AN ABSTRACT OF THE THESIS OF

Mouaffac Hamdy Shakashiro for the Ph. D. in Chemistry
(Name) (Degree) (Major)

Date thesis is presented March 30, 1965

Title THE DETERMINATION OF TITANIUM, ZIRCONIUM AND HAFNIUM IN MOLYBDENUM, NIOBIUM AND TANTALUM ALLOYS BY ION EXCHANGE

Abstract approved [redacted]
(Major professor)

New alloys containing refractory metals have been developed by the aero-space industry to meet the demand for thermally resistant materials. The chemical analysis of these alloys has been handled successfully by the use of ion exchange. Hydrofluoric acid, either alone or combined with hydrochloric acid, has here-to-fore been used to dissolve these alloys and complex their constituents, thus forming metal-fluoride anionic species which are preferentially adsorbed by the resin. Large volumes of eluents, made up of rather concentrated hydrofluoric-hydrochloric acid solutions, are necessary to separate the adsorbed species.

The anion exchange behavior of titanium, zirconium, hafnium, molybdenum, tantalum and niobium, in the aqueous and mixed solvent sulfuric-oxalic acid system, was studied for three reasons:

1. The lack of methods designed for the separation and

determination of small amounts of titanium, zirconium or hafnium in molybdenum, tantalum, and niobium base alloys.

2. The inconveniences associated with the use of hydrofluoric acid solutions.

3. The recent findings in ion exchange chromatography that the introduction of an organic solvent into the eluent enhances the chance of finding the proper conditions of separation.

The distribution coefficient concept and the plate theory were utilized to find the proper conditions of separation. The effect of oxalic acid concentration, sulfuric acid percentage and methanol percentage on the elution character of the six metal ions was investigated. It was found that greater adsorption is favored at low percentage of sulfuric acid and high concentration of oxalic acid. In the presence of both acids, methanol decreases the adsorption of molybdenum, titanium, tantalum and niobium, and increases the adsorption of zirconium and hafnium.

As a result of the previous studies, 17 separation procedures, involving different combinations of the six metals investigated, were developed using the concept of the minimum height column. These procedures were tested on synthetic metal mixtures and found adequate. The range in which some of these procedures could be used is wide. As low as 0.05% titanium and 0.05% zirconium could be separated from a molybdenum base alloy and determined accurately. Large amounts of constituents can be separated and determined as well.

In addition to designing these separation procedures, some conclusions were drawn regarding the complex formation involved:

1. Titanium does not form anionic complexes in the presence of sulfuric acid and needs high level of sulfate ion to form such complexes.

2. Zirconium sulfate complexes are more stable than the hafnium ones.

3. Molybdenum forms sulfato complexes which seem to be in slow equilibrium with some unadsorbable species.

4. All six metal oxalato complexes are stable at low hydrogen ion concentration. At high acidities these complexes break down due to the repression of the oxalic acid dissociation.

Methanol tends to increase the adsorption of metal ions from strong acid solutions. In the presence of oxalic acid, however, the adsorption decreases. This is, probably, due to the suppression of the dissociation of oxalic acid.

THE DETERMINATION OF TITANIUM, ZIRCONIUM AND HAFNIUM IN MOLYBDENUM, NIOBIUM AND TANTALUM ALLOYS BY ION EXCHANGE

by

MOUAFFAC HAMDY SHAKASHIRO

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1965

APPROVED:

[redacted]

Professor of Chemistry

In Charge of Major

[redacted]

Chairman of the Department of Chemistry

[redacted]

Dean of Graduate School

Date thesis is presented 3/30/1965

Typed by Muriel Davis

ACKNOWLEDGMENT

I wish to express my sincere gratitude to Dr. Harry Freund for his help, guidance and encouragement throughout the course of this work. The mere association with this gentleman has been a great experience for me. I hope I have gained some of his tireless drive and competitive attitude.

Thanks are also due to Mr. Richard Van Santen and coworkers in the analytical laboratory of Wah Chang Corporation, Albany, Oregon, for providing the Oxine method for the determination of hafnium and zirconium, for their gift of the pure elements and for their many helpful suggestions.

Appreciation is also extended to the Agency of International Development who sponsored and supported this work.

TABLE OF CONTENTS

II. THEORY AND METHOD OF CALCULATION

LIST OF FIGURES

LIST OF TABLES

THE DETERMINATION OF TITANIUM, ZIRCONIUM AND HAFNIUM IN MOLYBDENUM, NIOBIUM AND TANTALUM ALLOYS BY ION EXCHANGE

I. INTRODUCTION

The demand of the aero-space industry for thermally resistant materials of construction has led to the development of many new alloys. Space crafts and high speed jet engines contain alloys of molybdenum, titanium, zirconium, hafnium, niobium, tantalum and tungsten. New challenges are presented to the analytical chemist because of the complexity of such alloys and the erratic behavior of the elements once in solution. The solution and chemical separation of the alloys constituents has here-to-fore been carried out in hydrofluoric acid solutions, which present the usual troubles and hazards associated with the use of this acid.

Since its use for the separation of the nuclear fission products (72)ion exchange has been established as a superior analytical tool with great promise and potential, especially for difficult separations. The ion exchange separation of hafnium from zirconium (53) and tantalum from niobium (46) could be cited as examples. Prior to ion exchange, the separation of these couples by other analytical methods was one of the most tedious in chemistry. Trace analysis is another important field where ion exchange has proved to be of great value. In a recent study, Van Erkelens (73) has demonstrated that among the three available methods for trace analysis (paper chromatography, ion exchange and solvent extraction) ion exchange is to be preferred. Only when rapidity is of great value, solvent extraction is advantageous. Among other reasons mentioned for this preference, Van Erkelens cited the simplicity of the ion exchange process, the lack of restriction on the sample size and the availability of accurate, quantitative techniques for final measurement following the separations. Despite the great progress in modern analytical methods like activation analysis and x-ray fluorescence, only in a limited number of cases is the determination of micro constituents feasible without prior chemical treatment.

Very little has been published on the analysis of refractory alloys containing small amounts of titanium, zirconium or hafnium. Considerable work, however, has been reported on the ion exchange analysis of steel alloys containing refractory metals. Most of the work employs hydrofluoric-hydrochloric acid mixtures as eluents. According to Bandi *et al.* (2) the use of hydrofluoric acid has three serious disadvantages; the hazard of skin burns, the need for special laboratory equipment of plastic or platinum and the additional separation of fluoride from most metals prior to final determination. With this in mind, we have undertaken to study the anion exchange behavior of the refractory metal ions in the oxalic-sulfuric acid system using either aqueous or mixtures of aqueous-nonaqueous solvents. Thus in selecting the proper eluent three variables must be studied: the concentrations of the two acids and the percentage of the nonaqueous solvent. The selection of the sulfuric-oxalic acid medium for this anion exchange study and the introduction of a nonaqueous solvent into that medium can be best understood by reviewing the work that has been published on the separation of the refractory metals and on the use of mixed solvents in the ion exchange process.

Hydrofluoric Acid in the Anion Exchange Separation of Refractory Metals

Most separations involving these metals have been carried out in hydrofluoric-hydrochloric acid media. This is due to the fact that hydrofluoric acid is the only inorganic acid that can dissolve refractory alloys and subsequently form the negatively charged metallic complexes that can be absorbed on the resin.

Kraus and Moore (47) were the first to point out that hafnium and zirconium could be separated through the formation of fluoride complexes which were absorbed on a Dowex-1 resin column and then eluted preferentially with 0.5 M hydrofluoric-1 M hydrochloric acid solution. This separation was immediately confirmed and improved by Huffman and Lily (32) who separated macro amounts of hafnium and zirconium using 0.01 M hydrofluoric- 0.2 M hydrochloric acid solution as the eluent. The other difficult separation of tantalum and niobium was also reported first by Kraus and Moore (46). The use of hydrofluoric-hydrochloric acid mixtures in anion exchange expanded very rapidly thereafter and more difficult and complex separations were accomplished. The separations of zirconium-niobium (48), tantalum-niobium-protactinum (45), iron-tungsten-molybdenum (51) and few others were also reported by Kraus and coworkers. In addition to affecting these separations these pioneers drew some conclusions about the existing anionic species in the hydrofluoric-hydrochloric acid solutions.

Hague, Machlan and coworkers of the National Bureau of Standards have also contributed in this field. Separation procedures for steel alloys containing titanium, tungsten, niobium and molybdenum (27) and alloys containing zirconium, titanium, niobium and tantalum (28) have been developed by these researchers. Other separations involving refractory and classical alloying metals have been reported. Wilkins (77) has devised an anion exchange method that can separate nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium and tantalum from a high temperature alloy. Freund and Miner (19) separated trace amounts of aluminum from zirconium using 0.06 M hydrochloric- 0.8 M hydrofluoric acid solution. Sugawara (71) has recently developed an ion exchange procedure for the separation of trace amounts of titanium, zirconium, molybdenum in a tungsten base alloy using concentrated hydrofluoric-hydrochloric acid mixtures. Titanium and zirconium came out in the same fraction and were subsequently separated by solvent extraction. Large volumes of concentrated eluents were used, thus making the procedure unattractive.

Oxalic Acid in Anion Exchange Separations

Oxalic acid is known to form stable complexes with all refractory metals, but because these complexes are very stable large volumes of eluents are required for stripping. This problem has been attacked by using eluents containing either low concentrations of oxalic acid or oxalic-inorganic acid mixtures. The strong inorganic acid, successfully competing with the metal for the available ligand would thus decrease the extent of metal-ligand complexation. Waker and Baldwin (75) found that niobium is taken up on Dowex-1 from 0.4 M oxalic and then eluted with 1 M hydrochloric- 0.01 M oxalic acid solution. A separation procedure of niobium and zirconium is based on that principle. Speeke and Hoste (70) have shown also that niobium and tantalum could be separated either with 0.01 M oxalic- 2 M hydrochloric or 0.5 M oxalic-1 M hydrochloric on a Dowex-1 column. Bandi and coworkers (2) used different oxalic-citric-hydrochloric acid mixtures plus hydrogen peroxide to separate zirconium, titanium, niobium, tantalum, tungsten and molybdenum, with the zirconium and titanium coming out in the same fraction. Thus a second anion exchange step was required. It is evident, that with amounts as small as 0.1 mg of either of these two metals more accurate results would be obtained if the chemical manipulation were minimized. Other organic acids have also been used. Khopkar (36) used the selective uptake of zirconium from a 5% ammonium citrate at pH 2.7-3 solution to separate that metal from strontium, lead, cadmium and cesium, which do not form stable anionic complexes at that pH and thus pass into the effluent. Titanium and zirconium could also be taken up from an ascorbate solution by means of the ascorbate form of an anion exchange resin. This principle was used to determine titanium in natural water (38).

Sulfuric Acid in Anion Exchange Separations

Owing to the weak complexing character of the sulfate ion, but few metals are retained by anion exchangers from sulfate solutions. Generally this complex formation takes place only in dilute sulfuric acid medium. Korkisch and Farag (39) found that in 0.1 M sulfuric acid solution, zirconium, hafnium, vanadium, molybdenum, tungsten, uranium and tin (II) are taken up by the strongly basic Dowex-1 resin. Rajan and Gupta (60) were the first to separate hafnium and zirconium by preferrentially eluting their fluoride complexes with 0.52 M sulfuric acid. Later, however, this method was improved by Machlan and Hague (53) who used a sulfate form of Dowex-1 resin which was loaded with a solution of hafnium and zirconium in 3.5% sulfuric acid. Hafnium, which forms less stable sulfate complexes was eluted first by the 3.5% sulfuric acid solution and zirconium was then eluted with 10% sulfuric acid. The fact that uranium in sulfuric acid exists chiefly as the negatively charged complex $UO_2(SO_4)_2^{-2}$ led to the discovery of one of the best methods for the concentration of uranium. Kraus and Nelson (49) reported that iron (III) can be absorbed from a 0.01 M sulfuric acid solution and a method for the separation of aluminum and iron was developed.

Ion Exchange in Mixed Solvents

Adsorption of many elements increases when the fraction of aqueous component is decreased by the addition of a miscible organic solvent. This has led to the expansion of ion exchange separations into nonaqueous media. The first work reported is that of Bhatnager (4) and coworkers who studied the adsorption of benzoic acid by a resorcinol-formaldehyde resin in carbon disulfide, benzene, carbon tetrachloride, methanol, ethanol, acetone and water. Later, Robinson and Mills (62) tested a porous type anion exchange resin (Doulite A-2) and found that the dry resin can remove fatty acids from acetone and Shell Solvent. They also reported the effectiveness of the resin in the removal, from nonaqueous media, of whole salts capable of forming complexes with amines. Kressman and Kichner

(52) reported that cation exchange occurs readily in mixtures of water-acetone or ethanol. Prior to 1953 these were almost the only investigations that had been made on the exchange between resins and any solutes in nonaqueous media. Since that date, however, a steady expansion has occurred. This drive was ignited by Katzin and Gebert (34) who studied the absorption of acetone solutions of lithium chloride, lithium nitrate, cobaltous chloride and nickel nitrate on chloride and nitrate form anion exchange resins. They noted that the whole salt was absorbed and suggested that the salt was taken up as a complex anion:

$$R^+X^- + MX_2 \rightleftharpoons R^+(MX_3)^-$$

Although the separation of metals as chloro complexes from aqueous hydrochloric acid solutions by anion exchange resins is an established and valuable analytical procedure, the use of partially aqueous media, instead of aqueous, has resulted in improving the convenience and broadening the scope of this type of analytical separation. For example certain anion exchange separations here-to-fore carried out in concentrated hydrochloric acid medium now can be performed in dilute hydrochloric acid containing an appropriate amount of non-aqueous solvent. The separation of nickel and cobalt may be cited. In aqueous medium this separation has been achieved with 8 M hydrochloric acid (8) while, in mixed solvents, Fritz *et al.* (21)

performed the same separation using 82% ethanol-0.3 M hydrochloric acid solution. Also it was found that some of the elements which are not absorbed at all by any resin, no matter how concentrated their hydrochloric acid solution, could be absorbed easily from a mixed solvent medium. Scandium and yttrium, neither of which form anionic complexes in hydrochloric acid (50), were separated by Wilkins and coworkers (78) in ethanol-hydrochloric acid medium. Such success led to most of reported mixed solvent work being carried out in hydrochloric-organic solvent media. Fritz and Pietrzyk (21) determined the distribution coefficients of about 15 metal ions between the strongly basic 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. Korkisch and coworkers of the Analytical Institute of the University of Vienna have contributed significantly in this field. In one of the outstanding examples of the versatility of anion exchange separations in mixed solvents, these researchers studied the distribution of thorium, uranium, aluminum, titanium and scores of other metals between mineral acid-alcohol solutions and the resin Dowex-1. They developed, accordingly, seven separation methods for uranium and/or thorium from other elements (43). These different procedures are suitable for the assay of uranium and thorium in material of greatly varying composition. The anion exchange behavior of rare earths in mixed solvents has been studied by Korkisch, Hazan and Arrehnius (41), Fritz and Green (20) and Marple (54). Separation schemes for rare earths alone or with other elements employing different varieties of nitric acid-alcohol solutions were reported. Other invesitgations about rare earths were carried out in hydrochloric acid-alcohol solutions (16, 21) and sulfuric acid-ethanol solutions (17). Group I and II elements have also been studied. Fritz and coworkers have separated magnesium from calcium (23) and calcium from strontium (24) using different nitric acid-alcohol mixtures. In a recent investigation Ruch, Tera and Morrison (63) studied the behavior of both groups I and II in Dioxane-nitric acid medium and devised a simple procedure for the separation of group II metals. They were also able to separate group I elements from group II and reach some conclusions about the effect of the dielectric constant of the nonaqueous solvent upon the distribution coefficients of the investigated metal ions. Samuelson and Sjöström (66)used 60% ethanol as an eluent for the alkali metals from a column of Dowex-2 loaded with EDTA.

The anion exchange separation of transition elements in mixed solvents has been studied extensively. Fritz and Pietrzyk (21), Kojima (37), Yoshino and Kurimura (81), Korkisch and Janauer (42) and Fritz and Rettig (22) have developed numerous separation procedures for different combinations of transition metals using mineral acid-organic solvent solutions. Gallium, indium and aluminum were also separated (40). Burstall et al. (9) eluted gold (absorbed as the cyano complex) from an anion exchange column using an acetone eluent containing 5% hydrochloric acid and 5% water.

Very interesting results have been obtained by the study of cation exchange in mixed solvents, as, for instance, by Kember et al. (35) who developed a useful method for the separation of copper and nickel using acetone containing 4% hydrochloric acid and 10% water. Other cation exchange methods in nonaqueous and mixed solvents have been reviewed by Bonner (6).

From this survey we conclude that there has been no reported investigation on the anion exchange behavior of titanium, zirconium, hafnium, molybdenum, tantalum and niobium in the aqueous or mixed solvent sulfuric-oxalic acid media. Even in other media like the hydrofluoric-hydrochloric there are no reported procedures for the separation and determination of small amounts of titanium, zirconium and hafnium in refractory base alloys. After a thorough study of the effect of the concentration of both sulfuric and oxalic acids and the percentage of the non-aqueous solvent upon the absorption of these metal ions by the strongly basic anion exchanger Dowex 1-X8, such separation procedures and few others have been developed.

II. THEORY AND METHOD OF CALCULATION

Plate Theory and the Distribution Coefficients

Like any chromatographic process, ion exchange could be treated best by the plate theory which was originated by Martin and Synge (55). This approach was applied to the ion exchange phenomenon by Mayer and Tompkins (56) and later refined by Glueckauf (25).

According to this theory the column is considered to be made up of a large number of theoretical plates. Within each plate the concentration of the solute should be small and uniform, both in the resin and the interstitial volume. This calls for a small sample which would occupy roughly 0.6-3% of the total capacity of the resin. It has also been demonstrated that excellent separations are obtained when the ion exchange equilibrium is reached in each plate before the liquid flows to the next plate. The achievement of this equilibrium is favored by the use of slow flow rates and fine particle resins. Empirically, a flow rate of 0.7 ml/min/cm^2 of column cross section in aqueous solution would be suitable. Slower flow rates are necessary in mixed solvents because the time required to attain equilibrium is much longer. Shukla et al. (68) have found that the lower the water content the slower is the ion exchange process. This is certainly a major disadvantage of chromatographic separations in mixed solvents. In 50% methanol solutions a flow rate of 0.2-0.3 ml/min/cm^2 was found adequate. The resin Dowex 1-X8 with 200-400 mesh size which was used throughout this investigation meets the equilibrium requirement of a fine particle size very well. Whenever all these prerequisites are met the elution curve will closely resemble the bell shaped Gaussian Curve.

