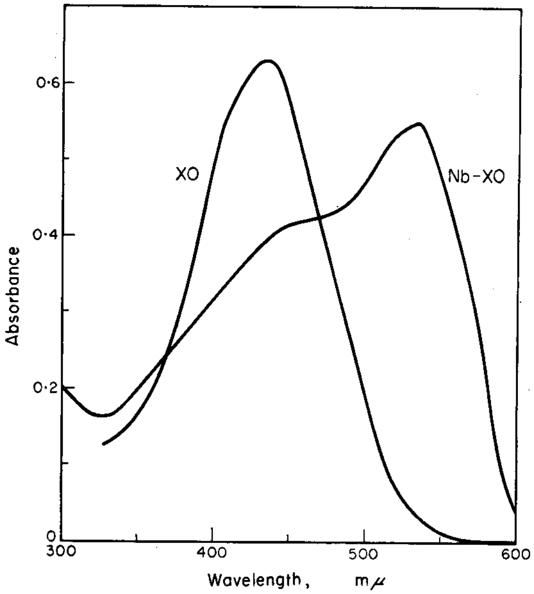

FIG. 1.—Absorption spectra.

Procedure

Calibration curve: Pipette 0 to 4·0 ml of $5 \times 10^{-4}M$ niobium solution into a 100-ml beaker, add 2·0 ml of $1 \times 10^{-3}M$ Xylenol Orange solution, 0·1 mmole of zinc-EDTA, 1 drop of 1·0M tartaric acid, and 2·0 ml of 1:1 formic acid. Adjust the pH of the solution to 2·7 and dilute to approximately 15 to 20 ml with water. Cover with a cover glass, heat to boiling on a hot plate for 10 to 15 min, remove and allow to cool to room temperature (do not cool rapidly with cold tap water). After gradual cooling, transfer to a 25-ml volumetric flask and make to volume with water. Measure the absorbance at 535 mμ against a reagent blank. Beer's law is followed. The presence of zinc-EDTA increases the absorbance slightly.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra for Xylenol Orange and its niobium complex are shown in Fig. 1. The maximum absorption for the niobium complex is at 535 mμ.

Effect of pH

A series of solutions containing 2·0 ml of $5 \times 10^{-4}M$ niobium solution, 2·0 ml of $1 \times 10^{-3}M$ Xylenol Orange solution, 0·1 mmole of zinc-EDTA, 1 drop of 1·0M tartaric acid, and 2·0 ml of formic acid were prepared. Sodium hydroxide was used for pH adjustment and the colour development was made by boiling and cooling as previously described. The optimum pH range is fairly narrow, the maximum colour development being found to occur at pH 2·4 to 2·8.

Effect of Xylenol Orange

The curve given in Fig. 2 has the same pattern as those previously reported, in that excess of Xylenol Orange tends to decrease the absorbance. Two ml of 1 × $10^{-3}M$ Xylenol Orange solution are recommended for 0 to 2 μmoles of niobium in 25 ml.

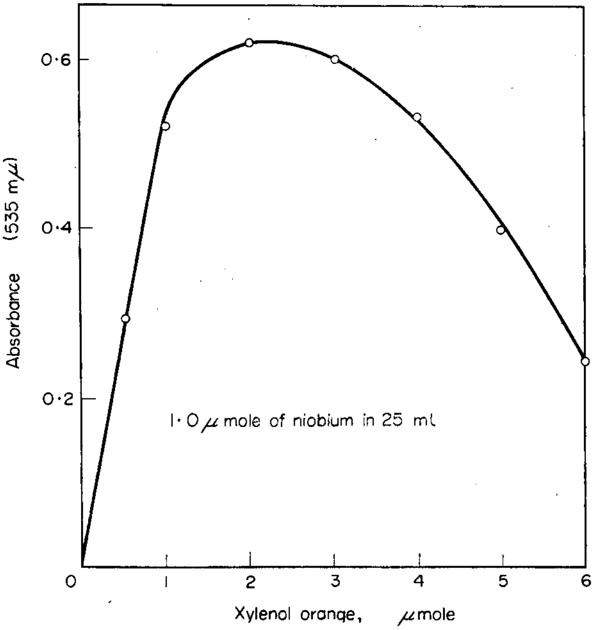

FIG. 2.—Effect of Xylenol Orange.

Effect of temperature

Previously, the colour reaction of niobium and Xylenol Orange was reported to be insensitive,[1] because the test was carried out in the absence of tartaric acid and at room temperature. Later it was reported that niobium gives a sensitive colour reaction with either Xylenol Orange or Methylthymol Blue upon heating in the presence of tartaric acid.[3] By heating for 10 to 15 min there results a linear relationship between the absorbance and temperature below 80°. The absorbance increases slightly at temperatures above 80°, the maximum colour development requiring a temperature of 90 to 100°. It is noted that the maximum colour development also requires a gradual cooling after boiling; therefore, the solution should not be cooled rapidly. Reproducible results were obtained by letting the solution cool at room temperature for 30 min or longer.

Effect of time

It was found that for 1·0 μmole of niobium the boiling time should be longer than 7 min; however, a longer time of boiling does not change the absorbance. It is recommended that the solution be boiled for 10 to 15 min in order to ensure maximum colour development.

Effect of volume

It was noted that irregular absorbancies resulted by using too small or too large a volume of solution during the boiling period. The optimum volume of the solution during boiling is 15 to 20 ml when 2 ml of 1 × $10^{-3}M$ Xylenol Orange solution and the specified amounts of other reagents are added.

Effect of tartaric acid and citric acid

The presence of tartaric acid is necessary for the colour development. Apparently, without tartaric acid, niobium is easily hydrolysed at pH 2 to 3; at lower pH values niobium cannot compete with protons to form the Xylenol Orange complex. Tartaric acid seems to serve as a solubilising agent to render niobium available for the complex formation; large amounts of tartaric acid do not inhibit the complex formation (see Fig. 3). Citric acid on the other hand inhibits the colour development. It is known that citric acid, in general, is a stronger complexing agent than tartaric acid. The big difference in their behaviour towards the complex formation of niobium and Xylenol Orange is rather surprising.

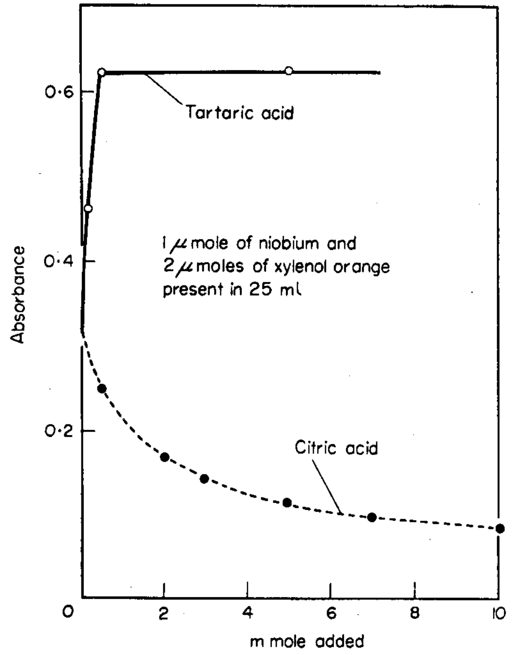

FIG. 3.—Effect of tartaric and citric acids.

Effect of EDTA and other complexing agents

As shown in Table II, acetate decreases the absorbance; it is believed that niobium forms a weak complex with acetate. EDTA also decreases the absorbance (Fig. 4). Oxalate, nitrilotriacetic acid (NTA), 1,2-diaminocyclohexanetetra-acetic acid (DCTA), and diethylenetriaminepenta-acetic acid (DTPA) completely prevent the colour development. Niobium has been studied polarographically in an EDTA medium indicating the formation of a niobium–EDTA complex.[5–7] It is surprising that NTA, generally believed a weaker complexing agent compared to EDTA, is more efficient than EDTA in preventing the niobium-Xylenol Orange reaction. It was thought that addition of a weak metal-EDTA complex might serve as an excellent masking agent to prevent interference from other heavy metals and at the same time give no decrease in absorbance at pH 2 to 3. Manganese^{II}-EDTA and zinc-EDTA were selected and their masking effects are given in Fig. 5. Manganese^{II}-EDTA is not a good masking agent in this case; however, the zinc-EDTA complex is an excellent one.

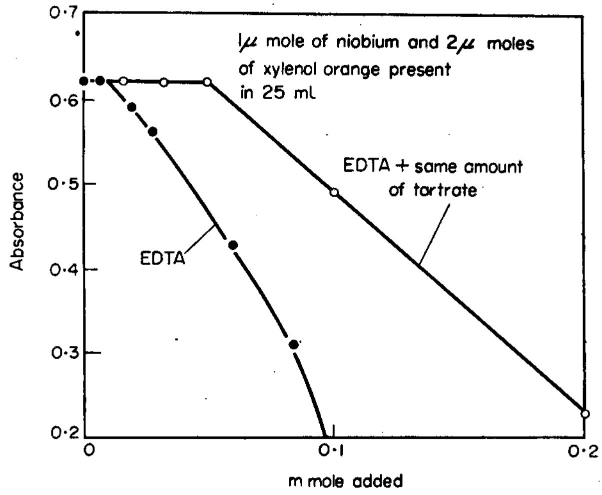

FIG. 4.—Effect of EDTA.

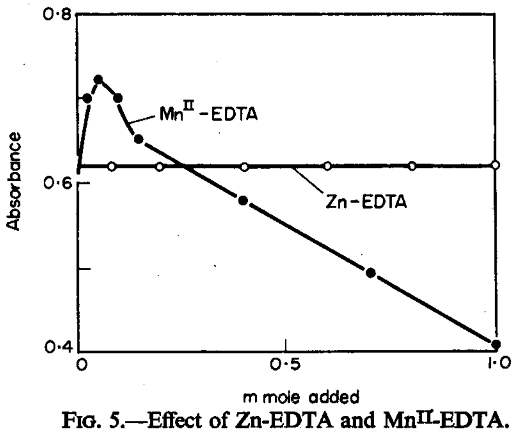

FIG. 5.—Effect of Zn-EDTA and Mn^{II}-EDTA.

This is because manganese^{II}-EDTA is a weaker complex than is the zinc-EDTA complex. The former has an apparent stability constant, $\log K_H = \log K - \log \alpha_H = 16{\cdot}5 - 10{\cdot}5 = 3{\cdot}1$ and the latter $\log K_H = 16{\cdot}5 - 10{\cdot}5 = 6{\cdot}0$, the latter being twice as stable as the former at pH 2·7. At pH 2·7 there is a sufficient amount of free EDTA dissociated from the manganese^{II}-EDTA complex to prevent the niobium-Xylenol Orange reaction. However, many metal ions, such as iron, copper, titanium, bismuth, zirconium, *etc*., can displace zinc from the zinc-EDTA complex, otherwise these ions would give coloured reactions with Xylenol Orange at pH 2·7. The zinc ion does not give any coloured reaction with Xylenol Orange at a pH below 3; and niobium cannot displace zinc to form free EDTA. The presence of tartrate prevents the hydrolysis of niobium and allows the toleration of some free EDTA. Addition of very small amounts of manganese^{II}-EDTA to give an "absorption maximum" remains unexplained.

Effect of anions

The effects of many common anions were studied; the results are shown in Table II. Most of the anions do not interfere. Surprisingly, nitrite completely inhibits the colour reaction of niobium and Xylenol Orange; however, no such effect was noticed when nitrite was added to the solution of the pre-formed niobium-Xylenol Orange complex. Large amounts of phosphate, pyrophosphate, arsenate, and traces of fluoride bleach the colour. Except for fluoride, the presence of less than 0·05 mmole of any of the anions does not interfere. Fluoride can be demasked* by addition of beryllium. The effect of acetate can be eliminated by addition of more tartrate (1 mmole). It should be emphasised that large amounts of sulphate and tartrate do not interfere; this is important because they are frequently used in keeping niobium in solution. Vanadate and tungstate do not interfere under the conditions described.

TABLE II.—DETERMINATION OF NIOBIUM IN THE PRESENCE OF ANIONS*

Anion Added	*Absorbance*	*Remark*
None	0·860	
Acetate	0·680	
	0·867	1 mmole of acetate; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Arsenate	0·335	
	0·865	0·05 mmole of arsenate; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Ascorbic acid	0·864	
Bromide	0·865	
Chloride	0·855	5 mmoles of chloride added.
Fluoride	0·845	2 mmoles of beryllium added.†
Iodide	0·870	
Molybdate	0·855	
Nitrate	0·870	
Nitrite	0·000	
Perchlorate	0·860	
Phosphate	0·480	
	0·848	0·05 mmole of phosphate added; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Pyrophosphate	0·122	
	0·854	0·05 mmole of pyrophosphate added. 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Sulphate	0·852	10 mmoles of sulphate added.
Vanadate	0·625	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
	0·851	0·075 mmole of Zn, 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.‡
Tungstate	0·865	

* Niobium taken: 1·35 μmoles; anion added: 1 mmole; Zn-EDTA added: 50 μmoles; tartaric acid added: 50 μmoles; volume: 25 ml.

† Fluoride is demasked by beryllium.

‡ The interference of vanadate may be caused by its oxidation of the dye or by its complex formation with niobium or the dye. Addition of free zinc ion is an example of demasking by forming a zinc-vanadate complex.

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* For a definition of the term "demasking", see K. L. Cheng, *Analyt. Chem.*, 1961, **33,** 783.

Effect of foreign metal ions

Xylenol Orange is a selective reagent in a relatively strong acidic medium; above pH 2·5 many metal ions give coloured reactions with Xylenol Orange. In order to increase its selectivity, suitable masking agents must be used. Most common metal ions do not interfere if zinc-EDTA and tartrate are added, as shown in Table III. Cerium^{IV} interferes because of its oxidising ability, but cerium^{III} does not. The interference of platinum^{IV} could not be masked by zinc-EDTA and tartrate. Tantalum and tin do not interfere.

TABLE III.—DETERMINATION OF NIOBIUM IN THE PRESENCE OF FOREIGN METALS.

Metal Added	*Absorbance*	*Remark*
None	0·860	
Al	0·868	0·2 mmole of Zn-EDTA and 1 mmole of tartrate added
$\mathrm{Sb^{III}}$	0·858	
Bi	0·860	
Cd	0·860	
Ca	0·865	
$\mathrm{Ce^{III}}$	0·470	
	0·850	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added
$\mathrm{Co^{II}}$	0·865	
$\mathrm{Cu^{II}}$	0·853	
Ga	0·850	
Hf	0·855	
In	0·860	
$\mathrm{Fe^{III}}$	0·858	
La	0·863	
$\mathrm{Pb^{II}}$	0·864	
$\mathrm{Hg^{II}}$	0·856	
Ni	0·700	
	0·720	0·1 mmole of Zn-EDTA and 0·05 mmole of tartrate added
	0·865	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added
$\mathrm{Pt^{IV}}$	0·700	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added; Pt forms a dark purple colour with Xylenol Orange.
$\mathrm{Ag^{I}}$	0·880	
Ta	0·850	0·1 mmole of Ta added; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Th	0·850	
$\mathrm{Sn^{IV}}$	0·800	
	0·865	1 mmole of tartrate added
$\mathrm{Ti^{IV}}$	1·50	
	0·870	0·2 mmole of Zn-EDTA added
$\mathrm{UO_2^{II}}$	0·852	
Zr	0·858	

* Niobium taken: 1·35 μmoles; foreign metal added: 10 μmoles; Zn-EDTA added: 50 μmoles; tartaric acid added: 50 μmoles; Volume: 25 ml.

Complex formation

It is difficult for niobium to react directly with Xylenol Orange, but it readily forms a coloured complex with Xylenol Orange upon heating in the presence of tartrate, which likely acts as a carrier.

Niobium forms chiefly a 1:1 complex with Xylenol Orange, as indicated by Job's method (Fig. 6). The formation constant was calculated from the curves in Fig. 6 based on the method used previously.[4] It was found to be 5·0 × 10^6 at pH 2·5. Because of its relatively low stability, it is easily understood why oxalate, pyrophosphate, phosphate and fluoride can bleach the colour reaction of niobium and Xylenol Orange.

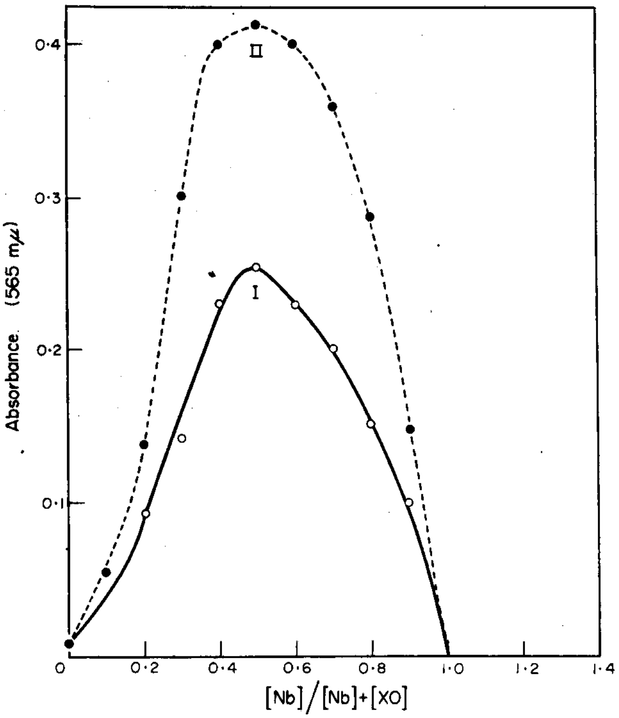
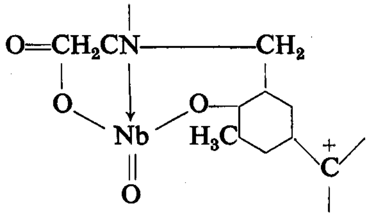


FIG. 6.—Job's curve.

I—Total concentration of niobium and Xylenol Orange = 4 × $10^{-5}M$.
II—Total concentration of niobium and Xylenol Orange = 8 × $10^{-5}M$.

Niobium has a tendency to form stable complexes with compounds having β-diketo, carboxylic acid, or phenolic groups. Therefore, it is believed that the phenolic, amine, and carboxylic groups of Xylenol Orange are involved in the chelation:



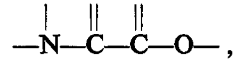
Methylthymol Blue, an analogue of Xylenol Orange, behaves similarly towards niobium, forming a red coloured complex upon heating in a weakly acidic medium in the presence of tartrate. That 3,3′-bis-[N,N-di(carboxymethyl)aminomethyl]thymolphthalein (Methylthymol Blue without the sulphonate group) gave no coloured reaction with niobium is not understood, at present.

For future synthesis of new colorimetric reagents for niobium, the present results suggest that replacement of the methyl group with a hydroxyl or carboxylic group on the phenolic ring of Xylenol Orange may result in more sensitive or more stable colorimetric reagents for niobium.

Just as with Xylenol Orange and Methylthymol Blue, it has been found that niobium reacts with 1-(2-pyridylazo)-2-naphthol (PAN) or with 4-(2-pyridylazo)-resorcinol

(PAR) at pH 2·5–3·0, on heating in the presence of tartaric acid, giving a sensitive red colour. The selectivity of these reactions can also be improved by adding Zn-EDTA.

It is interesting to note that the four dyes contain a common grouping,



$$-\overset{|}{N}-\overset{\|}{C}-\overset{\|}{C}-O-\,,$$

and that the same conditions for its formation apply. The Nb-PAN complex can be extracted by isoamyl alcohol.

Zusammenfassung—Der rote Niob-Xylenol Orange-Komplex wurde spectrophotometrisch untersucht. Der Komplex bietet die Grundlage für eine empfindliche und selektive Bestimmung von Spuren von Niob. Der Komplex bildet sich bei pH 2·4–2·8 in Gegenwart von Tartrat unter Erwärmen und hat einen molaren Absorptionskoeffizienten von 16,000. Die Stabilitätskonstante unter den gegebenen Bedingungen ist 5.0×10^6. Die meisten Metalle, einschliesslich Ta, V und W stören nicht, wenn Zn-ÄDTE und Tartrat als Maskierungsmittel zugesetzt werden. Fluorid, Nitrit, Oxalat, Pyrophosphat und Phosphat stören. Platin gibt eine dunkle Purpurfärbung und stört ebenfalls.

Résumé—Les auteurs ont étudié par spectrophotométrie le complexe rouge niobium-orangé de xylénol. Ce composé donne une réaction sensible et sélective pour le dosage de traces de niobium. Le complexe coloré formé par chauffage à pH 2,4–2,8 en présence de tartrate a une absorption molaire de 16.000 et une constante de formation de $5{,}0 \times 10^6$ dans le conditions étudiées. La plupart des métaux, dont le tantale, le vanadium et le tungstène ne gênent pas si on utilise le complexe zinc-EDTA et le tartrate comme agents complexants. Le fluorure, le nitrite, l'oxalate, le pyrophosphate et le phosphate gênent. Le platine donne une coloration pourpre foncée et gêne.

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UNTERSUCHUNGEN ÜBER DIE REAKTIONSFÄHIGKEIT VON CHROM UND TITAN MIT PYRROLIDINDITHIOCARBAMINAT

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Zusammenfassung—Es wird die Reaktionsfähigkeit von Titan in Abhängigkeit vom pH-Wert der Lösung und anderer anwesender Anionen und die Reaktionsfähigkeit von Chrom in Abhängigkeit von dem Bindungszustand des Chrom(III)-Ions und dem pH-Wert der Lösung jeweils mit Pyrrolidindithiocarbaminat untersucht. Die gewonnen Ergebnisse geben eine Erklärung für die zur Zeit sehr unterschiedlichen Beschreibungen der Reaktionsfähigkeit der beiden Metalle Chrom und Titan mit disubstituierten Dithiocarbaminaten.

EINLEITUNG

Das Studium der Literatur zeigt, daß bezüglich der Reaktion von Chrom bzw. Titan mit disubstituierten Dithiocarbaminaten sehr unterschiedliche Ansichten bestehen.

Titan

In Übereinstimmung mit der zeitlich vorhergehenden Literatur führt der eine von uns[1] 1955 an, daß das Titanion keine Reaktion mit einer Pyrrolidindithiocarbaminatlösung eingehe. Darauf aufbauend wurde eine Methode entwickelt,[2] die es ermöglicht, mit Hilfe von Pyrrolidindithiocarbaminat Schwermetalle in Eisen und Eisenerzen quantitativ von Titan abzutrennen. O. G. Koch[3] beschreibt eine Abtrennung der Schwermetalle von Titan in Titanmetall und Titanlegierungen auf dieselbe Weise. Demgegenüber stehen die Bericht von Rooney[4,5] aus 1958, denen zufolge eine Titandiäthyldithiocarbaminat-Verbindung besteht, die er sogar beschränkt dazu auswerten konnte, um im Gußeisen eine positive Trennung Titan von geringen Mengen Aluminium durchzuführen.

In der Tatsache allein, daß einerseits Diäthyldithiocarbaminat, andererseits Pyrrolidindithiocarbaminat verwendet wurde, ist nicht von vornherein eine Erklärung des Widerspruches zu suchen, da übereinstimmend aus sämtlichen Literaturangaben hervorgeht, daß sich die einzelnen Carbaminate nicht prinzipiell in iherm Verhalten verschiedenen Kationen gegenüber unterscheiden, sondern daß Differenzierungen nur im mengenmäßigen Ausmaß und in der Geschwindigkeit der Reaktionen liegen.

Chrom

Auch über die Fällbarkeit des Chroms bestehen zwei Ansichten. Malissa und Mitarbeiter[6] führen eine Chromdiäthyl-, sowie eine Chrompyrrolidindithiocarbaminatverbindung an, während Bode[7] für Diäthyldithiocarbaminat im pH-Bereich 4–11 keine Reaktion mit Chrom feststellen konnte, allerdings setzte er für seine Versuche

Kaliumchromalaun ein. Nach Gleu und Schwab[8] ist die Bildung der Chrompyrrolidindithiocarbaminatverbindung erst dann quantitativ, wenn man die Reaktion bei einem pH-Wert von 5 bei etwa 70°C mit Überschuß des Fällungsmittels durchführt und anschließend auch noch aufkocht.

VERSUCHE ZUR FÄLLUNG DES TITANS UND DES CHROMS MIT PYRROLIDINDITHIOCARBAMINAT

Titan

Versetzt man eine Titanylsulfatlösung von pH 1 mit einer 10%igen, wässrigen Pyrrolidindithiocarbaminatlösung, so tritt eine weiße Fällung auf, bestehend aus der freien Pyrrolidindithiocarbaminsäure. Puffert man aber die stark saure Lösung schrittweise mit Acetatpuffer, so zeigt sich bis pH 5keine Fällung einer gelben Pyrrolidindithiocarbaminatverbindung (Fällung rein weiß), im pH-Bereich 5 bis 6 jedoch wird der gefallene Niederschlag gelblich, wahrscheinlich zurückzuführen auf teilweise Mitfällung einer Titan-Pyrrolidindithiocarbaminatverbindung zusammen mit der freien Pyrrolidindithiocarbaminsäure.

Geht man umgekehrt vor, daß man nämlich die saure Lösung des Titanylsulfates zur ungepufferten, schwach alkalischen Pyrrolidindithiocarbaminatlösung hinzufügt, so erhält man einen grobflockigen gelborange gefärbten Niederschlag. Fügt man dazu nun 10%ige Schwefelsäure bis zur Erreichung eines pH-Wertes von 0, so kann man keine sichtbare Zerstörung der Fällung beobachten. Kocht man die das Titanpyrrolidincarbaminat enthaltende Lösung jedoch auf, so wird es sofort zerstört. In Chloroform ist die Verbindung ausgezeichnet löslich, doch zeigt sich, daß eine derartige Lösung, die anfänglich intensiv gelborange gefärbt ist, bei 1–2 stündigem Stehen vollkommen farblos wird, also nicht vorteilhaft für photometrische Zwecke geeignet ist.

Die Analyse der oben erwähnten gelborange gefärbten Titanpyrrolidindithiocarbaminatverbindung ergab:

	gefunden	theoret. bei Annahme einer Ti(Carb)$_3$
C	45,7–45,8%	37,1%
S	30,2–30,9%	39,5%
Ti	1,2– 1,5%	9,88%

Es ist noch zu untersuchen, um welche Verkettung des Titans mit dem Carbaminat es sich hiebei handelt bzw. ob es sich nicht nur um ein mit der freien Carbaminsäure bzw. deren Zersetzungsprodukten verunreinigtes Produkt handelt.

Je nach dem Verhältnis der Mengen an Titan und Pyrrolidindithiocarbaminat gelang es, durch einmalige Fällung größere oder kleinere Mengen Titan als „Titanpyrrolidindithiocarbaminat“ abzuscheiden. Selbst bei 10 fachen Überschuß des Fällungsmittels, bezogen auf die theoretisch notwendige Menge, war es aber nicht möglich, in einem Schritt eine vollständige Abscheidung zu erzielen. Es lag nun nahe, anzunehmen, daß der pH-Wert eine entscheidende Rolle bei der Fällung des „Titanpyrrolidindithiocarbaminates“ spiele, abgesehen vom Einfluß großen Fällungsmittelüberschusses.

Fällungsversuche in stark acetatgepufferten Titanylsulfatlösungen waren jedoch im pH-Bereich 1–6 weder dann erfolgreich, wenn die titanhältige Lösung mit dem Carbaminat versetzt wurde, noch, wenn umgekehrt vorgegangen wurde. Damit ist gezeigt, daß für die Fällbarkeit einer Titanpyrrolidindithiocarbaminatverbindung primär der Einfluß der Acetationen wichtig ist. Das erklärt sich zwangslos daraus, daß Titanionen große Neigung zur Bildung von Komplexverbindungen besitzen, die so stabil sind, daß sie nicht mehr auf Pyrrolidindithiocarbaminat ansprechen. Bekannt ist beispielsweise, daß selbst die Bildung des sehr beständigen Peroxodisulfatotitansäurekomplexes durch Anwesenheit großer Mengen an Acetationen teilweise unterbunden wird.

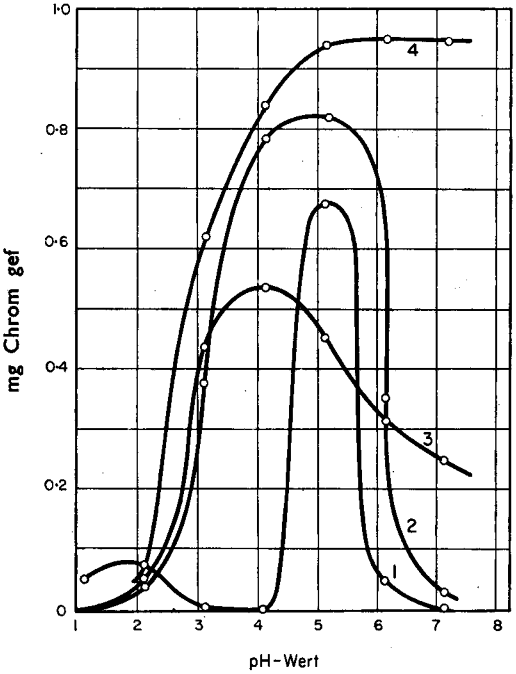

Abb. 1.—Abhängigkeit der Chrompyrrolidindithiocarbamatfällung vom pH-Wert
1—sofort titriert (A): 2—nach 16 Stunden (C):
3—nach 2 Stunden (B): 4—pH-Wert auf Ausgangswert zurückgebracht.

Der pH-Wert wurde nun der Reihe nach mit Natriumcitrat-, Glykokoll- und Urotropinpuffer variiert. In keinem Fall konnte eine „Titanpyrrolidindithiocarbaminatfällung“ erzielt werden. Erst bei sehr wenig Puffersubstanz trat teilweise Fällung auf.

Diese Zusammenhänge lassen die Widersprüche, die betreffs der Bildung einer „Titanpyrrolidindithiocarbaminatverbindung“ herrschen, von einer anderen Warte her betrachten. Malissa[1] und Koch[3] arbeiteten jeweils in stark acetatgepufferten Lösungen und erhalten in Übereinstimmung mit obigen Versuchen keinerlei Fällung des Titans. Rooney[4] beschreibt die Fällung erstens aus mit Glykokoll gepufferter Lösung und zweitens führt er an, daß nur so viel Puffer angewendet wurde, um eben den pH-Wert während des Vorganges konstant zu halten (Nähere Angaben fehlen).