The ion exchange separation of two or more ions, for which no information is available about their distribution between a particular eluent and a resin, could only be achieved by trial and error. The selection of column operating conditions and column dimensions are then often a matter of guesswork and usually result in "over separation", thus taking more time and chemicals than is really necessary. With the help of the distribution coefficients, plate theory could lead to the selection of the proper operating conditions for the separation of any pair of ions with any desired degree of purity.

The distribution coefficient, which may be used to predict the proper separation conditions of a particular solute from another, is defined as

$$C = \frac{\text{amount of solute in one gram of dry resin}}{\text{amount of solute in one ml of solution}}$$

Accordingly, the first practical step in devising a separation procedure is to determine the distribution coefficients of the metal ions that are to be separated. This can be done by measuring the distribution of a small amount of the metal ion (less than 0.1 milliequivalent per gram of dry resin) between a weighed amount of resin and a known volume of the proposed eluent.

These distribution coefficients can lead an experienced worker to an intelligent guess about the proper separation conditions and the dimensions of the column. This is particularly true when the ratio of one distribution coefficient to the other is larger than three. Let us assume that the three metal species A, B and C have distribution coefficients of 2, 15 and 200 respectively in a 2 molar sulfuric acid solution and the anion exchanger Dowex 1-X8. A good guess is a 6-8 cm column with an inside diameter of 2 cm filled with Dowex 1-X8. The reason for this choice could be understood empirically through relation (3) which will come later and the fact that the interstitial volume of such column is about 10 ml. According to this relation the volume U^* of eluent necessary to elute about half of solute A is 30 ml. Assuming that the elution curve of A is bell shaped it will take a volume of 20 ml to elute the second half of solute A if there is no tailing. This means that it will take about 50 ml of the 2 molar sulfuric acid to elute solute A. Regarding solute B, all that relation (3) tells is that the elution peak of this solute is at the 160 ml mark with no information about the width of the elution curve. Experience, however, tells that the elution curve of a species having a distribution coefficient of 15 is likely to begin at the 100 ml mark when a column of 10 ml interstitial volume is used. It should be pointed out that the elution curve will be certainly widened if a large amount of solute is used. The proper amount of solute is determined by the equilibrium requirements which were mentioned earlier. With this proposed column, for example, equal amounts of 0.25 milliequivalents of solutes A and B can be separated comfortably. It is presumed here that a load of 1% of the total capacity of the resin (which has a total capacity of 1.2 meq/ml wet resin) is small enough to attain equilibrium conditions. From the distribution coefficient of solute C we can also conclude that the eluent 2 molar sulfuric acid is not suitable for the elution of this solute because of the large volume needed for this elution. Another eluent for which species C has the smallest distribution coefficient possible should be used instead.

This guess should be tested and some modifications might be necessary if there is either an "over separation" or a "serious overlap" of the elution curves.

Calculation of the Minimum Height Column

A more systematic procedure for the determination of the optimum column is necessary especially when the distribution coefficients are close. A better criterion to indicate the separation characteristics of two species is the "separation factor" defined as the ratio of the distribution coefficients of these two species. Separation factors of less than two do not usually lead to "good guesses". This systematic procedure is based on the mathematical approach of the plate theory and the bell shaped elution curve.

Choosing the correct parameters in the Gaussian Curve equation the elution graph may be represented by the formula:

$$M = M^{*} e^{-\frac{P}{2} \frac{C + 1}{C} \left(\frac{U - U^{*}}{U^{*}}\right)^{2}} \qquad (1)$$

where

M = The molarity of the solute in the eluate.

M^{*} = The molarity of the solute in the eluate at the maximum of the elution curve.

C = The distribution coefficient of the solute.

P = The number of the theoretical plates in the column.

U = Volume of eluate, ml.

U^{*} = Volume of eluate at the peak of the elution graph, ml.

Rieman <u>et al</u> (61, p. 180) have calculated P in terms of other experimental parameters and found:

$$P = \left(\frac{2C}{C + 1}\right) \left(\frac{U^{*}}{U_a - U^{*}}\right)^{2} \qquad (2)$$

where U_a is the value of U at $M = \frac{M^*}{e}$. These parameters are illustrated in Figure 1. Mayer and Tompkins (56) have also shown:

$$U^* = CV + V \tag{3}$$

where V is the interstitial volume of the column measured in milliliters. It is apparent from relation (3) that U^* can be determined indirectly by measuring the distribution coefficient of the investigated species and the interstitial volume of the column. On the other hand, it could be determined from the experimental elution curve. The comparison of these two values was used to give an idea about the agreement between the theoretical treatment of the ion exchange process and the experimental results. Throughout this investigation it was found that a deviation of 2-10% exists, which is reasonably satisfactory.

Based on the preceding equations and the probability equation Rieman <u>et al</u> (61, p. 183) have calculated the minimum column length that will yield a quantitative separation of any pair of ions to any desired degree of purity. This is expressed by the relation:

$$\sqrt{H} = \frac{t}{C_2 - C_1}\left[\sqrt{\frac{C_2(C_2 + 1)}{p_2}} + \sqrt{\frac{C_1(C_1 + 1)}{p_1}}\right] \tag{4}$$

For C values higher than five an approximation could be made with an error of less than 0.5% and equation (4') could then be used instead.

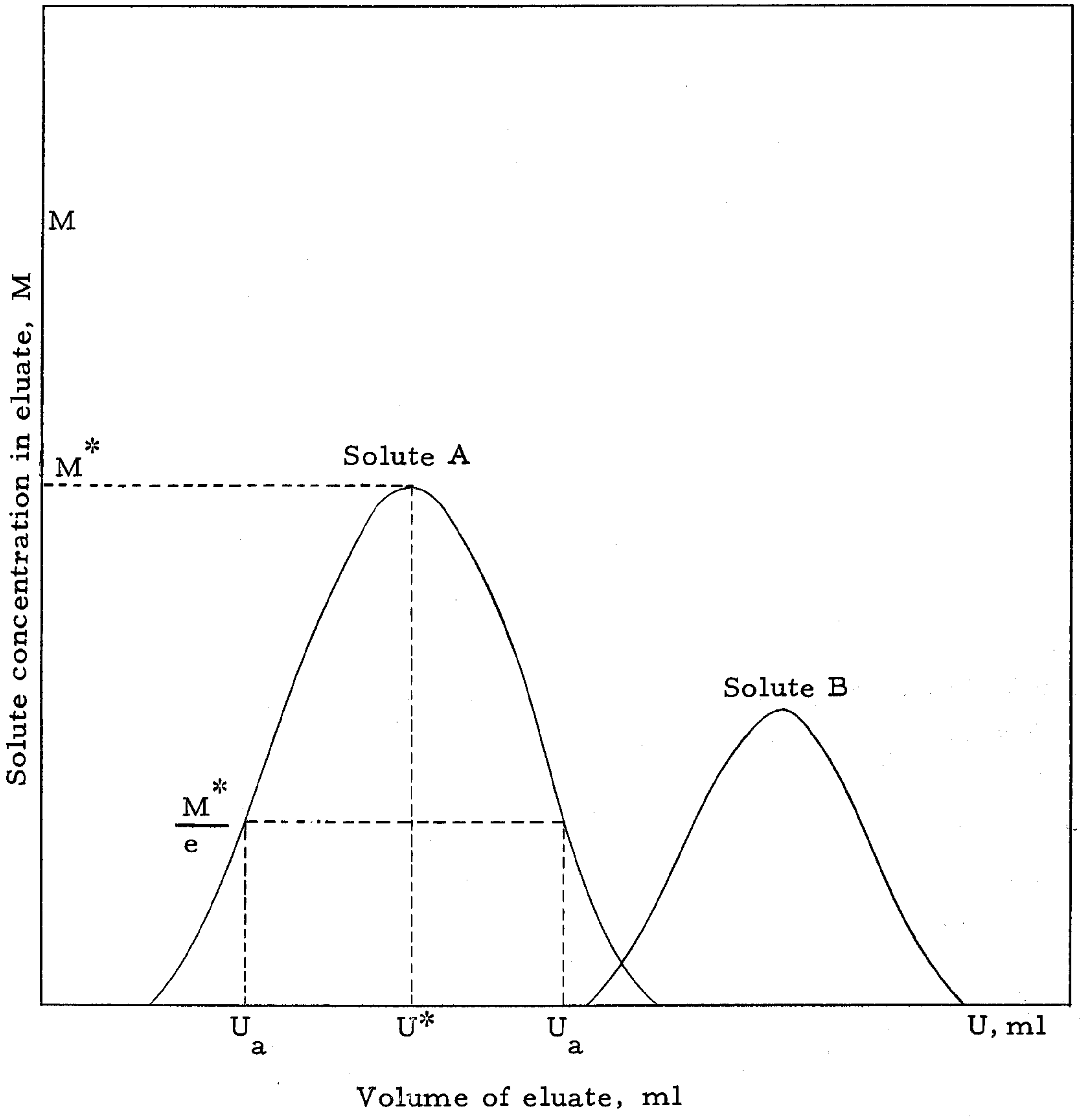

Figure I. Significance of Terms in the Elution Curve.

$$\sqrt{H} = \frac{t}{C_2 - C_1}\left[\frac{(C_2 + 0.5)}{\sqrt{p_2}} + \frac{(C_1 + 0.5)}{\sqrt{p_1}}\right] \qquad (4')$$

where:

H = The height of column necessary to achieve the desired separation, cm.

p_1, p_2 = Number of plates of solute 1 and solute 2 per cm of column.

t = Cross contamination factor.

It follows that

$$p_1 = \frac{P_1}{\ell} \qquad p_2 = \frac{P_2}{\ell} \qquad (5)$$

where ℓ is the length of column that contains P plates. In summary, the systematic procedure to find the minimum column length which can achieve a desired separation of two ions consists of the following steps:

1. The distribution coefficients of the two ions are measured in a range of concentrations of the proposed eluent.

2. A particular eluent is selected for which the separation factor (the ratio of the distribution coefficients) is as large as possible.

3. Each ion is eluted separately by that eluent through a given column of length ℓ . From the elution graph U^* and U_a could be determined and the number of theoretical plates involved is calculated from relation (2). Dividing these values by ℓ will give the number of plates p_1 and p_2 per cm for each solute.

4. The height of the column, H , is calculated using either relation (4) or (4'). The cross contamination factor, t, is determined by deciding on an acceptable value for the area under the curve and then referring to the normal curve of error in the

mathematical tables of the Handbook of Chemistry and Physics. For an example, if a 0.05% cross contamination factor is chosen as the limit of purity for a particular separation t would have a value of 3.29. If the constituents are present in the sample in widely differing amounts a smaller degree of cross contamination should be chosen. A value of 3.74 for t would correspond to a 0.01% cross contamination (61, p. 185).

Cornish (13) has suggested an interesting procedure for the determination of the optimum length of the column. The only experimental information needed, according to this procedure, is the separation factor of the two ions. This separation factor and the desired cross contamination factor are used to determine the number of the necessary plates from a prepared chart. The mesh size of the resin and the desired flow rate are then used to determine the height equivalent of a theoretical plate (HETP) from another chart. Subsequently, the number of plates multiplied by the height equivalent of a theoretical plate gives the optimum column length. The cross section of this column is determined, according to Cornish, by the amount of solutes to be separated. Unfortunately this simplified procedure of Cornish could not be applied successfully in this research. In one case a titanium-zirconium separation was developed using a 15 cm column with an inside diameter of 1.9 cm. The Cornish procedure predicted a 4 cm column with an inside diameter of less than 0.5 cm. This disagreement is probably due to the difficulty of attaining equilibrium in the sulfuric-oxalic complexing medium. It should also be remembered that the ion exchange process itself is a very complicated one because of the many factors that influence the absorption and the elution of a particular ion. In addition, the premises, upon which this calculation method is based, can seldom be fulfilled in all respects. This could be proved easily; two different species having the same distribution coefficients in two different eluents and two different forms of anion exchangers, will very rarely have the same elution curve.

Most of these reservations are not valid when the optimum column length is calculated according to the systematic procedure with the previously described four steps. The number of plates per cm, which is the reciprocal of the height equivalent of the theoretical plate is calculated from the experimental elution graph data. This means that all factors that affect that particular separation process are taken into account. In other words two separate elution processes for the two solutes are used to determine the optimum conditions for their separation. This is far superior to the prediction of these conditions from charts made on theoretical basis.

Throughout most of this investigation the systematic procedure has been used. In some cases, however, when the separation factor is large the conditions of the elution and the dimensions of the column were predicted directly without any calculations. In all cases the dimensions are chosen so that an interval of 50-80 ml of eluate is present between the last detectable portion of the first solute and the first detectable portion of the second solute, with the separation made at the middle point of this interval. This would achieve complete separation even if certain factors that influence the separation, such as flow rate and the percentage of the non-aqueous solvent are inadvertently a little different than expected.

III. THE DETERMINATION OF DISTRIBUTION COEFFICIENTS

Objective

The objective of this part of the investigation is to study the anion exchange behavior of titanium, zirconium, hafnium, molybdenum, niobium and tantalum in sulfuric-oxalic acid media using Dowex 1-X8 (200-400 mesh) as the anion exchanger. The study was conducted both in aqueous and partially aqueous solutions containing an organic solvent. Methanol was chosen as the organic solvent for reasons that will be discussed later. By varying the concentrations of the acids and the percentage of methanol the effect of these three factors on the elution of the six metal ions could be studied. It was hoped that such a study would lead to good separation procedures involving different combinations of these metals. Hopefully this study might also yield useful information on the formation of sulfate-oxalate complexes of these metals as well as information on the influence of the organic solvent on complex formation. The effect of sulfuric acid concentration on the nature and distribution of oxalate complexes of these metal ions would also be revealed.

Apparatus

1. For the colorimetric determinations of all six metals, three models of Beckman spectrophotometers were used depending

on their availability at the time of measurement and the spectral region of maximum absorbance. The Beckman model B was used frequently especially when the measurement was in the visible region of the spectrum. A Beckman model DB was also used in the visible and exclusively in the ultraviolet region for the molybdenum determination by the hydrogen peroxide method, where the maximum absorbance is at 330 mμ. The Beckman DU spectrophotometer was used at the start of the investigation until it was realized that the model B gave comparable results with less time and effort. The high precision associated with the DU is not necessarily needed because of the approximate calculations deduced from the plate theory.

2. A Labline automatic shaking bath with variable speed was used for equilibration studies. The speed was adjusted so that the contents of the stoppered Erlenmeyer flasks would mix thoroughly without splashing.

3. A Beckman Zeromatic pH meter equipped with calomel and glass electrodes was used for pH measurements.

Preparation of Metal Stock Solutions

Zirconium, Titanium and Hafnium

Separate stock solutions containing 1 mg metal per milliliter were prepared from the pure metals by dissolving 500 mg of each metal in a platinum dish with 1:1 nitric acid and the minimum amount of hydrofluoric acid, followed by fuming to dryness with sulfuric acid. The residue was then dissolved in 5% sulfuric acid, transferred quantitatively to a 500 ml volumetric flask and made up to volume with the 5% sulfuric acid solution. To check the exact metal content of the three solutions a Cupferron precipitation was performed. This is essentially the standardization procedure of Hillebrand, Lundell, Bright and Hoffman (31, p. 572). Exactly 50 ml of each of the stock solutions were used for analysis. These aliquots were diluted with water to 200 ml and sufficient sulfuric acid was added to bring the acidity to roughly 10% by volume. The resulting solutions were cooled to 5-10° C and then precipitated each with 50 ml of 6% cooled Cupferron solution. The precipitates were filtered and washed several times with a 1% Cupferron-3% sulfuric acid solution. The filter papers and precipitates were placed in previously weighed crucibles, dried in the oven and the paper burned off at 300° C with a final ignition at approximately 1200° C. The crucibles were cooled, weighed and the metal content of the stock solutions in mg/ml calculated. The recovery was better than 99% for all three metals.

Molybdenum

This metal can be dissolved without the use of hydrofluoric acid. The 1 mg/ml stock solution was prepared from pure metal obtained from the Wah Chang Corporation of Albany, Oregon. Five hundred milligrams of molybdenum powder were placed in a platinum dish (this could also be carried out in a 100 ml beaker) followed with 20 ml of 1:4 sulfuric acid. The dish was heated gently for about five minutes on a hot plate. Approximately 2 ml of concentrated nitric acid were added dropwise and the heating continued until the metal dissolved completely. The solution was evaporated and fumed until the volume of sulfuric acid had decreased to about 3 ml. The concentrated acid solution was cooled, diluted to about 20 ml with distilled water and transferred quantitatively to a 500 ml volumetric flask. Forty-seven milliliters of concentrated sulfuric acid and enough distilled water were finally added to make up to the mark. The exact molybdenum content per milliliter of this 10% sulfuric acid solution was determined gravimetrically by precipitation with α-benzoinoxime (31, p. 310). An aliquot of 50 ml of the stock solution was cooled to a temperature of 5-10° C. Twenty-five milliliters of 2% α-benzoinoxime in alcohol were added slowly with continuous stirring followed with sufficient bromine water to tint the solution a pale yellow. The excess of bromine water is present in order to counteract a tendency toward a slight reduction of molybdenum with consequent incomplete precipitation. Five milliliters of the α-benzoinoxime were then added with stirring to the cooled solution. A little macerated filter pulp was added and the solution was filtered through a close texture filter paper (Whatman no. 5). The precipitate was washed with 1% sulfuric acid solution, transfered to a previously weighed porcelain crucible, charred over a low gas flame and finally ignited to a constant weight at 550° C. The crucible was cooled, weighed and the metal content of the stock solution calculated. The recovery was 98-99%.