Im allgemeinen ist zu ersehen, daß Titan nur eine geringe Affinität bezüglich Pyrrolidindithiocarbaminat besitzt und es daher nur unter Einhaltung ganz spezieller Bedingungen zur noch nicht geklärten Reaktion gebracht werden kann.

Chrom

Ausgehend von einer Kaliumdichromatlösung wurde durch Reduktion mit Salzsäure und Wasserstoffperoxid eine Chrom(III)-haltige Lösung hergestellt. Von dieser Stammlösung (1 ml = 1 mg Cr) wurden 2 ml abpipettiert, mit 2 ml 20%iger Weinsäurelösung und 1 ml 50%iger Ammonacetatlösung versetzt und auf den jeweiligen pH-Wert eingestellt. Die Lösung wurde erwärmt und mit 2 ml 10%iger Natriumpyrrolidindithiocarbaminatlösung versetzt. Den hiebei ausgefallenen Niederschlag ließ man einige Zeit in der Wärme (60°C) absitzen und filtrierte dann ab. Nach Auflösung in Salpetersäure (1 + 1) wurde die Lösung fast bis zur Trockene eingedampft; und, um das Carbaminat restlos zu zerstören noch zweimal mit Salpetersäure, der etwas Wasserstoffperoxid zugesetzt war, aufgenommen und eingedampft. Hienach gab man nochmals etwas Wasserstoffperoxid zu und machte die Lösung mit NaOH alkalisch. Aus dieser Lösung wurden aliquote Teile nach dem Diphenylcarbazidverfahren auf Chrom untersucht.

TABELLE I.—FÄLLBARKEIT DES CHROMS ALS CHROMPYRROLIDINDITHIOCARBAMINAT IN ABHÄNGIGKEIT VOM pH-WERT DER LÖSUNG UND DER ABSETZZEIT

	Absetzzeit		
pH	A	B	C
1	0,052	0,003	0,002
2	0,007	0,049	0,039
3	0,001	0,440	0,381
4	0,001	0,545	0,787
5	0,686	0,400	0,825
6	0,055	0,320	0,355
7	0,001	0,253	0,035

Filtriert man sofort nach der Zugabe von Pyrrolidindithiocarbaminat und dem Aufkochen der Lösung ab (A), so erhält man bei Bestimmung des Chroms im verbliebenen Rückstand stark streuende Werte, die bei pH 5 ein Maximum zeigen. Läßt man hingegen 2 Stunden stehen (B), so nimmt die Zerstörung des anfangs gebildeten Chrompyrrolidindithiocarbaminates im stark sauren Bereich zu. Ab pH 3 macht sich jedoch schon die stabilisierende Wirkung des abgespaltenen Natriumions aus dem Carbaminat bemerkbar, indem es zu einer höheren Chrompyrrolidindithiocarbaminatausbeute führt, die ebenfalls zwischen pH 4 und 5 ihren Höchstwert hat. Nach sechzehnstündigem Stehenlassen (C) sind diese Effekte noch stärker ausgeprägt, ohne aber den Sollwert (1 mg) zu erreichen.

Da Messungen des pH-Wertes bei Versuchslösungen im pH-Bereich von 1–4 knapp vor der Filtration zeigten, daß eine Verschiebung des ursprünglichen Wertes zum Neutralpunkt hin erfolgt, wurden in einer weiteren Versuchsreihe sofort nach der Fällung die pH-Werte wieder auf ihren anfänglichen Wert zurückgebracht und dann noch zwei Stunden absitzen gelassen.

Tabelle II zeigt, daß bei den vorher angegebenen Bedingungen bei pH 1 Chrompyrrolidindithiocarbaminat praktisch nicht beständig ist, während ansonsten mit

TABELLE II.—FÄLLBARKEIT DES CHROMS ALS PYRROLIDINDITHIOCARBAMINAT IN ABHÄNGIGKEIT VOM pH-WERT DER LÖSUNG

pH	mg Cr gefunden
1	—
2	0,076
3	0,621
4	0,840
5	0,941
6	0,950
7	0,952

steigendem pH-Wert ein kontinuierliches Ansteigen der Chrompyrrolidindithiocarbaminatausbeute zu erkennen ist.

Weiters wurde eine Chrom(III)-haltige Lösung aus Kaliumchromalaun hergestellt und mit 10%iger Pyrrolidindithiocarbaminatlösung zu fällen versucht. Im pH-Bereich 2 bis 6 konnte keine Chrompyrrolidindithiocarbaminatfällung beobachtet werden. Es ist also zweifellos so, daß die Fällbarkeit oder die Nichtfällbarkeit eines Chrom(III)pyrrolidindithiocarbaminates stark von den jeweiligen Zustandsbedingungen des Metallions abhängig ist. Nur auf diese Weise kann verstanden werden, wie Bode[7] einerseits und Malissa[6] andererseits zu den bereits besprochenen verschiedenen Ansichten kommen konnten.

Chromatlösungen reagieren in der Kälte mit Pyrrolidindithiocarbaminat bei pH 2 bis 5 nicht. Erhitzt man jedoch auf ca. 70°C und versetzt mit großem Überschuß des Fällungsmittels, so zeigt sich anfänglich eine graublaue Trübung, die sich bei längerem Stehen verstärkt. Es wurde nun versucht, eine Fällung derart zu begünstigen, daß eine halbe Stunde lang kräftig umgeschüttelt wurde. Es zeigte sich, daß so eine Niederschlagsbildung erreicht werden kann. Die Filtration lieferte eine relativ feinkörnige graublaue Substanz, im Filtrat jedoch konnten noch große Mengen sechswertigen Chroms nachgewiesen werden. Der nicht vollständig gebildete Niederschlag dürfte zufolge seines Aussehens aus Chrom(III)pyrrolidindithiocarbaminat bestehen, dessen Bildung folgendermaßen zu verstehen ist. Sechswertiges Chrom wurde vorerst durch das Fällungsmittel zu dreiwertigem reduziert und dieses bildete dann allmählich im Laufe seines Entstehens die bekannte Chrom(III)pyrrolidindithiocarbaminatverbindung.

Summary—The dependence of the reactivity with pyrrolidinedithiocarbamate of titanium on pH and the presence of other ions, and of chromium^{III} on the state of binding of the chromium^{III} ion and on pH have been investigated. The results of this investigation provide an explanation of the hitherto very variable accounts of the reactivity of titanium and chromium with disubstituted dithiocarbamates.

Résumé—Les auteurs étudient l'influence du pH et de la la présence d'autres ions sur le pyrrolidinedithiocarbamate de titane et l'influence du pH et de l'état sous lequel se trouve le chrome (III) en solution sur le pyrrolidinedithiocarbamate de chrome (III). Les résultats obtenus permettent d'expliquer les différences rencontrées quant aux réactions du chrome et du titane avec les dithiocarbamates bisubstitués.

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THERMOGRAVIMETRY OF SOME URANIUM^{VI} 8-HYDROXYQUINOLATES

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Summary—The thermogravimetric behaviour of $UO_2(C_9H_6NO)_2.C_9H_6NOH$ and $[UO_2(C_9H_6NO)_2]_2.C_9H_6NOH$ prepared by precipitation from homogeneous solution with 8-acetoxyquinoline has been found to closely resemble that of $UO_2(C_9H_6NO)_2.C_9H_6NOH$ prepared by direct precipitation of uranium^{VI} with 8-hydroxyquinoline.

PREVIOUS thermogravimetric studies have been made by Duval[1] and by Wendlandt[2] with uranium 8-hydroxyquinolate prepared by conventional precipitation.[3] Duval found the precipitate to be thermally stable up to 157°. The molecule of crystallisation was removed above this temperature; an apparently stable quinolate, UO_2Q_2 (where $Q = C_9H_6NO$), exists in the range 252–346°. Beyond 346°, Duval's thermogram showed a rapid weight loss up to about 400°, followed by a slower loss that continued up to 947° which was the upper limit of the thermal analysis made by him. The subsequent investigation by Wendlandt[2] indicated that the unsolvated chelate began to decompose at 380°, that conversion to the oxide U_3O_8 was complete at 450°, and that no further weight loss occurred above this temperature. Neither author specified the heating rate that was used in the pyrolysis, but differences in this variable would not account for the marked discrepancy between their results above 400°.

The present paper describes thermogravimetric studies made with uranium 8-hydroxyquinolates precipitated from homogeneous solution with 8-acetoxyquinoline[4] at two different pH levels; the two precipitates formed appear to have the compositions $UO_2Q_2{\cdot}HQ$ and $(UO_2Q_2)_2{\cdot}HQ$. The thermogravimetric behaviour of the conventionally formed precipitate, *i.e.*, $UO_2Q_2{\cdot}HQ$ produced by 8-hydroxyquinoline, was also examined for comparative purposes.

EXPERIMENTAL

Preparation of precipitates for thermogravimetric analysis

The precipitates of uranium 8-hydroxyquinolate were prepared in accordance with the described procedures.[3,4] After the precipitates were washed and dried at 110° for 2 hr, they were weighed in order to confirm quantitative precipitation.

Thermogravimetric procedure

Approximately 100-mg portions of the precipitate, prepared as described, were transferred to crucibles freshly ignited at 850° and subsequently briefly stored in a desiccator. The samples were then subjected to a heating rate of 6°/min or 1°/min in a Stanton HTD thermobalance. Except where indicated, an air atmosphere was used. All data used in the preparation of the thermogravimetric curves in the following figures were corrected for buoyancy (experimentally determined for each crucible).

In some instances the heating programmes were interrupted in order to maintain a constant temperature for specified time periods.

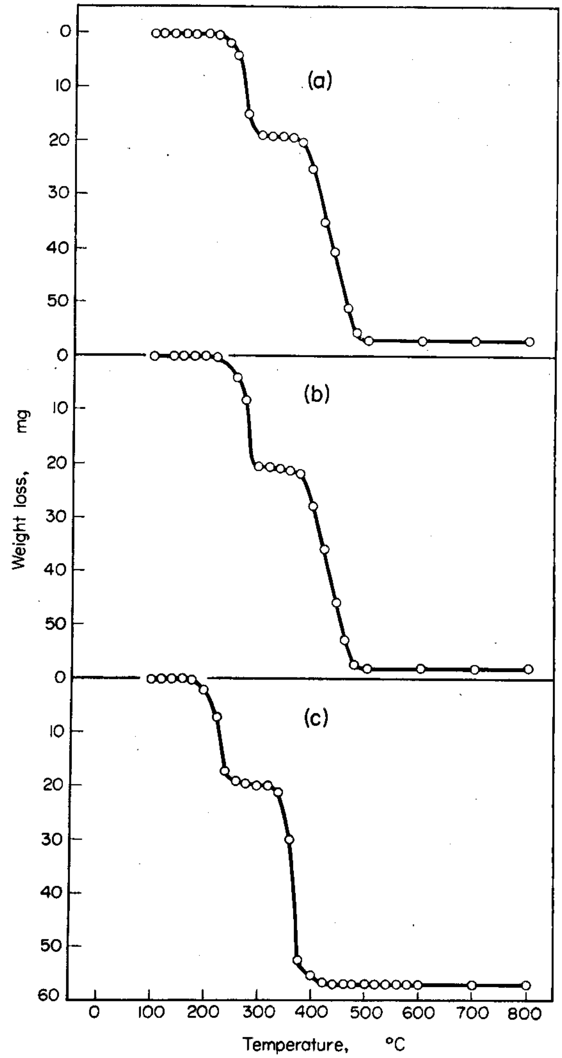

FIG. 1.—Thermogravimetric curves of uranium^{VI} 8-hydroxyquinolate:
(a) $UO_2Q_2 \cdot HQ$ prepared by conventional precipitation (heating rate: 1°/min; sample size: 96·2 mg).
(b) $UO_2Q_2 \cdot HQ$ prepared by PFHS (heating rate: 1°/min; sample size: 97·3 mg).
(c) $(UO_2Q_2)_2 \cdot HQ$ prepared by PFHS (heating rate: 1°/min; sample size: 99·7 mg).

RESULTS AND DISCUSSION

Weight loss-temperature data are shown in Fig. 1, respectively, for $UO_2Q_2 \cdot HQ$ prepared by conventional precipitation, $UO_2Q_2 \cdot HQ$ prepared by PFHS (precipitation from homogeneous solution) at pH 5·0, and $(UO_2Q_2)_2 \cdot HQ$ prepared by PFHS at pH 6·8; Fig. 2 shows the weight loss-time data of $UO_2Q_2 \cdot HQ$ held at 320° for many hr.

Thermogravimetric behaviour of $UO_2Q_2 \cdot HQ$ *prepared by PFHS and by conventional precipitation*

Precipitates prepared by PFHS and by conventional precipitation were found to behave in a quite similar manner for they were thermally stable up to about 200° [*cf.*

Figs. 1(a) and 1(b)]. Between 200° and 300°, the two precipitates apparently lost their molecules of crystallisation. The remaining organic material disappeared between 375° and 475° to form U_3O_8 which was stable above 500° and up to the 1200°-level to which the furnace was occasionally operated. The thermal behaviour of the conventionally formed precipitate (as well as that prepared by PFHS) agreed quite closely with Wendlandt's but not with Duval's observations. A quantitative analysis of several thermogravimetric curves is shown in Table I and indicates uncertainty in using UO_2Q_2 as a weighing form (in air) for the determination of uranium; in making the analyses for UO_2Q_2, the mid-points of the "plateaus" were used. There is also some uncertainty associated with U_3O_8 but in view of the horizontal nature of the final plateau, further work would be required to warrant any conclusion about the use of U_3O_8 as a weighing form in the present case. However, as shown in a previous investigation,[4] drying of the precipitate at 110°, *i.e.* the weighing form $UO_2Q_2{\cdot}HQ$, leads to quite satisfactory results.

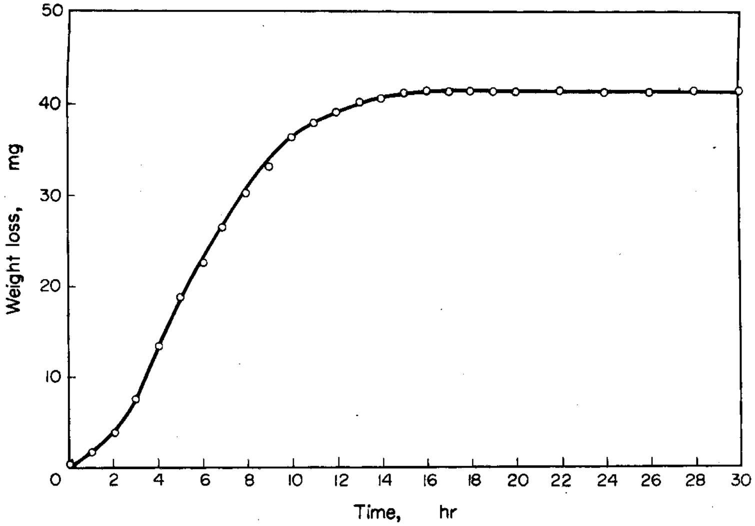

FIG. 2.—Weight loss of $UO_2Q_2{\cdot}HQ$ at constant temperature (320°; sample size: 124·5 mg).

TABLE I.—QUANTITATIVE ANALYSIS OF THERMOGRAVIMETRIC CURVES OF $UO_2Q_2{\cdot}HQ$

Sample weight, *mg*	96·2	97·3	68·6
Method of precipitation	Conventional	PFHS pH = 5·0	PFHS pH = 5·0
Heating rate of sample, °*C/min*	1	1	6
Weight loss for intermediate plateau, *mg*			
Observed	19·6	20·4	13·6
Theory[a]	19·8	20·1	14·2
Weight loss for final plateau, *mg*			
Observed	38·0	38·1	25·9
Theory[b]	38·0	38·4	27·0

[a] $UO_2Q_2{\cdot}HQ \rightarrow UO_2Q_2 + HQ$

[b] $3UO_2Q_2 \rightarrow U_3O_8$ + degradation products

Because of the presence of a non-horizontal "plateau" in the 300–375° region, the compounds obtained in this temperature range were further examined both by an alteration in the thermogravimetric technique and by bromination[5] to determine their 8-hydroxyquinoline content; only precipitates prepared by PFHS were brominated.

The heating programme was altered so that the temperature remained constant once 320° was reached; the choice was arbitrary although it can be seen from Figs. 1(a) and 1(b) that 320° is within a "plateau" region. The *orange* coloured precipitate prepared by PFHS (pH 5·0) slowly lost weight for about 18 hr after the 320°-level was reached. No weight loss was observed for the next 12-hr period as is shown by Fig. 2. The resulting *yellow* precipitate was analysed for carbon, nitrogen, hydrogen and uranium. Because UO_3 is yellow and U_3O_8 is dark olive drab (almost black), it was at first thought that the yellow compound was UO_3. However, the compound appeared to be a mixture of a uranium oxide and organic degradation products. The results are shown in Table II. Similar results were obtained with $UO_2Q_2{\cdot}HQ$ prepared by conventional precipitation.

TABLE II.—ELEMENTAL COMPOSITION OF THE YELLOW URANIUM COMPOUND OBTAINED UPON PROLONGED HEATING AT 320°

Element	N	H	C	U
Theory for UO_2Q_2, %	5·0	2·1	38·7	42·6
Observed[a], %	0·44	0·68	1·66	78·8[b]

[a] The initial sample of $UO_2Q_2{\cdot}HQ$ taken weighed 30·5 mg; the weight of yellow compound taken for microanalysis was 5·3 mg.
[b] Theory for U in UO_3 = 83·2%

When the previous experiment was repeated at two other temperatures, *i.e.*, at 260 and at 300°, different rates of weight loss were obtained although the overall results were essentially similar to those obtained at 320°.

In similar experiments, with several temperatures in the range 280–360°, the compounds obtained were also analysed by bromination for their 8-hydroxyquinoline content. The results in Table III show a continual variation, with temperature, of the mole ratio of 8-hydroxyquinoline to uranium. It is apparent that data obtained from the first thermogravimetric "plateau" cannot be used for the quantitative determination of uranium (weighed as UO_2Q_2) if the precipitate is heated in an air atmosphere where oxidation can occur.

TABLE III.—APPROXIMATE COMPOSITION OF URANIUM COMPOUND OBTAINED IN 280–360° TEMPERATURE RANGE

Temperature, °C	280	300	320	340	360
Mole Ratio: $\dfrac{\text{8-hydroxyquinoline}}{\text{uranium}}$	2·20, 2·29	1·88, 1·92	1·50, 1·73	1·26, 1·59	1·33, 1·49

When a nitrogen atmosphere was used, the compound did not lose weight when heated for a 20-hr period at 320°. The gravimetric data indicated the stable compound to be UO_2Q_2; the initial sample of $UO_2Q_2{\cdot}HQ$ which weighed 117·5 mg was observed to lose 24·2 mg in agreement with the theoretically expected loss of 24·2 mg.

$(UO_2Q_2)_2 \cdot HQ$ *Prepared by PFHS at* pH 6·8

The thermogravimetric curve shown in Fig. 1(c) for $(UO_2Q_2)_2 \cdot HQ$ is quite similar to that of Fig. 1(b) for $UO_2Q_2 \cdot HQ$. In addition, the weight loss-time curve for $(UO_2Q_2)_2 \cdot HQ$ was almost identical with that obtained for $UO_2Q_2 \cdot HQ$ at the 320°-level (*cf.* Fig. 2).

The data obtained from the middle of the "plateaus" of thermograms for (UO_2Q_2). HQ were not sufficiently accurate for gravimetric purposes (except at 110° as shown in the previous investigation[4]) for either UO_2Q_2 or U_3O_8 as weighing forms as is shown in Table IV (*cf.* with Table I). It is difficult from the data of Tables I and IV to determine if there is a significant difference in the behaviour of $(UO_2Q_2)_2 \cdot HQ$ and of $UO_2Q_2 \cdot HQ$ which might suggest different modes of solvation of the molecule of 8-hydroxyquinoline.

TABLE IV.—QUANTITATIVE ANALYSIS OF THERMOGRAVIMETRIC CURVES OF $(UO_2Q_2)_2 \cdot HQ$

Sample weight, *mg*	87·9	99·7
Method of precipitation	PFHS pH = 6·8	PFHS pH = 6·8
Heating rate of sample, *°C/min*	1	1
Weight loss for intermediate plateau, *mg*		
Observed	16·0	19·5
Theory[a]	10·1	11·5
Weight loss for final plateau, *mg*		
Observed	31·7	37·5
Theory[b]	38·7	43·9

[a] $(UO_2Q_2)_2 \cdot HQ \rightarrow 2UO_2Q_2 + HQ$

[b] $3(UO_2Q_2)_2 \rightarrow 2U_3O_8$ + degradation products

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Zusammenfassung—Das thermogravimetrische Verhalten von

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ und $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$

hergestellt durch Fällung aus homogener Lösung mit 8-Acetoxchinolin wurden als sehr ähnlich dem von $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ gefunden, welch letzteres durch direkte Fällung von Uran (VI) mit 8-Oxychinolin erhalten wurde.

Résumé—Les auteurs montrent que le comportement thermogravimétrique de

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ et de $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$

préparés par précipitation au moyen de la 8-acétoxyquinoléine est très sensiblement le même que celui de $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ préparé par précipitation directe de l'uranium (VI) au moyen de la 8-hydroxyquinoléine.

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NEW REDOX SYSTEMS—V*

OXIDATION OF URANIUM^{IV} WITH IRON^{III} IN 1,10-PHENANTHROLINE SOLUTIONS

INDIRECT COLORIMETRIC DETERMINATION OF URANIUM

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Summary—The oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline has been studied both potentiometrically and colorimetrically. Suitable conditions for the indirect colorimetric determination of uranium via ferroïn have been found.

IN previous parts of this series the oxidation of cobalt^{II} with iron^{III} in the presence of 1,10-phenanthroline and 2,2-bipyridyl were reported.[1,2] It has now been found possible to oxidise uranium^{IV} quantitatively with iron^{III} under similar conditions. Because uranium^{IV} and uranium^{VI} form weak complexes with 1,10-phenanthroline or practically do not react at all and because the intensely coloured ferroïn results, the following course of reaction can be presumed:

$$U^{IV} + 2(Fe^{III})Phen \rightarrow U^{VI} + 2(Fe^{II})\,Phen \tag{1}$$

The stoicheiometry of reaction (1) has been studied potentiometrically and especially colorimetrically. The obtained results have been utilised to develop a method for the indirect colorimetric determination of uranium^{IV}.

EXPERIMENTAL

Reagents

Standard uranium^{VI} solutions: Prepared from reagent grade $UO_2(NO_3)_2$ and their titre controlled gravimetrically as pyro-uranate. Before each test, suitable concentrations of uranium^{IV} were prepared by quantitative reduction of a standard uranium^{VI} solution with lead in 3*N* hydrochloric acid.[3]

Iron^{III} chloride solutions: Prepared from reagent grade $FeCl_3$ and their titre controlled gravimetrically as Fe_2O_3.

0·1*M* 1,10-*phenanthroline solution:* Prepared by dissolving 1·804 g of the analytically pure substance in water weakly acidified with sulphuric acid (resulting pH about 3) and diluting to 100 ml. Solutions of lower concentration were prepared by suitable dilution.

Buffer solutions: Prepared by neutralisation of the calculated quantity of trichloracetic, chloracetic or acetic acid with aqueous ammonia to the necessary pH, while a potentiometric control was maintained with a glass electrode. The resulting molarity of the solutions was 1.

Apparatus

The potentiometric measurements were carried out as previously.[1,2] The colorimetric measurements were carried out with a colorimeter Pulfrich with Elpho II (Carl Zeiss, Jena, E. Germany).

POTENTIOMETRIC RESULTS

In principle it is possible to oxidise uranium^{IV} in strongly acidic media with iron^{III} to uranium^{VI}. The comparatively high difference of standard potentials of the systems involved [$U^{IV}/U^{VI} = 0{\cdot}334$ V; $Fe^{II}/Fe^{III} = 0{\cdot}771$ V] allows the presumption of an

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* Part IV: see reference 2.

easy quantitative oxidation. In practice, however, the oxidation of uranium^{IV} with iron^{III} only proceeds sufficiently quickly for analytical use at increased temperatures. Thus the results of the potentiometric determination of uranium show considerable errors. Better results can be obtained when potassium thiocyanate is used as a catalyst.[4] In the presence of 1,10-phenanthroline the oxidation of uranium^{IV} to uranium^{VI} with iron^{III} proceeds quantitatively at room temperature in the pH range 1·5–5 and the stabilisation of the potential is practically instantaneous.

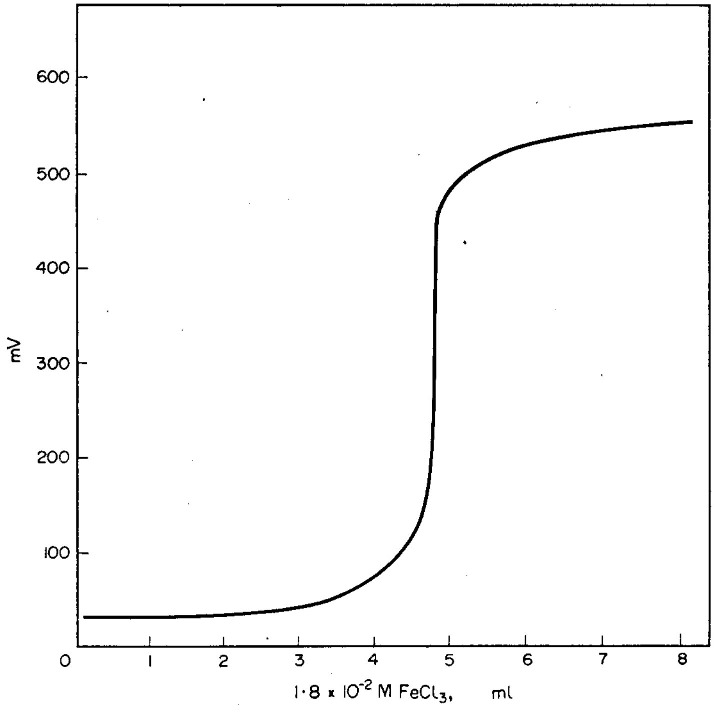

FIG. 1.—Oxidation of uranium^{IV} with iron^{III} chloride in 1,10-phenanthroline solution. (1 ml of 4·5 × 10^{-2}*M* uranium^{IV} solution; 5 ml of 0·1*M* 1,10-phenanthroline solution; pH 2; total volume: 100 ml; titrated with 1·8 × 10^{-2}*M* iron^{III} chloride solution in an atmosphere of nitrogen, Pt-electrode *vs.* SCE.)

The reaction velocity is influenced by the presence of 1,10-phenanthroline, which might be explained by the binding of the iron^{II} formed during the reduction of iron^{III} with uranium^{IV} and by the increasing of the formal potential of the Fe^{II}/Fe^{III} system to the value 0·810 V at pH 2.[1]

Fig. 1 shows the course of a potentiometric titration curve of uranium^{IV} with iron^{III} in the presence of an excess of 1,10-phenanthroline in an atmosphere of nitrogen. The procedure was carried out as follows:

A given amount of uranium^{VI} solution was reduced with 5 g of granulated lead in 3*N* hydrochloric acid and 1,10-phenanthroline solution added. The solution was cautiously neutralised to pH 0·5–1, then adjusted to *ca.* pH 2 in an atmosphere of nitrogen, a buffer solution of the same pH added and finally titration carried out with iron^{III} chloride solution.

It is evident from the potentiometric curve that the oxidation of uranium^{IV} occurs quantitatively and quickly under the given conditions with a change of two electrons.

The calculated formal potentials of the studied systems show that the reaction occurs in accordance with the supposed course (1).

COLORIMETRIC RESULTS

Because of the intense red coloration of ferroïn developed during (1) (it is proportional to the uranium concentration), the reaction can be easily followed colorimetrically. The oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline occurs considerably quicker than the oxidation of uranium^{IV} to uranium^{VI} with atmospheric oxygen and therefore it is not necessary to work in an inert atmosphere.

In the colorimetric study of reaction (1) the following procedure was used:

To the freshly prepared uranium^{IV} solution of pH < 1 a measured amount of iron^{III} chloride solution and 1,10-phenanthroline solution were added, and after adjustment of the pH to the chosen value, 5 ml of a suitable 1M buffer solution were added. The volume of the solution was adjusted to 25 ml and after 10 min the absorbance at 500–510 mμ was measured in a 5-cm cell against a blank solution prepared simultaneously with the sample and containing all of the reagents except the solution of uranium.

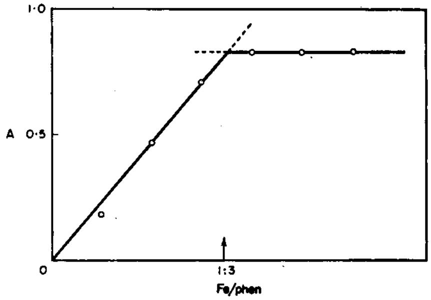

FIG. 2.—Dependence of the absorbance of Fe(Phen)$_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on the ratio of uranium: iron. (1 ml of $4{\cdot}5 \times 10^{-4}M$ uranium^{IV} solution; 1 ml of $0{\cdot}1M$ 1,10-phenanthroline solution; 2–10 ml of $1{\cdot}8 \times 10^{-4}M$ iron^{III} chloride solution; pH *ca.* 3; total volume: 25 ml; 5-cm cell; filter: $\lambda_{max} = 500$ mμ.)

Determination of the ratio of reacting components

The ratio of the reacting components was ascertained by the titration curve method. Fig. 2 shows that the quantitative oxidation of uranium in the presence of an excess of 1,10-phenanthroline requires a minimum ratio of uranium to iron of 1:2, which agrees with the results of the potentiometric titration. Fig. 3 shows the stoicheiometric amount of 1,10-phenanthroline necessary for the quantitative course of the reaction. The break in the curve at a ratio of iron:1,10-phenanthroline of 1:3 indicates that 1,10-phenanthroline is necessary only to bind the developed iron^{II} as the complex Fe(Phen)$_3^{2+}$.

From the results of the potentiometric and colorimetric studies and the fact that iron^{III} ions in a solution of pH 1·5–5 are bound with 1,10-phenanthroline as a hydroxo complex, the reaction can be described in detail by the equation:

$$U^{4+} + Fe_2(OH)_2(Phen)_4^{4+} + 2HPhen^+ \rightarrow UO_2^{2+} + 2Fe(Phen)_3^{2+} + 4H^+ \quad (2)$$

Influence of pH

The influence of pH on the ratio of reacting components of reaction (2) was also

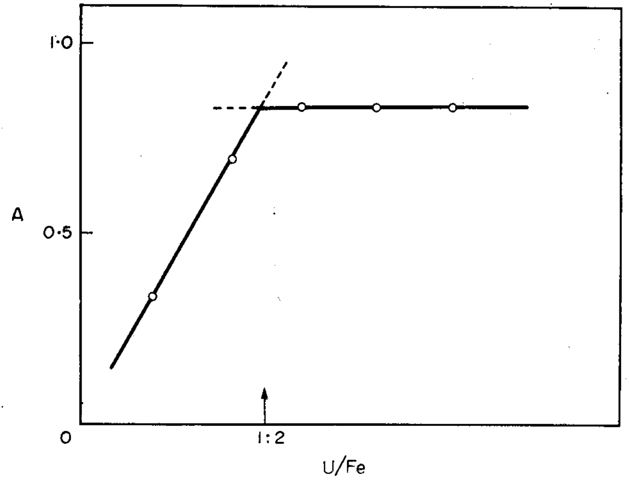

FIG. 3.—Dependence of the absorbance of Fe(Phen)$_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on the ratio of iron: 1,10-phenanthroline. (1 ml of 4·5 × 10^{-4}*M* uranium^{IV} solution; 8 ml of 1·8 × 10^{-4}*M* iron^{III} chloride solution; 2–10 ml of 5 × 10^{-4}*M* 1,10-phenanthroline solution; pH *ca.* 3; total volume: 25 ml; 5-cm cell; filter: λ_{max} = 500 mμ.)

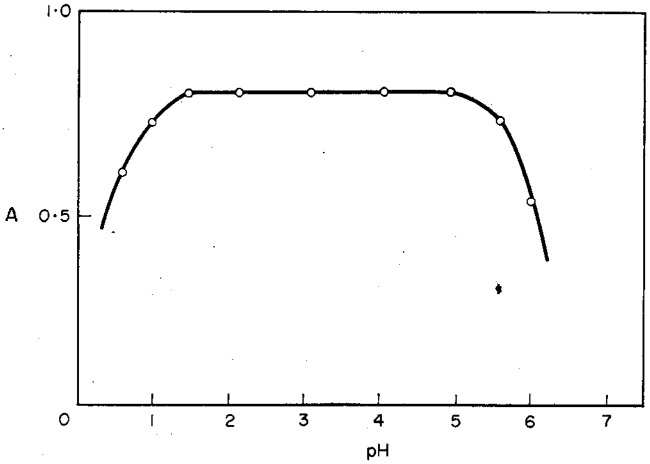

FIG. 4.—Dependence of the absorbance of Fe(Phen)$_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on pH. (1 ml of 4·5 × 10^{-4}*M* uranium^{IV} solution; 3 ml of 0·1*M* 1,10-phenanthroline solution; 8 ml of 1·8 × 10^{-4}*M* iron^{III} chloride solution; 5 ml of *ca.* 1*M* buffer solution; total volume: 25 ml; absorbance measured after 15 min; 5-cm cell; filter: λ_{max} = 500 mμ.)

followed colorimetrically. Fig. 4 shows that the oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline proceeds quantitatively at pH 1·5–5.

Indirect colorimetric determination of uranium

The results obtained show suitable conditions for the indirect colorimetric determination of uranium via the formation of ferroïn during the oxidation of uranium^{IV} according to equation (2). It is only necessary to emphasise here the need for keeping a certain order in addition of the various reagents to eliminate the atmospheric oxidation of uranium^{IV}.

Procedure: To the solution of uranium^{VI} add sufficient hydrochloric acid to bring the normality to about 3. Pass the solution through a lead reductor of suitable size or shake it for some min with a suitable amount of granulated lead. After separation of the lead, adjust the pH cautiously and with constant stirring to 0·5–1, then add immediately 1 ml of 0·01*M* iron^{III} chloride solution and 1 ml of 0·1*M* 1,10-phenanthroline solution. Adjust the pH to about 2 and add 5 ml of 1*M* buffer solution of the same pH. After 10 min measure the absorption at 500–510 mμ against a blank solution prepared simultaneously with the sample and containing all of the reagents except the solution of uranium. The preparation of the sample solution simultaneously with the sample is necessary to compensate for the yellow coloration of $[Fe_2(OH)_2Phen_4]^{4+}$, formed by an excess of ions, and the optical density of which depends on time.[1]

Evaluation of the results is carried out with a calibration curve obtained from the values of the extinction of a series of standard uranium solutions processed in the same way as the sample. With 1-cm cells and a filter with maximum transmittance at 500–510 mμ the calibration curve is linear over the range of 0–0·45 mg of uranium/50 ml. The sensitivity of the method can be raised by using longer cells.

Interferences

Iron^{II} and cobalt^{II} are the main interferences with the proposed indirect colorimetric determination of uranium. Iron^{III}, after reduction with lead to iron^{II}, forms ferroïn with 1,10-phenanthroline and cobalt^{II} is oxidised by iron^{III} in the presence of 1,10-phenanthroline in the same way as uranium^{IV}. Similarly, tin^{II}, molybdenum^{III} and tungsten^{III} all cause high results in the indirect determination of uranium.

Ions, *e.g.* copper^{II}, zinc^{II}, nickel^{II}, which form relatively stable complexes with 1,10-phenanthroline also interfere with the determination because they bind the 1,10-phenanthroline necessary for the quantitative course of reaction (2). The unfavourable influence of these ions can be removed by the use of an excess of 1,10-phenanthroline. By using 1 ml of 0·1*M* 1,10-phenanthroline it is possible to determine 0·038 mg of uranium/50 ml in the presence of 10 mg of nickel, 3·5 mg of copper and 3·5 mg of zinc with an error of ±2·5%.

Some ions, *e.g.* bismuth^{III}, influence the indirect colorimetric determination of uranium as ferroïn because they are hydrolysed under the conditions, while others, *e.g.* cadmium^{II}, silver^{I}, mercury^{I}, perchlorate, form insoluble complexes with 1,10-phenanthroline. The influence of the latter can be removed by a sufficient excess of complex-forming reagent, but even then the resulting precipitates disturb the colorimetry of ferroïn. Alkali metals, calcium^{II}, magnesium^{II}, barium^{II}, rare earth elements, beryllium^{II}, lead^{II}, manganese^{II}, aluminium^{III}, gallium^{III}, indium^{III}, thorium^{IV} and zirconium^{IV} have no influence even at high concentrations. The same applies for high concentrations of sulphates, chlorides and nitrates. Some results are shown in Table I.

TABLE I.—INDIRECT COLORIMETRIC DETERMINATION OF URANIUM

Taken		Uranium found, *μg*	Error, % (*rel.*)
Uranium, *μg*	Other metal, *mg*		
9·50	—	9·61	+1·2
38·0	—	37·2	−2·1
104·0	—	101·0	−3·0
38·0	Ni 10	37·1	−2·1
38·0	Cu 3·5	38·5	+1·0
38·0	Zn 3·5	38·0	±0·0
38·0	Be 85·0	37·8	−0·5
38·0	Pb 107·5	38·8	+2·1
38·0	Th 62·5	37·5	−1·3

The proposed method is convenient for the determination of small concentrations of uranium after its separation especially from iron and cobalt. It can be applied reliably even if 5-cm cells are used for the determination of 10 μg of uranium/25 ml.

Zusammenfassung—Die Oxydation von Uran (IV) durch Fe (III) in Gegenwart von 1,10-Phenanthrolin wurde potentiometrisch und kolorimetrisch studiert. Die optimalen Bedingungen für eine indirekte Bestimmung von Uran via Ferroin wurden ermittelt.

Résumé—L'oxydation de U(IV) par Fe(III) en présence de 1,10-phénanthroline a été étudié par potentiométrie et par spectrophotométrie. Les conditions optimales du dosage colorimétrique indirect de l'uranium au moyen de la ferroïne ont été déterminées.

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UNTERSUCHUNGEN AN REAGENZIEN FÜR NIOB UND TANTAL—I

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Zusammenfassung—Aus der Untersuchung einer großen Zahl hydroxylgruppenhaltiger organischer Substanzen konnten für weinsaure Lösungen als analytisch funktionelle Gruppierung für Niob und Tantal 2 Hydroxylgruppen in o-Stellung am aromatischen System erkannt werden. In gleicher Weise reagieren peri-Dihydroxynaphthalinderivate. Als Ergebnis der systematischen Untersuchungen wird Tribrompyrogallol als neues selektives und empfindliches Niobreagens gefunden.

BESTIMMUNG DER ANALYTISCH-FUNKTIONELLEN GRUPPE

Zu den noch keineswegs befriedigend gelösten Problemen der analytischen Chemie gehören auch die Methoden der Bestimmung von Niob und Tantal, besonders wenn diese beiden Elemente nebeneinander vorliegen.

Abgesehen von einigen anorgansichen Reagenzien werden meist Pyrogallol[2] und Brenzkatechin[3] für die Bestimmung der Erdsäuren benutzt, aber auch Phenylfluoron[4] u. a. werden in der Literatur empfohlen.

Auf der Suche nach geeigneten Reagenzien zur Bestimmung der Erdsäuren untersuchten Karjakin und Teleshnikowa[5] Phenole, Naphthole, Anthrachinonderivate u. a.. Als Komplexbildner benutzten sie Oxalat und Fluorid. Auf Grund ihrer Versuche empfahlen sie Pyrogallol, Brenzkatechin und Gallussäure zur Bestimmung der beiden Elemente.

Die nach dem Erscheinen der sowjetischen Arbeit beschriebenen neuen Reagenzien zeigten, daß eine nochmalige systematische Bearbeitung dieses Gebietes nützlich schien.

Im Rahmen dieser Untersuchung prüften wir sowohl aliphatische, wir aromatische Hydroxyverbindungen auf ihr Verhalten gegen Niob- und Tantal-Lösungen. Zur Beurteilung der Ergebnisse ist es noch von Bedeutung zu vermerken, daß die beiden Elemente als Tartratokomplexe eingesetzt wurden. Das Verhalten in oxalsaurer Lösung wurde zunächst nicht untersucht. Wegen der zu erwartenden pH-Abhängigkeit bei der Bildung der Komplexe führten wir die Untersuchungen sowohl im sauren, wie im neutralen und schwach alkalischen Gebiet durch.

Bei der Prüfung mit *weinsauren* Lösungen von Niob und Tantal ergaben

1. Mehrwertige aliphatische Alkohole (Glykol, Glyzerin, Mannit)	keine Reaktion
2. Einwertige Phenole und Derivate (Phenol, m-Kresol, Pikrinsäure)	keine Reaktion
3. Mehrwertige Phenole OH-Gruppen in m-Stellung (Phloroglucin, Resorcin, Orcin)	keine Reaktion

OH-Gruppen in p-Stellung (Hydrochinon)*	keine Reaktion
OH-Gruppen in o-Stellung (Brenzkatechin, Pyrogallol)	positive Reaktion
4. Einwertige Naphthole (α-Naphthol, β-Naphthol)	keine Reaktion
5. Mehrwertige Naphthole	
OH-Gruppen in m-Stellung (1.3-Dihydroxynaphthalin-5.7-disulfosäure)	keine Reaktion
OH-Gruppen in o-Stellung (2.3-Dihydroxynaphthalin)	positive Reaktion
OH-Gruppen in peri-Stellung (Chromotropsäure)	positive Reaktion
6. Dihydroxyanthracenderivate	
OH-Gruppen in o-Stellung (Alizarin, Chinalizarin)	positive Reaktion

Aus diesen Untersuchungen geht hervor, daß man o-ständige OH-Gruppen an aromatischen Ringen als analytisch- funktionelle Gruppen ansehen muß.

In einer weiteren Versuchsreihe prüften wir Substanzen, bei denen eine der Hydroxylgruppen durch Carboxyl-, Aldehyd- bzw. Methoxylgruppe ersetzt war. Bei keiner der Substanzen konnte in Gegenwart von Weinsäure eine Reaktion mit den Erdsäuren festgestellt werden.

Das Verhalten des Toluol-3.4-dithiols zeigte jedoch, daß o-ständige Sulfhydrylgruppen ähnlich wirken wie OH-Gruppen.

AUSWAHL GEEIGNETER REAGENZIEN

Zur Bestätigung des Ergebnisses der im ersten Abschnitt beschriebenen Versuche untersuchten wir im Anschluß daran eine größere Anzahl von Substanzen, die o-ständige Hydroxylgruppen enthalten mit dem Ziel, dabei geeignete Verbindungen für die photometrische Bestimmung zu finden.

Die Prüfung der Lösungen erfolgte durch photographische Aufnahme der Absorptionsspektren im Gebiet von ca. 350 bis 650 nm. Zur besseren Auswertung wurden die mittels Registrierphotometer erhaltenen Schwärzungskurven der Photoplatten herangezogen.

Da alle geprüften Reagenzien mit den Erdsäuren gelbe bis rote Verbindungen ergaben, sollen im folgenden nur die untersuchten Verbindungen aufgezählt werden, ohne daß zunächst auf die Absorptionsspektren eingegangen wird.

Wir prüften: Andrenalin, Alizarin, Brenzkatechin, Brenzkatechinviolett, Brompyrogallolrot, Carminsäure, Chinalizarin, Chromotropsäure, 2.3-Dihydroxynaphthalin, Dithiol, Gallussäure, Hämatoxylin, Phenylfluoron, Pyrogallol, Quercetin, Tiron, Tribrompyrogallol.

Für die weiteren Untersuchungen wählten wir aus diesem Sortiment die Stoffe aus, bei denen sich die Spektren der Metallkomplexe möglichst stark von denen der reinen

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* Das bekannte Verfahren zur Bestimmung von Niob in stark schwefelsaurer Lösung[6] beruht sicher auf einer Redox-Reaktion, kann also hier außer acht gelassen werden.

Reagenzien unterscheiden. Die Verhältnisse liegen natürlich besonders günstig, wenn die Reagenzlösungen farblos sind.

Unter diesen Gesichtspunkten erwiesen sich als besonders geeignet: Brenzkatechin, Chromotropsäure, Pyrogallol und Tiron.

Da—wie allgemein bekannt ist—die Einführung von Halogenatomen in organische Moleküle eine Farbvertiefung ergibt, untersuchten wir in diesem Zusammenhang das präparativ leicht zugängliche Tribrompyrogallol. Tetrabrombrenzkatechin, das ebenfalls leicht darstellbar ist, zeigt schlechte Löslichkeit und scheidet deshalb für analytische Zwecke aus. Die Untersuchung des Tribrompyrogallols ergab die erwarteten Effekte, so daß es mit in die Reihe der empfehlenswerten Reagenzien aufgenommen wurde.

AUFNAHME DER ABSORPTIONSSPEKTREN

Da zu erwarten war, daß die Färbung der Komplexe vom pH-Wert der Lösung abhängig ist, für die folgenden Untersuchungen aber die Bedingungen gefunden werden sollten, bei denen die Spektren im Sichtbaren eine maximale Farbintensität zeigen, prüften wir zunächst den Einfluß der Wasserstoffionenkonzentration.

Die Ergebnisse sind in Abb. 1 graphisch dargestellt.

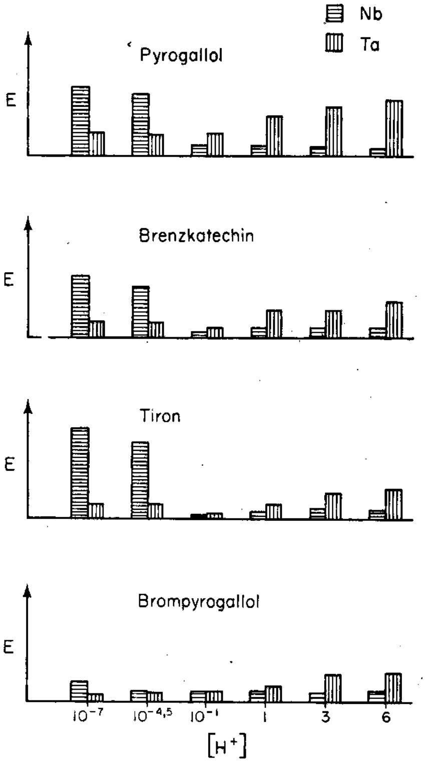


Abb. 1.—Absorption der Niob- und Tantalkomplexe bei $\lambda = 400$ nm in Abhängigkeit von der Wasserstoffionenkonzentration.

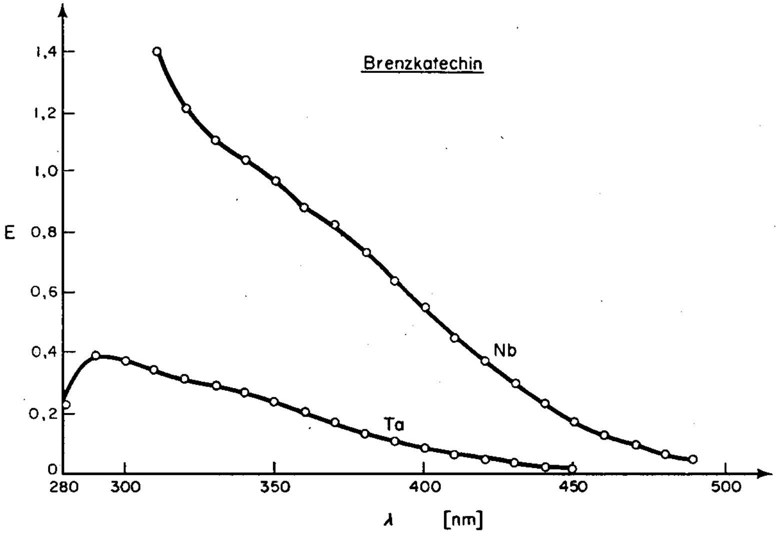
Das Schema, das nur einen qualitativen Vergleich zuläßt, zeigt, daß bei allen Reagenzien die Niob-Komplexe in neutraler, die Tantalkomplexe in stark saurer Lösung die intensivste Färbung aufweisen.

Im Zusammenhang mit diesen Versuchen stellten wir außerdem noch fest, daß die Färbungen nach spätestens 30 min ihr Maximum erreichen und dann für längere Zeit konstant bleiben. Zur Verhinderung der Oxydation des Pyrogallols mußte bei den Messungen im neutralen Gebiet den Lösungen etwas Natriumsulfit zugesetzt werden.

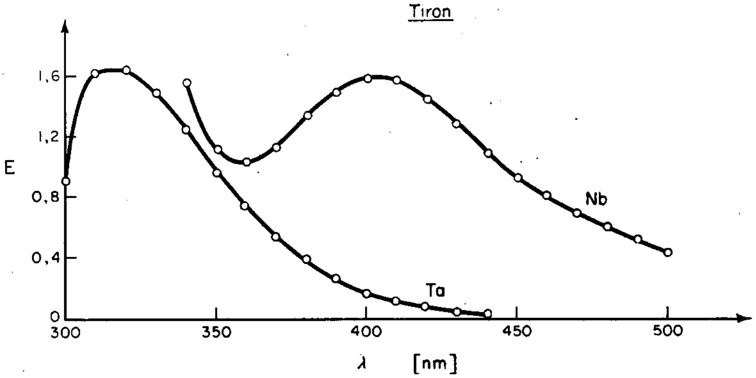
Bei dieser und allen weiteren Untersuchungen befanden sich im Vergleichsstrahlengang die reinen Reagenzlösungen der entsprechenden Wasserstoffionenkonzentration um deren Eigenabsorption im ultravioletten Spektralbereich auszuschalten.

Anschließend nahmen wir dann die Absorptionsspektren bei der Wasserstoffionenkonzentration auf, bei der wir vorher die höchste Extinktion gemessen hatten (Nb im Neutralen, Ta in 6*M* HCl).

Die Konzentration der Metallionen wählten wir dazu so, daß im Gebiet maximaler Extinktion gut meßbare Werte erhalten werden konnten. Die so erhaltenen Spektren sind in den Abb. 2a–e wiedergegeben.



(a)



(b)

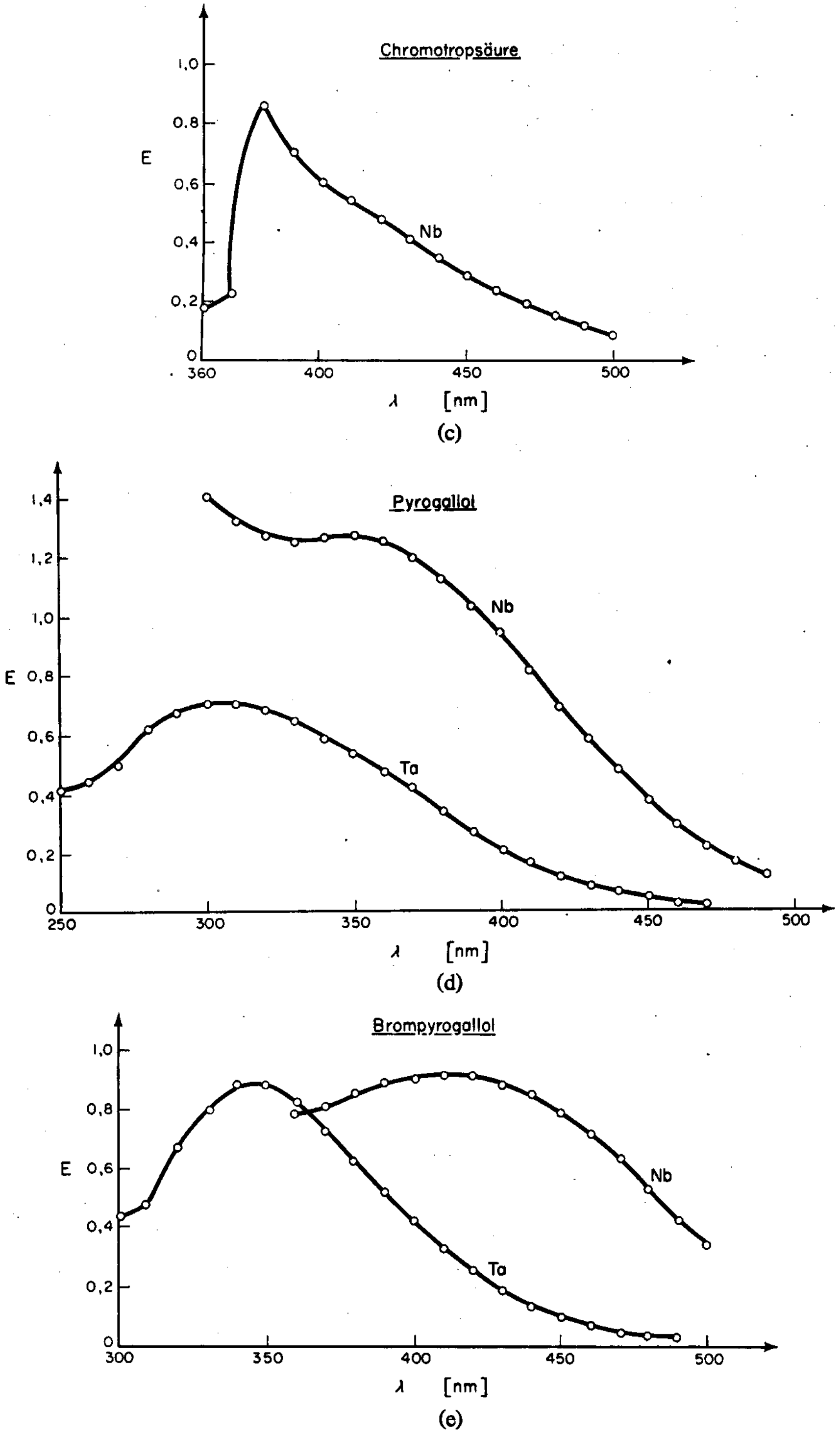


ABB. 2a–e.—Absorptionsspektren der Niob- und Tantalkomplexe.

In Tabelle I sind die Wellenlängen der Maxima der Spektren der Niob- und Tantalkomplexe zusammengestellt.

TABELLE I.—LAGE DER MAXIMA DER ABSORPTIONSSPEKTREN DER NIOB- UND TANTALKOMPLEXE

Reagens	Niob $\lambda_{\max}$, *nm*	Tantal $\lambda_{\max}$, *nm*
Brenzkatechin	350	295
Tiron	405	320
Chromotropsäure	380	
Pyrogallol	350	310
Tribrompyrogallol	410	345

Aus der Tabelle läßt sich ablesen, daß die Absorptionsmaxima der Tantalkomplexe stets bei kleineren Wellenlängen liegen als die der Niobverbindungen.

Für die Anwendung der Reagenzien sollen die Maxima der Nb- und Ta-Spektren möglichst weit auseinander liegen. In dieser Hinsicht ist das Tiron am günstigsten. Man kann aber erkennen, daß auch beim Tribrompyrogallol die Verhältnisse recht günstig liegen. Durch die Bromierung ist der Abstand der Maxima der beiden Spektren größer geworden (Nb von 350 auf 410 mm; Ta von 310 auf 345 nm).

In Tabelle II sind die Maximalkonzentrationen zusammengestellt bis zu welchen das Beersche Gesetz durch die untersuchten Erdsäurekomplexe erfüllt wird.

TABELLE II.—MAXIMALE KONZENTRATIONEN BIS ZU WELCHEN DAS BEERSCHE GESETZ ERFÜLLT WIRD

Reagens	Niob, *μg/ml*	Tantal, *μg/ml*
Brenzkatechin	100	2200
Tiron	60	250
Chromotropsäure	140	
Pyrogallol	50	1000
Tribrompyrogallol	30	2100

Ein quantitativer Vergleich der Brauchbarkeit der Reagenzien läßt sich am besten an Hand der molaren Extinktionskoeffizienten anstellen, die in Tabelle III enshalsen sind.

TABELLE III.—MOLARE DEKADISCHE EXTINKTIONSKOEFFIZIENTEN DER NIOB- UND TANTALKOMPLEXE MIT POLYPHENOLEN UND DERIVATEN DAVON

Reagens	neutral			sauer		
	λ, *nm*	Nb	Ta	λ, *nm*	Nb	Ta
Brenzkatechin	350	2640	227	295	801	143
Tiron	405	5060	93	320	641	1070
Chromotropsäure	380	1348	356			
Pyrogallol	350	5630	326	310	563	337
Tribrompyrogallol	410	6170	11	345	107	267

Um den Umfang der Störung der Meßwerte des einen Elementes durch das andere beurteilen zu können, sind auch die Extinktionskoeffizienten für Niob unter den für Tantal optimalen Bedingungen und umgekehrt bestimmt worden. Die Übersicht zeigt deutlich, daß unter den geprüften Reagenzien der Niob-Brompyrogallolkomplex den höchsten Extinktionskoeffizienten aufweist und hier die Störung durch Tantal außerordentlich gering ist.

Auf Grund dieser Befunde kann Tribrompyrogallol als neues Reagens für die photometrische Bestimmung von Niob empfohlen werden.

Andererseits ist zu erkennen, daß alle untersuchten Reagenzien sich in weinsaurem Medium nicht besonders gut zur Bestimmung des Tantals eignen, wobei das Tiron noch die günstigsten Ergebnisse zeigt. Auf Grund der Tatsache, daß im Tribrompyrogallol ein weitgehend selektives Reagens vorliegt, kann für die Simultanbestimmung von Niob und Tantal in weinsaurer Lösung folgendes Verfahren empfohlen werden.

1. Bestimmung des Niobs in neutraler Lösung bei 410 nm unter Verwendung von Tribrompyrogallol.
2. Bestimmung der Summe Niob + Tantal in $6M$ salzsaurer Lösung mit Tiron bei 320 nm.
3. Ermittlung der Extinktion des Niob-Tiron-Komplexes unter den Bedingungen von 2. aus einer gesondert aufgenommemen Störkurve.
4. Errechnung des Ta-Gehaltes aus der Differenz (Σ Nb + Ta) (bestimmt nach 2.) und dem Niobgehalt (bestimmt nach 1).

EXPERIMENTELLER TEIL

Apparaturen

Die spektrophotometrischen Messungen erfolen mit dem Universalspektrophotometer VSU 1 des VEB Carl Zeiss, Jena.

Herstellung der Lösungen der Erdsäuren

1. *Niob-Testlösung:* 3,3219 g des nach Brauer[7] gereinigten Niob(V)-oxids werden mit 30 g Kaliumhydrogensulfat im Quarztiegel aufgeschlossen und in 150 ml Weinsäurelösung (200 g/l) unter Erwärmen gelöst. Darauf Auffülen mit Wasser auf 250 ml. Die so erhaltene Lösung ist $0{,}1M$ an Niob. 1 ml = 9,3 mg Niob.

2. *Tantal-Testlösung:* 5,5234 g reinstes Tantal(V)-oxid werden mit 70 g Kaliumhydrogensulfat zwei Stunden im Quarztiegel geschmolzen. Zum Ende des Aufschlusses muß der Verlust an Schwefeltrioxid durch Zugabe einiger Tropfen konzentrierter Schwefelsäure ausgeglichen werden. Die erkaltete Schmelze wird mit 250 ml Weinsäurelösung (200 g/l) etwa 5 min zum Sieden erhitzt, abgekühlt und im Meßkolben auf 250 ml aufgefüllt. Die so erhaltene Lösung ist $0{,}1M$ an Tantal. 1 ml = 18,1 mg Tantal.

3. *Tribrompyrogallol:* Die Herstellung des Reagenses erfolgte nach einer Vorschrift von Hlasiwetz.[8] 12,6 g Pyrogallol wurden mit 50 g Brom in einer Reibschale verrieben und das nicht verbrauchte Brom auf dem siedenen Wasserbad abgedampft. Das Rohprodukt wurde aus siedendem Wasser umkristallisiert und getrocknet.
Schmelzpunkt: nach Literatur 168–170°; gefunden 170°.

4. *Reagenzlösungen*

Brenzkatechin	20%ig in Wasser
Pyrogallol	20%ig in Wasser
Tiron	20%ig in Wasser
Chromotropsäure	1%ig in Wasser
Tribrompyrogallol	10%ig in Äthanol

Summary—On examination of a wide range of hydroxylic organic compounds it has been found that two hydroxyl groups in the *ortho* position to each other in an aromatic system act as a functional analytical group for niobium and tantalum. *peri*-Dihydroxynaphthalene derivatives react similarly. After a systematic examination, tribromopyrogallol is proposed as a new selective and sensitive reagent for niobium.

Résumé—Au cours de l'étude d'un grand nombre de composés organiques oxhydrilés, il a été constaté qu'en présence d'acide tartrique, les composés possédant deux groupements oxhydriles en ortho sur un noyau aromatique présentaient des propriétés analytiques spécifiques pour le niobium et le tantale. Les dérivés du péri-dihydroxynaphtalène réagissent d'une manière analogue. Après une étude systématique, le tribromopyrogallol est proposé comme un nouveau réactif spécifique et sensible du niobium.