Niobium and Tantalum

Separate stock solutions containing 1 mg metal/ml were prepared from the pure metals by dissolving 250 mg of each with 20 ml of 1:1 hydrofluoric acid and 3 ml of concentrated nitric acid in a platinum dish. The resulting fluoride solution was fumed with 10 ml of concentrated sulfuric acid to a final volume of about 3 ml. Fuming to dryness is undesirable because the dry sulfate residue, is then very difficult to dissolve. This partial fuming was repeated three times to ensure the complete removal of hydrofluoric acid. In the case of niobium the walls of the dish were washed down with 5 ml of 1M oxalic acid followed by the addition of 20 ml of the same solution. The platinum dish was heated gently until the niobium residue was dissolved completely. The tantalum sample was treated in a similar manner except that 1 M ammonium oxalate solution was used in place of the1 M oxalic acid solution. Tantalum, when present in comparatively large amounts, seems to complex more readily with ammonium oxalate than with oxalic acid. The contents of the two dishes were then transfered to two separate 250 ml volumetric flasks followed by the addition of 22 ml of concentrated sulfuric acid to each flask. After cooling, enough distilled water was added to bring the volume to the mark. Thus, the final solution was 0. 1 M in total oxalate and 10% in sulfuric acid. The exact metal content of each solution was determined in a similar manner to that of zirconium.

Pretreatment of Anion Exchange Resin

The anion exchange resin Dowex-1 "Analyzed Reagent", 200-400 mesh, having eight percent divenylbenzene crosslinkages was used. This strongly basic resin is commercially available in the chloride form, with a moisture content of 40%. The preparation of this resin for the use in the distribution coefficient studies was carried out in the following manner: Approximately 100 gr of resin were transfered to a 500 ml beaker and suspended in 250 ml of 5% hydrochloric acid. Unless otherwise specified all the acid percentages are by volume. The coarser fraction was allowed to settle for ten minutes and the fines removed by decantation. This process was repeated several times, until most of the fine material was removed. The beaker contents werethen transfered to a 30 cm high glass column, with an inside diameter of 2. 54 cm (1 inch) and whose stem was plugged with glass wool. To remove the remaining fines the loaded column was washed with 100 ml of 10% nitric acid followed by alternate 100 ml washings of 10% and 25% hydrochloric acid. Finally the transfer of the chloride form into the sulfate form was accomplished by washing with 5% sulfuric acid. The complete removal of the chloride ion was followed by testing portions of the eluate with silver nitrate solution. The resin bed was washed with about 500 ml of distilled water, transfered to a Buchner funnel and filtered by suction. To remove organic material that might be present, the resin was washed with 200 ml of absolute alcohol and 200 ml of reagent acetone respectively while still on the Buchner funnel. The resin was finally air dried to a constant weight. The water content of such treated resin is 5-10% by weight.

Colorimetric Procedures

Titanium

A few measurements were carried out using the hydrogen peroxide method (67, p. 870). The low sensitivity of the peroxide method led to adoption of the Tiron method of Yoe and Armstrong (80). This method is about 20 times more sensitive than the hydrogen peroxide method, permitting detection of less than 0. 1 p. p. m. Titanium.

Reagents

Tiron solution: Four grams of disodium-1,2-dihydroxybenzene-3, 5-disulfonate (Tiron) were dissolved and diluted to 100 ml with distilled water. This water clear solution becomes pale yellow after aging several weeks and should then be discarded.

Buffer solution: A buffer solution having a pH of 4.7 was prepared by mixing equal volumes of 1 M acetic acid and 1 M sodium acetate solutions.

Standard titanium solution: A titanium solution containing 0.01 mg/ml was prepared from the stock solution prepared earlier (p. 24), by diluting with 5% sulfuric acid.

Dilute ammonium hydroxide solution: Ten ml of the concentrated ammonium hydroxide solution (28%) were diluted to 100 ml with distilled water.

Procedure

The calibration curve was prepared by transfering 0.0, 1.0, 2.0, 5.0, 7.0, 8.0 and 10.0 ml of the standard titanium solution to 100 ml thoroughly cleaned beakers followed with 5 ml of the Tiron reagent solution. Sufficient dilute ammonium hydroxide solution was then added to make the solution neutral to Congo red paper. The contents were quantitatively transfered to 50 ml volumetric flasks and 5 ml of the buffer solution were added. The flasks were finally made up to volume with distilled water and the absorbances were measured against distilled water at 410 mμ using 1 cm matched cells.

To measure the titanium content of the unknown solution an appropriate aliquot of that solution was treated in the same manner and the titanium content was read from the calibration curve. Although Yoe and Armstrong listed the limit of interference of oxalic acid as 500 p. p. m., it was observed that about 4-5 times as much could be tolerated without any significant difference in absorbance readings. Oxalic acid was destroyed, however, when the content was greater than 2000 p. p. m.

Zirconium and Hafnium

Three different spectrophotometric methods were used until it was learned that R. Van Santan and coworkers of the analytical laboratory of Wah Chang Corporation, Albany, Oregon, had developed a superior method employing Oxine. The first method used was the Alizarine Red S method (67, p. 968). Due to the inconsistancy of the results the Chloranilic method (67, p. 976) was then employed. Finally, the Xylenole Orange method of Cheng(10) was adopted because he claimed that hafnium could be determined in presence of zirconium by masking the zirconium content of the sample with hydrogen peroxide (11). Although Cheng's procedure could not be reproduced neither here nor in Wah Chang analytical laboratory, Xylenole Orange was found superior for the separate determination of zirconium and hafnium than the previous methods. This is probably due to the fact that trace amounts of sulfate ion could be tolerated according to this procedure. In these three methods hafnium and zirconium colored chelates were developed in dilute hydrochloric or perchloric acid solutions. Due to the fact that the exchange studies were carried out in sulfuric-oxalic acid media the complete removal of the sulfate or oxalate was necessary. The Xylenole Orange method can tolerate only 2 micro moles of sulfate ion in 25 ml flask. Removal of excess sulfate was accomplished by the precipitation of zirconium or hafnium as hydrates with ammonium hydroxide and the subsequent separation of these hydrates from their solution by centrifuging. Repeated centrifuging and washing of these hydrates was necessary to ensure efficient removal of sulfate or oxalate ions. Failure to remove these anions would result in erratic results when hafnium or zirconium is determined with either alizarine red S or chloranilic acid. The Xylenole Orange method is superior to the two previous methods because it is practically impossible to remove all traces of these complexing anions.

Despite this advantage of the Xylenole Orange method it is not suitable when the zirconium or hafnium level of a large volume of eluate is less than 1 mg. Actually in the anion exchange separation of less than 0. 1% zirconium and 0. 1% titanium in a molybdenum base alloy, which will be described later, the eluate fraction of zirconium contained only 0. 1 mg of that metal. No spectrophotometric method that includes a precipitation step and five or six washings of the centrifuged precipitate can possibly give accurate results. A method which can determine such small amount of zirconium or hafnium with a minimum of chemical manipulation is necessary. Fortunately such method, based on the extraction, with chloroform, of zirconium and hafnium Oxinate, was in the process of development in Wah Chang analytical laboratory (74) during our work on those alloys. This determination can be carried out in presence both of sulfuric and oxalic acids and posseses a high sensitivity (0.1 p. p. m. metal detectable).

Reagents

Tartaric acid solution: Twenty grams of Reagent Grade tartaric acid were dissolved and diluted to 100 ml with distilled water.

Ammonium chloride solution: Twenty-five grams of Reagent Grade ammonium chloride were dissolved and diluted to 100 ml with distilled water.

Oxine-acetone solution: Five grams of Analytical Reagent 8-hydroxyquinoline (Oxine) were dissolved and diluted to 100 ml with acetone.

Ammonium hydroxide solution: Fifty ml of concentrated ammonium hydroxide were diluted to 100 ml with distilled water.

Reagent Grade chloroform: This reagent was used as received.

Standard zirconium and hafnium solutions: Solutions containing 0.01 mg metal/ml were prepared from an appropriate stock solution prepared earlier (p. 24) by dilution with 5% sulfuric acid.

Procedure

The calibration curve for either hafnium or zirconium was prepared by transfering 0.0, 1.0, 2.0, 5.0, 7.0, 8.0 and 10.0 ml of the standard solution to thoroughly cleaned 100 ml beakers, followed by 5 ml of the 20% tartaric acid solution and 5 ml of the 25% ammonium chloric solution. Sufficient distilled water was added to each beaker to permit the potentiometric measurement of pH with a glass electrode. The pH was brought to 9.0 by the dropwise addition of concentrated ammonium hydroxide solution from a burette. One milliliter of the 5% oxine solution was then added and the solutions were permitted to stand for a period of 45 minutes. The solution was then transfered to a 100 ml separating funnel, 25 ml of the Reagent Grade chloroform added, and the mixture was shaken well for a period of about two minutes. The chloroform layer was then transfered to a dry 25 ml volumetric flask and the absorbance was read at 386 mμ against a blank which was prepared in exactly the same manner.

The zirconium or hafnium content of an unknown solution was determined by taking an appropriate aliquot and treating it according to the previous procedure.

Molybdenum

Although the thiocyanate method is more sensitive, the hydrogen peroxide method (69, p. 377) was found adequate and simple. This method is based on the formation of a pale yellow peroxymolbdic acid which has a maximum absorbance at 330 mμ. The Beckman spectrophotometer model DB was used for these UV measurements. Because oxalic acid decreases the color intensity of the molybdenum complex the amount of this acid was kept constant throughout the calibration curve and all subsequent determinations. The amount of sulfuric acid present was also found to decrease the absorbance of the complex but to a lesser degree, thus making it necessary to maintain a constant sulfuric acid level.

Reagents

Sulfuric acid solution: Ten ml of concentrated sulfuric acid were diluted to 100 ml with distilled water.

Reagent Grade 3% hydrogen peroxide.

One tenth molar oxalic acid solution.

Standard molybdenum solution: Ten ml of the molybdenum stock solution prepared earlier (p. 25)were diluted to 100 ml with 10% sulfuric acid solution.

Procedure

The calibration curve was prepared by transfering 0.0, 1.0, 2.0, 5.0, 7.0, 8.0 and 10.0 ml of the standard molybdenum solution to 25 ml volumetric flasks followed by 1 ml of the 1 M oxalic acid and enough 10% sulfuric acid to bring the final content to 1 ml of concentrated sulfuric acid in each flask. Two ml of 3% hydrogen peroxide were then added and the flasks were made up to volume with distilled water. Absorbance measurements were made at 330 mμ, against a water blank.

To determine the molybdenum content of any solution an appropriate aliquot of that solution was transfered to a 25 ml volumetric flask and treated in the same manner. The final solution should be 0.04 M in oxalic acid and 4% by volume in sulfuric acid.

Niobium

Both niobium and tantalum form soluble, yellow complexes with pyrogallol in ammonium oxalate solution. Tantalum, however, has maximum absorbance in the acid pH region while niobium absorbs most strongly in a slightly alkaline solution. Based on this fact Wood and Scholes (79) developed a colorimetric method for the determination of niobium. This method was adopted for this investigation with some modifications to suit the sulfuric-oxalic acid system in which the exchange studies were made.

Reagent

Pyrogallol-sodium sulfite solution: Four grams of Reagent Grade pyrogallol and 10 grams of Reagent Grade sodium sulfite were dissolved and diluted to 100 ml with distilled water.

Dilute ammonium hydroxide solution: Twenty ml of concentrated ammonia were diluted to 100 ml with distilled water.

Sulfuric-oxalic acid solution: A 10% sulfuric acid in 0.1 M oxalic solution was prepared by mixing 100 ml concentrated sulfuric acid with 100 ml of 1 M oxalic acid and diluting with distilled water.

Standard niobium solution: Ten ml of the stock nobium solution prepared earlier (p. 27) were diluted to 100 ml with the 10% sulfuric-0.1 M oxalic acid solution.

Procedure

The calibration curve was prepared by transfering 0.0, 1.0, 2.0, 5.0, 7.0, 8.0 and 10.0 ml of the standard niobium solution to thoroughly cleaned beakers followed by adding the proper volume of the 10% sulfuric-0.1 M oxalic solution to have a final volume of 10 ml in each beaker. Ten milliliters of distilled water were then added followed by enough 20% ammonium hydroxide solution to bring the pH to 2.5. At this point 10 ml of the 4% pyrogallol-10% sodium sulfite solution were added, and the pH was adjusted again to 6.4-6.5 with the 20% ammonium hydroxide solution. By the addition of the main amount of 20% ammonia, before the pyrogall solution, the evolution of sulfur dioxide is avoided. The beaker contents were then transfered to 50 ml volumetric flasks and adjusted to the mark with distilled water. The absorbance measurements were taken at 410 mμ against water.

To determine the niobium content of a solution, an appropriate aliquot of that solution was transfered to a 50 ml volumetric flask and tested in the same manner. Like molybdenum the final solution should be 0.04 M in oxalic acid in 4% by volume in sulfuric acid.

Tantalum

Pyrogallol seems to be the best reagent for the colorimetric determination of this element which is lacking in characteristic color reactions. Recently a new method (33) has been developed for this determination based on the extraction of the tantalum-malachite green complex with benzene which has a maximum absorbance at 635 mμ. Although this method is more sensitive the pyrogallol method was preferred because of its simplicity.

Reagents

Pyrogallol solution: Twenty grams of Reagent Grade pyrogallic acid, four grams of Reagent Grade ammonium oxalate and 2. 5 ml of concentrated sulfuric acid were dissolved and diluted to 100 ml with distilled water.

Ammonium oxalate solution: Four grams of Reagent Grade ammonium oxalate were dissolved and diluted to 100 ml with distilled water.

Sulfuric-oxalic acid solution: A 10% sulfuric 0. 1 M oxalic acid solution was prepared by mixing 100 ml concentrated sulfuric acid with 100 ml of 1 M oxalic acid and then diluting with distilled water.

Standard tantalum solution: Ten ml of the stock tantalum solution prepared earlier (p. 27) were diluted to 100 ml of 0. 1 M oxalic-10% sulfuric by adding the proper amounts of both acids and then completing the volume with distilled water.

Procedure

The calibration curve was prepared by transfering 0. 0, 1. 0, 2. 0, 5. 0, 8. 0 and 10. 0 ml of the standard tantalum solution to 25 ml volumetric flasks, followed with the proper volume of the 10% sulfuric-0. 1 M oxalic acid solution to have a final volume of 10 ml in each flask. Five ml of the 4% ammonium oxalate solution were then added and 10 ml of the pyrogallol reagent solution completed the volume of each flask to the mark. Absorbance measurements were taken at 400 mμ against water.

To determine the tantalum content of a solution an appropriate aliquot of that solution was treated according to the previous procedure. Here, too, the final solution should be 0. 04 M in oxalic acid and 4% in sulfuric acid because these acids affect the absorbance readings to some extent.

Procedure of Distribution Coefficient Determination

The distribution coefficient, which is defined as the metal ion uptake of 1 gram dry resin divided by the metal ion content of 1 ml external solution, was determined by the batch method. Approximately 1 gr of the air dried resin prepared earlier (p. 28) was placed in a 125 ml glass stoppered Erlenmeyer flask, followed by exactly 5 ml of the metal stock solution and the proper amounts of dilute acids and water to bring the final volume to 50 ml. In the mixed solvents studies, varying amounts of methanol were also added. For example, titanium run in 6% sulfuric - 0. 025 M oxalic - 50% methanol was carried out by placing the following reagents in the 125 ml Erlenmeyer flask:

One gram air dried resin.

Five milliliters of the titanium stock solution
(1 mg metal/ml in 5% sulfuric acid).

Twenty-five milliliters of Reagent Grade methanol.

Two-and-a-half milliliters of 0. 5 M oxalic acid.

Eleven milliliters of 25% sulfuric acid.

Six-and-a-half milliliters of distilled water.

The stoppered flask was shaken for a period of time depending on the amount of methanol present. An over night period (about 12 ± 1 hours) was found adequate for runs containing up to 70% methanol. Only few experiments with higher methanol percentage were carried out. In such cases 24 hour shaking was satisfactory. For exchange studies conducted in aqueous solutions equilibrium could be reached within a few hours. To ensure the attainment of equilibrium, however, all aqueous experiments flasks were shaken for six hours. The five milligrams metal ion amount present in each flask represents as high as 0.1045 milliequivalent in the case of titanium and as low as 0.0276 milliequivalent in the case of tantalum which has the highest atomic weight among the six metal ions investigated. Taking into account the fact that the resin has a total exchange capacity of approximately 2 meq/g of dry resin (5-10% moisture content) it was concluded that the metal ion load of any of these runs occupies between 5.2% and 1.4% of the total capacity of the resin. Only titanium occupies a little high percentage of the exchange cites of the resin. All other five metal ions are within the equilibrium requirements of the plate theory. The high percentage of titanium was tolerated, however, because this metal does not form strongly stable anionic complexes at the specified acid concentrations used for separations and hence is not tightly held by the resin. When equilibration was achieved, the content of each stoppered flask was filtered into a 50 ml volumetric flask. Two milliliters of distilled waters were used to wash each stoppered flask then poured on the resin present in the filter paper. The final volume was 46-48 ml. The loss of solution is apparently due to mixing and evaporation.

Depending on the sensitivity of the spectrophotometric method used, a suitable aliquot was taken from each flask for analysis. In the case of titanium, hafnium and zirconium, one ml aliquot was quite enough while in the case of molybdenum, tantalum and niobium 10 ml aliquot was necessary. Because a 10 ml aliquot could be measured more accurately than a 1 ml aliquot, the titanium, hafnium, and zirconium solutions were diluted ten times and 10 ml aliquots were used.

To illustrate how the distribution coefficient was finally calculated,the case of titanium in 6% sulfuric-0. 025 M oxalic could be cited. The final volume of the solution after six hours shaking was 48 ml and the analysis of 1 ml aliquot of this solution with Tiron showed that the 48 ml contained 4. 57 mg titanium.

$$C = \frac{5 - 4.57}{\frac{4.57}{48}} = 4.5$$

It is clear that this result is approximate because the exact volume of the solution in equilibrium with the 1 gr resin is not accurately known. Owing to the approximate character of the calculations and results based on the plate theory, these numbers are quite adequate.

A check on the validity of these distribution coefficient values and their agreement with the experimental elution curves is made later. In mixed solvent experiments methanol was evaporated from the analyzed fraction of the solution by heating. For each metal ion, the resin remaining on the filter papers was flushed into a beaker. When this resin accumulated to about 50 gr it was packed in a column and the metal ion was eluted completely by a suitable eluent, so that the resin could be used again.