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DETERMINATION OF METALS IN METAL CHELATE COMPOUNDS*

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Summary—A rapid and convenient method of determining the metal content of metal chelate compounds is reported. The sample is decomposed with mixed acids in an open tube, and the freed metal ion is titrated with EDTA. Of the mixed acids investigated, a 3:1 mixture of nitric acid (62%) and perchloric acid (60%) is found to be effective in most cases.

THE determination of the metal content of solid metal chelate compounds has been done in various ways. The classical method of dry ashing, with or without sulphuric acid, cannot be recommended as the standard procedure, since there is a danger of sublimation of sample. There remains the further problem of choosing the weighing forms, metal oxide or sulphate, if the determination is finished gravimetrically.

Since the development of EDTA titration techniques for the determination of metals, many papers have been published on the application of this method to the determination of metals in chelate compounds. In these methods, the samples are at first decomposed by wet-digestion processes. Once the ligand molecule is decomposed and the free metal ion is released into solution, the subsequent metal titration can be done without difficulty.[1,2] In order to decompose the metal chelates without loss of sample, various procedures have been proposed. For example, samples may be decomposed by a modified Kjeldahl digestion method, by fuming nitric acid in an open or a sealed tube, or by the Schöniger flask combustion method.[3–5] Most of the chelates which are difficult to decompose can be degraded satisfactorily either by the Kjeldahl method or by modified Carius method with fuming nitric acid in a sealed tube.[6] However, in the case of the Kjeldahl method, excess sulphuric acid often causes trouble in the subsequent metal titration; and the Carius decomposition is time-consuming. Decomposition of the sample with fuming nitric acid in an open vessel often results in a violent spontaneous combustion which causes splashing of the sample. The Schöniger method seems attractive in its simplicity, but the method is only applicable to chelates of the alkaline earths, zinc, cadmium or mercury, because other metals form alloys with the platinum wire, or form insoluble oxides.[3]

The present investigation was carried out to find the most practical method of determining the metal content of chelate compounds. For the sake of simplicity in the analytical procedure, the methods investigated are all wet-digestion processes in open vessels. Of these, the following digestion procedures are found to give satisfactory results: (1) with fuming or concentrated nitric acid, (2) with a mixture of concentrated nitric acid and concentrated sulphuric acid, (3) with a mixture of concentrated

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* Contribution No. 26. This work was supported partly by a grant provided by the Ministry of Education, Japanese Government.

nitric acid and perchloric acid, and (4) with a mixture of fuming nitric acid, concentrated sulphuric acid and perchloric acid.

Although the last of these procedures offers the most complete and smooth decomposition, it has a drawback in that insoluble sulphate may result from barium and lead chelates. Procedures (1) and (2), if carried out carefully, also provided satisfactory results for most of the metal chelates investigated. Procedure (3), employing a mixture of nitric acid and perchloric acid, was found to be the most useful for a wide variety of samples.

Although these procedures were originally developed for the determination of metals in metal chelate compounds, they may also be useful for such samples as the metal salts of organic acids or other organometallic compounds.

EXPERIMENTAL

Reagents

Decomposition mixtures

(1) Fuming nitric acid.
(2) A mixture of 15 ml of nitric acid (62%) and 15 ml of hydrogen peroxide (30%).
(3) A mixture of 15 ml of nitric acid (62%) and 15 ml of sulphuric acid (95%).
(4) A mixture of 18 ml of nitric acid (62%) and 6 ml of perchloric acid (60%).
(5) A mixture of 15 ml of fuming nitric acid, 15 ml of sulphuric acid (95%) and 5 ml of perchloric acid (60%).

Reagents for EDTA titration

0·005M *EDTA solution*: Dissolve about 1·86 g of disodium ethylenediaminetetraacetate dihydrate in distilled water to make 1 litre, and standardise against 0·01*M* standard zinc sulphate solution at pH 10 using Erio T as indicator.

Metallochromic indicators: Erio T, Patton and Reeder's Dye, Xylenol Orange, and Pyridylazonaphthol (PAN). Conditions for the metal titrations are listed in Table I. Sodium was determined on an aliquot of the decomposed solution, by precipitation as sodium zinc uranyl acetate, followed by the EDTA titration of zinc in the precipitate.[7,8]

Other reagents

Analytical grade unless otherwise stated. Demineralised water is used throughout the experiments.

Procedure

Weigh about 10–20 mg of sample into a small test tube (10 mm in diameter and 12 cm in length). To this, add 10 drops of decomposing acid drop by drop. Care should be taken not to leave any sample on the wall of the tube, otherwise it will be incompletely decomposed, or will be lost by

TABLE I.—CONDITIONS FOR THE METAL TITRATIONS

Metal ion	Indicator	Buffer and pH
Mg	Erio T	NH_3—NH_4Cl, 10
Ca	Patton and Reeder	KOH 13
Sr	Erio T, Mg-EDTA	NH_3—NH_4Cl, 10
Ba	Erio T, Mg-EDTA	NH_3—NH_4Cl, 10
Zn	Erio T	NH_3—NH_4Cl, 10
Cd	Erio T	NH_3—NH_4Cl, 10
Hg^{II}	Xylenol Orange	Urotropin, 6
Cu	PAN	Acetate, methanol, 2·5
Ni	PAN, Cu-EDTA	Acetate, 3, (100°)
Pb	Xylenol Orange	Urotropin, 6
	Erio T (Back titration with Zn)	NH_3—NH_4Cl, 10
Bi	Xylenol Orange	HNO_3, 1–3

sublimation during the decomposition process. Hold the tube at a 45° angle, and heat very carefully at the bottom by a microburner. Shake the tube continually to avoid explosive boiling. At the first stage of decomposition, evolution of nitrogen oxides is observed, then fuming of sulphuric acid or perchloric acid follows. Continue heating for about 5–10 min until only a few drops of the liquid remain in the tube.

After cooling, wash the content of the tube into a titration flask, and dilute for the metal titration. The conditions of titration for each metal are summarised in Table I.

If the sample contains a relatively large ligand or one difficult to decompose, it is sometimes necessary to repeat the decomposition with a few additional drops of the acid.

RESULTS AND DISCUSSION

The relative ease of sample decomposition depends greatly on the kind of metal chelates investigated, and some examples of metal determinations are listed in Table II–IV.

Simple chelate compounds can be decomposed by nitric acid if heating is applied slowly. If the sample is heated in a wide open vessel such as a crucible or beaker, in place of a narrow tube, loss of sample occurs during the violent spontaneous decomposition reaction, which often occurs at a later stage in the decomposition process.

In the case of nitrilotriacetate chelates, the sample can be decomposed satisfactorily by a mixture of nitric acid and hydrogen peroxide, but not by nitric acid only. As shown in the examples, the sodium content can also be determined on an aliquot of the resulting solution. Determination of the metal content of such metal chelates cannot be achieved by the classical gravimetric methods after dry ashing.

TABLE II.—METAL DETERMINATION AFTER DECOMPOSING WITH FUMING NITRIC ACID

Sample	Metal, %	
	Calcd.	Found.*
$Bi(NH_2CH_2CH_2S)_2(NO_3)$	49·37	49·3
$Ni(NH_2CH_2CH_2S)(OH_2)_3(NO_3)$	23·40	23·6
$Ni(NH_2CH_2CH_2S)_2$	26·96	26·8
$Pb(NH_2CH_2CH_2S)(OH_2)_5NO_3)$	45·74	46·0
$Hg(NH_2CH_2CH_2S)(OH_2)_2(NO_3)$	53·51	53·8

* The values reported in Table II–IV are the average of two to five determinations.

TABLE III.—METAL DETERMINATION AFTER DECOMPOSING WITH A MIXTURE OF NITRIC ACID AND HYDROGEN PEROXIDE

Sample	Metal, %		Na, %	
	Calcd.	Found	Calcd.	Found
NaMgNTA* $\cdot 3.5H_2O$	8·16	8·10	7·72	7·68
NaCaNTA$\cdot 3H_2O$	14·02	14·02	7·54	7·50
NaSrNTA$\cdot 4H_2O$	23·5	24·0	6·22	6·12
NaBaNTA$\cdot 3{\cdot}5H_2O$	33·4	34·0	5·59	5·50
NaNiNTA$\cdot 3{\cdot}5H_2O$	17·6	17·0	6·91	6·68
NaCuNTA$\cdot 2{\cdot}5H_2O$	19·9	20·6	7·22	7·06
NaZnNTA$\cdot 3{\cdot}5H_2O$	19·3	19·4	6·67	6·60
NaCdNTA$\cdot 3H_2O$	30·3	31·0	6·15	6·08
NaPbNTA$\cdot 3H_2O$	43·9	44·2	4·87	4·80

* NTA designates trivalent anionic form of nitrilotriacetic acid, $N(CH_2COO)_3^{-3}$.

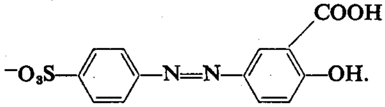
In most cases, a mixture of nitric acid and perchloric acid is found to be a most effective oxidising agent, reacting smoothly. No violent reaction is observed with a mixture containing perchloric acid or sulphuric acid, but the mixture containing sulphuric acid gives insoluble precipitates in the case of lead and barium chelates. However, this is not a serious defect since those precipitates can be dissolved in alkaline EDTA solution, making it possible to determine them by a back-titration technique.

TABLE IV.—METAL DETERMINATION AFTER DECOMPOSING WITH NITRIC ACID, OR WITH MIXTURES WITH SULPHURIC ACID OR PERCHLORIC ACID

Sample	Decomposing acid.*	Metal, %	
		Calcd.	Found
Bis(acetylacetonato)-Cu^{II}	(1)	24·27	24·1
Bis(acetylacetone)-	(1)	22·23	22·0
ethylenedi-imino-Cu^{II}	(3)	22·23	22·2
Bis(salicylaldi-imine)-	(1)	16·30	15·6
diethylenesulphido-Cu^{II}	(4)	16·30	15·5
$Mg(SAS)_2.8H_2O$†	(4)	3·00	3·01

* Number of acid stands for the number of the decomposition mixture as listed under Reagents.

† SAS designates a mono-anionic form of sulphophenylazo-salicylic acid,



In some instances, such as metal chelates of sulphophenylazosalicylic acid, decomposition with the mixture of nitric acid and perchloric acid is not complete and it is necessary to repeat the digestion with an additional amount of acid.

Zusammenfassung—Eine schnelle und einfache Methode zur Bestimmung des Metallgehaltes von Chelatverbindungen wird mitgeteilt. Die Probe wird im offenen Rohr mit einem Säuregemisch zersetzt und das Metall mit ADTE titriert. Von den untersuchten Säuremischungen wurde die folgende als sehr wirkungsvoll gefunden: 3 Teile (62%) Salpeter—und 1 Teil (60%) Perchlorsäure.

Résumé—Les auteurs proposent une méthode rapide et commode pour le dosage d'un métal contenu dans un complexe. L'échantillon est décomposé par un mélange d'acides en tube ouvert, et le métal, libéré, est titré par l'E.D.T.A. Parmi les mélanges d'acides étudiés, le mélange de 3 parties d'acide nitrique (62%) et d'une partie d'acide perchlorique (60%) s'est révélé le plus efficace dans la majorité des cas.

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EXTRACTION AND DETERMINATION OF IRON AS THE BATHOPHENANTHROLINE COMPLEX IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS*

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Summary—A spectrophotometric method for determining iron in the range 0·001–0·125% in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of iron to the bivalent state with ascorbic acid and hydroxylamine hydrochloride, the red complex formed between iron^{II} and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) is extracted into *n*-amyl alcohol and the absorbance of the resulting extract is determined at 536 mμ. Interference from copper is eliminated with thiourea. Cobalt, cadmium, nickel, manganese and zinc also interfere but the amounts of each of these impurities present in the four high-purity metals described are so low that their interference effects are negligible in the proposed method. Highly reproducible and precise results can be obtained with careful control of the pH during reduction and extraction.

INTRODUCTION

THE development of a suitable spectrophotometric procedure for the determination of trace amounts of iron in high-purity niobium, tantalum, molybdenum and tungsten metals has been undertaken at the Mines Branch laboratories as part of a project to determine impurities in these metals.

Despite the large number of spectrophotometric methods which have been proposed for the determination of small amounts of iron, very few have been applied in matrices of the above metals. Hastings *et al.*[1] determined iron in tantalum metal with *o*-phenanthroline. Crawley and Aspinal[2] used bathophenanthroline for the determination of iron in tungsten metal. Recently Gahler *et al.*[3] described a method for determining iron in niobium, tantalum and tungsten metals with bathophenanthroline in which iron is reduced with sodium dithionite and the iron^{II}-bathophenanthroline complex is extracted into chloroform. Their procedure could probably be extended to the determination of iron in molybdenum metal but this was not attempted because the present investigation was nearing completion at the time their paper was published. Prior to this time no single method was found in the literature which was directly applicable to all four metals under consideration.

At the beginning of this investigation it was decided that the development of a single procedure applicable to all four metals would require similar methods of dissolution and solution preparation, as well as a chromogenic reagent capable of forming an extractable iron complex. The use of an extraction procedure would be necessary

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to remove the coloured iron complex from the background colour exhibited by molybdenum solutions and also possible turbidity from partial hydrolysis of niobium and tantalum solutions. The extraction step would increase the sensitivity of the method and also make it possible to remove iron from solutions of the required agents, thus reducing the blank essentially to zero.

It is known that the four high-purity metals dissolve in hydrofluoric and nitric acids and form soluble complexes with ammonium tartrate.[2,4,5] Therefore, these reactions were utilised for the decomposition procedure and solution preparation. Bathophenanthroline was chosen as the chromogenic reagent because of its sensitivity and reported specificity.[6] It was first proposed by Case,[7] and investigated as an analytical reagent by Smith, McCurdy and Diehl[8] who applied it to the determination of iron in municipal water supples. The iron^{II}-trisbathophenanthroline complex has a molar extinction coefficient of 22,400 at 533 mμ[8] and can be extracted into iso-amyl, *n*-amyl and *n*-hexyl alcohols, and nitrobenzene.[6]

The present paper describes the successful use of bathophenanthroline in determining iron in high-purity niobium, tantalum, molybdenum and tungsten metals. Copper, cobalt, cadmium, nickel, manganese and zinc were found to interfere in this method. In the aliquot taken for analysis up to 10 μg of each of these interfering cations can be tolerated, while the tolerance level for copper alone is 50 μg.

EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model DU.
pH meter: Leeds and Northrup, Cat. No. 7664, a.c. operated.
Centrifuge: Canlab clinical type.

Reagents

Standard iron stock solution: Dissolve 0·1000 g of electrolytic iron in 10 ml of 1:1 sulphuric acid. Dilute to 500 ml with water and store in a polyethylene bottle.

Pre-reduced standard iron solution: Dilute 5 ml of the stock solution together with 1 ml of 10% ascorbic acid solution to 200 ml with water. Prepare fresh as needed (1 ml of this solution ≡ 5 μg Fe).

Bathophenanthroline, 0·001*M solution*: Dissolve 0·167 g of 4,7-diphenyl-1,10-phenanthroline (G. Frederick Smith Chemical Co.) in 250 ml of ethyl alcohol. Dilute to 500 ml with water and store in a polyethylene bottle.

Ammonium tartrate, 25% *iron-free solution:* Dissolve 125 g of ammonium tartrate and 1 g of hydroxylamine hydrochloride in approximately 350 ml of water. Add 10 ml of bathophenanthroline solution, allow to stand for 1 hr, then extract three times with 15-ml portions of a 3:1 mixture of chloroform and *n*-amyl alcohol. Extract the iron-free solution three times with chloroform to remove excess *n*-amyl alcohol. Filter, dilute to 500 ml with water and store in a polyethylene bottle.

Boric acid, 5% *iron-free solution:* Dissolve 50 g of boric acid in approximately 800 ml of hot water. Cool, dissolve 1 g of hydroxylamine hydrochloride in this solution, then add 20 ml of bathophenanthroline solution and allow to stand for 1 hr. Extract with chloroform and *n*-amyl alcohol as described for the ammonium tartrate solution. Filter, dilute to 1 litre with water and store in a polyethylene bottle.

Hydroxylamine hydrochloride, 10% *iron-free solution:* Dissolve 10 g of hydroxylamine hydrochloride in approximately 60 ml of water. Add 5 ml of bathophenanthroline solution and allow to stand for 10 min. Extract three times with 8-ml portions of a 3:1 mixture of chloroform and *n*-amyl alcohol, then three times with chloroform to remove excess *n*-amyl alcohol. Filter and dilute to 100 ml with water. Prepare a fresh solution weekly.

Ascorbic acid, 10% *solution:* Dissolve 10 g of ascorbic acid (Analytical Reagent, British Drug Houses Ltd.) in water and dilute to 100 ml. Prepare a fresh solution every second day. (The iron content of this reagent is sufficiently low that purification is unnecessary.)

Thiourea, 5% *solution:* Dissolve 10 g of thiourea (Analytical Reagent, Fisher Scientific Co.) in water and dilute to 200 ml.

n-Amyl alcohol: The *n*-amyl alcohol used must be free from oxidising agents such as peroxides. Test each new bottle before use by the addition of potassium iodide and starch solution to a dilute hydrochloric acid wash of the alcohol. If the presence of peroxides is indicated distil according to the method described by Russel and Hart[9] for iso-amyl alcohol. Analytical reagent *n*-amyl alcohol obtained from Mallinckrodt Chemical Works was found to be free from peroxides.

Chloroform: Analytical reagent, obtained from Fisher Scientific Co.

General experimental procedure

Calibration curve. Pipette 20 ml of 25% ammonium tartrate solution, 40 ml of 5% boric acid solution, 20 ml of 10% ascorbic acid solution, and 10 ml of 10% hydroxylamine hydrochloride solution into a 250-ml beaker. Adjust the pH of the resulting "base" solution to 5·5 with concentrated ammonia solution using a pH meter, and dilute to volume with water in a 200-ml volumetric flask. Add a 20-ml aliquot of this solution to each of six 60-ml separatory funnels which are marked at 25 ml. Then, by burette, add to the last five funnels 1, 2, 3, 4 and 5 ml, respectively, of the pre-reduced standard iron solution. The first funnel contains the blank. Dilute the contents of each funnel to the 25-ml mark with water and swirl to mix. (Because *n*-amyl alcohol and water are soluble in each other to a certain extent the total volume should be carefully controlled.) Add to each funnel 2 ml of 5% thiourea solution, mix and allow to stand for 5 min. Add 4 ml of 0·001*M* bathophenanthroline solution, mix and allow to stand for 15 min. Then add, by pipette, 10 ml of *n*-amyl alcohol, stopper and shake for 2 min. Allow 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the *n*-amyl alcohol extracts into 15-ml centrifuge tubes and centrifuge for 30 sec. Determine the absorbance of each extract against the blank as the reference solution, using 1-cm cells in a Beckman DU spectrophotometer, at a wavelength of 536 mμ. Plot micrograms of iron *vs.* absorbance.

Procedure for niobium, tantalum, molybdenum and tungsten metals. In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker (tetrafluoroethylene-Dynalab Corp., Rochester, N.Y.), add 5 ml of water and 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon watch glass. Then through the lip of the beaker add concentrated nitric acid slowly, 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. (If all of the sample does not go into solution with the above procedure, then omit the preliminary addition of the 5 ml of water and dissolve directly with the hydrofluoric and nitric acids). Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. (For molybdenum metal and a separate reagent blank, add at this point, 2 ml of concentrated hydrochloric acid and heat until the dark brown coloration disappears and the solution becomes pale yellow). Add 3 ml of formic acid to destroy excess nitric acid[10] and heat gently until the evolution of oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water and evaporate to approximately 5 ml. Add 10 ml of water and 10 ml of 25% ammonium tartrate solution, and heat gently without boiling for 5–10 min, at which point the solution should be clear. Add 20 ml of 5% boric acid solution and allow to stand for 20 min. (If the iron determination cannot be completed the same day, allow to stand overnight at this point.) Add 2 ml of 1:1 sulphuric acid, mix, and add 10 ml of 10% ascorbic acid solution and 5 ml of 10% hydroxylamine hydrochloride solution. Mix, allow to stand for 10 min, then adjust the pH to 5·5 with concentrated ammonia solution using a pH meter. Transfer to a 100-ml volumetric flask and dilute to volume. Transfer a suitable aliquot (4-20 ml) of both sample and blank solutions, depending on the iron concentration of the sample, to 60-ml separatory funnels. Dilute to the 25-ml mark with water and proceed with the iron extraction as described for the calibration curve. Measure the absorbance of the sample against the reagent blank and determine the iron content of the aliquot by reference to the calibration curve. 1 μg of iron = 0·001% when 20-ml aliquots of sample are taken.

RESULTS

Extraction of the coloured complex

Although the iron^{II}-bathophenanthroline complex can be extracted into various organic solvents,[6] *n*-amyl alcohol was chosen for the present work because of its ready availability.

In preliminary experiments with pure iron solutions, it was found that up to 25 μg of iron contained in a 25-ml volume of solution could be extracted quantitatively over the pH range 3 to 7 in a single stage with 10 ml of *n*-amyl alcohol. The extraction of larger amounts of iron was not attempted because of the high optical density of the resulting extract.

Factors influencing formation of the iron complex and its subsequent extraction from solutions of the high-purity metals

Reductant. Hydroxylamine hydrochloride is often used for the reduction of iron^{III} in spectrophotometric procedures. However, when the effectiveness of this reducing agent was tested on samples of niobium, tantalum, molybdenum and tungsten metals which were decomposed according to the described procedure, and to which standard additions of iron had been made, excessive time (up to 4 hr) was required for complete reduction of the iron.

Ascorbic acid was tested under similar conditions as a possible reductant and the results of these experiments indicated that this reagent was capable of reducing iron more rapidly than hydroxylamine hydrochloride. However, after the iron^{II}-bathophenanthroline complex was extracted into *n*-amyl alcohol, there was a tendency for the colour to fade. This was considered to be caused by low solubility of ascorbic acid in *n*-amyl alcohol and the consequent atmospheric oxidation of the iron^{II} complex.

Because the organic extracts from the tests previously performed with hydroxylamine hydrochloride showed no inclination for colour fading over a 24 hr period, it was considered that a mixture of hydroxylamine hydrochloride and ascorbic acid would be effective in bringing about immediate and complete reduction of iron and producing a stable extract. A series of tests performed on synthetic solutions of the metals employing the two reducing agents showed that the above conditions were fulfilled.

Effect of pH. Experiments to determine the effect of pH on the formation and extraction of the iron^{II}-bathophenanthroline complex from solutions of the high-purity metals, were performed with molybdenum solutions, because it was considered that the optimum conditions for determining iron in molybdenum metal would also be applicable to the other three metals. Because many bathophenanthroline methods for iron recommend a pH of 4 or 5·5[6,8,11,12,13] for the extraction of the iron complex, tests were carried out at both pH values on synthetic samples prepared by decomposing 0·5-g portions of molybdenum metal of low iron content according to the described dissolution procedure. Known additions of iron were made after the formic acid treatment, followed by the amounts of ammonium tartrate, boric acid, and reducing agents specified in the proposed procedure. After adjusting the pH, the solutions were diluted to the mark with water in 100-ml volumetric flasks. Appropriate aliquots of the resulting solutions were made up to 25 ml with water, 4 ml of 0·001*M* bathophenanthroline solution[6] were added, and the iron complex was extracted with 10 ml of *n*-amyl alcohol. The total iron content of these solutions was determined by reference to calibration curves prepared from "base" solutions of the same pH (described under *Calibration Curve*). The results of these tests are given in Table I.

Table I shows that the recovery of iron from molybdenum solutions is incomplete when the iron complex is formed and extracted at pH 4, but at pH 5·5 total recovery of the added iron was obtained indicating complete reduction and complete formation of the iron complex.

Tests carried out at pH 5·5 on synthetic niobium, tantalum and tungsten samples showed that complete recovery of the added iron was obtained for the niobium and tungsten samples, but the results for the tantalum samples were low. Tests performed with tantalum solutions adjusted to pH 4 and pH 7 also yielded low results. However, when more bathophenanthroline was added to the aqueous phase remaining after extraction of these solutions, increased colour formation was observed after several hr, indicating that prior to the extraction step the reduction of the added iron was incomplete. Further investigation with tantalum solutions showed that this was because of the pH at which the reducing agents were added. The pH of the sample solutions after dissolution according to the described procedure and addition of ammonium tartrate and boric acid was found to be approximately 3. At this pH reduction of iron was complete in niobium, molybdenum and tungsten solutions, but was incomplete in tantalum solutions. However, when the pH was lowered to 1 with sulphuric acid before reduction, complete recovery of the added iron was obtained.

TABLE I.—EFFECT OF pH ON EXTRACTION OF IRON FROM SYNTHETIC MOLYBDENUM SAMPLES

Sample	Fe found, %	
	pH 4	pH 5·5
Mo	0·0079	0·0083
Mo + 0·010% Fe	0.0176	0·0182
Mo + 0·025% Fe	0·0311	0·0335
Mo + 0·050% Fe	0·0438	0·0575
Mo + 0·100% Fe	0·0880	0·1085

The results of the foregoing experiments show that the development of a single method for determining iron which would be applicable to all four metals described, would require that reduction takes place at approximately pH 1 followed by pH adjustment to 5·5 for the formation and extraction of the iron complex.

Effect of diverse metal ions

Smith, McCurdy and Diehl[8] state that bathophenanthroline is more or less specific for iron and that the only metal cations which form bathophenanthroline derivatives are copper and cobalt, which do not interfere under the conditions of their procedure. Cobalt is described as forming a light yellow complex which is not extracted from acid solution. Copper also forms a yellow derivative, copper^{I}-bisbathophenanthroline, in neutral or alkaline solution, which is transformed on acidifying the solution to colourless copper^{I}-monobathophenanthroline. They state further, that at pH 4 the copper^{I}-mono derivative is extracted but is colourless, and that copper, in quantities up to 250 μg, does not interfere.

More recent investigations have shown that bathophenanthroline is not specific for iron. Guest and Roloson[12] in determining iron in uranium-bearing materials employing hydroxylamine hydrochloride as reductant, found that copper is a very serious interferent at pH 4, and that bathophenanthroline forms a copper complex in preference to the iron complex. Gahler *et al.*[3] found that copper, cobalt, nickel and manganese interfere to the extent that they consume reagent. Tests carried out in this laboratory corroborated these results and showed that cadmium and zinc also interfere.

Preliminary tests with copper were carried out at pH 4 as recommended by Smith *et al.*[8] Varying amounts of copper solution and a constant known amount of pre-reduced iron solution were added to aliquots of "base" solution which had been adjusted to pH 4. (Reduction of the iron prior to addition to the "base" solution ensures that all of the iron will be present in the reduced form at the given pH). After diluting the resulting solutions to 25 ml with water, 4 ml of 0·001 *M* bathophenanthroline solution were added and the iron complex was then extracted with 10 ml of *n*-amyl alcohol. The results of these tests (Table II) show the magnitude of the copper interference. At the concentration of bathophenanthroline employed, as little as 5 μg of copper will enhance the iron result, and at higher levels (250 μg) the bathophenanthroline is preferentially complexed by the copper. Amounts of copper in excess of 250 μg were found to give negative absorption readings.

TABLE II.—EFFECT OF COPPER ON EXTRACTION OF IRON WITH BATHOPHENANTHROLINE AT pH 4†

Cu taken, *μg*	Fe found, *μg*
5	10·9
10	11·4
25	13·2
50	16·0
100	20·7
250	1·0*

* Bathophenanthroline preferentially complexed by copper.

† Concentration of iron present: 10 μg.

The possibility that the four high-purity metals under consideration could contain trace amounts of copper had to be taken into account; consequently, some means was required for complexing copper and preventing its reaction with bathophenanthroline. It is known that small amounts of copper can be masked with thiourea,[14] therefore this reagent was investigated as a possible complexing agent. The tests described in the preceding paragraph were repeated with the addition of thiourea prior to the addition of the bathophenanthroline. The results of these tests (Table III) show that for small amounts of copper, thiourea successfully inhibits the formation of the copper^{I}-bathophenanthroline complex.

TABLE III.—EFFECT OF THIOUREA ON THE EXTRACTION OF IRON IN THE PRESENCE OF COPPER AT pH 4

Cu taken, *μg*	Fe found, *μg*
10	10·2
25	10·1
50	10·1
100	10·1
250	10·7

Concentration of iron present: 10 μg.
Amount of thiourea added: 0·100 g.

The effectiveness of thiourea in eliminating interference from copper was tested for concentrations of iron up to 25 μg at pH 5·5, because this is the pH required for extracting iron from solutions of the four high-purity metals. Results show (Table IV) that up to 50 μg of copper can be tolerated in test solutions at this pH.

TABLE IV.—EFFECTIVENESS OF THIOUREA IN COMPLEXING COPPER AT pH 5·5

Fe taken, μg	Fe found, μg	
	Cu taken, 100 μg	Cu taken, 50 μg
0	0·3*	0·2*
5	5·3†	5·3
10	9·9	10·2
15	14·5	14·9
20	18·7	19·6
25	23·5	24·5

* Extracts were yellow.
† Extract had a slight orange tinge.

Tests carried out with cobalt, cadmium, nickel, manganese and zinc showed that their interference effects are not as serious as that from copper. No attempt was made to find ways of eliminating these elements because spectrographic results on 22 samples of high-purity niobium, tantalum, molybdenum and tungsten metals showed these impurities and also copper to be present in small amounts, *i.e.* less than 0·01 %. The determination of the quantity of each impurity which could be tolerated at the bathophenanthroline concentration used in the proposed procedure would have little significance with regard to the present investigation because small amounts of each impurity do occur in the same sample. Therefore, tests were carried out to determine the maximum amount of the six interfering elements which could be present together in equal amounts in solutions of the four metals without affecting the iron results. Solutions of the high-purity metals were prepared as described under *General Experimental Procedure*. Then, varying quantities of a solution containing equal amounts of copper, cobalt, cadmium, nickel, manganese and zinc were added to three 20-ml aliquots of each of these solutions, and the total iron content of the resulting aliquots was determined as described in the proposed method. Also, in order to determine the effect of the combined interfering elements at levels of iron greater than are present in the metals themselves, and approaching the upper limit of the calibration curve, the above tests were repeated with the addition of a known amount (15 μg) of standard pre-reduced iron solution. Table V gives the results of these tests for niobium only, and also the results of tests carried out in an identical manner with 50 μg of copper alone which was previously shown (Table IV) to have no appreciable effect in test solutions. Tests performed with tantalum, molybdenum and tungsten solutions under the same conditions yielded similar results.