Results

Due to the fact that sulfuric acid, oxalic acid and methanol concentrations influence the distribution coefficients, one parameter was varied while the other two were kept constant. In Figure II the distribution coefficients of titanium, hafnium, zirconium, and molybdenum are plotted as functions of sulfuric acid percentage. The absence of niobium and tantalum from this figure is explained by the fact that the ionic species of these two metals hydrolyze in dilute sulfuric acid. It is noted that titanium, of the four metals does not form any stable aniomic species even in 2% sulfuric acid solution. Hafnium forms more stable anionic species with sulfuric acid. As

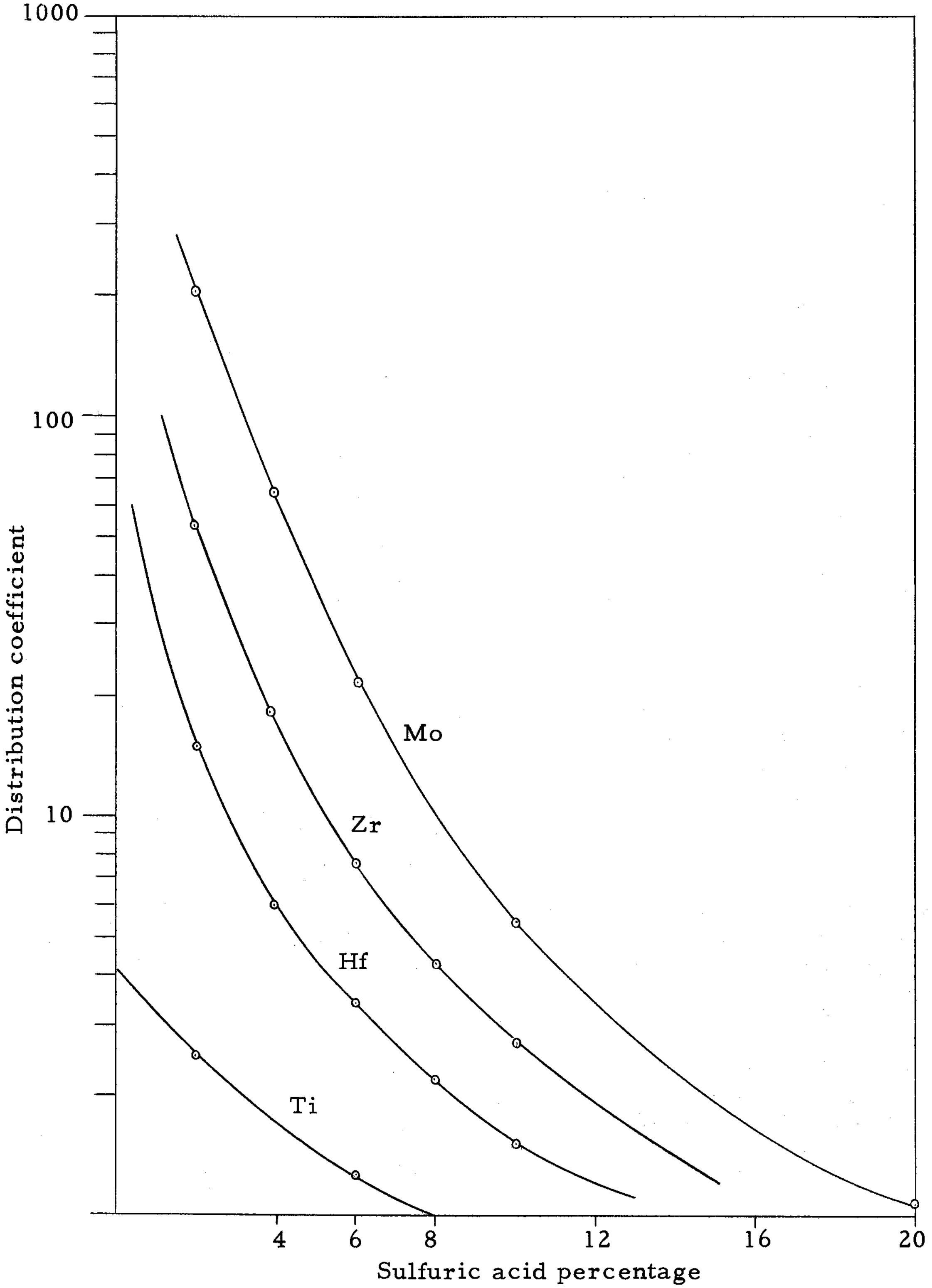

Figure II. Distribution Coefficients of Titanium, Zirconium Hafnium and Molybdenum vs. Sulfuric Acid Percentage.

a matter of fact when a load consisting of a mixture of 25 mg titanium and 25 mg hafnium in 25 ml of 2% sulfuric acid, was absorbed on a 15 x 1.9 cm column, a large fraction of the titanium passed through the column with the sample solution. The sulfate anionic species of zirconium are also stronger than the hafnium anionic species and around the 3% level the difference in the values of the distribution coefficients is sufficient to make the separation of hafnium and zirconium possible (see procedure no. 18 in Table 1, page 74). Molybdenum, of the four metals, forms what seems to be the strongest anionic species in sulfuric acid. An elution study, however, made on a 20 x 2.54 cm column, showed that at the 3% sulfuric acid level (C = 110) very small amounts of molybdenum were eluted prematurely. This is evident in Figure III.

For all these four metal ions an increase in the sulfuric acid percentage tends to suppress the formation of the metal-sulfate anionic species.

The introduction of a small amount of oxalic acid increases the distribution coefficients especially at low sulfuric acid percentages. This is quite evident from Figures IV and V. These figures indicate that titanium begins forming stable oxalate complexes as the level of the oxalic acid increases. Molybdenum also appears to be strongly complexed by oxalic acid. The premature elution of molybdenum which was noticed earlier when the metal is complexed by sulfuric

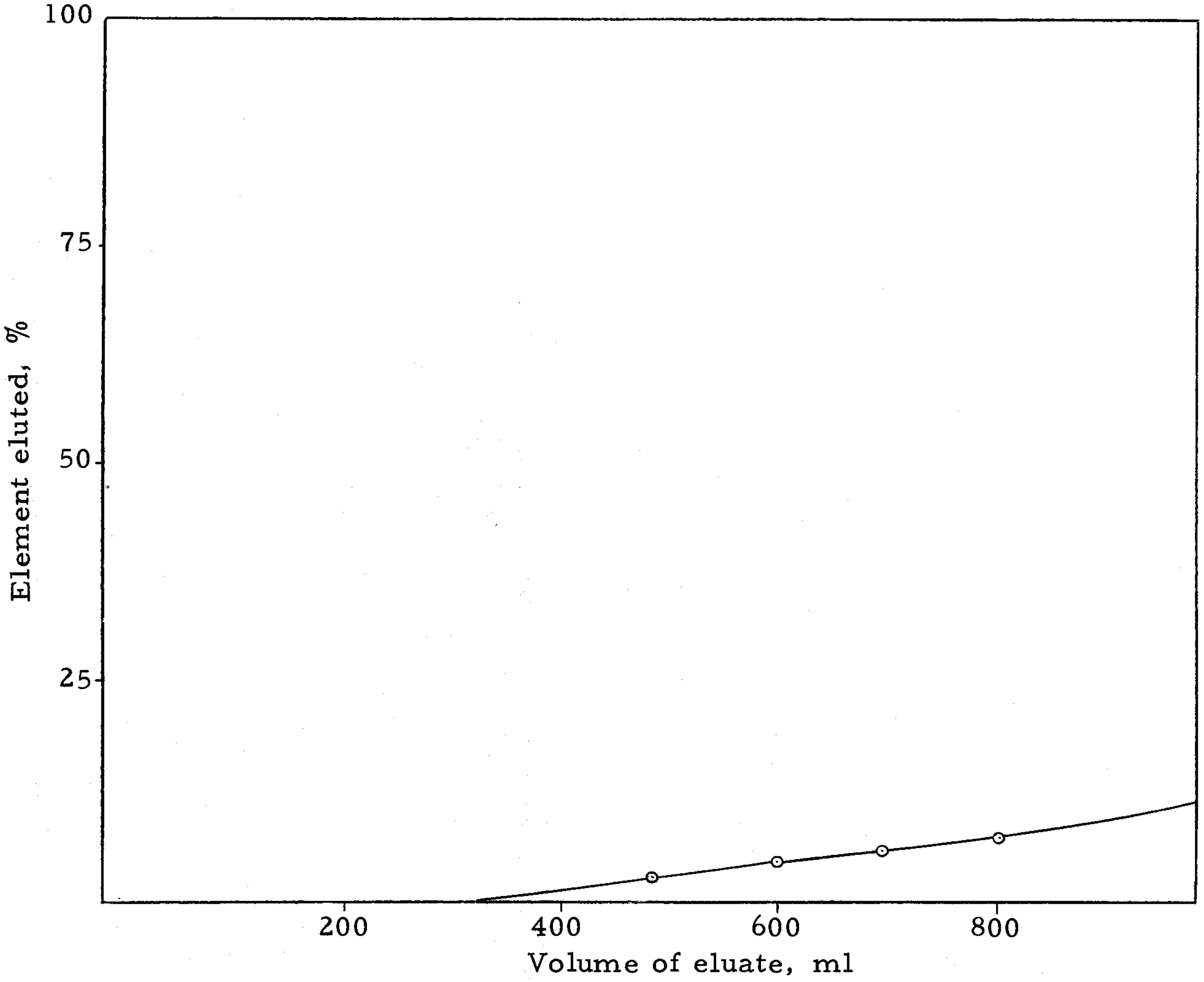

Figure III. The Premature Elution of 25 mg of Molybdenum by 3% Sulfuric Acid Through a 20 x 2.54 cm Column

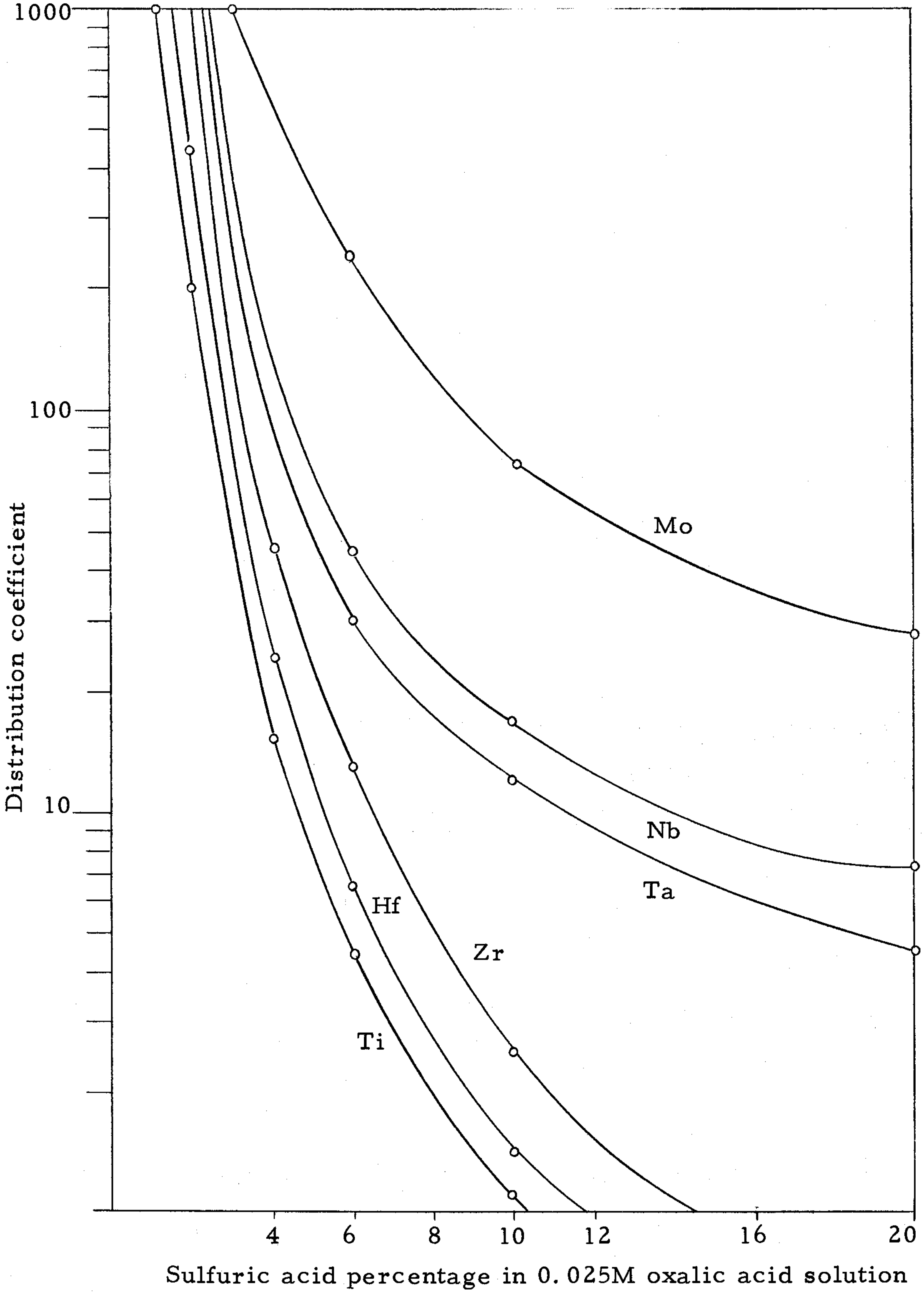

Figure IV. Distribution Coefficients of the Six Metals vs. Sulfuric Acid Percentage in 0.025M Oxalic Acid Solution.

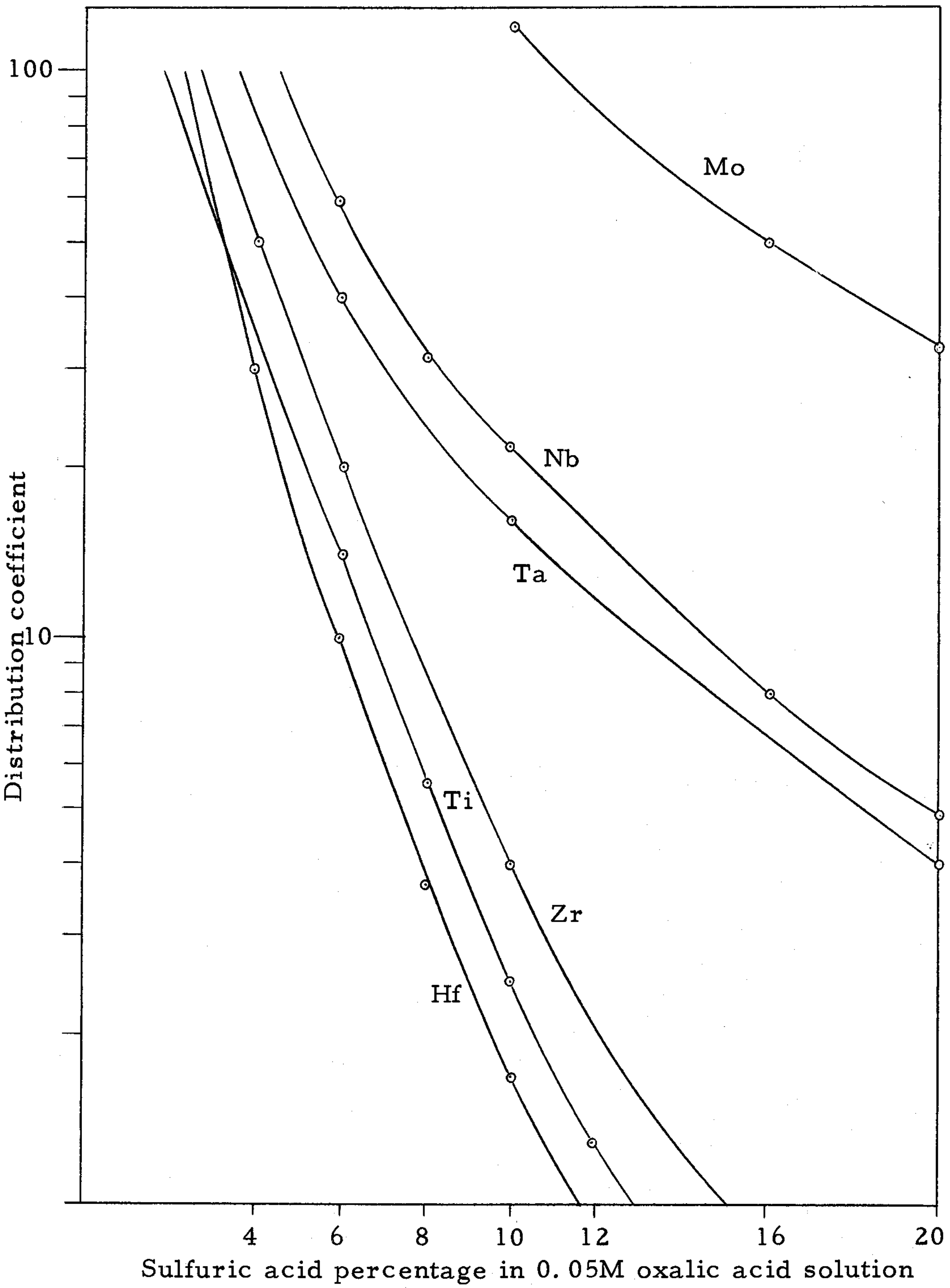

Figure V. Distribution Coefficients of the Six Metals vs. Sulfuric Acid Percentage in 0. 05M Oxalic Acid Solution.

acid only, is not observed at all in presence of oxalic acid.

Niobium and tantalum form stable complexes with oxalic acid. The stability of these complexes, however, is intermediate between the complexes of zirconium, hafnium and titanium on one hand and molybdenum on the other hand.

The effect of oxalic acid on the complex formation of the six metals is illustrated more clearly by Figure VI. The sulfuric acid level is kept constant at an optimum value of 6% which is not high enough to affect the formation of the exalate complexes nor low enough to yield complexes of its own. It is noticed that up to 0.05 M oxalic acid the distribution coefficients increase rapidly while at concentrations higher than 0.05 M oxalic acid the increase is less rapid.