The results in Table V and also those obtained with synthetic tantalum, molybdenum and tungsten samples show that in samples of the four metals analysed according to the proposed procedure, up to 50 μg of copper alone, or 10 μg each of copper, cobalt, cadmium, nickel, manganese, and zinc may be present together in the aliquot taken for extraction without appreciably affecting the iron result. These

TABLE V.—EFFECT OF INTERFERING CATIONS ON THE DETERMINATION OF IRON BY THE PROPOSED METHOD IN SYNTHETIC NIOBIUM SAMPLES

Sample	Total Fe present, %	Fe found, %
Nb + 0·005% each of Cu, Co, Cd, Ni, Mn, Zn	0·0064 (4)	0·0063
Nb + 0·01%* each of Cu, Co, Cd, Ni, Mn, Zn	0·0064	0·0062
Nb + 0·02% each of Cu, Co, Cd, Ni, Mn, Zn	0·0064	0·0062
Nb + 0·015%* Fe + 0·005% each of above	0·0214	0·0213
Nb + 0·015% Fe + 0·01% each of above	0·0214	0·0208
Nb + 0·015% Fe + 0·02% each of above	0·0214	0·0185
Nb + 0·05%* Cu	0·0064	0·0063
Nb + 0·015% Fe + 0·05% Cu	0·0214	0·0212

Figure in parenthesis indicates number of replicate determinations.

* 10, 15 and 50 μg, respectively, for 20-ml extraction aliquots.

tolerance limits are adequate for the level of these impurities present in high-purity samples of the four metals, but they could be increased somewhat by increasing slightly the thiourea and bathophenanthroline concentrations. However, experiments performed with molybdenum solutions using 0·100 and 0·250 g of thiourea in combination with 2 ml of a 0·01*M* solution of bathophenanthroline in ethyl alcohol were unsuccessful. The extracts obtained were milky in appearance and did not clear on being centrifuged.

Application to synthetic niobium, tantalum, molybdenum and tungsten samples for iron contents up to approximately 0·1%

In order to determine its accuracy for higher levels of iron concentration, the proposed method was applied to the analysis of a series of synthetic samples in which the added iron concentration varied from 0·01 to 0·10%, and which were prepared from the same four metals used in the preceding tests. The standard iron solution was added after the formic acid treatment. The results obtained are given in Table VI.

TABLE VI.—RECOVERY OF IRON BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Fe present, %	Fe found, %	Sample	Total Fe present, %	Fe found, %
Nb + 0·010% Fe	0·0164	0·0167	Ta + 0·010% Fe	0·0166	0·0163
Nb + 0·025% Fe	0·0314	0·0314	Ta + 0·025% Fe	0·0316	0·0318
Nb + 0·050% Fe	0·0564	0·0568	Ta + 0·050% Fe	0·0566	0·0562
Nb + 0·100% Fe	0·1064	0·1089	Ta + 0·100% Fe	0·1066	0·1060
Mo + 0·010% Fe	0·0179	0·0174	W + 0·010% Fe	0·0156	0·0166
Mo + 0·025% Fe	0·0329	0·0330	W + 0·025% Fe	0·0306	0·0310
Mo + 0·050% Fe	0·0579	0·0555	W + 0·050% Fe	0·0556	0·0563
Mo + 0·100% Fe	0·1079	0·1064	W + 0·100% Fe	0·1056	0·1070

DISCUSSION

Table VI shows that the results obtained by the proposed bathophenanthroline method agree favourably with the total calculated percentage of iron present in the range of values up to approximately 0·1%.

In the proposed procedure the iron^{II}-bathophenanthroline complex is extracted in a single stage with a fixed quantity of *n*-amyl alcohol. Because *n*-amyl alcohol is soluble to a certain degree in water, the absorbancy of the resulting extract therefore depends on the density and volume as well as the pH of the aqueous phase remaining after extraction. Therefore, preparation of a suitable calibration curve for determining iron in the four high-purity metals would require that extraction of known amounts of iron for plotting the reference curve should take place under essentially the same conditions as the iron is extracted in the samples. The use of a pre-reduced standard iron solution together with 20-ml aliquots of a "base" solution adjusted to pH 5·5, and consisting of the reagents required in the sample preparation, ensures that the sample conditions regarding reduction and extraction pH's and density and volume of the aqueous phase, will be duplicated in the calibration solutions for amounts of iron up to 0·025%. The presence of greater than 0·025% iron in samples of the four metals necessitates extraction of a smaller aliquot of the sample solution than 20 ml. Dilution of a smaller aliquot to 25 ml with water prior to extraction of the iron complex is accompanied by a variation in pH and density, and if extremely accurate analysis is required, the absorbancy of the resulting extract should be determined by reference to a calibration curve prepared by using the same size aliquot of the "base" solution. However, when a 4-ml aliquot of sample solution is diluted to 25 ml with water the density diminishes, and the pH decreases from 5·5 to approximately 4·6. These combined effects were shown to produce a maximum positive error of 0·002% at the 0·10-% iron level in test solutions when extraction was carried out at pH 4·6. This is felt to be within the experimental error of the method.

The proposed procedure is suitable for samples containing between 0·001 and 0·125% of iron, but material containing larger amounts could also be successfully analysed simply by reducing the initial sample weight. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Eine spektrophotometrische Methode zur Bestimmung von Eisenspuren in hochreinem Niob, Tantal, Molybdän und Wolfram wird beschrieben. Nach Lösen der Probe wird Eisen mittels Ascorbinsäure und Hydroxylamin reduziert, der rote Komplex mit Bathophenanthrolin (4,7-Diphenyl-10-phenanthrolin) wird geformt, in n-Amylalkohol ausgeschuttelt und die Absorbtion bei 536 mμ gemessen. Störungen durch Kupfer werden mittels Thioharnstoff ausgeschaltet. Co, Cd, Ni, Mu und Zn stören ebenfalls, doch sind die in hochreinen Metallen vorhandene Mengen so gering, dass der Einfluss vernachlässigt werden kann. Die Resultate sind sehr präzise, wenn die Einstellung des pH der Lösung während Reduktion und Extraktion genau bewerkstelligt wird.

Résumé—Les auteurs décrivent une méthode spectrophotométrique de dosage de traces de fer dans le niobium, le tantale, le molybdène et le tungstène de haute pureté. Après mise en solution de l'échantillon et réduction du fer à l'état(II) par l'acide ascorbique et le chlorhydrate d'hydroxylamine, le complexe rouge formé entre le fer ferreux et la bathophénanthroline (4,7-diphényl-1,10-phénanthroline) est extrait

par l'alcool amylique. La mesure est effectuée à 536 mμ. L'interférence du cuivre peut être éliminée par la thiourée. Le cobalt, le cadmium, le nickel, le manganèse et le zinc genent également mais les quantités de chacune de ces impuretés présentes dans les quatre métaux de haute pureté considérés sont si faibles que leur influence est négligeable. Des résultats reproductibles et précis peuvent être obtenus par un contrôle soigné du pH lors de la réduction et de l'extraction.

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PRECIPITATION FROM MIXED SOLVENTS—I

ALUMINIUM 8-HYDROXYQUINOLATE

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Summary—The precipitation of aluminium 8-hydroxyquinolate from a buffered acetone–water system has been effected by the volatilisation of the acetone. The use of this procedure results in a precipitate with physical characteristics superior to that obtained in the conventional manner and allows more efficient separation from interfering cations. Separations of 10-mg quantities of aluminium from an equal amount of cadmium as well as separations of 25-mg quantities of aluminium from at least 420 mg of magnesium and twice that amount of calcium can easily be accomplished. These results compare favourably with those obtained by hydrolysis of 8-acetoxyquinoline. A procedure is described for the quantitative determination of 2–10 mg of aluminium.

THAT controlled precipitation can lead to increased crystallinity, greater ease of handling and greatly improved separation from diverse ions has long been known. For these reasons the method of slow, direct addition of precipitants has given way, in many cases, to the methods of precipitation from homogeneous solution (PFHS).[1] In the case of the precipitation of aluminium with 8-hydroxyquinoline, such techniques as the *in situ* generation of the precipitant by hydrolysis of 8-acetoxyquinoline[2,3] and the gradual reduction of solubility by a slow pH change[4] have been employed. In general, the application of such techniques has been restricted by the disadvantages that (1) some of the reagents used for the *in situ* generation are relatively exotic and expensive, (2) the rate of the *in situ* generation is usually pH-dependent as is the solubility of the final precipitate, and there may not be a range where these two characteristics both have useful values, or (3) when the pH is changed over a large range to effect the precipitation of the desired ion it also effects the precipitation of undesired diverse ions.

The method herein described is based upon the observation that the presence of relatively large amounts of miscible organic solvents retards the precipitation of certain materials, particularly chelated metallic ions. Volatilisation of the organic component then leads to the precipitate eventually displaying only its aqueous solubility. In a preliminary report on this work[5] it was shown that the employment of this technique permitted the direct addition of the precipitant and that the subsequent volatilisation of the organic solvent from the buffered solution effected the gradual formation of the precipitate. In this manner the advantages of the more conventional forms of PFHS were retained while the disadvantages which have been mentioned were eliminated.

In this paper the general utility of precipitation from a mixed solvent system was investigated as it applied to the case of aluminium 8-hydroxyquinolate. This system was chosen since it permitted comparisons with the conventional means of precipitation and with the earlier method of precipitation by the controlled hydrolysis of the

8-acetoxyquinoline. Of particular interest are comparisons relating to the physical characteristics of the precipitate and comparisons of separations from diverse ions.

EXPERIMENTAL

Reagents

Aluminium: An aluminium solution was prepared from reagent-grade $AlK(SO_4)_2 . 12H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey). A value of 9·99 ± 0·03 mg of aluminium per 10 ml of solution was obtained by conventional precipitation of the aluminium with 8-hydroxyquinoline.[6]

Cadmium: A solution containing 1 mg of cadmium per ml was prepared by weighing C.P. Grade $Cd(NO_3)_2 . 4H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey).

Magnesium: A solution containing 300 mg of magnesium per 25 ml was prepared by weighing Reagent-grade $MgSO_4 . 7H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey).

Calcium: A solution containing 1000 mg of calcium per 25 ml was prepared by weighing Reagent grade $Ca(NO_3)_2 . 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

8-*Hydroxyquinoline:* A 5% solution in 2*N* acetic acid was prepared by adding 5·7 ml of glacial acetic acid to 2·50 g of the reagent-grade material (Fisher Scientific Company, Fair Lawn, New Jersey); after a gentle warming and agitation to dissolve the reagent, the solution was diluted to 50 ml with distilled water. In some cases it was desired to add this reagent without introducing further acid into the system. In these instances a solution was prepared by dissolving 10 g of 8-hydroxyquinoline in 90 ml of acetone.

All other chemicals were reagent-grade. It was noted that certain lots of reagent-grade acetone required distillation in order to remove an unidentified water-insoluble residue.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes was used for all pH measurements.

Procedure

Aluminium precipitation: Samples of 2 to 10 ml of the aluminium solution (containing approximately 2 to 10 mg of aluminium) were mixed with 50 ml of distilled water in a 250-ml beaker. To this solution were added 60 ml of acetone, 4 ml of the 5% 8-hydroxyquinoline solution, and 40 ml of 2*N* ammonium acetate. The resulting solution was placed on a water bath at 70–75° and left uncovered for 3 hr. Visible precipitation began in about 15 min. At the end of the evaporation period the samples were removed from the bath, allowed to cool, and filtered through medium-porosity sintered-glass crucibles. The precipitates were washed three times with distilled water and dried for 3 hr at 135–140°; the product was weighed as anhydrous $Al(C_9H_6ON)_3$. The pH of the filtrates was found to lie in the range 5·5–5·6.

Analysis of ten samples of 10 ml each by this method yielded an average value of 9·97 mg of aluminium with a standard deviation of 0·03 mg. In addition, samples of from 2 to 10 ml were analysed with the results summarised in Table I.

Cadmium co-precipitation: In order to study the effect of pH upon the co-precipitation of cadmium various amounts of sodium acetate–acetic acid or ammonium acetate–acetic acid solutions were added to solutions containing approximately 10 mg of aluminium and 10 mg of cadmium. The resulting solutions were either diluted to 175 ml and precipitated by the addition of 8-hydroxyquinoline according to the conventional method[6] or were treated with 60 ml of acetone, 3 ml of a 10% solution of 8-hydroxyquinoline in acetone and sufficient water to bring the total volume to 175 ml.

Table I.—Quantitative determination of aluminium from a water-acetone mixture

Aluminium added, *mg*	Aluminium precipitated, *mg*
1·99	1·98
3·99	4·02
4·99	4·98
5·98	6·00
6·98	7·00
7·98	8·00
9·97	10·04

Average error 0·03 mg

Samples treated by the second method were then heated for 3 hr at 70–75°, filtered, dried and weighed as before. In both methods of treatment sufficient precipitant was added to provide a 20% excess of 8-hydroxyquinoline over that required to precipitate completely both aluminium and cadmium and in both methods the values of the final pH of the filtrates were measured. Figure 1 presents the results obtained in this manner. Additional studies were then made in the pH range 4·7–4·9, using solutions which contained 10 ml of the aluminium solution and 10, 15 or 20 ml of the cadmium solution. To these mixtures were added 60 ml of acetone, 20 ml of 5*N* acetic acid, 40 ml of 3*M* sodium acetate and 5·5 ml of 5% 8-hydroxyquinoline in acetone. The resulting solutions were treated as before and the results are included in Table II.

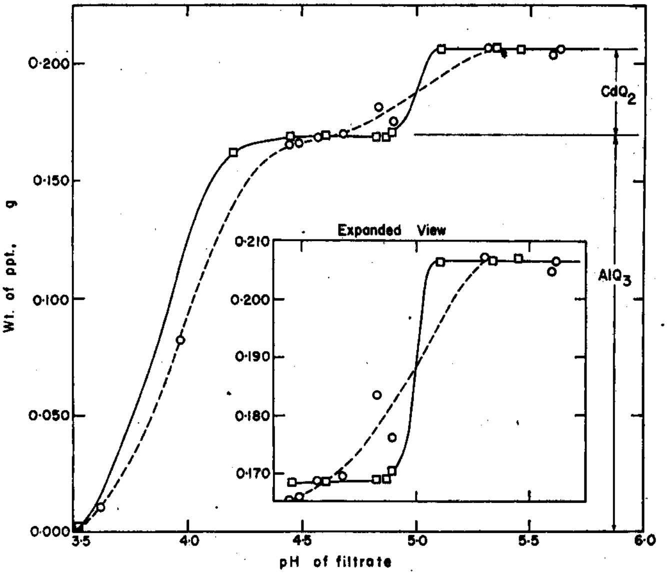

FIG. 1.—Weight of precipitate, g, versus pH of filtrate.
□ Evaporation method. ○ Direct addition method.

TABLE II.—EFFECT OF DIVERSE CATIONS ON ALUMINIUM DETERMINATION FROM A WATER–ACETONE SYSTEM

Aluminium present, *mg*	Diverse ion added	Weight of diverse ion, *mg*	Weight of diverse ion precipitated, *mg*
10	Cd	10	<0·1*
10	Cd	15	7·3*
10	Cd	20	13·0*
25	Mg	240	<0·1
25	Mg	300	<0·1
25	Mg	360	<0·1
25	Mg	420	<0·1
25	Ca	800	<0·1
25	Ca	1000	5·5
25	Ca	1200	1·4
25	Ca	1400	2·0

* Average of two samples. Filtrate pH of 4·8.

Magnesium co-precipitation: Twenty-five ml of the standardised aluminium solution were treated essentially as described in the aluminium procedure, except that 240–420 mg of magnesium were added. In addition, there was added a 20% excess of 8-hydroxyquinoline over that required to precipitate aluminium completely. Fifty ml of 2*M* ammonium acetate were used as a buffer. The values of pH for the filtrates were 5·2–5·3, and the results are included in Table II.

Calcium co-precipitation: Twenty-five ml of the standardised aluminium solution were treated essentially as described in the aluminium procedure, except that 800–1400 mg of calcium were added. In addition, there was added a 20% excess of 8-hydroxyquinoline over that required to precipitate aluminium completely. Fifty ml of 2*M* ammonium acetate were used as a buffer. The values of pH for the filtrates were 5·1–5·2, and the results are included in Table II.

RESULTS AND DISCUSSION

Precipitation of 2–10 mg of aluminium by this method gives quantitative results, and a highly crystalline precipitate is produced, which is much more easily filtered and washed than that obtained by conventional methods. In these respects the precipitates obtained by the evaporation method closely paralleled those obtained by the hydrolysis of 8-acetoxyquinoline. The use of 24·98-mg samples of aluminium also yields quantitative results, even in the presence of a large excess of magnesium or calcium, and despite the fact that rather high concentrations of the precipitating agent were present.

The results of the cadmium co-precipitation study are shown in Fig. 1. It should be noted that for this study two highly interfering ions were chosen to illustrate the effectiveness of the method of precipitation from mixed solvents in reducing co-precipitation. The curve obtained using the conventional method of direct addition shows no distinct break, and no pH at which separation is possible. Although the useful pH range is not wide, the proposed method of precipitation from mixed solvents should permit the separation of 10 mg of aluminium from 10 mg of cadmium at pH's between 4·7 and 4·9. The results in Table II show this to be the case when samples are analysed by the method described in the cadmium procedure. These separations are comparable with, if not better than, those obtained by PFHS utilising the hydrolysis of 8-acetoxyquinoline when 1·8 mg of cadmium was precipitated from a sample containing 10 mg of aluminium and 10 mg of cadmium.[2] Under the same conditions the direct addition method precipitated 2·7 mg of the cadmium.

The results of the magnesium and calcium co-precipitation studies are shown in Table II. These results are comparable to those recently obtained by hydrolysis of 8-acetoxyquinoline.[3]

Upon the addition of the acetone to the water-aluminium-calcium mixture the solution became quite cloudy, probably because of the decreased solubility of the inorganic salts in the resultant water-acetone mixture. The subsequent addition of 8-hydroxyquinoline and ammonium acetate solutions did not noticeably affect this cloudiness and only after prolonged heating at the evaporation temperature (70–75°) did the solutions become clear. Even under these rather adverse conditions the separation of aluminium from calcium was highly effective.

The behaviour of the water-aluminium-magnesium mixture upon the addition of acetone was similar to that of the system containing calcium, with the exception that a very brief heating at 60–65° was sufficient to remove all turbidity.

CONCLUSIONS

The results presented clearly illustrate the utility of the method of precipitation from mixed solvents in the analysis of aluminium. This method not only yields precipitates of superior physical characteristics to those obtained by the conventional method, but also permits the selection of any desired pH without concern about the possibility of altering the rate of the precipitation. In addition it has been possible to achieve these improvements while using only equipment and reagents commonly available in most laboratories.

Additional work with other cations, precipitants, and solvent systems is under way, and will be the subject of future papers.

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Zusammenfassung—Die Fällung von Al-Oxinat aus gepufferter Azeton-Wasserlösung durch Verdampfen des Azetons wird beschrieben. Ein Niederschlag mit stark verbesserten physikalischen Eigenschaften wird erhalten. Trennung von 10 mg Al von einer gleichen Menge Cd und Trennung von 25 mg Al von mindestens 420 mg und zweimal soviel Ca kann leicht bewerkstelligt werden. Die Ergebnisse lassen sich sehr wohl mit denen vergleichen, die nach der Methode der Hydrolyse von 8-Azetoxychinolin erhalten werden. Eine Arbeitvorschrift zu Bestimmung von 2–10 mg Al wird mitgeteilt.

Résumé—La précipitation de l'oxinate d'aluminium à partir d'un mélange eau–acétone au milieu tamponné a été effectuée par volatilisation de l'acétone. Le procédé permet d'obtenir un précipité dont les caractéristiques physiques sont supérieures à celles obtenues par la méthode traditionnelle et conduit à une séparation plus efficace. La séparation de 10 mg d'aluminium d'une quantité égale de cadmium, ou de 25 mg d'aluminium d'au moins 420 mg de magnésium et deux fois cette quantité de calcium peut être effectuée aisément. Ces résultats se comparent favorablement à ceux obtenus par l'hydrolyse de la 8-acétoxyquinoléine. Une méthode est décrite pour le dosage quantitatif de 2 à 10 mg d'aluminium.

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APPLICATION OF THE RADIOACTIVE IONISATION DETECTOR TO THE DETERMINATION OF PERMANENT GASES BY GAS CHROMATOGRAPHY AND SOME USES IN STUDIES OF CHEMICAL KINETICS

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Summary—It has been found possible to determine volumes of hydrogen, methane, and carbon dioxide within the range 0·1–1·0 ml at S.T.P. and carbon monoxide and nitrogen within the range 0·1–0·4 ml at S.T.P. with an accuracy of around 5% in a gas chromatograph using the radioactive ionisation detector, provided that the detector temperature and the rate of carrier gas flow through the column are maintained between stated limits. Results of experiments on the sensitivity of the instrument to oxygen, sulphur dioxide, ethane, propane and n-pentane are also reported. Particular attention has been directed towards selecting the most suitable parameter of the response peaks for use in quantitative analysis.

Some particular applications of the argon chromatograph in studies of chemical kinetics involving permanent gases are described, and a method for the removal of corrosive gases from mixtures to be analysed is discussed.

INTRODUCTION

THE radioactive ionisation detector (argon detector) for use in gas chromatography was originally developed for the determination of small amounts of those vapours which have an ionisation potential less than that of argon. Lovelock, who developed the detector,[1] has listed[2] some of the substances to which it does not respond normally, and these include hydrogen, nitrogen, oxygen, carbon dioxide and carbon monoxide. Lovelock also states[2] that the response of the detector to methane and to ethane is very much less than to the higher hydrocarbons. The simplicity and stability of the detector have made it desirable that the gases which it does not normally detect should be brought within its range, and a number of suggestions to this end have been made. Willis[3] has found that a controlled concentration of ethylene in the argon stream increases the sensitivity of the detector to the permanent gases; Berry[4,5] and Wiseman[6] have discussed the use of helium in ionisation detectors.

The present article discusses the determination of permanent gases in a standard argon detector, while avoiding the necessity for adding traces of ethylene to the gas stream or the added expense of using helium as the carrier gas. In addition to indicating the degree of accuracy which might be expected outside the range of substances for which the argon ionisation detector was designed, the present account is also concerned with some particular applications. A preliminary report on the use of the argon detector for the analysis of hydrogen-methane mixtures has already been given.[7] It is emphasised, however, that comparatively large volumes of permanent gases (0·1–1·0 ml at S.T.P.) must be used to obtain satisfactory responses. Since the disturbance peak on the introduction of each sample is very small, the instrument has found particular application in kinetic studies in which it was necessary to analyse mixtures containing 2–4 components at intervals of 4–8 min.

EXPERIMENTAL

A diagrammatic sketch of the apparatus used to control argon flow and inject the sample is shown in Fig. 1. A sample of gas was connected through A to a McLeod gauge so that a known pressure of gas in the known volume B could be displaced into the previously evacuated sampling volume.

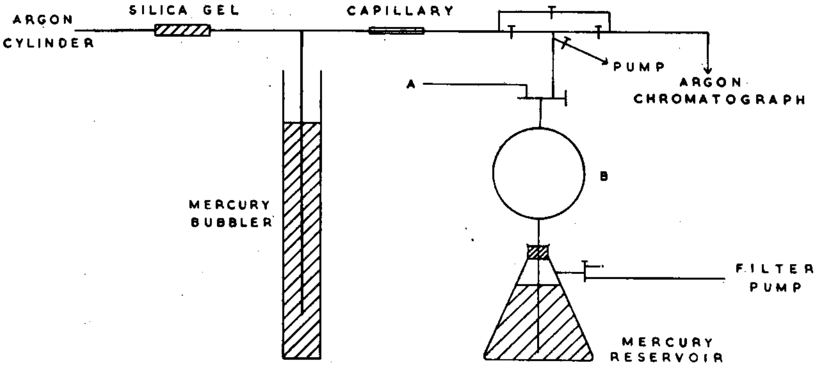

FIG. 1.—Apparatus used to inject samples into the argon gas stream.

Care was taken when making the apparatus that the glass around the tap (2 mm) in the sampling volume was shaped in such a way that gas bubbles were not trapped by the mercury, thus ensuring that the whole of the measured dose was swept from the sampling volume when the argon stream was deflected through it. The author used the apparatus to follow the kinetics of a gas-solid reaction occurring in a small reaction vessel attached at A, volumes being arranged so that 85–90% of the gas in the reaction vessel was withdrawn by a single stroke of the Toepler pump.

A standard Pye Argon Chromatograph was used throughout the work; the source contained radium-D but newer models now contain strontium-90. The rate of flow of cylinder argon (supplied by British Oxygen Co. Ltd.) was determined by the head of mercury in the bubbler and the capillary tube shown in Fig. 1. A single chromatographic column of charcoal (100–120 mesh B.S.S. standard screen) 80 cm long was used throughout almost all the work.

For quantitative calibrations of the chromatograph the following gases were used: cylinder hydrogen, purified by diffusion through heated palladium; cylinder nitrogen (oxygen free) passed through a liquid nitrogen trap; cylinder methane, carbon monoxide, carbon dioxide, ammonia and liquified sulphur dioxide, each condensed in liquid nitrogen, outgassed, the first-boiling fraction evacuated, and a sample withdrawn for study. All gases were shown to be free from appreciable amounts of impurities, by gas chromatographic analysis, before being studied in detail.

RESULTS

Unless otherwise stated, the response of the chromatograph refers to that found at 2000 v with a 10-mv bobbin in the recorder and the detector held at 20 ± 2° with a flow of 30 ± 2 ml/min of argon through the 80-cm charcoal column, and "×10" scale of sensitivity of the detector. Deflections of the recorder in the same direction as that found for hydrocarbons (*e.g.*, benzene) will be termed "positive" and those in the opposite direction "negative".

Hydrogen

Sharp negative peaks were obtained (sketch given in ref. 7) and the most satisfactory parameter for quantitative studies was the distance from the maximum of the very small initial positive "kick" to the maximum of the large negative peak which immediately followed it, *i.e.*, the height of the steep front of the peak. Fig. 2 shows a composite plot of peak height against volume of hydrogen injected from 9 separate sets of calibrations made at intervals over a period of 12 months. The scatter of results on Fig. 2 is greater than that observed on any set of calibrations made at any one time, because response tended to vary slightly over an extended period of time, and results from calibrations under slightly different sets of operating conditions have been included on Fig. 2. The following factors have been found to influence the peak height:

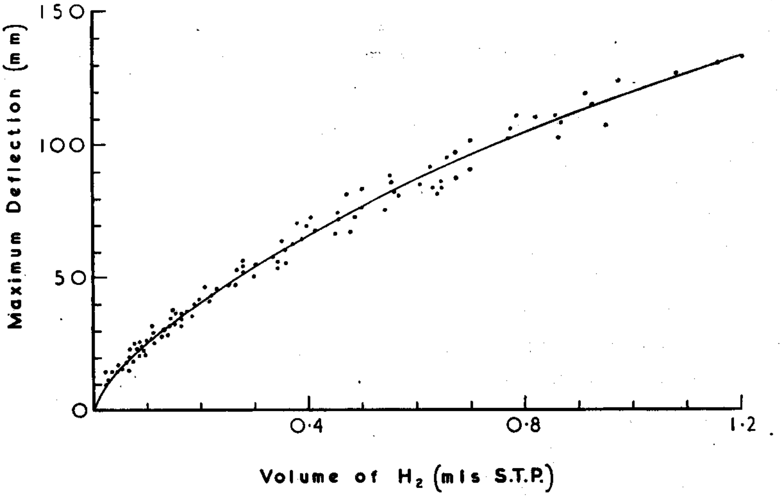

FIG. 2.—Calibration plot of maximum peak height of detector deflection against volume of hydrogen injected.

1. *The presence of air:* After the column was allowed to stand in air for some weeks, the sensitivity of the detector to hydrogen, under the same operating conditions used to determine the results on Fig. 2, showed a reduction of deflection from 20 mm at 0·1 ml to 30 mm at 1·0 ml at S.T.P. On another occasion the calibrations found immediately after regreasing the taps of the apparatus gave deflections less than those expected from Fig. 2. The degree of reproducibility of calibrations was considerably increased through baking out the column to 200° in an argon stream and cooling overnight in argon. This was repeated every night during quantitative work.

2. *Temperature:* Calibration curves at 24° and 29°, under otherwise identical conditions, were similar in shape, but the maximum deflections at 24° were some 5–7 mm less than those at the higher temperature for samples 0·1–1·0 ml at S.T.P.

3. *Argon flow rate:* A calibration plot at a flow of 17 ml/min of argon gave deflections which were 10 mm less than those found at 30 ml/min of argon within the range 0·1–1·0 ml at S.T.P.

4. *Voltage*: Deflections for detection at 1750 v were about half those at 2000 v.

Provided that calibrations are repeated at regular intervals, that air is excluded from the column, and that the column is regularly baked to remove impurities, that temperature is maintained constant (say 20 ± 2°) and that flow rate is maintained constant (say 30 ± 2 ml/min), the argon chromatograph is capable of giving a quantitative measure of hydrogen, accurate to ±5%.

Methane

Methane gave a positive deflection, very much smaller than that found for an equal volume of a higher hydrocarbon. The most satisfactory parameter of the response peak to use in quantitative analysis differed with the concentration range. At low concentrations, 0·01–0·10 ml at S.T.P., maximum peak height was found to be very nearly directly proportional to the volume admitted; there was a *very slight* curve in the same sense as in Fig. 2. This peak height was slightly affected by argon flow rate, but both the curvature of the calibration graph and the sensitivity increased with temperature (the peak height for 0·05 ml at S.T.P. of methane was 34 mm at 20° and 52 mm at 38°).

At concentrations $>0{\cdot}1$ ml at S.T.P. the peak first broadened, then showed pronounced inversion. Here the most satisfactory parameter for use in quantitative work was peak "area", found by adding (*i*) the small initial negative kick (*a*), (*ii*) the maximum positive deflection (*b*), and (*iii*) the distance of the maximum inverted distance below height *b* (*c*), and multiplying by the peak width (*w*) measured at $\frac{1}{2}(a + b + c)$ (*i.e.*, assuming that the peak has been formed by a "folding over" process). Such "areas" were directly proportional to the volume of methane injected but were very sensitive to:

1. *Temperature:* The height at which peak inversion occurred (*b* above) was very sensitive to temperature. A calibration plot of "areas", with column and detector at 37°, was almost parallel to a similar plot at 20°, but was displaced to the equivalent of 0·15 ml at S.T.P., which, in estimating volumes in the range 0·20–1·0 ml at S.T.P., represents a very large error.

2. *Argon flow rate:* Reduction of argon flow rate from 30 to 18 ml/min, under otherwise identical conditions, resulted in such a large increase in *w* that the apparent peak "area" for a given dose was almost doubled.

3. *Detector voltage:* Reduction of detector voltage 2000 to 1750 v caused the value of *b* to be halved and the apparent peak "areas" were almost halved.

From a series of calibrations made at intervals over 12 months it was found that reliable, reproducible calibrations could be obtained, provided that detector temperature and argon flow rate were both standardised. Calibrations for methane were found to be slightly more sensitive to these variables than the corresponding results for hydrogen, but, with care, it was found possible to achieve an estimated accuracy of ±5%. In cracking studies, where methane was virtually the only product, volumes estimated by the above technique agreed, to within about 7%, with those calculated from volumetric measurement of the quantity of hydrocarbon cracked.

Preliminary work using cylinder helium in place of argon as the carrier gas showed that the response to methane was similar in magnitude to that found in an argon stream.

Carbon dioxide

Carbon dioxide was determined after elution from the column thermostatted at 100° by the jacket in the instrument as supplied. A negative deflection was found; typical response peaks are sketched in Fig. 3. Each peak could be divided into three parts: (*i*) an initial "kick", (*ii*) a peak with a well defined maximum which depended on the volume of carbon dioxide injected, and (*iii*) a second, broader maximum the height of which did not vary appreciably with the volume of gas injected. Two parameters of response peaks were found suitable for determinations:

(*a*) the height of peak (*ii*), measured using the top of peak (*iii*) as the zero peak height; *x* in Fig. 3 where *x* is positive for large volumes of carbon dioxide (A) and negative for smaller volumes (B). A linear relation was found between x and the volume of carbon dioxide injected in the range 0·15–1·0 ml at S.T.P. It was not, however, found practicable to measure volumes of carbon dioxide less than 0·15 ml at S.T.P. by this method.

(*b*) peak "area" measured by maximum peak height above the base line, y, multiplied by peak width at $y/2$. The latter calibration was more satisfactory in the determination of volumes greater than 1·0 ml at S.T.P., and a linear relation was found between "area" and volume of gas injected.

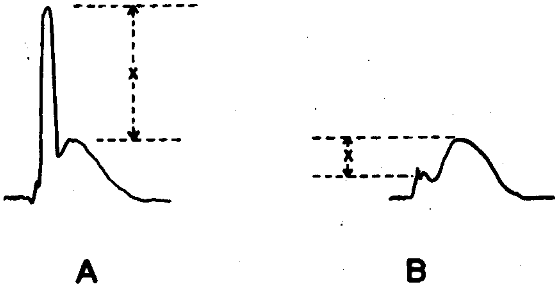

FIG. 3.—Detector response shape for carbon dioxide. Dose A was larger than dose B.

The carbon dioxide response peak was sensitive to the presence of impurities; for example peak shape was altered when sulphur dioxide was being eluted from the column simultaneously. Provided that conditions are controlled, and that care is taken to exclude impurities such as sulphur dioxide, determinations could be made with an estimated accuracy of ±5%.

Carbon monoxide

Carbon monoxide, detected on elution from the column at 100°, gave a sharp negative peak, similar in appearance to that of hydrogen; but the calibration plot of peak height against volume injected was very much more curved than in Fig. 2. At volumes greater than 0·4 ml at S.T.P. the plot became so flat that this parameter could no longer be regarded as satisfactory for use in quantitative work. Calibrations made with a 5-month interval, in the range 0–0·4 ml at S.T.P., using the column at 100°, and a flow of 25 ± 1 ml/min of argon, were coincident. It is concluded from these results that the instrument can be used for the determination of carbon monoxide with about the same degree of accuracy as that of hydrogen, provided that the same accuracy of control of operating conditions is observed.

A study of the effect of impurities on the deflection given by carbon monoxide showed (*i*) that simultaneous elution of small traces of ammonia from the column increased the apparent deflection. In one example studied, the calibration plot was apparently increased by about 40 mm throughout most of its length by a very small amount of ammonia which was simultaneously eluted; and (*ii*) that a carbon monoxide peak, eluted while a sulphur dioxide peak was being simultaneously eluted, had a maximum peak height the same distance above the extrapolated zero deflection line as would have been expected in the absence of the sulphur dioxide peak. The sulphur dioxide trace merely rendered invisible the lower portion of the peak. Small amounts of carbon monoxide could not be determined while sulphur dioxide was being eluted.

Nitrogen

A single calibration for nitrogen showed that it gave a negative peak identical in shape with that given by cabon monoxide; and the calibration plot for nitrogen detected at 20° was almost coincident with that of carbon monoxide at 23° except that the deflection for the former was marginally lower than that of the latter in the flattened region (more than 0·4 ml at S.T.P.).

Sulphur dioxide

When eluted from the charcoal column at 100°, sulphur dioxide gave a large negative peak with a long tail. A plot of maximum peak height against volume of gas injected showed an initial steep rise (0–0·2 ml at S.T.P.) followed by a decreasing rate of increase of peak height with increase in volume injected (0·2–1·0 ml at S.T.P.). This calibration was only acceptable for a dose which was eluted *after* the recorder had returned to its original zero reading; any overlap of peaks vitiated the calibrations.

Ethane, propane and n-pentane

All three compounds showed a positive response, and plots of peak "area" (height × width at half height) against volume of gas injected were, within experimental error, linear over the range 0–0·003 ml at S.T.P. The instrument is very much more sensitive to these compounds than to the substances discussed earlier, and the calibration plots showed scatter arising from difficulties in handling and measuring small doses of gas. Results, expressed as the mean "area" of response peaks (mm^2) for samples of 0·001 ml at S.T.P. of gas for calibrations over a range of detector voltages are summarised in Fig. 4.

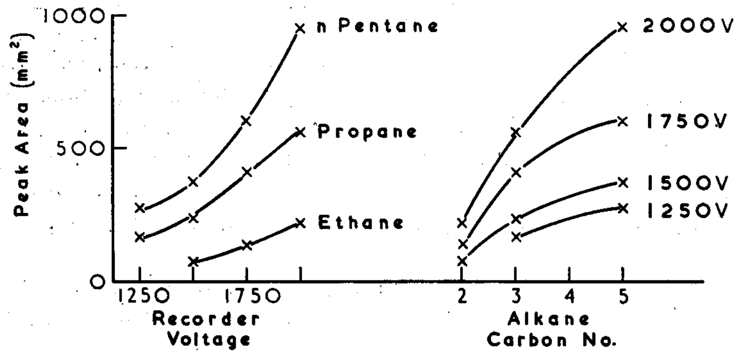

FIG. 4.—Plot of peak "areas" (see text for definition) against detector voltage for 0·001 ml at S.T.P. for ethane, for propane and for n-pentane.

Oxygen

Attempts to use the instrument for the determination of oxygen were unsuccessful. A large negative peak was observed, but conditions for quantitative work were not established.

Ammonia

Large positive peaks were observed which had a long tail. As noted earlier (see *Carbon monoxide*), traces of ammonia can make analyses of permanent gases unreliable.

Hydrogen sulphide

Large positive peaks arising from hydrogen sulphide were observed during analysis of hydrogen sulphide-hydrocarbon mixtures when a dinonylphthalate supported on a "Celite" column was used as the stationary phase. Small traces of hydrogen sulphide eluted simultaneously with hydrocarbons apparently increased the hydrocarbon response peak height. Quantitative investigations of this effect were not made but it was clear that sensitivity to hydrocarbons was increased by the presence of traces of hydrogen sulphide.

DISCUSSION

The ionisation potentials of the substance discussed above, listed in volts in decreasing order of magnitude, are:[8]

Hydrogen	15·6	Nitrogen	15·51
Methane	14·5	Carbon dioxide	14·4
Carbon monoxide	14·1	Sulphur dioxide	13·1
Ethane	12·8	Oxygen	12·5
Metastable argon[2]	11·7		
Ammonia	11·2	Hydrogen sulphide	10·42

Any quantitative theory for the detector response characteristics cannot be directly based on the values of ionisation potential alone, since both the shape of the peak and the calibration plots for hydrogen, nitrogen and carbon monoxide were similar, but differed from those of methane and carbon dioxide, which have ionisation potentials between those of nitrogen and carbon monoxide; and, furthermore, the characteristics of methane and carbon dioxide did not resemble each other. The quantitative response of the detector may be expected to be dependent on (*i*) the ionisation potential of the compound and the average life-time of the excited species, (*ii*) the concentrations and nature of all impurities in the detector at the same time (specific examples have been noted above when the effect of various impurities on individual gases were discussed), and (*iii*) the variation, with time, of concentration of material as it is eluted from the column (this accounts for the marked "tailing" of the sulphur dioxide peak). The complexity of these factors make quantitative calculations difficult, but it may be noted that most of those substances which have ionisation potentials greater than 11·7 v produce negative peaks, showing that they cause a fall in the standing current of the detector.

Negative peaks were found to give adequate accuracy for use in quantitative analysis provided that the concentration of impurities (*e.g.*, air) was carefully controlled, the temperature of the column and detector were maintained constant (say $\pm 2°$) and the flow rate was constant (say 30 ± 2 ml/min). Those compounds for which peak width was used as a response parameter were very sensitive to flow rate. All peaks were sensitive to detector temperature; McWilliam,[9] quoting results of Lovelock, James and Piper,[10] has noted that the absolute sensitivity of the argon detector is very dependent on temperature. The results of the present work show that the determination of hydrogen, methane, nitrogen, carbon monoxide and carbon dioxide may be made with an estimated accuracy of about 5% provided that the conditions stated are observed. To produce an increase in accuracy, more accurate control of the detector temperature would be necessary.

The sensitivity of the instrument to the ethane-pentane series is seen (Fig. 4) to increase markedly with detector voltage (also noted for hydrogen and methane) and with chain length; the latter effect is readily explained by the ionisation potentials of the compounds. Although the ionisation potentials of both methane and ethane are greater than that of argon, a positive response is found, but this is very much less than for the higher hydrocarbons, in agreement with the data of Lovelock.[2]

Since the responses obtained in the present study may result from or may be sensitive to the presence of impurities in the argon supply it is necessary to repeat calibrations for each substance with each new argon cylinder used. In the author's experience, however, calibration curves for the determination of hydrogen and methane were constant, within experimental error, for several different argon cylinders.

Application of the argon chromatograph to kinetic studies

The almost complete absence of disturbance peaks when a sample is injected, and the rapid re-establishment of equilibrium conditions in the detector after interruption of the argon flow, made the apparatus useful for studying the kinetics of reactions involving permanent gases, where it is desirable to make frequent analyses of the products (*e.g.*, ref. 11). Using the apparatus under conditions described above, with the charcoal column held at 22°, it was possible to analyse one sample of a hydrogen-methane mixture every 6 min. The only other product in the particular reaction studied was ethane, which had a retention time of some 2·5 hr. The effect of this on subsequent analyses could be eliminated by removing the column from its jacket and heating (while the flow of argon was maintained) with a bunsen flame so that a hot zone moved slowly from the top to bottom of the column; the column was cooled in the argon flow and reconnected to the detector, and after some 10 min hydrogen-methane analyses were resumed. The same column, held at 100°, could be used to follow kinetics of the ethane formation reaction if samples were withdrawn at accurately controlled intervals (see ref. 11).

A similar technique was used to study the dissociation of ammonia on a solid catalyst, the column being removed and heated just before the expected time of elution of the ammonia peak. Repeated heating of the column was necessary here, however, to ensure complete removal of ammonia, traces of which vitiated the detector response calibrations for hydrogen and nitrogen.

Retention times on the charcoal column were such that quantitative analyses of the following product mixtures could be made at approximately 10-min intervals by selection of appropriate length of column, operating temperature and argon flow rate: hydrogen-carbon monoxide-carbon dioxide-methane; hydrogen-nitrogen-methane; methane-ethane. Calibrations must be repeated under each new set of operating conditions.

Corrosive gases

The potential radioactive hazard which could result from damage to the detector by corrosive gases in mixtures to be analysed makes it necessary to remove any corrosive material before it enters the radioactive chamber. In a particular study where the products of the reaction to be studied consisted of ethane and higher hydrocarbons in addition to appreciable quantities of hydrogen chloride, the author found that the corrosive products could be removed by passing the gas to be analysed through a bed (20 × 2 cm) of sodium hydroxide pellets after the injection of the gas into the argon stream, but before it passed through the column. This procedure invariably increased the width of the peak. No peaks attributed to hydrogen chloride were found on the chromatograph trace and it was concluded that this gas was quantitatively removed by the alkali. Hydrogen sulphide could be removed similarly, but it was necessary to replace the alkali with fresh material frequently, since traces of hydrogensulphide were detected in the effluent gases some 30–40 min after the sample was injected when analyses were made using a dinonylphthalate column (120 cm long). Elution of traces of hydrogen sulphide was shown by a slight positive rise in the base line, accompanied by a marked rise in sensitivity of the apparatus for the detection of hydrocarbon. It was found that the sodium hydroxide could be changed quickly with little influence on the identification of substances having comparatively large retention distances but quantitative studies would undoubtedly be subject to very considerable errors.

A single detector containing radium-D was used throughout all the work reported in the present paper. It gave excellent service for some two years, during which it was operated at 2000 V and was frequently heated for short periods to 200°. Subsequently some 100–200 doses (of around 0·8 ml at S.T.P.) of each of the corrosive gases hydrogen sulphide, water vapour and sulphur dioxide were passed through it at 20–100°. This treatment is more severe than the apparatus may be reasonably expected to withstand, but no appreciable radiation, above the background, was found on routine monitoring of the detector, though internal examination finally showed that corrosion had started, and the makers recommended that the detector should be replaced. On fitting a new 20-millicurie ^{90}Sr source to the instrument, there was an appreciable rise in the radiation detected outside the case, and additional shielding was fitted around the outside of the detector case.

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Zusammenfassung—Es wurde gefunden, dass die chromatographische Bestimmung von Wasserstoff, Methan, Kohlenmonoxyd, Kohlendioxyd und Stickstoff im Bereich 0·1–1·0 ml (Normalbedingungen) mit einer Genauigkeit von etwa 5% möglich ist. Ein radioaktiver Ionisationsdetector wurde verwendet und die Strömungsgeschwindigkeit des Trägergases wurde innerhalb bestimmter Grenzen konstant gehalten. Ergebnisse über die Untersuchung der Empfindlichkeit des Instrumentes gegenüber Sauerstoff, Schwefeldioxyd, Äthan, Propan und n-Pentan werden ebenfalls mitgeteilt. Besonderes Augenmaek wurde darauf gerichtet die bestgeeigneten Parameter fur das Kurvenmaximum bei quantitaiven Bestimmungen festzulegen. Einige besondere Anwendungsmöglichkeiten des Argon-Chromatographen bei kinetischen Studien mit permanenten Gasen, sowie eine Methodezur Entfernung korrodierender Gase von Analysengemischen werden behandelt.

Résumé—L'auteur montre qu'il est possible de mesurer quantitativement des volumes d'hydrogène, de méthane, d'oxyde de carbone, de gaz carbonique et d'azote compris entre 0,1 et 1,0 ml dans les conditions normales de température et de pression, avec une précision de 5 pour 100 en utilisant un chromatographe en phase gazeuse muni d'un détecteur à ionisation dans la mesure où la température du détecteur et la vitesse du gaz porteur à travers la colonne sont maintenus dans des limites déterminées. Les résultats d'essais de détermination de la sensibilité de l'instrument pour l'oxygène, le gaz sulfureux, l'éthane, le propane et le n-pentane sont également donnés. L'auteur s'est particulièrement attaché à déterminer le paramètre le plus commode permettant d'agir sur les pics en vue de la mise au point d'analyses quantitatives. Quelques applications particulières du chromatographe à l'argon dans les études de cinétique chimique sont décrites et une méthode permettant l'élimination de gaz corrosifs dans les mélanges à analyser est discutée.

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SHORT COMMUNICATIONS

Contributions to the basic problems of complexometry—X:* Determination of nickel and cobalt in the presence of iron, copper and some other metals

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THE problem of successive determination of nickel and cobalt in the same solution has not yet been satisfactorily solved, especially in the presence of iron, copper and other elements, which need to be considered in the analysis of alloys. A few years ago[1] a procedure utilising the high stability of the cobalt^{III}-EDTA complex (pK 40·7) was proposed.[2] The complex of tervalent cobalt with EDTA is formed very easily in an alkaline medium by hydrogen peroxide oxidation and Schwarzenbach[3] ascribes to it the composition $Co(OH)Y.^{2-}$ The original determination of nickel and cobalt was based on the different reactivity of $Co(OH)Y^{2-}$ and NiY^{2-} complexes with potassium cyanide. The former does not react, while the latter quantitatively forms a nickel-cyanide complex. The sum of nickel and cobalt can be determined indirectly by adding an excess of EDTA in an ammoniacal medium, then titrating the excess of EDTA with magnesium chloride using Eriochrome Black T as indicator. After the oxidation of cobalt with hydrogen peroxide and screening nickel with potassium cyanide, a second titration is carried out with magnesium chloride to determine the EDTA liberated from the NiY^{2-} complex.

The complex $Co(OH)Y^{2-}$ is coloured intensely blue so that this procedure can be used only for amounts of cobalt not exceeding 10 mg in 100–150 ml of solution to be titrated. Iron must not be present and it cannot be screened with triethanolamine (TEA) because of the reaction of the Fe-TEA complex with the indicator. Other elements also interfere.

In an acidic medium there also exists a ruby red complex, $Co(H_2O)Y^-$ or CoY^-. Indirect determination of cobalt is then possible even in a relatively acidic medium where many elements do not interfere. Kinnunen and Wennestrand[4] use a back-titration of added excess EDTA with thorium nitrate and Xylenol Orange as indicator. Flaschka and Ganchoff[5] titrate the added excess EDTA with bismuth and follow the titration photometrically using Pyrocatechol Violet as indicator. Neither of these methods makes possible the determination of cobalt in the presence of iron. Their practical application is therefore very limited.

In solving the given problem a return was made to the original method of determination of nickel and cobalt in an alkaline medium, elaborated in 1953, when only Eriochrome Black T was known as a complexometric indicator. Today there are other very suitable indicators for a strongly alkaline medium *e.g.* Thymolftalexon or Fluorexon (Calcein). In a solution of potassium hydroxide (pH 12) traces of calcium give with Fluorexon a very intense green fluorescence which is easily discernible even in the presence of the highly coloured cobalt complex CoY^-. The strongly alkaline medium also permits the masking of iron as a colourless TEA complex. Further, it has been found that thioglycollic acid (TGA), which does not react with the nickel- and cobalt-EDTA complexes, masks other elements which may be present, *e.g.* copper, lead, bismuth, zinc, *etc.* Under these conditions the new method becomes highly selective for cobalt and nickel.

EXPERIMENTAL

Reagents

0·05*M* EDTA solution and 0·05*M* solutions of cobalt and nickel nitrates, copper sulphate, iron^{III} chloride and lead nitrate were prepared from reagent grade chemicals and their strengths controlled by complexometric titrations.

Fluorexon (CHEMAPOL, Prague, Czechoslovakia) diluted with potassium nitrate (1:100), 0·5% Xylenol Orange (Chemapol), 1*M* potassium hydroxide, 20% triethanolamine, 15% thioglycollic acid (Merck, Darmstadt, Germany), 20% thiourea, solid potassium cyanide and urotropine.

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* Part IX: *Talanta*, 1962, **9**, 23.

Determination of the sum of nickel and cobalt

Although the solutions of nickel- and cobalt-EDTA complexes are coloured, the indirect determination of both elements is possible in three different ways:

(a) By back-titration with lead nitrate at pH 5–5·5 to a Xylenol Orange end-point.

(b) By back-titration with a calcium salt at pH 10–11 to a Thymolftalexon end-point.

(c) By back-titration with a calcium salt at pH 12–13 to a Fluorexon end-point.

All of these colour changes are very sharp at the end-point, even at high concentrations of both elements. With Xylenol Orange it is possible to determine 50 mg of cobalt or nickel in 100 ml of titrated solution and with the other two methods the maximal permitted concentration of both elements is about the same. The first method has the advantage that the alkaline earth elements do not interfere if masked by fluoride. In the second method iron and aluminium do not interfere if screened with TEA. A combination of methods (a) and (c) is more suitable for practical application if one expects the presence of other elements.

Procedure. (a) To a slightly acid solution add a small excess of 0·05*M* EDTA and a few drops of Xylenol Orange. Add solid urotropine to adjust the pH to 5–5·5, then titrate with 0·05*M* lead nitrate solution to an intense red-violet coloration.

Procedure. (c) To a slightly acid solution add a small excess of EDTA and 1*M* KoH to its final concentration 0·1*M* (after suitable dilution). After addition of Fluorexon titrate the solution with calcium salt to the appearance of a vivid yellow-green fluorescence. Titration in diffuse day light is recommended.

Determination of nickel in presence of cobalt

As has been already stated, the cobalt^{III}-EDTA complex is inactive against potassium cyanide, while the nickel-EDTA complex reacts quantitatively. The determination of nickel can be carried out in one of two ways.

After determination of the sum of nickel and cobalt according to *Procedure* (*c*), add 1–5 ml of 3% hydrogen peroxide, mix thoroughly and set aside for 5 min. The solution becomes coloured blue, then add 0·2–0·5 g of potassium cyanide and after 5–10 min titrate the liberated EDTA with a calcium salt to a green fluorescence, which is very clearly visible at the edge of the surface in strongly coloured solutions. Alternatively, oxidise cobalt first, as described, titrate the excess of EDTA with calcium, and after addition of potassium cyanide titrate once more. In this simple way we determine both nickel and cobalt.

Determination of nickel and cobalt in the presence of iron

In a strongly alkaline medium tervalent iron forms a colourless complex with TEA even in the presence of EDTA. The addition of EDTA on the contrary is useful here, because these solutions are free of colloidal iron hydroxide.[7]

Procedure. To the acid solution of iron, cobalt and nickel, add a sufficient amount of EDTA, 20 ml of 20% triethanolamine solution, and 1*M* potassium hydroxide to a final concentration of 0·1*M*. The sum of nickel and cobalt is determined by back-titration with a calcium salt. This titration can be carried out with hydrogen peroxide before or after oxidation. For screening nickel, potassium cyanide must be added after the addition of peroxide.

Determination of nickel and cobalt in the presence of copper

The determination of the sum of nickel and cobalt, then of copper presents no difficulties as recently described.[6] It is based on the sum of all three elements by back-titration with calcium and on the masking of copper with TGA in the same solution. If we wish to determine cobalt besides nickel, we must oxidise cobalt with hydrogen peroxide before the addition of TGA. In its presence the oxidation of cobalt is not quantitative, but once the complex $Co(OH)Y^{2-}$ is formed it is not reduced with TGA at all or only very slowly.

Procedure. To the slightly acid solution add an excess of EDTA, potassium hydroxide and hydrogen peroxide as described above. After oxidation (5 min) add 5–10 ml of a neutralised solution of 15% thioglycollic acid and titrate with calcium salt using Fluorexon as indicator. After addition of potassium cyanide, determine nickel.

Determination of nickel and cobalt in the presence of iron and copper

The procedure described below is actually a combination of the two foregoing procedures. It has to be emphasised that copper forms very stable complexes with EDTA as well as with TEA, so that its determination in an alkaline medium is impossible. It is, however, possible to mask copper with TGA and it is known that TGA forms intense red complexes with iron in an alkaline medium. The presence of TEA and potassium hydroxide prevents the latter reaction.

Procedure. To the solution containing all four elements add an excess of EDTA, 20 ml of 20% triethanolamine, enough $1M$ potassium hydroxide, 1–5 ml of 3% hydrogen peroxide and after 5 min 5–10 ml of neutralised 15% thioglycollic acid. By back-titration with calcium salt the sum of cobalt and nickel is obtained. After addition of 0·2–0·5 g of potassium cyanide, continue the titration with calcium salt (determination of nickel).

The above method gives good results. All colour changes at the end-point are sharp, but are unfavourably influenced by high concentrations of ammonium and sodium salts.[6] The complex $Co(OH)Y^{2-}$ is very stable, but tends to react with TGA and with potassium cyanide (reduction and complex formation). This unfavourable influence is observed only 30 min after the end of the titration and is therefore without practical value.

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Summary—A complexometric determination of nickel and cobalt in the same solution has been devised. It is based on the determination of the sum of nickel and cobalt by back-titration of added excess EDTA in a strongly alkaline medium with calcium chloride using Fluorexon (Calcein) as indicator. After oxidation of cobalt with hydrogen peroxide to form the cobalt^{III}- EDTA complex and screening of nickel by potassium cyanide, the liberated EDTA corresponding to the amount of nickel present is titrated with further calcium chloride. High concentrations of iron and aluminium are screened with triethanolamine. Copper and other heavy metals are screened with thioglycollic acid.

Zusammenfassung—Die komplexometrische Bestimmung von Kobalt und Nickel in derselbeu Lösung wird beschrieben. Zuerst wird die Summe Co + Ni in alkalischem Medium ermittelt, indem der Ueberschuss von ÄDTE mit Calciumchloridlösung gegen Fluorexon-(Calcein)-Indicator zurücktitriert wird. Nach Oxydation des Kobalts zum dreiwertigen Komplex mittels Wasserstoffperoxyd wird Nickel durch Zusatz von Kaliumcyanid maskiert und die freiwerdende Menge ÄDTE mit Calcium titriert. Selbst grosse Mengen von Eisen und Aluminium können mit Triäthanolamin maskiert werden. Kupfer und andere Schwermetalle werden mit Thioglykolsäure ausgeschaltet.

Résumé—Les auteurs ont mis au point le dosage complexométrique du nickel et du cobalt présents dans la même solution. Il est fondé sur la détermination de la somme du nickel et du cobalt par titrage en retour de l'E.D.T.A. en milieu fortement alcalin par le chlorure de calcium en présence de calcéine comme indicateur. Après oxydation du cobalt en complexe EDTA-Co(III) par l'eau oxygénée, le nickel est complexé par le cyanure de potassium; l'E.D.T.A. libéré, qui correspond au nickel présent est titré à nouveau par le chlorure de calcium. Le fer et l'aluminium même présents en grandes quantités, sont complexés par la triéthanolamine. Le cuivre et les autres métaux lourds sont complexés par l'acide thioglycolique.

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Beobachtungen am Verbrennungsverlauf organischer Substanzen

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Bei der Durchführung von Kohlenstoff—und Schwefelbestimmungen nach der relativkonduktometrischen Methode, wie sie bereits des öfteren beschrieben wurde,[1-5] ergeben sich weitere auswertbare Möglichkeiten dieser neuen Arbeitstechnik, die im folgenden in Kürze ihrem Wesen nach aufgezeigt werden sollen.

Die relativkonduktometrische Methode beruht auf der Leitfähigkeitsdifferenzmessung in zwei Zellen, die eine gefüllt mit unbegaster, die andere gefüllt mit der mit CO_2 oder SO_2 begasten Absorptionslösung. Die Aufzeichnung dieser Leitfähigkeitsdifferenzen erfolgt mittels automatisch registrierendem Schreiber, der ein Integral über das während einer Verbrennung auftretende Gas bzw. die durch dessen Absorption in geeigneten Lösungsmitteln verursachte Leitfähigkeitsdifferenz liefert. Das heißt somit, diese integrierende Aufzeichnung findet auf jeden Fall statt, ob nun die Verbrennung rasch oder langsam erfolgt, wobei unter "rasch" eine Zeitdauer von weniger als 1/2 Minute, unter "langsam" eine von 1/2 Minute bis zu einer Stunde und mehr verstanden wird.

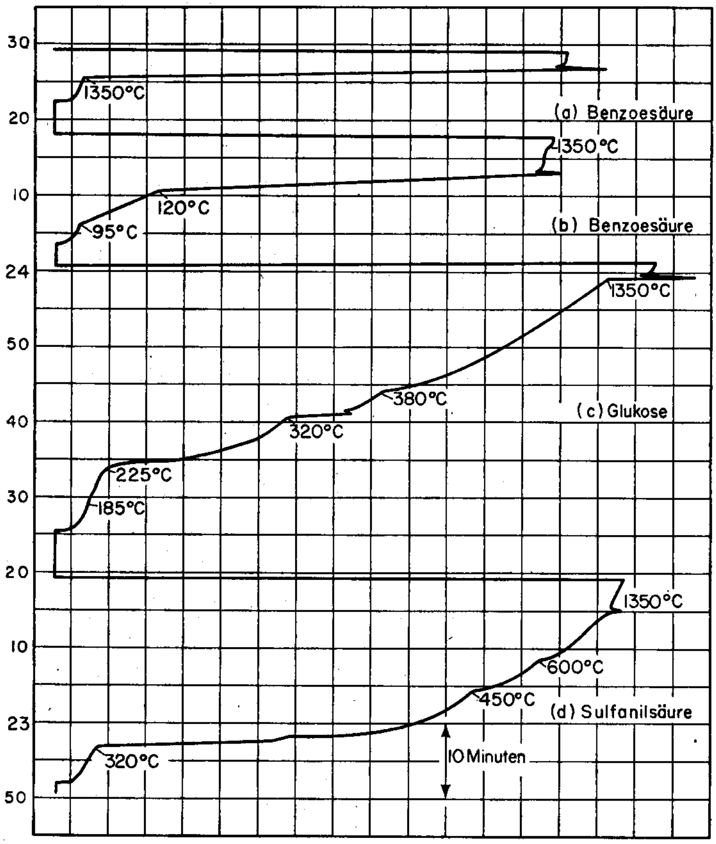

Abb. 1.—Registrierung von Kohlenstoff-Bestimmungen in einigen Einwaagen organischer Substanzen.

Es liegt im Interesse des Analytikers, die Verbrennung rasch durchzuführen, erstens, weil die Resultate bei explosionsartig verlaufenden Verbrennungen infolge der eindeutigeren Aufzeichnung durch den Schreiber weniger streuen und zweitens, weil die Stärke dieser Methode vor allem in der kurzen Dauer einer einzelnen Bestimmung liegt.