The introduction of methanol into the oxalic-sulfuric system produces some interesting effects. Figure VII shows the distribution coefficients of the six metals in the 6% sulfuric-0.05 M oxalic as functions of the percentage of methanol present in the solution. The 6%-0.05 M level was chosen mainly because this combination was found the most suitable for the separation of tertiary alloys containing hafnium. Similar experiments were carried out at the 6%-0.025 M and other sulfuric-oxalic levels. The shapes of the curves were similar to those of Figure VII except that the differences between the distribution coefficient values were not great enough for

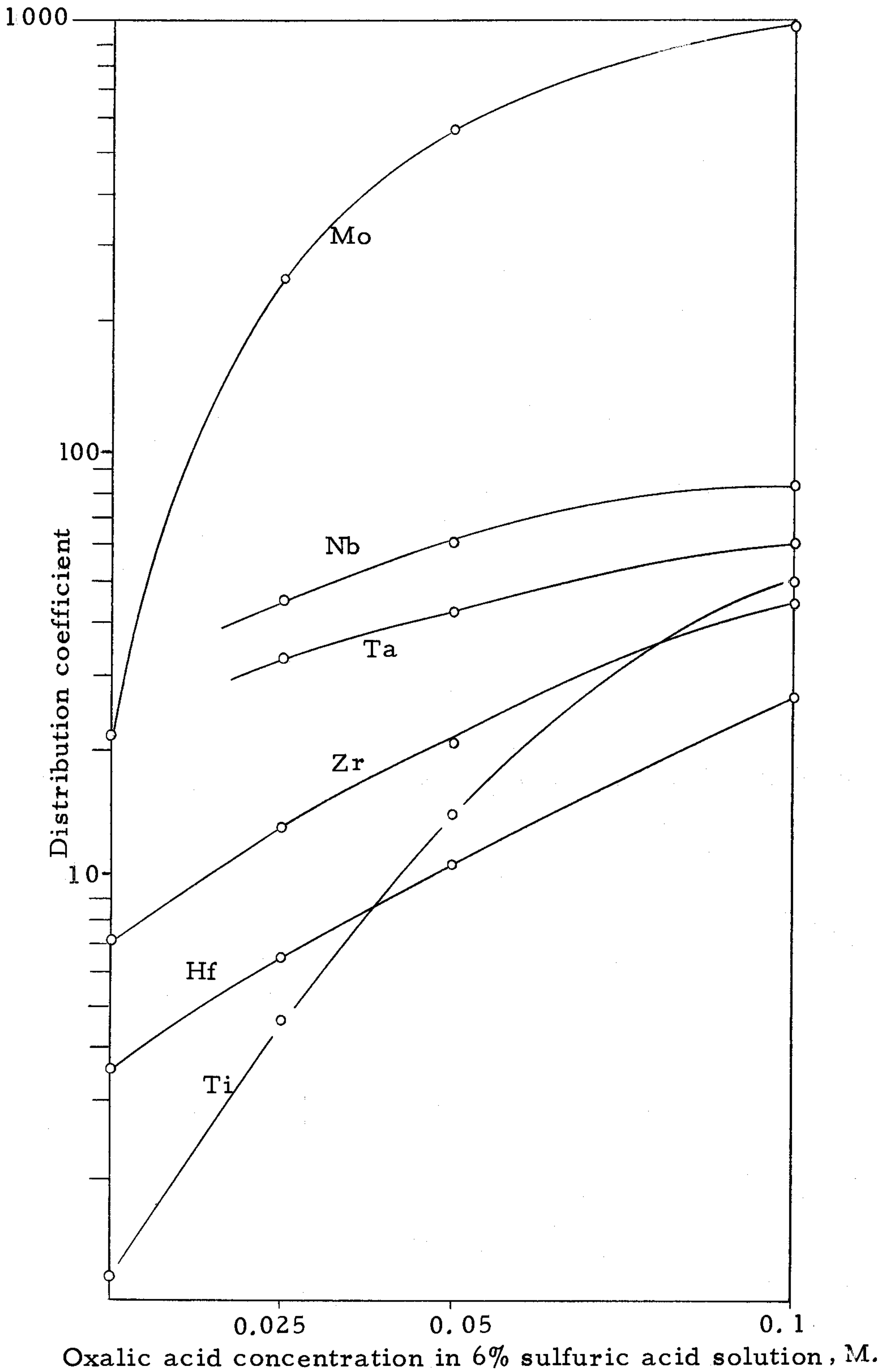

Figure VI. Distribution Coefficients of the Six Metals vs. Oxalic Acid Concentration in 6% Sulfuric Acid Solution.

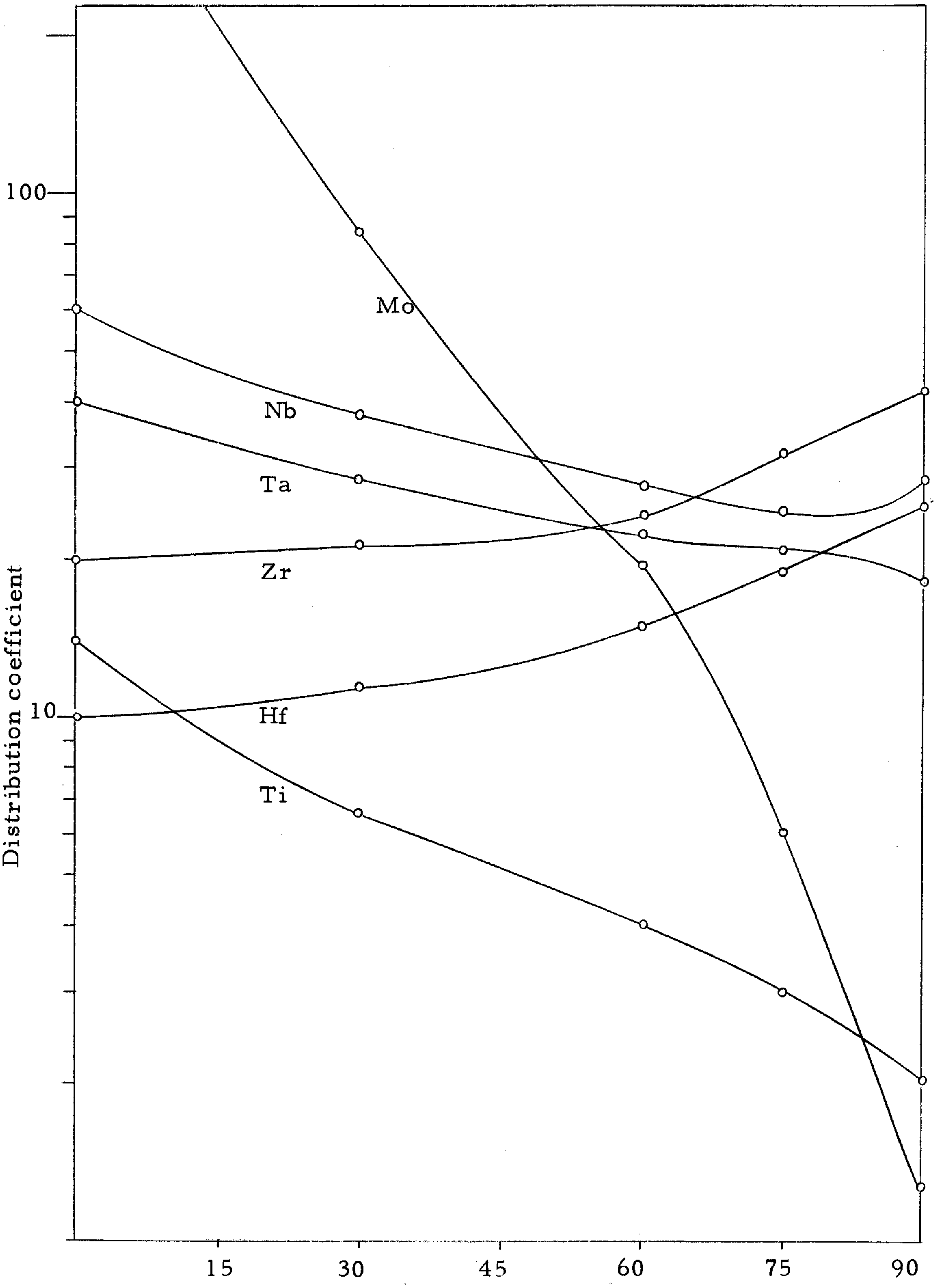

Figure VII. Distribution Coefficients of the Six Metals vs. Methanol Percentage in the 6% Sulfuric-0.05M Oxalic Acid Solution.

separations involving hafnium in tertiary alloys. Analysis procedures for tertiary alloys involving zirconium were developed from earlier figures without the introduction of the nonaqueous solvent.

Figure VIII shows the distribution coefficients of the four metal ions involved in the nonaqueous separations, plotted as functions of the sulfuric acid percentage. This figure shows the reason for choosing the 6% sulfuric acid for Figure VII studies; at higher percentages sulfuric acid tends to suppress the formation of the complex anions, and at lower percentages it complicates the study by forming complexes of its own.

Finally, in order to see which complexes are affected by the addition of the nonaqueous solvent, a few distribution coefficient measurements were performed in the absence of oxalic acid. In Figure IX the distribution coefficients of titanium, zirconium, hafnium and molybdenum are plotted as functions of methanol percentage in 6% sulfuric acid only.

In the next section it is shown how these different distribution coefficients could be used to design practical separation procedures for different combinations of the investigated metals.

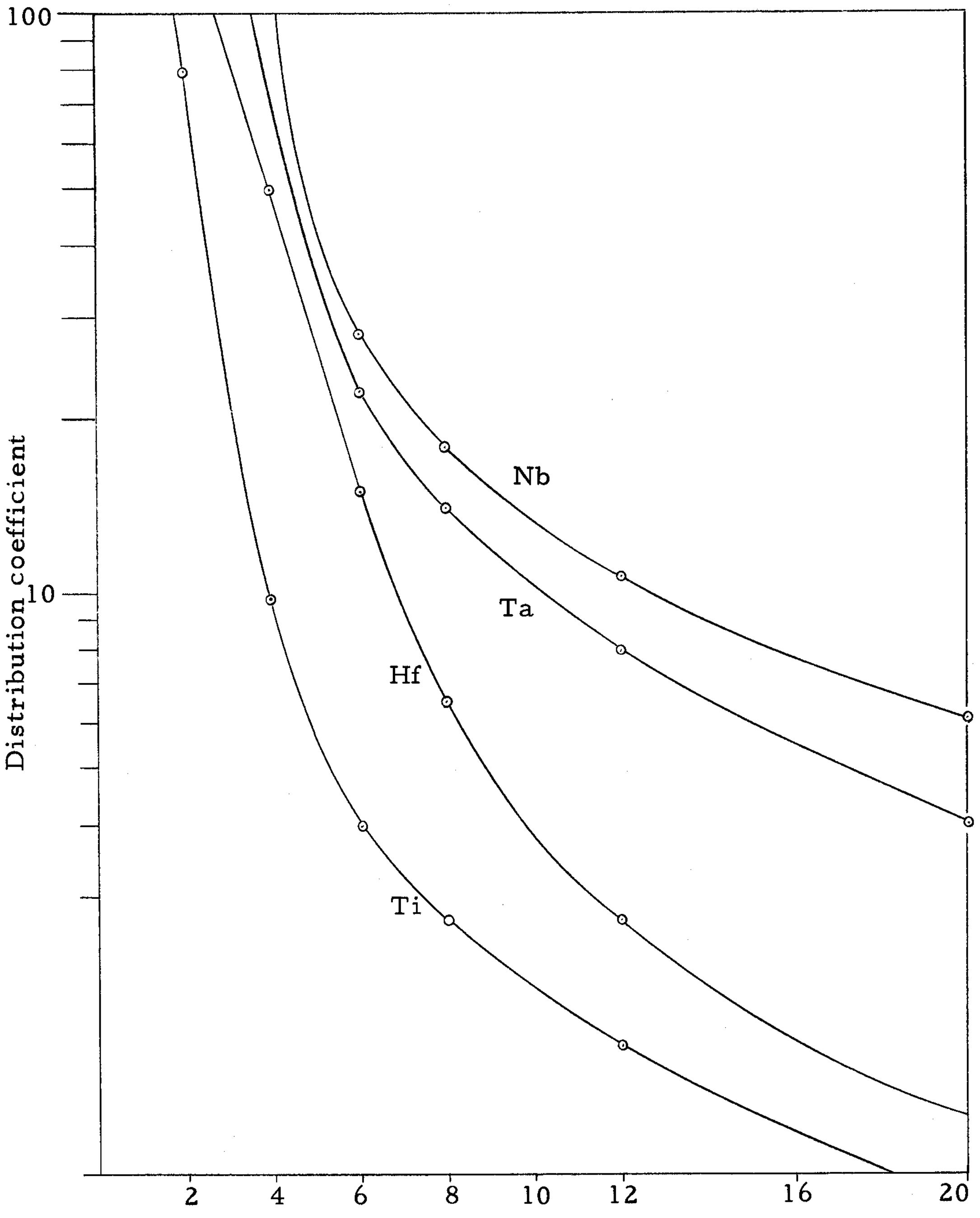

Figure VIII. Distribution Coefficients of Titanium, Hafnium, Niobium and Tantalum vs. Sulfuric Acid Percentage in the 0.05M Oxalic Acid-60% Methanol Solution.

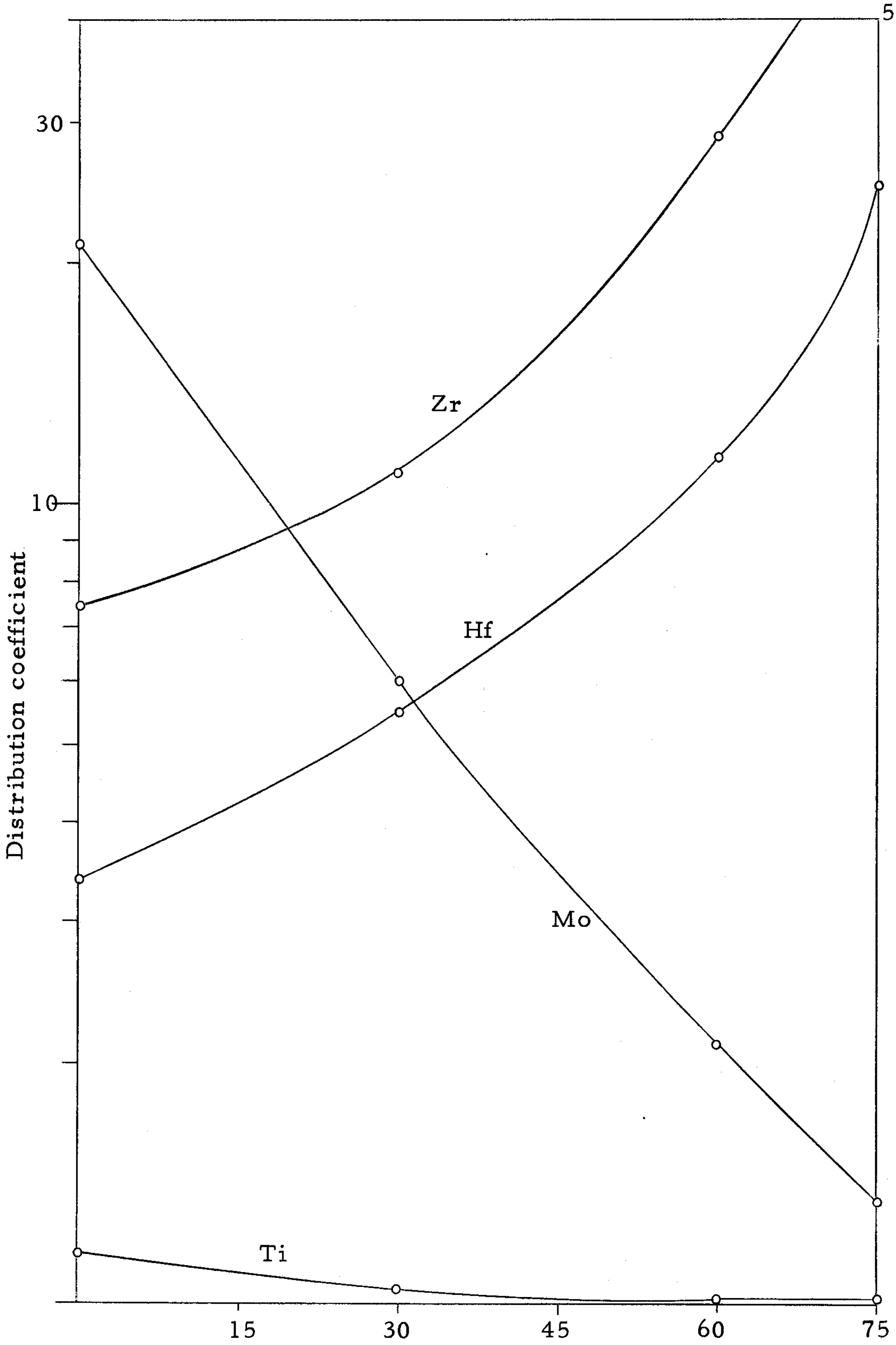

Figure IX. Distribution Coefficients of Titanium, Hafnium, Zirconium and Molybdenum vs. Methanol Percentage in 6% Sulfuric Acid Solution.

IV. SEPARATION PROCEDURES

General

Using the information provided by the previous distribution coefficient studies, numerous separation procedures were developed. Although this investigation was, at the start, directed toward finding suitable procedures for the analysis of small amounts of titanium, hafnium and zirconium in molybdenum, tantalum or niobium base alloys, many of the developed procedures lend themselves to the separation of comparatively large amounts of all constituents. It should also be mentioned that a procedure designed for the separation and determination of less than 1% titanium and 1% zirconium in a niobium base alloy for example, could, equally well, be used for the determination and separation of more than 1% titanium and 1% zirconium by simply using a smaller sample.