Nun scheint aber ein weiterer großer Vorteil dieser Methode darin zu bestehen, daß man—ohne Rücksicht auf die Zeitfrage—bei sogenannten "gelenkten Verbrennungen" fraktionierte und temperaturkontrollierte Verbrennungsabläufe auch mit sehr geringen Substanzmengen (etwa 1 mg) studieren kann. Wird nämlich die zu verbrennende Probe nicht plötzlich von 20°C auf 1350°C gebracht, sondern durch langsames Einschieben mit geeigneten Vorrichtungen dieser Temperaturbereich in 1, 2, 10, 20 Minuten oder beliebig länger durchlaufen, so erhält man an Stelle einer waagrechten Linie eine in mehreren Stufen bzw. Kurven aufsteigende Aufzeichnung auf dem Registrierstreifen, die bei Einhaltung der gleichen Versuchsbedingungen für die einzelnen Substanzen reproduzierbar ist und die möglicherweise Kohlenstoff-bzw. Schwefelanteilen mit bestimmten Bindungscharakter in der Substanz entspricht.

An Hand von einigen Beispielen von Verbrennungen und ihren Aufzeichnungen durch den Schreiber möge das Gesagte veranschaulicht werden. Siehe dazu Abb. 1: Registrierung des Kohlenstoff-Gehaltes einiger Einwaagen verschiedener organischer Substanzen.

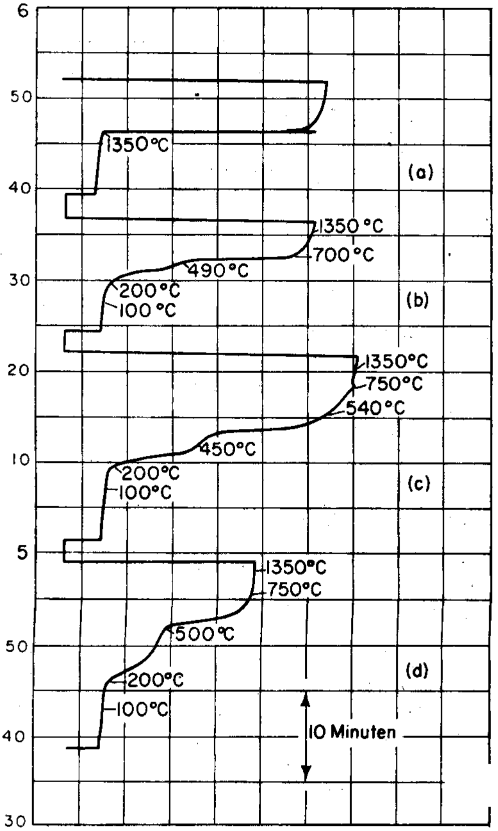

Abb. 2.—Registrierung von Schwefel-Bestimmungen in einigen Einwaagen eines schweren Heizöles (3,6% S).

Die erste Aufzeichnung zeigt den Verbrennungsablauf von Benzoesäure unter den üblichen Bedingungen (Abb. 1a), d.h. rasches Einschieben der Probe in den auf 1350°C erhitzten Verbrennungsofen. Die Verbrennung und Registrierung erfolgt in diesem Fall unter Berücksichtigung einer Überkonzentrationsspitze in max. 2 Minuten.

Die zweite Aufzeichnung (Abb. 1b) zeigt die Verbrennung der gleichen Substanz, wobei aber das Einschieben in den Ofen stufenweise erfolgt. Man kann auf diese Weise eine ungefähre Zersetzungstemperatur der Substanz ermitteln und weiters eine stufenweise Verbrennung durchführen, wobei in jeder durchschrittenen Temperaturstufe ein gewisser Prozentsatz des Kohlenstoff-Gehaltes der Substanz in CO_2 übergeht. Der Aufzeichnung entnimmt man, daß unter den gegebenen Bedingungen die Zersetzung der Benzoesäure bei 95°C einsetzt, bei 120°C zu 95 % verlaufen ist und beim Einschieben auf 1350°C nur mehr ein kleiner Restbetrag an Kohlenstoff registriert wird. Das Verhältnis des Kohlenstoffes in der COOH-Gruppe zum Kohlenstoff im Ring, ist 1:6. Die auf die waagrechte projizierten, den freiwerdenden Kohlenstoffmengen entsprechenden Strecken 95–120°C und 120–1350°C verhalten sich ebenfalls etwa wie 1:6. Inwieweit es sich hier um einen Effekt, welcher durch den Verdampfungs-bzw. Zersetzungsbeginn der betreffenden Substanz hervorgerufen wird bzw. um echte Unterschiede im C-Bindungscharakter, müßte noch geklärt werden.

Die dritte Aufzeichnung (Abb. 1c) gibt den Verbrennungsverlauf von Glukose wieder. In diesem Fall beginnt die Zersetzung erst bei 185°C, ist bei 225°C zu 35%, bei 320°C zu 50% und bei 1350°C zu 100% vor sich gegangen. Eine Interpretation der Stufenbildung muß genaueren Untersuchungen vorbehalten bleiben.

Die vierte Aufzeichnung (Abb. 1d) zeigt die Verbrennung von Sulfanilsäure. Der Zersetzungsbeginn liegt in diesem Fall erst bei 320°C, bei welcher Temperatur ca. 75% des Gesamt-Kohlenstoffes freigemacht werden. Die restlichen 25% werden stufenweise bis zu einer Endtemperatur von 600°C erfaßt,

Entsprechendes dazu läßt sich auch bei Schwefelbestimmungen feststellen.

Versuche, bei denen Sulfonal verwendet wurde, zeigen beispielsweise, daß bei Einschieben einer Einwaage in den kalten Ofen und langsamen Anheizen auf 1350°C nur 4,27% der zu erwartenden Schwefel-Menge vom Schreiber registriert wurden, während der Großteil der Probe weit unter der Siedetemperatur vergaste und vom Sauerstoffstrom weggeführt wurde, ohne in SO_2 übergeführt worden zu sein.

Bei einem weiteren Versuch, durchgeführt in einem auf 600°C erhitzten Verbrennungsrohr, konnten auch nur 8,70% des Schwefelwertes erfaßt werden. Auch bei dieser Temperatur scheint die Geschwindigkeit der Verbrennung noch zu klein zu sein, um zu verhindern, daß unzersetzte Substanzmengen vom Sauerstoff-Strom aus der heißen Zone weggeführt werden, noch bevor sie zu SO_2 umgesetzt werden konnten.

Erst Versuche, die bei einer Ofentemperatur von 1350°C durchgeführt wurden, ergaben je nach Versuchsbedingungen eine 95–100% ige Registrierung der zu erwartenden Schwefel-Mengen.

An Hand von Verbrennungen von Erdölprodukten, durchgeführt durch langsames Einschieben der Proben in den heißen Ofen (im Verlauf von 5–20 Minuten und mehr) kann analog zu den Kohlenstoff-Bestimmungen gezeigt werden, daß man auch damit differenzierte Verbrennungen erhält. Bild 2 zeigt Registrierungen von Schwefel-Bestimmungen in einigen Einwaagen von einem schweren Heizöl.

Die Aufzeichnungen a und b (Einschieben einer Einwaage im Verlauf von 1 bzw. 5 Minuten) zeigen noch keine Differenzierung in verschieden flüchtige Anteile. Erst bei einer Einschiebedauer von 10 bzw. 20 Minuten (Aufzeichnung c und d) treten stufenweise Registrierungen auf. Zwischen Raumtemperatur und 200°C scheinen dabei keine wesentlichen Anteile an flüchtigen Schwefelverbindungen zu verbrennen. Im Temperaturbereich von 200–500°C vergasen bzw. verbrennen Produkte, die etwas mehr als 35% des Gesamtschwefels enthalten und der Rest wird zwischen 500–750°C in SO_2 übergeführt. Über dieser Temperatur bis 1350°C waren keine schwefelhaltigen Verbindungen mehr zu erfassen.

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Zusammenfassung—Es wird eine neue Anwendung der relativkonduktometrischen Methode zur Kohlenstof- und Schwefel-Bestimmung aufgezeigt, die darauf beruht, durch langsame gelenkte Verbrennung eine differenzierte Erfassung einzelner Fraktionen des Kohlenstof- und Schwefelgehaltes organischer Substanzen zu ermöglichen.

Summary—A new application of the relative-conductimetric method for the determination of carbon and sulphur is described. The method consists in a slow programmed combustion and trapping of the different fraction. Thus it is possible to analyse the various fractions of the organic material for their carbon and sulphur content.

Résumé—Une nouvelle application de la conductimétrie relative au dosage du carbone et du souffre est décrite. La méthode consiste en une combustion lente er programmée à la suite de laquelle les différentes fractions sont recueillie. Il est ainsi possible de doser les diverses fractions de carbone et de soufre des substances organiques.

Copper^{II} catalysis of 8-acetoxyquinoline hydrolysis

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A METHOD for the precipitation of metal 8-hydroxyquinolates in homogeneous solution utilising the hydrolysis reaction of 8-acetoxyquinoline has recently been established.[1,2] The possibility that complexes of this reagent with metal ions might participate in such hydrolysis was considered in the present study of the effects of copper^{II} ion on the kinetics of the hydrolysis of 8-acetoxyquinoline.

EXPERIMENTAL

The 8-acetoxyquinoline, PFHS grade, was obtained from the Burdick and Jackson Laboratories and used without further purification.

Each of the hydrolysis reactions was carried out in a 20:1 mixture by volume of an appropriate aqueous buffer solution and a freshly prepared solution of 8-acetoxyquinoline in absolute ethanol. The ionic strengths of the stock aqueous buffers, with the exception of the most concentrated perchloric acid solution, were set at 0·10 by the addition of sodium perchlorate. An acetate buffer, a phosphate buffer, and two borate buffers having identical concentrations of borate ion, comprised the stock solutions of pH greater than 4. The other aqueous stock solutions were prepared from perchloric acid. Copper perchlorate was used in the preparation of the stock solutions containing copper ion.

Rate constants were measured spectrophotometrically. At appropriate time intervals, optical density measurements were taken of samples of the reaction mixtures, which were kept in a constant temperature bath maintained at 25·0°. Samples of the pH 3·05 reaction mixtures, initially 0·00002*M* in ester concentration, were transferred to a 10-cm absorption cell for measurement. Initial ester concentrations in the other reaction mixtures were in the range of 0·0001*M* to 0·0003*M*. Samples of these solutions were taken in a 1-cm absorption cell.

The conjugate acid of 8-acetoxyquinoline has an absorption maximum at 313·5 mμ ($\log \epsilon = 3·77$). The free base has maxima at 313·5 mμ ($\log \epsilon = 3·46$), 300 mμ ($\log \epsilon = 3·56$), and 288 mμ ($\log \epsilon = 3·62$). The variation of absorbancy at each of these wavelengths was in conformity with Beer's law in the concentration range studied. Hydrolysis to 8-hydroxyquinoline in solutions of pH less than 4 was followed at 313·5 mμ. Other rate measurements were made at 285·0 mμ.

A pK_a value of 3·14 ($\pm$0·05) for the 8-acetoxyquinolinium ion was determined by measuring changes in molar extinction coefficient with pH at 313·5 mμ.

KINETIC DATA FOR THE HYDROLYSIS OF 8-ACETOXYQUINOLINE

pH*	Measured first order rate constants, *min*$^{-1}$ × 10^3			Calculated† first order rate constants, *min*$^{-1}$ × 10^3		
	Cu^{2+} absent	0·0146*M* Cu^{2+}	0·0292*M* Cu^{2+}	Cu^{2+} absent	0·0146 *M*Cu^{2+}	0·0292*M* Cu^{2+}
	1·36‡					
1·05	0·36			0·37		
1·45	0·32			0·31		
2·05	0·41		0·46	0·40		0·44
2·35	0·57		0·70	0·56		0·69
2·67	0·82	1·04	1·30	0·84	1·08	1·32
3·05	1·34		3·4	1·33		3·4
4·72	2·64			2·66		
6·79	2·76			2·73		
8·80	3·5			3·5		
9·20	4·5			4·6		

* The pH reading at reaction completion for the copper-free reaction mixtures. The corresponding readings for the mixtures containing copper were 0·00–0·04 pH units lower, presumably because of copper chelation with 8-hydroxyquinoline. The largest pH differences were found at pH 2·67, where the ratios of initial ester concentration to hydrogen ion concentration were the highest. Kinetic calculations for any copper catalysed reaction accompanied by a substantial pH change were based only on the rate data collected during the first half of the reaction.

† See DISCUSSION

‡ In 0·9*M* perchloric acid.

The pH measurements were taken with a Beckman Model G pH meter standardised with Beckman pH 4 buffer solution for measurements above pH 4. A reaction solution of known acid concentration served to standardise the pH meter for measurements below pH 4. A Cary Model 11 spectrophotometer was used for the rate measurements.

DISCUSSION

The kinetic measurements established that the hydrolysis of 8-acetoxyquinoline is first order in 8-acetoxyquinoline. It was found that the variation of the first order rate constant with pH and copper concentration under the conditions studied could be expressed by a sum of terms corresponding to several catalysed and uncatalysed hydrolysis reactions. These included the hydrogen ion catalysed reactions of the ester and of the ester cation, the hydroxide ion catalysed hydrolysis of the ester, the hydrolysis without hydrogen ion or hydroxide ion catalysis but possibly involving intramolecular base catalysis by the amine function, and the hydroxide ion catalysed reaction of the 1:1 copper-ester complex. If K_a, the acid dissociation constant for the 8-acetoxyquinolinium ion, is introduced, the reaction terms may be written in the form

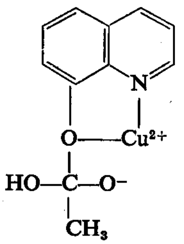
$$k = \frac{1}{(\mathrm{H}^+) + K_a}\left\{k_1(\mathrm{H}^+)^2 + K_a\left[k_2(\mathrm{H}^+) + k_3 + \frac{k_4(\mathrm{OH}^-)}{K_w} + \frac{k_5(\mathrm{OH}^-)(\mathrm{Cu}^{++})}{K_w}\right]\right\}$$

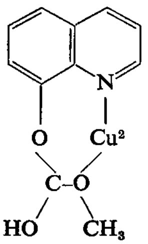
where

$k_1 = 0{\cdot}0017$ litre mol^{-1}min^{-1}
$k_2 = 0{\cdot}276$ litre mol^{-1}min^{-1}
$k_3 = 0{\cdot}00272$ min^{-1}
$k_4 = 1{\cdot}2 \times 10^{-12}$ mol litre^{-1}min^{-1}
$k_5 = 0{\cdot}00014$ min^{-1}

Values of the first order rate constant, k, calculated from the pH, the measured pK_a value of 3·14, and the k_1, k_2, k_3, k_4, and k_5 values given above, are listed in the table of kinetic data and compared with the measured constants.

The copper catalysed hydrolysis was found to be first order in 8-acetoxyquinoline (as the free base), first order in copper ion, and first order in hydroxide ion. It was surprising to find the order in hydroxide ion in view of the very low concentrations of this ion available for a reaction with the 1:1 copper-ester complex in the pH range studied. The order in hydroxide ion suggests that such a reaction would be a rate determining step if a mechanism analogous to one described[3] for the hydroxide ion catalysed hydrolysis reactions of other esters were followed. Possible structures for the reaction intermediate if some stabilisation by chelation is assumed are:





An investigation of the effects of other metal ions on the hydrolysis of 8-acetoxyquinoline is in progress.

Acknowledgement—Support of this research by the United States Public Health Service is gratefully acknowledged. The authors wish to thank Mr. Robert Brook for technical assistance.

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Summary—The hydrolysis of 8-acetoxyquinoline in dilute acid solution has been found to be subject to copper$^{\mathrm{II}}$ catalysis. The catalysed reaction is first order in 8-acetoxyquinoline (as the free base), first order in copper ion, and first order in hydroxide ion. It is proposed that a copper chelate is a reaction intermediate in the hydrolysis.

Zusammenfassung—Es wurde gefunden, dass die Hydrolyse von 8-Acetoxychinolin in verdünnter Säure durch Kupfer(II) katalysiert wird. Die katalytische Reaktion ist erster Ordnung in Bezug auf Acetoxin (als freie Base), Kupfer und auch Hydroxylion. Es wird angenommen, dass sich ein Kupferchelat als Zwischenprodukt bildet.

Résumé—L'hydrolyse de la 8-acétoxyquinoléine en solution acide dilué est catalysée par le cuivre(II). La réaction catalysée est du premier ordre à l'égard de la 8-acétoxyquinoléine (en tant que base libre), des ions cuivriques et des ions oxydriles. La formation d'un complexe du cuivre est proposée comme réaction intermédiaire lors de l'hydrolyse.

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Talanta, 1962, Vol. 9, pp. 1063 to 1066. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Talanta

SIR,

Anybody with even a modicum of interest in analytical chemistry must, I think, peruse *Talanta* quite often. I wonder how many readers have been puzzled—as the writer is—by the meaning of this title. It certainly is more lively and appealing than the variety of *Archives—Memoirs—Acta—Journal—Zeitschrift* to which one has become accustomed since time immemorial—but what *does* it mean? Its editors and authors may be talented—the Journal may be worth a talent of gold—but why the plural Ταλαντα? And why was this title chosen? The writer dug out his old Greek dictionary, consulted the British Encyclopedia and the Oxford Dictionary, but no explanation was forthcoming. It might therefore perhaps not be out of place if the editor would give an explanation, either as a subtitle, or somewhere on the cover or in the table of contents, either of each issue or at least from time to time, and so end this tantalising frustration. At the birth of the Journal, an explanation was probably given to midwives and bystanders but many readers may have missed this stage and so perhaps *repetitio est mater studiorum.*

In spite, however, of this ethmological uncertainty, *vivat, crescat, floreat* Ταλαντα!

I am, Sir, Yours, *etc.*

WILLIAM STROSS

1, *Haydon Hill House,*
Bicester Road,
Aylesbury, Bucks. England.
16 *June* 1962.

Dear Dr. Stross,

Your enquiry, coupled with various other friendly enquiries in the past, leads me to believe that an explanation of the name of our Journal might be of interest to a wider public.

When we first projected the journal it was thought of as a sister journal to the already established *Tetrahedron.* It was, therefore, felt that it would be very appropriate if we had a Greek name to go with *Tetrahedron,* and one which was as closely associated with analytical chemistry as *Tetrahedron* is with organic chemistry. Apart from this, we felt that it would be a very considerable advantage to have a name which did not actually contain the terms "analysis" or "analytical"; for the purpose of indicating references, it was desirable to choose a title which could not be confused with any of the existing journals in analytical chemistry.

We consulted our Greek experts (we ourselves lay little claim to classical scholarship) and pointed out that the determination of the parts of a whole is fundamental to analytical chemistry. Their first suggestion was *Stoicheion.* We were tempted to accept this because it means quite precisely "element"; but we found that none of us could consistently spell the word correctly! The experts next said that the Greek word for a balance was *Talanta* (related to the Greek "talent" which, of course, was originally a weight of gold or silver). The rather obvious confusion with the word "talent", as used in its more conventional sense, appealed to our sense of humour, or whatever one might call it! We tried the name out on various people and they were rather intrigued by it; it seemed to fit in very well with *Tetrahedron*; and, therefore, we adopted it. I think it is true that most people do not understand the implication of it. But the cover design was, in its first rough draft, designed by us to include the Greek form of the name in order to give some sort of clue about the origin of the word.

Incidentally, the little vignette of balance which appears inside the cover is the result of a considerable amount of searching on the part of our Greek experts for an actual picture of a *Greek* balance. It is surprising how hard it was to track down one—we could get Egyptian balances and Roman balances, but this must be one of the very few authentic instances of an illustration of a Greek balance.

Tailpiece: It is curious to find how many people cannot spell the present name of the Journal correctly. We are quite startled to find how often people refer to it as "*Tantala*" and often speculate about what *would* have happened had we settled for *Stoicheion*!

Yours sincerely,

CECIL L. WILSON
(Editor-in-Chief)

The iodometric estimation of tin

SIR,

The accurate estimation of tin by titration with a standard solution of iodine has been attempted by many workers and the subject has, accordingly, a very large literature. No attempt is made here to survey the literature, although much of it has been consulted.

The method that seemed to us to be the most promising is that adopted in British Standard Method 1121, Parts 20 and 22; here the tin is reduced by aluminium foil in the presence of antimony, and the stannous tin is titrated with potassium iodate in the presence of potassium iodide. The method was applied in the following way: To a 250-ml conical flask, fitted with a side tube reaching to the bottom of the flask through which nitrogen (oxygen free) was passed throughout the experiment, was added an aliquot of stannic chloride solution containing 83·91 mg of tin, 40 ml of hydrochloric acid (sp. gr. 1·16), 2 ml of antimony chloride solution,* and sufficient water to bring the total volume to about 100 ml. One gram of aluminium foil was added in small amounts, the solution being kept warm to assist the reaction. After the last piece of aluminium had been added, the flask was attached to a reflux condenser and, when the aluminium had dissolved, the liquid was boiled for 30 min to redissolve the tin. The flask was then cooled, the condenser was removed, 10 ml of 10% potassium iodide were added, and the solution was titrated with standard 0·05*N* potassium iodate solution using starch as indicator. The results were reasonably consistent (28·68 ± 0·05 ml) but were 1% less than theoretical.

Similar results were obtained using nickel foil instead of aluminium and antimony. In these experiments strips of nickel foil (with a surface area of 12 in.^2 and etched with a solution of hydrochloric acid and sodium chloride) were added and the solution was boiled under reflux for 2 hours before cooling and titrating.

Finally, Kolthoff's[1] method of reducing the tin with iron (reduced) and antimony was tried. This method gave consistent results and the titres were theoretical (*viz.* 1 ml of 0·05*N* iodate = 2·97 mg of tin). The experiment was carried out in a similar manner, and in the same apparatus, using 1 g of iron (reduced), added all at once, and 1 ml of antimony chloride solution, the solution being boiled under reflux until the iron had dissolved and for 20 min afterwards.

Järvinen[2] drew attention to the necessity of adding a sufficient excess of iron and we have found that with 180 mg of tin the titres are low, but that the theoretical result is obtained when the quantity of iron is doubled. If antimony is not present we found, as did Järvinen, that much larger amounts of iron are necessary. On the other hand, if the amount of hydrochloric acid is reduced from 40 ml to 10 ml, the theoretical titre is obtained using 1 g of iron. There was no blank in any of the above titrations.

* Add 5 ml of sulphuric acid (sp. gr. 1·84) to 500 mg of powdered antimony and fume the mixture until no free antimony remains. After cooling, dissolve the white residue in a mixture of 20 ml of hydrochloric acid (sp. gr. 1·16) and 50 ml of water, and dilute the solution to 100 ml.

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24 *July* 1962.

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[1] I. M. Kolthoff, *Z. analyt. Chem.*, 1921, **60,** 452.
[2] K. K. Järvinen, *ibid.*, 1923, **62,** 189.

Sodium thiosulphate solutions

SIR,

IN a recent standard textbook,[1] the following statement appears, concerning the preparation of sodium thiosulphate solutions.

"Solutions of sodium thiosulphate keep very well indeed if made up in carbon dioxide-free boiled demineralized or distilled water. On no account should carbonates be added to the solution to make it keep better as recommended by some authors. The addition of carbonates actually has the reverse effect."

We have habitually made an addition of 0·01 % w/v of sodium carbonate in preparing thiosulphate solutions, and it has not been our experience that this is deleterious. For example, a solution prepared in distilled water[2] in equilibrium with atmospheric carbon dioxide and containing 0·01 % sodium carbonate, which was carefully standardised potentiometrically against potassium iodate and cross checked with potassium bromate, had a factor of 1·0077 ± 0·0002 on 6th June 1955. The solution was stored in a polythene-screw-capped brown glass Winchester. Rather more than seven years later this solution was independently restandardised, and had a factor of 1·0068 ± 0·0002 on 1st August 1962. The solution remained perfectly clear and free from sediment.

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11 *August* 1962

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The oxygen flask method at low halogen levels

Sir,

THE use of the Oxygen Flask method for the determination of halogens in organic substances has been encouraged in numerous publications[1] since its re-introduction in 1955. It is noteworthy however, that no systematic study of the limitations of the method has been made. The writer wishes to stimulate critical consideration of the combustion conditions and the blank values in this method, especially with regard to its possible application at halogen levels below 10^{-5} g equiv.

The very nature of the combustion conditions engenders doubt about their efficiency; and experience of the method in routine use indicates that liquid, refractory, and high-halogen-content substances are not always completely combusted. Various expedients facilitate their correct analysis, but these detract from the value of the determination as a routine method. In particular, liquid substances have no universally satisfactory way of combustion, the probability of the escape of vapour before or during burning being high in all the published methods.

The blank value from the substance wrapping material has hitherto either been ignored or been assumed to be small and constant. It is certain, however, that this value is not very reproducible, and is often a serious limiting factor of the accuracy of the method. This is particularly so at the halogen level mentioned above, where the blank value amounts at a minimum to approximately 5 % of this level (see Table).

The magnitude and variability of the value are increased if finger stalls are not worn by the analyst. If a halogen-differentiating finish is coupled with the method,[2] the blank value makes bromide and iodide analysis possible but chloride analysis impossible. The reagents used in the method contribute a constant blank of the order of 8×10^{-8} g equiv of Cl^-, which is of little significance The avoidance of a wrapping material, as in carbon determinations,[1] is not recommended on account of the poor combustion conditions, and reduction in the material size introduces serious handling problems.

Material	Average Cl^- content, $g\ equiv \times 10^{-7}$
(*a*) "Whatman" filter paper, No. 541 (1·5 in^2.)	7
(*b*) Double water washed (*a*) (1·5 in^2.)	5
(*c*) "Whatman" filter paper, No. 1 (1·5 in^2.)	5
(*d*) "Kleenex" tissue (1·5 in^2.)	14
(*e*) Tracing paper (1·5 in^2.)	18
(*f*) "Sellotape" (1·0 in^2.) + fuse of (*a*) (0·5 in^2.)	4 + 2
(*g*) "Eli Lilly" Gelatin Capsule No. 5 + (*a*) (1·5 in^2.)	8 + 7
(*h*) "Parke, Davis" Gelatin Capsule No. 5 + (*a*) (1·5 in^2.)	3 + 7

In conclusion, it is recommended that a tube combustion procedure be generally adopted at this halogen level. It provides more ideal combustion conditions, a constant reagent blank value, and relatively easy handling of liquid substances, in comparison with the Oxygen Flask method. Even at the micro-determination halogen level (5×10^{-5} g equiv), a tube combustion procedure is recommended.

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28 *September* 1962

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BOOK REVIEWS

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

This is a series of monographs on the radiochemistry of the elements. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radiochemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

The major part of the monograph is taken up by the latter section, and a critical selection of the known radiochemical techniques for each element has obviously been made. A number of the procedures have originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has, in some of the monographs, been covered up to 1962.

This series will be of particular interest to the radiochemist or the analytical chemist. It will also be of value to the biochemist and the physicist who often use radiochemical techniques in the solution of specific problems.

The most recent additions to the series now available are:

The Radiochemistry of Silicon. W. T. Mullins and G. W. Leddicotte. January, 1962. $0.50.
The Radiochemistry of Osmium. G. W. Leddicotte. October, 1961. $0.50.
The Radiochemistry of Iridium. G. W. Leddicotte. October, 1961. $0.50.
The Radiochemistry of Platinum. G. W. Leddicotte. October, 1961. $0.50.
The Radiochemistry of Tellurium. G. W. Leddicotte. October, 1961. $0.50.
The Radiochemistry of Tungsten. W. T. Mullins and G. W. Leddicotte. September, 1961. $0.50.
The Radiochemistry of Vanadium. J. L. Brownlee, Jr. December, 1960. $0.75.
The Radiochemistry of Gold. J. F. Emery and G. W. Leddicotte. May, 1961. $0.50.
The Radiochemistry of Germanium. J. A. Marinsky. July, 1961. $0.50.
The Radiochemistry of Lead. W. M. Gibson. August, 1961. $1.75.
The Radiochemistry of Niobium and Tantalum. E. P. Steinberg. August, 1961. $0.75.
The Radiochemistry of Selenium. G. W. Leddicotte. April, 1961. $0.50.
The Radiochemistry of Polonium. P. E. Figgins. January, 1961. $0.75.
The Radiochemistry of the Transcurium Elements. G. H. Higgins. October, 1960. $0.50.
The Radiochemistry of Cobalt. L. C. Bate and G. W. Leddicotte. September, 1961. $1.00.
The Radiochemistry of Potassium. W. T. Mullins and G. W. Leddicotte. November, 1961. $0.50.
The Radiochemistry of Silver. D. N. Sunderman and C. W. Townley. November, 1961. $0.75.
The Radiochemistry of Aluminium and Gallium. J. E. Lewis. April, 1961. $0.50.
The Radiochemistry of Titanium. Chong Kuk Kim. March, 1961. $0.50.

In the same series the following publications dealing with radiochemical techniques have appeared:

Low-level Radiochemical Separations. T. T. Sugihara. April, 1961, $0.50.
Separations by Solvent Extraction with Tri-n-octylphosphine Oxide. J. C. White and W. J. Ross. February, 1961. $0.75.
Liquid-Liquid Extraction with High Molecular Weight Amines. F. L. Moore. December, 1960. $1.00.
Rapid Radiochemical Separations. Y. Kusaka and W. Wayne Meinke. December, 1961. $1.25.

The following publications are now also available:

Radio-active Contamination of Materials Used in Scientific Research. J. R. DeVoe. Publication 895. 1961.
A Cross-Referenced Index of Radiochemical Teaching Experiments Applicable to Chemistry. G. R. Choppin. Publication 905. 1961.

R. J. Magee

Progress in Nuclear Energy, Series IX: Analytical Chemistry, Volume 2. Edited by C. E. CROUTHAMEL. Pergamon Press Limited, Oxford, 1961. pp viii + 400. £5. 0. 0.

IT will be recalled that Volume 1 of Progress in Nuclear Energy, Series IX, reproduced the analytical chemistry papers presented at the 1958 Geneva Conference on *Peaceful Uses of Atomic Energy*. Volume 2 comprises eight review articles covering a wide range of subject matter, as follows:

1. *Recent Advances in Counting Techniques*, by C. Gastrousis, R. Heinrich and C. E. Crouthamel (79 pages)
2. *Magnetic Resonance Spectroscopy, Applications of Electron Spin Resonance Spectroscopy to Organic and Inorganic Chemistry*, H. A. Elion and L. Shapiro (75 pages).
3. *Recent Advances in the Separation and Analysis of the Transuranium Elements*, by D. C. Hoffman (43 pages).
4. *Applications of Liquid-Liquid Extraction in Inorganic Chemistry*, by D. F. Peppard (23 pages).
5. *Flame Photometry and Atomic Absorption Spectroscopy*, by J. W. Robinson, (32 pages).
6. *Recent Advances in Ultraviolet, Visible and Infrared Spectrometry*, by J. C. White, (55 pages)
7. *Particle Interactions with Matter; Backscattering and Excitation of Characteristic X-rays*, by R. H. Müller (24 pages).
8. *Ion Exchange Chromatography*, by J. E. Salmon (42 pages).