Based on the systematic procedure for finding the minimum column height (p. 15) 18 different schemes have been developed for widely different mixtures of the six metals. As mentioned earlier a majority of space alloys are molybdenum, tantalum, or niobium base alloys. This explains why most of the tertiary metal mixtures procedures (shown later in Table I) have been designed for the analysis of such base alloys. The other binary mixtures procedures are the first of their kind in the sulfuric-oxalic system. These binary procedures are distinguished by the wide range over which they could be used. The molybdenum-zirconium procedure (no. 13 in Table I) for example, could be used to determine small amounts of zirconium in molybdenum base alloy or small amounts of molybdenum in a zirconium base alloy. It could also be used for the separation and gravimetric determination of large amounts of both metals in the same sample. It will be shown in such cases, that only the amount of eluent should be increased to compensate for the broadening of the elution curves.

Experimental

Ion Exchange Column

The ion exchange column was made of glass tube ranging in diameter from 1. 9 to 2. 54 cm, sealed to a 4 cm long glass tube with an inside diameter of about 5 mm. The resin is supported on a plug of glass wool fitted into the column near the bottom. A 15 cm high column with a 1. 9 cm inside diameter refers to the resin bed height and not to the actual height of the glass column which is usually about 4-6 cm higher than the resin bed column. This extra height is necessary to get a continuous eluent head starting from the top of the funnel which contains the eluent and ending at the top of the resin bed.

The eluent is introduced through a 500 ml funnel whose stem is attached to a 5 cm capillary tube by a 50 cm long piece of rubber tubing. The capillary tube is plugged into a rubber stopper which closes the top of the glass column tightly. The capillary tip is immersed under the surface of the eluent present on top of the resin to establish the liquid head necessary for the flow of the eluent. The flow rate of the eluent is controlled by the height of the funnel and the bore of the capillary tube. The flow rate also depends strongly on the cross sectional area of the resin bed and the resin particle size. In order to get clean separations moderate flow rates should be used. For aqueous elutions of tertiary metal mixtures carried out in either 15 x 1.9 cm columns or 20 x 2.54 cm columns, a flow rate of 1.5-2 ml/min is satisfactory for the elution of the first two constituents of the mixture. For a binary mixture the first constituent only is eluted with 1.5-2 ml/min rate. In all cases the last constituent is eluted faster at a rate of 2-3 ml/min. When the eluent 6% sulfuric-0.05 M oxalic-60% methanol is used the rate should not exceed 1.5 ml/min, because equilibrium is slowly achieved in presence of methanol.

Ion Exchange Resin

The strongly basic resin Dowex 1-X8 chloride form (200-400 mesh) was used in all separations. The pretreatment of this resin and its transfer into the sulfate form was mentioned earlier (p. 28). After the transfer into the sulfate form and while the resin was still on the column, about 200 ml deionized water was passed through. The resin bed was then flushed into a beaker and kept under water permanently. To pack a column for an aqueous separation, the outlet was first plugged with a piece of glass wool and the resin slurried in the beaker with a covering water. The slurry was then poured along the wall of the column allowing the particles to settle forming the bed. In the case of separations using mixed solvents the water content of the beaker was discarded and the resin slurried with about 50 ml of the preconditioning mixed solvent, then poured along the walls of the column. This step prevents channelling which is caused by the change in swelling due to the methanol content of the eluent. If, despite this step, channelling takes place (which appears like small bubbles through the glass column) the resin bed should be flushed into a beaker with the same eluent, conditioned once more and then returned to the column. Channelling decreases the efficiency of the resin and frequently results in tailing. After the column is drained to the top of the resin bed it is preconditioned with a suitable volume of the first eluent used for the separation. The volume used depends on the size of the resin bed.

On completion of the separation, the resin is returned to the sulfate form by passing 200-400 ml of 10% sulfuric acid solution.

The complete removal of oxalate could be checked by $KMnO_4$. This was necessary in separations involving niobium and tantalum for after elution of either metal, some oxalate would still be held by the resin. In the case of molybdenum alloys, however, this is not necessary because the final eluent is 20% sulfuric acid. When the column is not in use, 200 ml of deionized water is passed and the last portion of this water is kept on top of the resin with the stopcock of the funnel shut so that the resin bed is not exposed to the air. When the column is used for elutions involving methanol, it is recommended that the bed be flushed into a beaker and the column repacked. This will eliminate any bubbles and help resettle the particles.

Sample and Loading

For molybdenum alloys, an appropriate sample size (see Table I) was weighed accurately and heated gently in a platinum dish with 15 ml of 1:4 sulfuric acid. A few drops of nitric acid and a minimum of hydrofluoric acid were added to dissolve the sample. The clear solution was then fumed to dryness and dissolved with a suitable volume of the first eluent. To load this sample it was then transfered quantitatively to the top of the resin bed through a 10 x 1 cm glass tube that ends up with a small capillary tube. A thin layer of glass wool on the top of the resin helped achieve even absorption of the sample. The slow uptake of the sample was favorable in order to attain equilibrium conditions. After loading, the column wall was washed with about 5 ml of the eluent. Elution was then carried out.

For a tantalum or niobium alloy the appropriate amount was weighed accurately and dissolved in a platinum dish with 2-4 ml of hydrofluoric acid plus a few drops of nitric acid. After complete dissolution, 5-7 ml of sulfuric acid were added and the solution fumed to a volume of 1 or 2 ml. If there is any uncertainty about the exact remaining volume it is recommended to underestimate it so that the final percentage of sulfuric acid in the sample load would be a little higher. Enough sulfuric acid was then added to have the final necessary volume of this material. Sufficient water, oxalic acid and methanol, in the case of mixed solvents separations, were then added to make a final volume of 50 ml which was loaded on the column in the manner described for the molybdenum alloy.

Eluents

The eluent 6% sulfuric-0.025 M oxalic acid solution, was prepared by mixing 60 ml of concentrated sulfuric acid with about 800 ml water in a 1 liter volumetric flask. After cooling, 25 ml of 1 M oxalic acid was added and the volume adjusted to one liter with water. In the case of mixed solvent solutions, like the 6% sulfuric-0.05 M oxalic-60% methanol, only 200 ml of water was added after the 60 ml of sulfuric acid. Six hundred ml of methanol and 50 ml of 1 M oxalic were then added to the cooled solution and the volume adjusted to one liter with water.

Collection of Fractions and Plotting the Elution Curve

The elution curve characteristic of a metal was prepared by collecting the eluate in fractions, which could then be analyzed to determine the metal content. This information is necessary to draw the elution curve of that particular metal species. From this elution curve the numerical values of U_a and U^* (p. 18) could be deduced. These parameters are essential for the calculation of the minimum height column necessary to achieve separation. A Research Specialties automatic fraction collector, Model 1205 A, was used to collect these fractions. This very helpful instrument was indispensible to check the whole separation scheme and determine where the elution, of any constituent, starts and where it ends. The instrument used for this investigation is a constant volume type based upon the siphon principle, illustrated in Figure X. The main body A of the syphon pipet receives the eluate drops from the resin column. When this eluate builds up in A it starts to compress the small volume of air present in compartment B which, in turn, pushes the electrolyte up in compartment C. The amount of electrolyte present in C and the height of the electrodes are maintained so that the electrical connection between the electrolyte and the electrodes takes place shortly

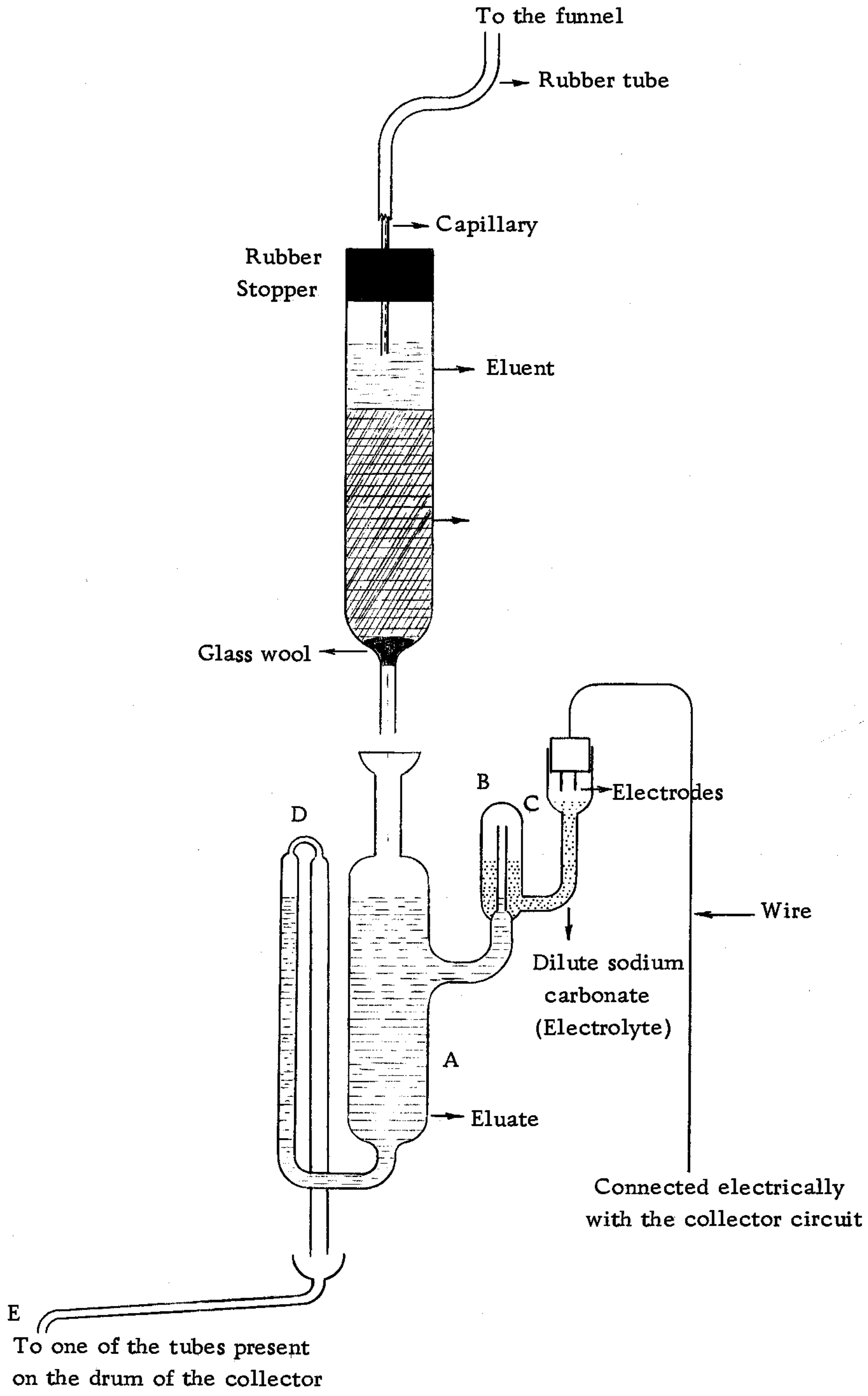

Figure X. Schematic Diagram of the Resin Column and the Syphon Pipet.

before the level of the liquid, in the syphon, reaches D. When the circuit is closed the drum moves and places an empty tube at the tip of the handle E. Seconds later when the eluate level reaches D it syphons through and the new tube receives the fraction. A syphon of 10 ml delivery volume was used when the volume of eluent necessary to elute a constituent did not exceed 200 ml. Otherwise a 20 ml-syphon was used. In drawing the elution curve of a species, using the 20 ml syphon it should be noted that the value of U for any given fraction, n, is not 20 n but 20 (n-0. 5). This is because the value of U pertains to the mid point, not the end, of a fraction. The constant-volume fraction collector has a disadvantage in that each fraction is invariably contaminated by the previous fraction.

To draw the elution curve a suitable portion of each fraction was analyzed by a suitable spectrophotometric method. When the information provided by the elution curve was not intended to be used for any quantitative calculations then the curve could be determined empirically. In the case of titanium, for example, the intensity of the color produced by adding 1 ml of 3% hydrogen peroxide to each fraction gives an adequate picture about where the elution starts, peaks and ends. In the case of zirconium and hafnium, the volume of precipitate produced by adding ammonium hydroxide to each fraction (or a portion of it) yields the same information. For molybdenum, 1 ml of 10% potassium thiolyanate and 2 ml of 10%

stannous chloride in dilute hydrochloric acid give an amber to orange-red color when traces of this metal are present in the fraction. Tantalum and niobium were examined each by its appropriate spectrophotometric method described earlier.

Determination of Interstitial Volume

To check the agreement between the U^* value deduced from experimental elution curve and the theoretical U^* value based on the relation

$$U^* = CV + V$$

it was necessary to determine the interstitial volume V of the resin column. As mentioned earlier, this check would provide some information on the reliability and usefulness of the plate theory.

This volume, the void space in the resin bed, was determined by filling the interstices of the column (chloride form) with 0.1 M hydrochloric acid followed by washing with water until all hydrochloric acid was removed. The number of milliliters of 0.1 M sodium hydroxide necessary to neutralize this amount of acid is the interstitial volume of the column. No correction was needed for penetration. This is due to the high degree of crosslinkage of the Dowex 1-X8 resin. It was found that the interstitial volume occupies 44% of the whole resinbed volume. Thus the product of the bed volume of the column multiplied by 0.44 yielded the numerical value of V.

The Development of Separation Procedures

The systematic procedure, described earlier (p. 19) was used for the determination of the minimum height column necessary to achieve a particular separation. A molybdenum base alloy with small amounts of titanium and zirconium was the first alloy for which a separation procedure was devised.

The first step was the determination of distribution coefficients of the different metal species in a wide range of concentrations and percentages of sulfuric acid, oxalic acid and methanol. It should be mentioned here that although all the reported distribution coefficient measurements were made in less than 0.1 M oxalic acid, many other determinations were carried out at higher oxalic acid levels. Later, however, it was realized that only at low levels of oxalic acid was the separation factor high enough to achieve the desired separations.

The second step was to seek a favorable separation factor, greater than two for titanium-zirconium and for zirconium-molybdenum. A glance at Figure II indicated that an aqueous solution of 4% sulfuric acid or less should be a good eluent. The premature leaking, of molybdenum, however, (see Figure III) prohibited the use of dilute sulfuric acid solutions as eluents for tertiary molybdenum base alloys.

The presence of small amounts of oxalic acid in the dilute sulfuric acid solutions increased the distribution coefficients considerably but, more importantly, prevented the bleeding of molybdenum (Figures IV and V). At exactly 6% sulfuric-0.025 M oxalic the picture was most promising. The separation factor of titanium-zirconium was close to three and for zirconium-molybdenum was more than 18. It should be noted here that at 4% sulfuric-0.025 M oxalic the separation factor of titanium-zirconium was also about three. This eluent, however, is inferior to the 6%-0.025 M because it tends to broaden the elution curves of titanium and zirconium owing to the high C values, which indicate that the metal anion complex is held tightly by the resin.

The third step was the elution of a mixture containing 5 mg titanium and 10 mg zirconium using a 10 x 1.9 cm resin column through which the proposed eluent was passed. Molybdenum will not be eluted because it is held very tightly by the resin (C = 240). A syphon with 10 ml delivery volume was used to supply the fractions for colorimetric analysis. Figure XI shows the resulting elution curve. It is clear that a little longer column would result in a larger interval between the end of the titanium curve and the start of the zirconium curve.

The fourth step was to calculate the minimum height column, using the relations found on pages 17 and 19. From the values

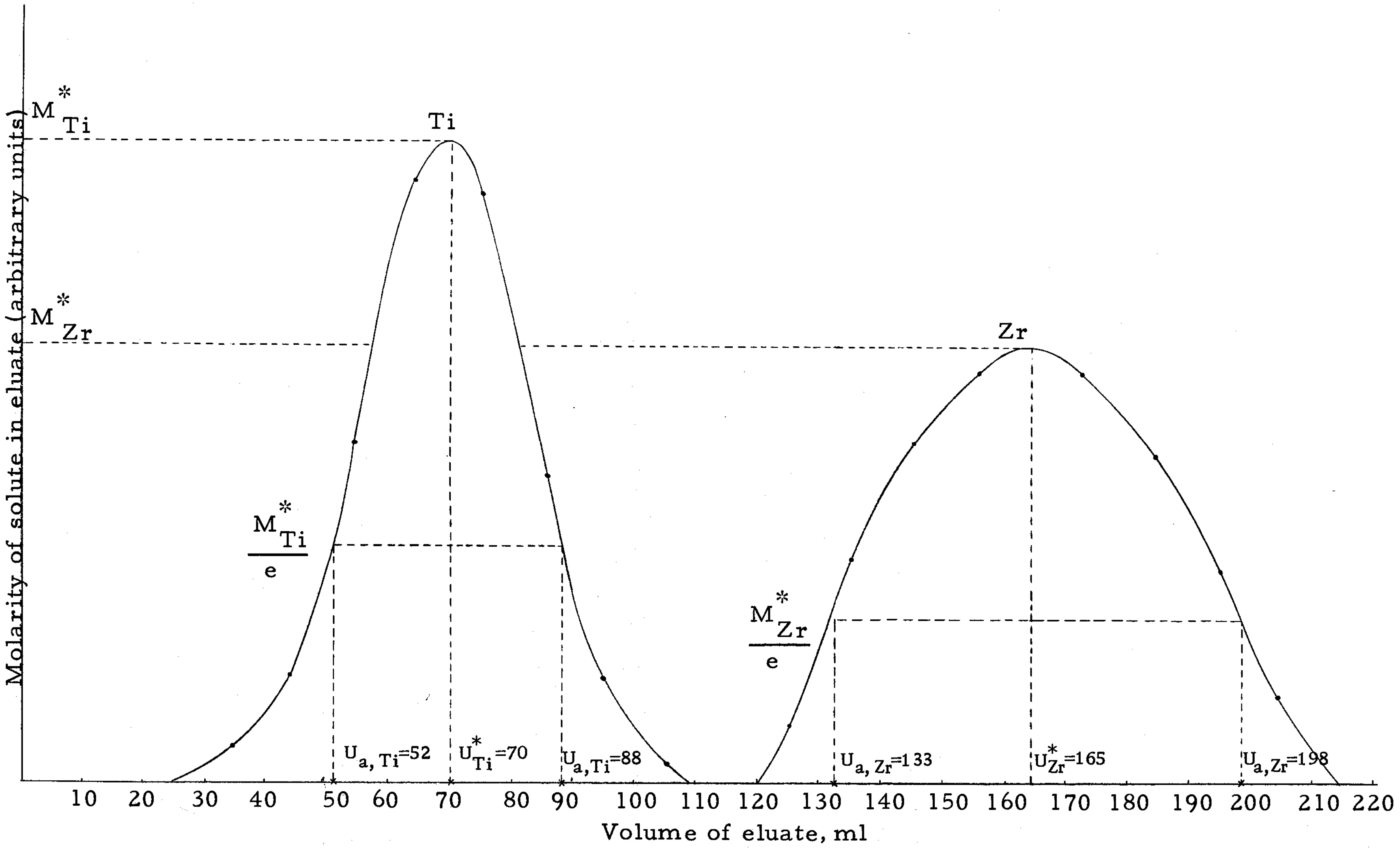

Figure XI. The Elution of 5 mg Titanium and 10 mg Zirconium on a 10 x 1.9 cm Column Using 6% Sulfuric-0.025M Oxalic Acid as Eluent. Rate of Flow 1.5-2 ml/min deduced from Figures IV and XI, relation (2) gives:

$$P_{Ti} = 25 \text{ plates} \qquad P_{Zr} = 48 \text{ plates}$$

Since the length of used column is 10 cm:

$$p_{Ti} = \frac{25}{10} = 2.5 \text{ plate/cm}, \quad p_{Zr} = \frac{48}{10} = 4.8 \text{ plate/cm}$$

Using these values in relation (4) and setting the limit of cross contamination at 0.05%, the minimum column height was found to be 13 cm. A cross contamination limit of 0.01% requires a 17 cm high column. A compromise height of 15 cm was adopted.