As these titles suggest, the phrase "nuclear energy" has been interpreted in its widest sense; indeed, Chapters 2, 5 and 8 touch only incidentally on the nuclear energy field, though it can be argued with considerable truth that virtually every element has occupied the interest of nuclear scientists in one way or another and therefore commanded the attention of their analytical colleagues. The present volume should be of wide appeal and several of the chapters will be of value to analytical chemists outside the nuclear field.

Chapter 1 deals with the gas ionisation proportional spectrometer, solid state spectrometry and scintillation spectrometry. It strikes an excellent balance between theory and practice and will be welcomed by the chemists in the radiochemical field who constantly struggle to keep abreast of the advances achieved by their colleagues in counting techniques. Chapter 2 is an eminently readable introduction to magnetic resonance and electron spin resonance spectroscopy and indicates clearly the potential of a technique which as yet remains a highly specialised "tool of the future" to the vast majority of analysts. The separation and determination of the transuranium elements have presented some formidable problems and in Chapter 3 Hoffman reviews a now extensive literature in a balanced and workmanlike manner.

Peppard's chapter on liquid-liquid extraction, though rather surprisingly the shortest of the volume, is a scholarly and concise presentation. Dealing almost entirely with nuclear chemistry, its principal objective is to familiarise the analyst with the wealth of solvent extraction data which has become available in recent years and to discuss critically its potential analytical value. Inevitably the principal coverage is accorded to the wide variety of acidic phosphorus esters and organic phosphinic acids which have received such extensive study. The mode of operation and practical application of these substances is presented with commendable clarity.

In Chapter 5, Robinson reviews in detail the present status of flame photometry (with particular reference to high temperature flames) and atomic absorption spectroscopy. The latter is discussed under the heading *Recent Advances in Flame Photometry* and could give rise to the misleading impression that atomic absorption spectrometry is limited to flame excitation. Chapter 6, by White, reviews recent advances in ultraviolet, visible and infrared spectrometry under three main headings: *Status of Ultraviolet and Visible Spectrophotometric Methods for Selected Elements*, *Advance in Infrared Absorption Analysis* and *Absorption Spectrophotometry of Molten Salts*. The first two call for little comment but the third is a most valuable contribution. It considers in detail the many practical problems of obtaining spectra of melts. It is supported by some excellent diagrams and should be compulsory reading for those wishing to enter this relatively new field.

In Chapter 7, *β-particle Interactions with Matter*, the reader is led easily through the many facets of β-backscattering and the β-particle excitation of *bremsstrahlung* and characteristic X-rays. The analytical applications of the latter *vis-a-vis* the conventional X-ray methods are critically considered. The chapter is mainly of a broad general nature and could well have some appeal at student level.

Ion Exchange Chromatography, the subject of Chapter 8, has been a particular favourite of authors of review articles during the past decade and apart from some recent applications in the period 1957–1960 the present contribution contains little that cannot be readily found elewhere. The author has recognised this limitation and has incorporated a *résumé* of the basic operational principles of the diverse forms of ion exchange and the whole is presented clearly and succinctly.

Undoubtedly specialist readers in the various fields reviewed in this volume will find grounds for justifiable criticism on matters of detail, but on the whole the book is intended to command the attention of a much wider audience interested in, but not necessarily closely associated with, those aspects of analytical chemistry which have received such impetus from the demands of nuclear science. To such an audience the book can be recommended; it is well produced and contains copious reference to the original literature. A notable omission from the work is electrochemical analysis, and it is to be hoped that this will be rectified in a subsequent volume.

J. K. Foreman

Microdiffusion Analysis and Volumetric Error. E. J. Conway. 5th revised edition, Crosby Lockwood and Son Ltd., London, 1962. Pp xviii + 467, 42s.

In a review of the 4th revised edition of *Microdiffusion Analysis* (*Talanta*, 1959, **2**, 98), the present reviewer drew attention to the responsibility of an author to his readers to provide a periodically revised text. The continued success of a book depends very much on how effective the revision is. With Professor Conway's book, the publishing history reflects how well the techniques of microdiffusion analysis have been received by successive generations of chemists and biochemists, and how great is the present interest in the subject.

A comprehensive review of this book is uncalled for. The reviewer has no intention of preaching to the converted, but for those who have little or no experience of microdiffusion analysis, it may suffice to state that here is the one authoritative text on the subject which not only contains all the important and relevant material from the earlier editions, but also has the advantage of containing much new material incorporated into the text since the 4th edition appeared in 1957. The revision is by no means superficial; Professor Conway lists in his preface the several new applications of the technique which are now included in the text. Attention has also been given to developments in the design and construction of the microdiffusion cells. This revision will be welcomed by all those familiar with the methods of microdiffusion analysis not only because of the increased utility of the book to themselves, but also because they can confidently recommend an up-to-date account of the technique to their students and colleagues as yet uninitiated to the methods.

W. I. Stephen

The Collected Works of Irving Langmuir; Vol. 7, Protein Structures; Vol. 8, Properties of Matter; Vol. 9, Surface Phenomena. General Editor, Guy Suits. Pergamon Press Limited, Oxford, 1961. Pp xlii + 227; xxix + 251; and xxi + 521. 100/- net per volume.

The publication of the works of Irving Langmuir in twelve volumes is a worthwhile task only because of the importance of Langmuir's contributions to the subjects which he investigated. The importance of his work stems not only from the clarity and brillance of his publications but also from the inspiration and influence which they had on others who followed after him. Perhaps the most valuable effect of the present volumes will be to induce more people to read some of Langmuir's work in the original form rather than to rely on the accounts condensed and distilled from one textbook to the next—a process which may retain the essence but certainly destroys the flavour of his work.

Each volume has one or two introductory chapters by authorities in the respective fields. Dr. Harry Sobotka in Volume 7 gives a fairly extensive survey describing the influence of Langmuir's work on protein structures on subsequent research. Dean Henry Eyring's introduction to Volume 8 is more personal in character and Volume 9, which is divided into two parts, has articles by Professor N. K. Adam relating to evaporation, condensation and adsorption and by Dr. W. A. Zisman on monomolecular films.

The volumes are clear, readable and well-produced. The division of the papers into the respective volumes is perhaps not ideal; *e.g.*, some of those in Volume 8 are very closely related to many in Volume 9, but the problem of the appropriate grouping of the work is obviously difficult. The method of charging the same sum for each volume seems completely unjustifiable except on grounds of administrative convenience. The price of 100/- for a substantial volume like No. 9 seems high enough but, since Volumes 7 and 8 are considerably smaller, one is left with the conclusion that they are grossly over-priced.

C. Kemball

The Determination of Stability Constants. FRANCIS J. C. ROSSOTTI and HAZEL ROSSOTTI. McGraw-Hill Book Co. Inc., New York, 1961. pp. 425. 97s.

MANY of the remarkable advances in theoretical inorganic chemistry in the last decade rest heavily on the results of a great deal of experimental work on the determination of the stability constants of metal complexes in solution. This book gives an account of the many experimental methods which may be used and describes in detail the computational procedures whereby stability constants are derived from the primary experimental results. It is the first authoritative work on this subject. The authors are specialists who have been closely associated with two of the major schools of solution co-ordination chemistry.

There are eighteen chapters. The first five, which include a brief survey of background and basic principles, are mainly concerned with the generalised methods of evaluation of step formation constants in simultaneous equilibria. The use of secondary concentration variables, "degree of formation" and "ligand number", and of graphical methods such as that of "normalised curve fitting" are treated in detail. Chapters 6-15 deal with the various physico-chemical techniques which may be applied to stability constant determination in mononuclear systems. All make use of some measurable property of the system which changes in a definite way with the degree of complex formation. Those described include potentiometry, solubility, liquid-liquid partition, ion-change and optical and kinetic methods. The final three chapters are concerned with mixed and polynuclear systems.

Throughout, the treatment is critical. For example, some indication of the suitability of a particular experimental or computational method in different circumstances is usually given. It is the authors' view that in the past much work has been poorly designed and that mathematical analysis of data, often incomplete, has not always been carefully carried out. Most of the common pitfalls can be avoided by a careful reading of this volume. For example, the importance of covering a wide range for each of the concentration variables, where several simultaneous equilibria are involved, is stressed, as is also the need for maintaining an environment of constant ionic strength for the control of activity coefficients. The choice of background electrolyte for a given investigation, and the significance of stoicheiometric, as compared with thermodynamic, equilibrium constants are discussed.

While the stimulus for this book has unquestionably been the rapid and growing interest in the solution chemistry of metal complexes, the mathematical techniques described are, of course, applicable to any system of equilibrium, *e.g.*, dissociation of acids and bases, ion association, hydrogen bond formation and equilibria involving relatively large aggregates of molecules and ions such as micelles, *etc.*, though not all of these are treated specifically. Rather more might have been included on measurements in mixed and non-aqueous solvents.

For the sake of exactness the authors have adopted a rather formal mathematical presentation requiring the use of a great number of different symbols, many of them confusingly alike. Probably this was unavoidable; it does not, however, make for easy reading, and most readers would welcome a greater use of illustrative examples.

The bibliography seems very comprehensive and the book is attractively produced. It is intended for research workers, in a variety of fields, actively concerned with equilibria in solution; few can afford to be without it.

S. M. NELSON

Talanta, 1962, Vol. 9, pp. 1071 to 1074. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this Section should be sent directly to the Associate Editor)

AUSTRALIA

Tuesday–Friday 20–23 *August* 1963: **Fourth Australian Spectroscopy Conference:** *Spectroscopy Committee of Australian Academy of Science.* Australian National University, Canberra.

The Conference will cover all aspects of pure and applied spectroscopy. It is hoped to have separate sessions on the following fields of spectroscopy: Atomic Emission, Atomic Absorption, Infrared and Raman, Microwave, Nuclear Magnetic, Nuclear Quadrupole and Electron Spin Resonance, Molecular Electronic, Spectra of Molecules of Biological Interest, Astrophysical Spectroscopy and Mass Spectrometry. The use of spectroscopy as an analytical tool will be featured.

Conference papers should represent original and unpublished work. It is hoped to allow 20 min for presentation of papers and 10 min for discussion. Titles of proposed papers should be submitted before 28 February 1963 and abstracts (150 to 200 words) before 15 May 1963 to the Secretaries for Collection and Publication of Abstracts, Dr. C. H. Williams and Mr. D. J. David, Division of Plant Industry, C.S.I.R.O., Canberra. There will also be a limited number of invited review papers. The principal invited speaker will be Dr. G. Herzberg, F.R.S., Director, Division of Pure Physics, National Research Council of Canada.

AUSTRIA

Friday 14 *December* 1962: **Review of Catalysts in Determination of Carbon and Hydrogen in Organic Compounds:** Dr. G. Kainz: *Österreichische Gesellschaft für Mikrochemie.* Wien.

The *Österreichische Gesellschaft für Mikrochemie* and *Verein Österreichischer Chemiker* announce that they will sponsor an **International Congress on Analytical Chemistry** during the first week of *October* 1965.

There will be 6 plenary lectures and 80 other lectures, the main topics being *Measurements in the Range* 10^{-6}–10^{-12} g and *Automation in Analytical Chemistry.* Application has been made for the patronage of I.U.P.A.C. for the Conference.

HUNGARY

Friday–Saturday 21–22 *December* 1962: **Analytical Chemistry Congress:** Budapest.

The following papers will be delivered after the opening of the Congress by Professor E. Schulek:

Recent Developments in Spectrum Analysis.	T. Török
New Methods in Spectrum Analysis: Use of the Plate Electrode and A.C. Arc Examination.	T. Kantor
Problems of Enrichment in Spectrum Analysis of Solutions.	O. Szakács
Recent Spectrophotometers.	G. Svehla
Use of Spectrophotometry in Steroid Hormone Research.	A. Szabö
Differential Spectrophotometry.	A. Páll and G. Svehla
Use of Atomic Absorption Spectrophotometry in Metal Analysis.	L. Koltai and G. Svehla
Spectrophotometric Method for Determination of Carbon Content of Organic Compounds	L. Török
New Methods in Radiochemical Analysis.	E. Körös
Recent Developments in Thermogravimetric Analysis.	F. Paulik
Special Instruments of Organic Analysis.	L. Mázor
Automatic Titrimeters	I. Buzás
Analytical Use of Catalytic Reactions.	J. Laszlovszky
Recent Developments in Polarographic Analysis.	G. Farsang
Recent Developments in Gas Chromatography.	J. Takács

Further details can be obtained from Dr. L. Mázor, Institute for General Chemistry, Technical University, Budapest XI, Gellért tér 4, Die V. **Ungarische Tagung für Emissionsspektralanalyse** wurde von 9 bis 11 August 1962 in Miskolc abgehalten (Siehe *Talanta*, 1962, **9**, 402 und 628).

Zusammenfassende Vorträge:

Die Anhaltspunkte und Möglichkeiten der heimischen Einführung der direktanzeigenden optischen Emissionsspektralapparate.	T. Török
Die Bedeutung der Emissionsspektroskopie im Eisenhüttenwesen.	L. Paksy
Uber die wirtschaftliche Bedeutung der Spektralanalyse für die Stahlindustrie.	B. Weszprémy
Die Spektralanalyse von Schlacken.	E. Gegus
Spektralanalyse der Reinmetalle.	S. Kerekes
Die Rolle der spektroskopischen Materialprüfung in der Eisen- und Stahlindustrie.	G. Szikora

Die Texte dieser Hauptvorträge werden in der Ungarischen Zeitschrift fur Hüttenwesen (*Kohászati Lapok*) erscheinen.

Originale Kurzvorträge:

Erfahrungen und Anwendungsmöglichkeiten des ARL-Quantovacs.	T. Vogel
Die Anwendung einer Schmelzelectrode zur spektral-analytischen Bestimmung kleiner Mengen von Antimon und Arsen in Blei.	B. Holińska
Vakuumspektrometrische Qualitätskontrolle von Stahl.	H. Eischer
Verstellbare Blende mit Stufenfilter zur qualitativen Spektralanalyse.	O. Szakács
Spektrographische Untersuchung archäologischer Funde aus der Kupfer- und Bronzezeit.	K. Zimmer, Z. L. Szabó und P. Patay
Die Spektralanalyse von Aluminiumlegierungen unter Anwendung von geeigneten Analysenverfahren.	Z. Czajka
Eine neue, Schwärzungsunterschieden der Manganlinien beruhende Methode zur Bestimmung des Mangangehaltes von Aluminiumlegierungen—I.	L. Péter
Höhere Nachweisempfindlichkeit von Eisen bei Untersuchungen mit der doppelt rotierenden Funkenstrecke in Argon.	W. Guttmann
Eine spektrographische Methode zur quantitativen Bestimmung von Kupfer, Zink und Blei in Erzen.	M. Gralikowski and J. Podsiadlo
Probenahme bei der Spektralanalyse.	M. Gál
Eigenschaften und Verwendung der hochohmigen Spektralkohlenelektroden.	S. Meluš and S. Országh
Anwendungen der Röntgenfluoreszenz-Spektrometrie in der Stahlindustrie.	H. Eischer
Über eine erhebliche Verkürzung der Zeitdauer der spektrographischen Schnellanalysen.	W. Klimecki

Die Texte dieser Kurzreferate erscheinen in der Decembernummer der Ungarischen Zeitschrift for Chemie (*Magyar Kémiai Folyóirat*).

Weitere Auskunft ist in Dr. K. Zimmer, G.T.E., V. Szabadság tér 17, Budapest, zu erhalten.

UNITED KINGDOM

Wednesday 19 *December* 1962: **Mass Spectrometry:** *Institute of Physics and Physical Society.* Imperial College of Science and Technology, London. 9.30 a.m.

The provisional programme is as follows:

New Instrumental Techniques of Isotope Analysis.	H. W. Wilson
Field Emission and Ionisation Studies.	A. J. B. Robertson
Study of Ions and Radicals in Flames.	T. M. Sugden
Theory of Mass Spectra.	G. R. Lester
Application of High Resolution Techniques in Mass Spectrometry.	R. D. Craig
Mass Spectrometric Analysis of Very Small Quantities of the Noble Gases.	M. H. Dodson

The Honorary Secretary for the Meeting is Mr. R. M. S. Hall, Central Electricity Generating Board, Research Laboratories, Cleeve Road, Leatherhead.

Thursday 10 *January* 1963: **Annual General Meeting:** *Western Section, Society for Analytical Chemistry,* followed by Joint Meeting with *Bristol and District Section, Royal Institute of Chemistry:* **New Developments in Chelatometry—A Review of Methods and Reagents related to EDTA:** T. S. West. University, Bristol. 5.30 p.m. and 6.30 p.m.

Wednesday 23 *January* 1963: **London Discussion Meeting:** *Microchemistry Group, Society for Analytical Chemistry. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 24 *January* 1963: **Recent Advances in Polarography:** G. F. Reynolds: *Midlands Section, Society for Analytical Chemistry* and *Birmingham and Midlands Section, Royal Institute of Chemistry.* North Staffordshire Technical College, Stoke-on-Trent. 7.00 p.m.

Friday 25 *January* 1963: **Annual General Meeting:** *Scottish Section, Society for Analytical Chemistry.* Glasgow. 1.30 p.m.

Saturday 26 *January* 1963: **Annual General Meeting** followed by **Address of Retiring Chairman,** Mr. J. Markland: *North of England Section, Society for Analytical Chemistry. Old Nags Head Hotel,* Lloyd Road, Manchester. 2.15 p.m.

Wednesday–Thursday 17–18 *April* 1963: **First International Meeting in Questioned Documents.** London School of Pharmacy.

The draft programme is:

1. *Writing Materials—Paper/Instruments/Inks.*
2. *Laboratory Examinations—Chemical/Photographic/Optical.*
3. *Recent Advances/Problems in Q.D. Examinations.*

The Role of the Q.D. Examiner as an Expert Witness.

Further information is available from P. G. Baxter, 55 Cresent Road, Brentwood, Essex, England or from O. Hilton, 15 Park Row, New York 38, N.Y., U.S.A.

Wednesday–Tuesday 17–23 *July* 1963: **Fifth International Pesticides Congress.** Friends House, West Central London.

The programme will be divided into six Topics, one of which is entitled *Pesticide Residue Analysis.* The papers under this Topic will be concerned with modern analytical methods, special emphasis being given to those techniques having a wide application to current problems. The subjects envisaged are:

1. *Clean-up Processes* (including *Oxygen-Flask Combustion*).
2. *Biological and Enzymatic Methods.*
3. *Infrared Methods.*
4. *Chromatographic Methods.*
5. *Electroanalytical and New Methods.*

Opening papers for the above subjects are being arranged and other papers relating to new work in any of them are also invited. Details of (a) title of paper, (b) heading under which it is offered, and (c) three copies of a summary (150–250 words) must be sent, not later than 2 January 1963, to either Dr. H. Egan, Laboratory of the Government Chemist, Clement's Inn Passage, London, W.C.2 or to Dr. E. A. Parkin, Pest Infestation Laboratory, London Road, Slough, Bucks. Time allowed for presentation will be up to 20 min, and 5–10 min will be allowed for discussion.

General enquiries about the Congress should be directed to the Congress Honorary Secretary, Lt.-Col. F. J. Griffin, 14 Belgrave Square, London, S.W.1.

British Standards Institution announces the following **Revised British Standard:**
B.S. 1427: 1962: *Routine control methods of testing water used in industry* (Price: 12s.6d.). This covers methods of test for the following:

1. Alkalinities
2. Aluminium
3. Ammonia (free and saline)
4. Calcium
5. Chloride
6. Residual chlorine (free and total)
7. Colour
8. Dissolved oxygen
9. Dissolved salts
10. Electrical conductivity
11. Free carbon dioxide
12. Hardness
13. Hydrazine
14. Iron
15. Magnesium
16. Nitrite
17. pH value
18. Phosphates
19. Silica
20. Specific gravity
21. Sulphate
22. Sulphite

UNITED STATES OF AMERICA

Tuesday 8 *January* 1963: **Analysis of Solids by Vacuum Spark Mass Spectroscopy:** A. J. Ahearn: *New York Section, Society for Applied Spectroscopy.* Hotel Manhatten, 44 Street and 8 Avenue, New York. 8.00 p.m.

Monday–Thursday 21–24 *January* 1963: **International Symposium on Advance in Gas Chromatography.** Sheraton-Lincoln Hotel, Houston, Texas.

The programme is as follows:

Monday morning 21 *January*	
A Sensitive Ionisation Cross-Section Detector for Gas Chromatography.	J. E. Lovelock
Use of Catalytic Combustion Filaments for Qualitative Gas Chromatography.	O. F. Folmer
A New Radioactive Gas Chromatographic Detector for Identification of Strong Oxidants.	B. J. Gudzinowicz
Monday afternoon, 21 *January*	
Capillary Columns—Trials, Tribulations and Triumphs. Informal Conference	D. H. Desty
Gas Chromatography and Inorganic Chemistry.	C. S. G. Phillips
A New Column System for Gas Chromatography.	R. P. W. Scott
A New Concept in Gas Chromatography.	H. R. Felton
Tuesday morning, 22 *January*	
Theoretical and Practical Considerations on Choice of Solvent and Filling of Analytical and Preparative Columns.	E. Bayer
Rapid Scanning Mass Spectrometry: Continuous Analysis of Fractions from Capillary Gas Chromatography.	J. A. Dorsey
Studies on Efficiency of Packed Gas Chromatographic Columns.	D. D. DeFord
Recirculated Column for Preparative-Scale Gas Chromatography.	M. J. E. Golay
Tuesday afternoon, 22 *January*	
Diffusion and Mass Transfer Coefficients in Packed Gas Chromatographic Columns.	J. H. Purnell
Advances in the Theory of Plate Height in Gas Chromatography.	J. C. Giddings
Storage and Complete Automatic Computation of Gas Chromatographic Data.	H. W. Johnson, Jr.
Wednesday morning, 23 *January*	
Spreading of "Air Peaks" in Capillary and Packed Gas Chromatographic Columns.	J. H. Knox
Capillary Adsorption Columns.	R. D. Schwartz
New Types of Columns in Gas Chromatography.	I. Haslasz
Wednesday afternoon, 23 *January*	
A Simple Compact Gas-Radio Chromatogram.	A. T. James
Radio Assay of Gas Chromatographic Compounds Labelled with Tritium.	A. Karmen
Quantitative Aspects of Gas Chromatographic Separations in Biological Studies.	E. C. Horning
Thursday morning, 24 *January*	
Analysis of Flavours by Gas Chromatographic Techniques.	A. I. M. Keulemans
Electron Capture Spectrometry of Biological Compounds.	S. R. Lipsky
Determination of Lead Alkyls by Electron Capture.	H. J. Dawson
Applications of the Methylene Insertion Reaction to Component Analysis of Hydrocarbons.	I. Dvoretzky

Further information may be obtained from Dr. A. Zlatkis, Department of Chemistry, University of Houston, Texas.

Talanta, 1962, Vol. 9, p. 1075. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Contribution to the basic problems of complexometry—Part XI. Determination of titanium, iron and aluminium in the presence of each other: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (1 *October* 1962)

Improved method for calculation of error in quantitative spectrophotometric measurements: G. SVEHLA, A. PALL and L. ERDEY. (1 *October* 1962)

The oxygen flask method at low halogen levels: C. TOMLINSON. (1 *October* 1962)

Use of the argon gas chromatograph in the quantitative determination of carbon in steel: A. K. GALWEY. (1 *October* 1962)

Determination of methylol group in phenolic resins by titration with sodium methoxide and infrared absorption spectroscopy: NAOKI YOSHIMI, MASAYOSHI YAMAO, and SHIGEYUKI TANAKA. (4 *October* 1962)

New principle of activation analysis separations I. Theory of substoicheiometric separations: JAROMÍR RŮŽIČKA and JIŘÍ STARÝ. (9 *October* 1962)

A new reductimetric reagent: Iron^{II} in a strong phosphoric acid medium—Part III: Titration of vanadium^{IV} or vanadium^{V} with iron^{II} at room temperature. Determination of chromium^{VI} and vanadium^{V} in the same solution. G. GOPALA RAO and L. S. A. DIKSHITULU. (9 *October* 1962)

Titrimetric micro determination of carbon in aqueous solutions and in organic compounds: D. C. WHITE. (12 *October* 1962)

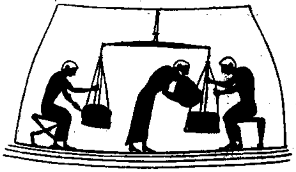
Interference of silicon in the determination of phosphorus by the vanadomolybdate method: ROBERT B. LEW and FREDI JAKOB. (15 *October* 1962)

1-Isonicotinoyl-2-salicyldene hydrazine as a new chelatometric reagent: SARVAGYA S. KATIYAR and S. N. TANDON: (25 *October* 1962)

TALANTA

An International Journal of Analytical Chemistry

VOLUME 9, 1962



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SUBJECT INDEX

AUTHOR INDEX

(*Names of authors of books reviewed are in italics*)

ERRATA

Page 1, last line of Summary: the formula should read $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

Page 9, footnote: the reference should read *Zhur. analit. Khim.*, 1959, **14** (5), 574.

Page 26, line 2: for *Sajó method*[4] read *Sajó method*[5].

Page 76, footnote: the reference should read *Talanta*, 1961, **8**, 720.

Page 85: reference 1 should read G. Frederick Smith, *Talanta*, 1962, **9**, 65.

Page 176: the legend for Fig. 1 is under Fig. 2 and *vice versa*.

Page 282: lines 25–27 should be deleted.

Page 225: the author in reference 4 should read J. S. HETMAN.

Page 328: the legend for Table II should read *Determination of copper in presence of nickel*^{II} *or iron*^{III}.

Page 405, line 13: for 1933 read 1923.

Page 295: the journal in reference 2 should read *Ind. Eng. Chem.*

Page 355, title, Summary, first paragraph and under Reagents: for 5-(3-*nitrophenylazo*)*salicylate* read 5-(4-*nitrophenylazo*)*salicylate*.

Page 359, Fig. 5: for 5-(3-*nitrophenylazo*)*salicylate* read 5-(4-*nitrophenylazo*)*salicylate*; also, the nitrophenylazo group should be shown in the 5-*position* and not in the 4-*position*.

Page 363, Zusammenfassung: for 5-(3-*nitrophenylazo*)*salizylsäure* read 5-(4-*nitrophenylazo*)*salizylsäure*.

Page 364, Résumé: for 5-(3-*nitrophénylazo*)*salicylique* read 5-(4-*nitrophénylazo*)*salicylique*.

Page 452, second paragraph of Introduction: the reagent should read *N*-(1-*naphthyl*)*ethylenediamine dihydrochloride*.

Page 457, caption to Fig. 1: the final sentence should read *Reagent solutions contain* $2{\cdot}5 \times 10^{-5}$ *mole of* $Cu(NO_3)_2$ [*or* $CuCl_2$] *and* $8{\cdot}5 \times 10^{-5}$ *mole of di-octen in hexone medium.*

Page 381, line 5: for *stimulate* read *simulate*.

Page 384: the heading on the last column of Table III should refer to the footnote by reading *Corrected*[a].

Page 387, line 8 of Introduction: this should read *complex fluoride ions. All of the fluoride, both free and in the form of tantalum complex, complexes with boron.*

Page 449, Preliminary Communication by F. Vydra and V. Marková: *Received* 13 *February* 1962. *Accepted* 22 *February* 1962.

Page 609: reference 11 should read *Talanta*, 1962, **9**, 581.

Page 813, Fig. 1: higher curve is for *concentrated hydrochloric acid* and lower curve for *constant boiling hydrochloric acid.*

Page 815, line 4 of *Comparison of results between methods and with standards:* for *oxide* read *iodide*.

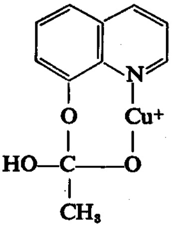
Page 817, line 2 under Table V: for 057 read 0·057.

Page 835, paper by G. Gopala Rao, P. V. Krishna Rao and K. S. Murty: *Accepted* 1 *June* 1962.

Page 917: this paper is actually *Part II* of the series.

Page 919, last line: for *expression* (1) read *equation* (1).

Page 1060: the second formula should be



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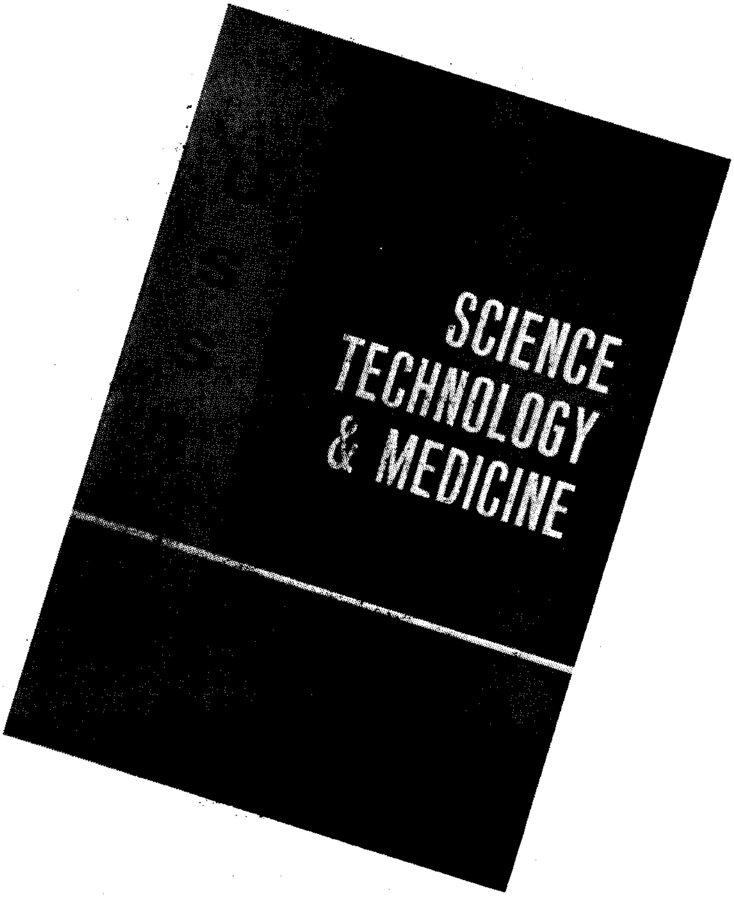
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