The fifth and final step was to check this proposed procedure. This was done by preparing a mixture of 5 mg titanium and 10 mg zirconium in 25 ml of 6% sulfuric acid-0.025 M oxalic acid solution which was transfered to a 15 x 1.9 cm column. The shape of the elution curve was similar to that of Figure XI except that the titanium curve started at the 45 ml point and ended at the 140 ml point. The zirconium curve started at the 185 ml point and ended at the 295 ml point. All these volumes are measured starting from the eluate of the load itself.

This result leads to the conclusion that the systematic procedure is useful and that the plate theory is reliable despite many of the approximations in both the theoretical and experimental approaches to the problem.

Depending on the relative amounts of metals separated, three different procedures (1, 2, and 3 in Table I) were developed. When large amounts of titanium and zirconium are present some modifications are necessary because of the broadening of the elution curves. A larger column was used in procedure (3) due to the comparatively large amounts of all the sample constituents.

It is noticed that zirconium, in these procedures,was eluted with 10%-0.025 M instead of the 6%-0.025 M solution. This is because the 10%-0.025 M solution will elute zirconium faster (C = 2.5) and at the same time does not appreciably influence molybdenum (C = 70).

Separation procedures of titanium and zirconium in niobium or tantalum base alloys (procedures 7 and 9 in Table I) were developed along the same lines. Larger columns were necessary because tantalum and niobium are not held as tightly as molybdenum. Instead of the 10%-0.025 M, the eluent 10%-0.05 M is used to elute zirconium in procedure 9 because tantalum has a higher distribution coefficient in the second eluent than in the first (see Figures IV and V).

When hafnium replaces zirconium in the alloys, the procedures just developed are no longer suitable. This is evident from Figures IV and V. Since the hafnium distribution coefficient curves are close to those of titanium, the separation factor is less than two. This requires a very long column and large volumes of eluents. The problem was solved, however, by introducing methanol into the eluent. The fact that methanol affects the stabilities of titanium and hafnium oxalate complexes in opposite directions (Figure VII) was the key to the development of separation procedures for alloys containing hafnium and titanium.

For the binary mixtures the dimensions of the columns were chosen so that there is always 50-80 ml gap between the last detectable traces of the first solute and the first detectable traces of the second solute.

Separation Procedures

Table I describes 18 separation methods for different combinations of the six metals investigated. The first column describes the kind of alloy or metal mixture for which the procedure was designed. It is important to mention that these procedures could be applied also when the starting mixture is in the oxide form. The second column, in this table, specifies the size of sample and the final solution in which it is contained after being dissolved and fumed as mentioned earlier (p. 59). The resin bed dimensions are described in the third column. This resin is always in the sulfate form at the start. To prepare this resin for a run it is preconditioned with a suitable volume of the first eluent which will be used later. The amount of eluent necessary to elute each constituent is specified in the fourth column. The eluate of the sample itself should be

TABLE I. Separation Procedures of Metal Ion Mixtures on Dowex 1-X8, 200-400 Mesh, Sulfate Form

Metal Mixture	Sample Size and Load	Column Dimensions Height x Inside Diameter cmxcm	Elution[c]	Use and Determination Method
(1) Ti-Zr-Mo	100 mg in 50 ml of 6%-0.025M[a]	15 x 1.9 Preconditioned with 200 ml of the 6%-0.025M[b]	Ti-110 ml of 6%-0.025M Zr-160 ml of 10%-0.025M Mo-500 ml of 20%[d]	For Mo base alloys containing less than 1% Ti and 1% Zr.[e] Ti with Tiron. Zr with Oxine.
(2) Ti-Zr-Mo	10-20 mg in 25 ml of 6%-0.025 M	The same	Ti-150 ml of 6%-0.025 M Zr-200 ml of 10%-0.025M Mo-300 ml of 20%	For Mo alloys containing more than 1% and 1% Zr. Ti with Tiron. Zr with Oxine.
(3) Ti-Zr-Mo	50-100 mg in 50 ml of 6%-0.025M	20 x 2.54 Preconditioned with 300 ml of the 6%-0.025M	Ti-270 ml of 6%-0.025M Zr-300 ml of 10%-0.025M Mo-600 ml of 20%	For alloys containing more than 20% of either Ti or Zr. Ti and Zr gravimetrically with Cupferron. Mo gravimetrically with α-benzoinoxime.
(4) Ti-Hf-Mo	100 mg in 50 ml of 6%-0.05M-60%	20 x 2.54 Preconditioned with 300 ml of the 6%-0.05M-60%	Ti-230 ml of 6%-0.05M-60% Hf-200 ml of 10%-0.025M Mo-700 ml of 20%	For Mo base alloys containing less than 1% Ti and 1% Hf. Ti with Tiron. Hf with Oxine
(5) Ti-Hf-Mo	10-20mg in 25 ml of 6%-0.05M-60%	The same	Ti-275ml of 6%-0.05M-60% Hf-250ml of 10%-0.025M Mo-500 ml of 20%	For Mo base alloys containing more than 1% Ti and 1% Hf. Ti with Tiron. Hf with Oxine.
(6) Ti-Hf-Mo	40-60mg 25ml of 6%-0.05-60%	The same	Ti 315 ml of 6%-0.05M-60% Hf-250 of 10%-0.025 Mo-600 of 20%	For gravimetric analysis of Mo-Hf-Ti alloy. Hf and Ti by Cupferron. Mo by α-benzoinoxime.

TABLE I. Continued

Metal Mixture	Sample Size and Load	Column Dimensions Height x Inside Diameter cm x cm	Elution	Use and Determination Method
(7) Ti-Zr-Nb	⩽ 25 mg[f] in 50 ml of 6%-0.025M	20 x 2.54 Preconditioned with 300 ml of 6%-0.025M	Ti-250 ml of 6%-0.025M Zr-240 ml of 10%-0.025M Nb-600 ml of 20%-0.1M	For Nb base alloys containing more than 0.2% of either Ti or Zr. Ti with Tiron. Zr with Oxine.
(8) Ti-Hf-Nb	⩽ 25 mg[f] in 50 ml of 6%-0.05M-60%	20 x 2.54 Preconditioned with 300 ml of 6%-0.05M-60%	Ti-250 ml of 6%-0.05M-60% Hf-220 ml of 8%-0.05M Nb-600 ml of 20%-0.1M	For Nb base alloys containing more than 0.2% Ti and 0.4% Hf. Ti with Tiron. Hf with Oxine.
(9) Ti-Zr-Ta	⩽ 25 mg[f] in 50 ml of 6%-0.025M	20 x 2.54 Preconditioned with 300 ml of the 6%-0.025M	Ti-250 ml of 6%-0.025M Zr-240 ml of 10%-0.05M Ta-500 ml of 20%-0.025M	For Ta alloys containing more than 0.2% of either Ti or Zr. Ti with Tiron. Zr with Oxine.
(10) Ti-Hf-Ta	⩽ 25 mg[f] in 50 ml of 6%-0.05M-60%	20 x 2.54 Preconditioned with 300 ml of the 6%-0.05M-60%	Ti-250 ml of 6%-0.05M-60% Hf-220 ml of 8%-0.05M Ta-500 ml of 20%-0.025M	For Ta alloys containing more than 0.2% Ti and 0.4% Hf. Ti with Tiron. Hf with Oxine.
(11) Ti-Mo	⩽ 50 mg in 25 ml of 3%	15 x 1.9 Preconditioned with 200 ml of 3%	Ti-100 ml of 3%. 110 ml if the amount of Ti exceeds 25 mg. Mo-300 ml of 20%	For any combination of Ti and Mo. Ti with Tiron or Cupferron depending on the amount[g]; Mo with thiocyanate or α-benzoinoxime.
(12) Hf-Mo	⩽ 50 mg in 25 ml of 10%-0.025M	10 x 1.9 Preconditioned with 150 ml of the 10%-0.025M	Hf-150 ml of 10%-0.025M 175 ml if the amount of Hf exceeds 25 mg. Mo-250 ml of 20%	For any combination of Hf and Mo. Hf with oxine or Cupferron. Mo with thiocyanate or α-benzoinoxime.

TABLE I. Continued

Metal Mixture	Sample Size and Load	Column Dimensions Height x Inside Diameter cm x cm	Elution	Use and Determination Method
(13)[h] Zr-Mo	≤ 50 mg in 25 ml of 10%-0.025M	10 x 1.9 Preconditioned with 150 ml of the 10%-0.025M	Zr-175 ml of 10%-0.025M 200 ml if the amount of Zr exceeds 25 mg. Mo-250 ml of 20%	For any combination of Zr and Mo. Zr with Oxine or Cupferron depending on the amount. Mo also with thiocyanate or -benzoinoxime.
(14) Ti-Nb	≤ 50 mg in 50 ml of 6%-0.025M	15 x 1.9 Preconditioned with 200 ml of 6%-0.025M	Ti-225 ml of 6%-0.025M 250 ml if the amount of Ti exceeds 25 mg. Nb-300 ml of 20%-0.1M 350 ml if the amount of Nb exceeds 25 mg	For niobium alloys. Ti with Tiron or Cupferron. Nb with Cupferron.
(15) Hf-Nb or Zr-Nb	≤ 50 mg in 50 ml of 10%-0.025M	15 x 1.9 Preconditioned with 200 ml of 10%-0.025M	Hf or Zr-200 ml of 10%-0.25M 225 ml if the amount of Hf or Zr exceeds 25 mg Nb-300 ml of 20%-0.1M 350 ml if Nb exceeds 25 mg	For niobium alloys. Hf or Zr with Oxine if the amount is small. Hf, Zr and Nb with Cupferron if the amount is large.
(16) Ti-Hf	≤ 100 mg in 25 ml of 2%	15 x 1.9 Pre conditioned with 200 ml of 2%	Ti-125 ml of 2% 150 ml if the amount of Ti exceeds 50 mg Hf-160 ml of 8% 200 ml if the amount of Hf exceeds 50 mg	For any combination of Ti and Hf. Small amounts of Ti with Tiron. Hf with Oxine. Large amounts of both with Cupferron.
(17) Ti-Zr	≤ 100 mg in 25 ml of 3%	15 x 1.9 Preconditioned with 200 ml of 3%	Ti-140 ml of 3% 160 ml if the amount of Ti exceeds 50 mg Zr-200 ml of 10% 225 ml if the amount of Zr exceeds 50 mg	For any combination of Ti and Zr. Ti with Tiron or Cupferron. Zr with Oxine or Cupferron.

TABLE 1. Continued

Metal Mixture	Sample Size and Load	Column Dimensions Height x Inside Diameter cm x cm	Elution	Use and Determination Method
(18) Hf-Zr	500 mg in 3.5%	22 x 2.54 Preconditioned with 200 ml of 3.5%	Hf-550 ml of 3.5% Zr-250 ml of 10%	For mixtures containing less than 20% Zr. Hf and Zr by Cupferron. Two anion exchange steps are required for mixtures containing 20-80% Zr.[i]

---

[a] The solution composition expressed as 6%-0.025 M refers to a 6% sulfuric acid solution in 0.025M oxalic acid. When there is a third number in the expression, it should refer to the percentage of methanol in the mixture.

[b] The starting resin is Dowex 1-X8 (200-400 mesh) in the sulfate form.

[c] For a tertiary metal mixture the rate of elution of the first constituent is 1.5 - 2 ml/min if the elution is performed with an aqueous eluent. This rate should not exceed 1.5 ml/min if the elution is carried out with a mixture containing methanol. The second constituent is eluted at a rate of 1.5-2 ml/min and the third and final constituent is always eluted faster at a rate of 2-3 ml/min. For a binary metal mixture the elution rate of the first constituent is also 1.5-2 ml/min, with the second constituent eluted with a faster rate of 2-3 ml/min.

[d] The eluate of the first constituent should always be combined with the load eluate for further analysis to determine the content of this constituent in the metal mixture. For example; the 50 ml of load eluate should be combined with the 110 ml of 6%-0.025M solution to determine the titanium content of the sample in procedure no. (1).

[e] The smallest amount of either titanium or zirconium that could be determined within 1% accuracy is 0.05 mg. For hafnium this amount is 0.1 mg.

[f] The sample size depends on its content of both Ti and Zr. This size is chosen so that the amount of Ti or Zr present in the sample is less than 5 mg.

[g] Titanium is determined colorimetrically with Tiron if the amount of the metal, present in the sample is 0.05-10 mg. Larger amounts are determined with Cupferron. The same thing applies to zirconium and hafnium which are determined by Oxine or Cupferron, except that the lower limit for hafnium is 0.1 mg instead of 0.05 mg. Molybdenum is determined colorimetrically with thiocyanate when the sample content of the metal is 1-10 mg and gravimetrically with α-benzoinoxime when larger amounts are present.

[h] Samples as large as 200 mg could be used in procedures (12) and (13) provided that larger amounts of eluents are employed. The broadened elution curves could be determined qualitatively as explained earlier (page 63). This applies also to Ti-Mo separation if it is performed according to procedure (12). The premature elution of Mo prohibits the use of procedure (11) when large amount of Mo is present in the sample.

[i] This procedure was established by Machlan and Hague (53).

combined with the eluate of the first separated constituent. The last column, in Table I, sets the range of the alloy constituents in which the scheme is used. It also provides information about the analytical method used for the determination of each constituent.

In order to clarify any ambiguity about this table, one of the listed procedures will be described in detail. This is procedure (1) used for the analysis of less than 1% titanium and 1% zirconium in a molybdenum base alloy. Weigh accurately 100 mg of the alloy and dissolve it in a platinum dish with 15 ml of 1:4 sulfuric acid, 1 ml nitric acid and two drops of hydrofluoric acid. Fume to dryness and dissolve the residue in 50 ml of the 6% sulfuric-0. 025 M oxalic acid solution. Set up the resin column by passing 200 ml of the 6%-0.025 M solution through 15 x 1. 9 cm, resin in the sulfate form. Place a small piece of glass wool on top of the resin bed and transfer the sample quantitatively to the column through a 10 x 1 cm glass tube pulled to a fine tip. Wash the walls of this tube and the walls of the column with about 5 ml eluent. Collect the eluate of the sample and the wash and complete the titanium elution by passing 110 ml of the 6%-0. 025 M solution with a flow rate of 1. 5-2ml/min. The combined 165 ml contains the titanium fraction, which is determined colorimetrically with Tiron. An aliquot of 20 ml is adequate if the alloy contains around 0. 5% titanium. Zirconium is eluted next with 160 ml of 10% sulfuric-0. 025 M oxalic acid solution, also at a rate of

1.5- 2 ml/min. An aliquot of 10 ml is taken for the colorimetric determination of zirconium with Oxine if the percentage of this metal in the original alloy is around 1%. Finally molybdenum is eluted with 500 ml of the 20% sulfuric acid solution at a rate of 2-3 ml/min.

In order to prepare the column for another run, 200 ml of deionized water is passed through the resin bed. The column content is then flushed into a beaker, swirled for a while and then returned back to the column. If a second run is to be performed 200 ml of the 6%-0.025 M is then passed. Otherwise, the resin column is kept permanently under a water layer with the stopcock of the funnel shut off. When the analysis involves either niobium or tantalum, 300 ml of 10% sulfuric acid should be passed through the column after the final elution. This step is necessary to return the column to the sulfate form and to remove any oxalate species present.

In agreement with Machlan and Hague (53) it is recommended that each column be calibrated to determine the volume of solution needed to elute each constituent. This is necessary because the resins and column loadings vary somewhat with different lots of resin. This step is particularly recommended when the separation involves large constituents that are determined gravimetrically after the separation.

RESULTS AND DISCUSSION

The Analysis of Synthetic Mixtures

To check the reliability of the designed procedures three or more separations were performed according to the specifications and parameters of each scheme present in Table I. Samples were made up of pure metals obtained from Wah Chang Corporation, Albany, Oregon. A Mettler H 15 balance was used to weigh amounts larger than 10 mg with accuracy of 0. 1 mg. A keyboard type microbalance was used for weighing amounts of 1-10 mg with an accuracy of better than 0. 02 mg. For amounts smaller than 1 mg of any constituent the standardized stock solution was diluted properly and an adequate aliquot was added to the other constituents of the sample after dissolution.

Each eluate was collected in a suitable size-clean beaker and analyzed either colorimetrically or gravimetrically depending on the size of the sample and the percentages of its constituents. Generally, when the constituent weighed less than 10 mg a colorimetric method was used for the determination. Gravimetric methods were used for larger constituents.

When a colorimetric method was used for the determination a suitable aliquot was taken for analysis. The size of the aliquot depended on the amount of metal species present in the eluate and the sensitivity of the prospective spectrophotometric method. In the case of titanium, for example, an aliquot containing as small as 0.05 mg metal was quite adequate. An amount of 0.1 mg titanium determined with Tiron according to the procedure described earlier (p. 29) has an absorbance of 0.52.

Zirconium is equally sensitive and an aliquot containing 0.05 mg of this metal is quite adequate for the determination with Oxine. Hafnium is about one-half sensitive compared to zirconium and consequently the aliquot used for analysis should contain around 0.1 mg of this metal. In all three cases a concentration step, such as evaporation, is necessary if the sample content of the determined metal is less than 0.5 mg. The thiocyanate method (67, p. 644) used for the determination of small amounts of molybdenum in procedures 11, 12 and 13 is very sensitive and an aliquot, of the molybdenum eluate containing 0.05 mg is adequate. No concentration step is recommended here because the molybdenum eluate fraction contains rather large amounts of sulfuric acid.

For gravimetric analysis of titanium, zirconium, hafnium, and niobium a cupferron precipitation was performed. Molybdenum was precipitated with α-benzoinoxime. Both precipitation procedures were described earlier (pages 25 and 26). Tables II, III, IV and V show the results obtained on the analysis of such synthetic mixtures

TABLE II. Analysis of Synthetic Base Alloys Containing Titanium and Zirconium[a]

Synthetic Alloy	Procedure no.[b]	Sample Weight mg	Titanium			Zirconium		
			Present mg	Found mg	Recovery %	Present mg	Found mg	Recovery %
Molybdenum Base Alloy	1	100	0.050	0.050	100	0.080	0.079	98.8
		100	0.250	0.245	98	0.050	0.049	98
		100	1.000	0.985	98.5	1.000	0.99	99
Molybdenum Base Alloy	2	20	1.000	0.99	99	1.000	0.98	98
		20	3.50	3.45	98.6	2.10	2.12	101
		10	4.00	3.94	98.5	0.200	0.196	98
		15	0.500	0.520	104	5.00	4.97	99.4
Niobium Base Alloy	7	25	0.500	0.505	101	0.100	0.985	98.5
		25	4.54	4.46	98.2	1.58	1.57	99.4
		20	2.10	2.08	99	4.50	4.35	96.6
		15	4.95	4.89	98.8	0.800	0.805	100.6
Tantalum Base Alloy	9	20	0.050	0.049	98	0.500	0.500	100
		15	3.14	3.10	98.7	3.80	3.73	98.3
		15	4.75	4.68	98.6	1.15	1.14	99.2
TZM Alloy[c]	1	100	0.50	0.50	100	0.080	0.079	98.8

[a] All determinations were carried out colorimetrically.

[b] These numbers refer to the listed procedures in Table I.

[c] A space alloy obtained from the Wah Chang Corp., Albany, Oregon.

TABLE III. Analysis of Synthetic Base Alloys Containing Titanium and Hafnium[a]

Synthetic Alloy	Procedure no.	Sample Weight mg	Titanium			Hafnium		
			Present mg	Found mg	Recovery %	Present mg	Found mg	Recovery %
Molybdenum Base Alloy	4	100	0.100	0.992	99.2	0.100	0.097	97
		100	0.500	0.490	98	0.500	0.49	98
		100	1.000	1.000	100	1.000	0.975	97.5
Molybdenum Base Alloy	5	20	0.500	0.500	100	0.800	0.790	98.8
		15	2.54	2.41	95	4.60	4.52	98.4
		10	3.02	3.08	98.2	1.80	1.78	98.9
Niobium Base Alloy	8	20	0.200	0.196	98	0.200	0.188	94
		15	1.57	1.55	98.7	3.32	3.27	98.5
		15	3.18	3.10	97.5	1.58	1.58	100
Tantalum Base Alloy	10	20	0.200	0.202	101	0.400	0.395	98.7
		20	4.40	4.29	97.6	1.75	1.73	99
		15	1.000	1.000	100	1.000	0.970	97

[a] All determinations were carried out colorimetrically.

TABLE IV. Analysis of Synthetic Alloys Containing Molybdenum, Titanium and Zirconium or Hafnium[a]

Procedure no.	Sample Weight mg	Present mg	Found mg	Recovery %	Present mg	Found mg	Recovery %	Present mg	Found mg	Recovery %
		Molybdenum			Titanium			Zirconium		
3	50.0	15.0	14.8	98.6	15.0	14.7	98	20.0	19.9	99.5
	70.0	30.0	28.9	96.5	20.0	19.8	99	20.0	19.5	97.5
	85.0	35.0	34.7	99.2	20.0	19.4	97	30.0	30.4	101.2
		Molybdenum			Titanium			Hafnium		
6	40.0	15.0	14.7	98	10.0	9.75	97.5	15.0	14.9	99.3
	50.0	25.0	24.3	97.2	12.0	11.8	98.3	13.0	13.2	101.5
	60.0	30.0	29.8	99.4	15.0	13.9	92.6	15.0	14.6	97.3

[a] All determinations were carried out gravimetrically.

TABLE V. Analysis of Synthetic Binary Alloys[a]

Binary Alloy	Procedure no.	Sample Weight mg	Present mg	Found mg	Recovery %	Present mg	Found mg	Recovery %
				Titanium			Molybdenum	
Titanium-Molybdenum	11	50.0	25.0	24.8	99.2	25.0	24.3	97.2
		30.0	29.0	--	--	1.00	1.00	100
		25.0	0.250	0.245	98	24.75	--	--
				Hafnium			Molybdenum	
Hafnium-Molybdenum	12	50.0	30.0	29.5	98.3	20.0	19.8	99
		40.0	1.00	0.99	99	39.0	--	--
		40.0	38.0	--	--	2.00	1.97	98.5
				Zirconium			Molybdenum	
Zirconium-Molybdenum	13	50.0	25.0	24.6	98.4	25.0	25.2	100.8
		30.0	0.500	0.500	100	29.5	--	--
		30.0	29.0	--	--	1.00	0.97	97
				Titanium			Niobium	
Titanium-Niobium	14	50.0	30.0	29.2	97.3	20.0	20.0	100
		25.0	2.42	2.38	98.4	22.6	--	--
				Hafnium			Niobium	
Hafnium-Niobium	15	40.0	25.0	24.5	98	15.0	14.8	98.7
		25.0	4.56	4.52	99.2	20.4	--	--
				Zirconium			Niobium	
Zirconium-Niobium	15	50.0	25.0	24.9	99.6	25.0	24.1	96.4
		40.0	3.20	3.14	98.2	36.8	--	--
				Titanium			Hafnium	
Titanium-Hafnium	16	100.0	60.0	59.5	99.2	40.0	39.7	99.2
		50.0	1.52	1.50	98.8	48.5	--	--
		20.0	19.2	--	--	0.800	0.780	97.5
				Titanium			Zirconium	
Titanium-Zirconium	17	80.0	40.0	39.4	98.5	40.0	40.3	100.8
		30.0	26.5	--	--	3.54	3.45	97.5
		30.0	8.10	8.08	99.7	21.9	--	--

---

[a] Amounts exceeding 10 mg were determined gravimetrically. Smaller amounts were determined colorimetrically.

and the TZM alloy obtained from Wah Chang Corporation, Albany, Oregon.

Evaluation of the Separation Procedures

The proceeding separation results indicated that the new procedures are quite satisfactory for the practical analysis of numerous combinations of refractory metals. Within an error of ±1%,as little as 0.05% of either titanium or zirconium in a molybdenum base alloy, could be determined. Some of these procedures, like procedures (12) and (13), can be used for the analysis of mixtures containing small amounts of either components of the mixture as well as for comparatively large amounts of both of them.

As these separations are performed without the use of hydrofluoric acid as an eluent, this is quite an advantage over many of the procedures currently used which employ mixtures of this acid with hydrochloric acid for elution. The use of hydrofluoric acid is associated with many inconveniences which were mentioned earlier.

The time necessary to perform one of these separations and the subsequent analysis of the different constituents depends on the procedure itself and on whether the constituents are determined gravimetrically or colorimetrically after the separation. Gravimetric determinations consume more time than colorimetric ones. To cite an example the analysis of the TZM alloy, which is a molybdenum base alloy containing small amounts of titanium and zirconium, takes about eight hours to perform. Assuming that the column was already prepared and preconditioned, about one hour is necessary to dissolve the sample, fume it and prepare it for loading, 30 min - 1 hour for the loading itself, three hours for the elution of titanium and zirconium and two hours for the colorimetric determination of zirconium and titanium. Molybdenum is eluted during these determinations. Separation procedures employing methanol as a mixed solvent in the eluent consume about four hours more. This is due to the large volumes of eluents needed, the slower rate of elution and the time necessary for the evaporation of methanol from the aliquots taken for analysis.

The success of the sulfuric oxalic acid system in handling the usually troublesome refractory alloys should establish that system as a suitable one which should be investigated further and applied to the separation of other metallic mixtures. The only limitation encountered in this investigation is the restriction on the sample size in the case of tantalum and niobium alloys containing titanium and hafnium or zirconium. This was necessary to prevent any possible contamination of the eluted constituents.

Complex Formation

When an ion exchanger is brought into contact with a solution containing different ionic species, exchange of ions will take place until equilibrium is established. As a result, some counter ions are exchanged and retained by the resin in preference to others. This selectivity is due to one or several of the following reasons:

1. The Donnan potential, a purely electrostatic effect, results in preference for the counter ion of higher valence, particularly when the ion exchange capacity is high and the external solution is dilute.

2. The specific interactions between a counter ion and the fixed ionic groups (ion pair formation or strong complexation) result in a preference of this ion.

3. The sieve action on one hand and the tendency of the elastic matrix to contract on the other hand, imposes some limitations on the size of the sorbed counter ions.

4. The complex formation of the counter ion with the co-ion affects the selectivity of the ion exchanger profoundly. This selectivity is closely related to the stability of the complexes formed. Measurements of the ion exchange equilibria in the presence of complexing agents have been used for calculating complex stability constants.

Due to this complex formation the separation of complexed metal species can be achieved by adjusting the complexing ligand concentration which, in turn, determines the fraction of the metal which is present as sorbable complex anions.

The sulfuric-oxalic acid system, as a complexing medium, is a rather complicated one due to the fact that both acids are able to form complexes with the investigated metal ions. The stability of these complexes depends greatly on the concentration of both acids. Generally, sulfuric acid can form anionic complexes with titanium, zirconium, hafnium and molybdenum only at low acid concentrations. Oxalic acid, on the other hand, seems to form very stable complexes with all the six investigated metal ions. These complexes are formed at as low as 0.025 M oxalic acid concentration and their stability increases at higher acid concentrations.

Sulfate Complexes

It is clear from Figure II that titanium, among the four metal ions investigated forms the weakest anionic species, if any, at very low concentrations of sulfuric acid. Beukenkamp (3) found that titanium is present in the form of $Ti(OH)_3^+$, $Ti(OH)_2^{++}$, $Ti(OH)_2HSO_4^+$, and $Ti(OH)_3HSO_4$ in sulfuric acid solution. Using electrolytic techniques Nabivanets (57) found that, in sulfuric acid solution of less than 0.1 M, all of the titanium species migrate toward the cathode, indicating the formation of positively charged species. This author also studied the titanium complexes formed in a sodium sulfate solution acidified with 0.2 M perchloric acid. He found that the titanium complexes present are TiO^{+2}, $TiOSO_4$ and $TiO(SO_4)_2^{-2}$, with the last anionic species predominant at sulfate concentrations higher than one molar. Consequently it seems reasonable that the titanyl ion TiO^{++} requires high level of the sulfate ion to form the anionic complex $TiO(SO_4)_2^{-2}$. This level is not available at high concentrations of sulfuric acid where the predominant species is HSO_4^-.

Hafnium and zirconium, when compared with titanium, seem to form more stable anionic complex species at low concentrations of sulfuric acid. At 2% sulfuric acid which corresponds to 0. 37 M, zirconium is almost completely absorbed by the resin while hafnium is absorbed to an extent of about 90%. This is in complete agreement with Machlan and Hague (53) and Rajan and Gopta (60) who found that the anionic zirconium complexes with sulfuric acid are more stable than those of hafnium.

The composition of the zirconium and hafnium species present in sulfuric acid solution is not well known, because the metal ion is involved in three reactions simultaneously: hydrolysis, polymerization and complexation. The hydrogen ion concentration of the solution is the main factor that determines the extent of each of these reactions. Conick and Mcvey (12) found that in 2 M perchloric acid the average zirconium species at low metal ion concentration ($4.7 \times 10^{-5} - 5.1 \times 10^{-4}$M) has a charge somewhere between +3 and +4 and is not polymerized. This corresponds to a mixture of Zr^{+4} and $ZrOH^{+3}$ or possibly ZrO^{++}. At higher zirconium concentrations there is abundant evidence that zirconium is polymerized and considerably more hydrolyzed in the polymers than when present as the monomer. Due to the very close similarity of hafnium and zirconium the polymer might contain both metal ions in the same structure when a mixture of both metals is in solution. This is apparently the reason why Machlan and Hague (53) needed two anion exchange steps to separate zirconium from hafnium when the original mixture contained more than 20% zirconium. This separation was carried out in 3.5% sulfuric acid solution. Connick and Mcvey also studied the stability of the zirconium complexes formed with the sulfate ion in the 2 M perchloric acid. They found that at bisulfate concentration of 10^{-2} M the zirconium complex present is mainly $ZrSO_4^{++}$ while on increasing the bisulfate concentration to 0.3 M the zirconium compound $Zr(SO_4)_3^{=}$ is formed. Before going any further it should be noticed that it is the sulfate rather than the bisulfate ion which is present in such complexes. The attachment of either Zr^{+4} or ZrO^{++} to a bisulfate ion should make the hydrogen ion readily ionizable. Just as the attachment of one hydrogen ion in sulfuric acid makes the other hydrogen a strong acid. Ryabchikov et al. (65) found very similar results to those of Connick and Mcvey. Using ion exchange techniques they found that, at 0.1 M sulfuric acid concentration and hydrogen ion concentration of 2.33 M, zirconium forms $Zr(SO_4)^{+2}$, $Zr(SO_4)_2$ and $Zr(SO_4)_3^{-2}$ while hafnium forms $Hf(SO_4)^{+2}$ and $Hf(SO_4)_2$ only. They also reported that the metal complexes are actually hydrates of the type $M(SO_4)_n^{4-2n} \cdot (H_2O)_m$ where the sum of n and m is equal to the coordination number of the quadruply charged metal ion which is generally 6. This leads to the belief that zirconium and hafnium, in sulfuric acid solution, form complexes of the type

$$M(SO_4)_n^{4-2n} \cdot (H_2O)_m \text{ or possibly } MO(SO_4)_n^{2-2n} \cdot (H_2O)_m \,.$$

The concentration of sulfuric acid is the main factor that determines the value of n. Assuming that the complex formation is represented by the following equilibrium:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^=$$

$$nSO_4^= + M^{+4} \rightleftharpoons M(SO_4)_n^{4-2n}$$

The bisulfate ion should be present in moderate amounts so that it furnishes the sulfate ion which complexes the metal ion. High acidity, however, suppresses the first dissociation equilibria and consequently inhibits the formation of the metal sulfate anionic species. In other words both the metal and the hydrogen ions are competing for the sulfate ion.

Figure II shows that molybdenum, among the four metals, appears to form the most stable complexes with sulfuric acid. Such anionic complexes, however, seem to be involved in a slow hydrolysis or polymerization process that leads to the formation of some cationic or neutral species. This slow equilibrium is probably the cause of the premature elution of molybdenum which was observed earlier (p. 46). The nature of molybdenum-sulfate anionic species is not known. It was reported (14, p. 800) that, on cooling a hot saturated solution of MoO_3 in concentrated sulfuric acid, the molybdenyl sulfate, MoO_2SO_4, crystalizes out. By treating this compound with alkali metal sulfate solutions, complex salts of the formulas $M^I_2[Mo_2O_6(SO_4)]$ and $M^I_2[Mo_2O_4(SO_4)_3]$ have been obtained. In this investigation the treatment of molybdenum goes through the same path except that the cooled concentrated sulfuric acid solution of molybdenum was dissolved in dilute sulfuric acid solution instead of the alkali metal sulfate solution. This, probably, produced the same anionic species reported previously except that hydrogen ions replaced the alkali metal ions outside the coordination sphere.

Oxalate Complexes

Due to the chelating character of the oxalate ion it forms a great many stable coordination compounds, usually acting as a bidentate group. The complexing power of the oxalate ion greatly exceeds that of the sulfate ion. Consequently when both ions are involved in the formation of a particular complex with some metal ion it can be assumed that the oxalate metal complex is dominant. In this sense the sulfuric acid would act only as a supplier of the hydrogen ion thus controlling the dissociation of oxalic acid and the amount of oxalate ion available for the complex formation.

Comparing Figure II on one hand with Figures IV and V on the other hand, it is concluded that the introduction of small amounts of oxalic acid into the sulfuric acid solution results in the formation of more stable complexes. As the concentration of sulfuric acid increases the stability of these complexes goes down due to the suppression of the dissociation of oxalic acid.

$$H_2C_2O_4 \rightleftharpoons 2H^+ + OX^=$$

$$mOX^= + M^{+n} \rightleftharpoons [M(OX)_m]^{n-2m}$$

M^{+n} in the last equilibrium denotes a simple metal ion or a partially hydrolyzed metal ion.

It is interesting to notice that the titanium curve in Figure V is above the hafnium curve. The position of the two curves is reversed in Figure IV which leads to the conclusion that titanium forms more stable oxalate complexes than hafnium. No premature elution of molybdenum was observed when oxalic acid is present, indicating the existence of a stable complex. As a matter of fact molybdenum, among the six metal ions investigated, forms the most stable anonic complexes with oxalic acid. These complex species persist even at high sulfuric acid concentration (C = 27 in 20% sulfuric-0.025 M oxalic acid solution). By increasing the oxalic acid concentration at a constant sulfuric acid level (6% in Figure VI), a state is reached where the distribution coefficients level out. Apparently, at that point essentially all the available metal ions have been complexed with oxalic acid.

The composition of the complexes depends mainly on the concentrations of the two acids. In the case of titanium, Figure IV indicates that no significant level of titanium anionic species is present in the 6%-0.025M solution. This is in agreement with Babko and Dubovenko (1) who found that at pH $\leqslant 1$ titanium forms the simple complex $TiOC_2O_4$ with oxalic acid. Although their studies were conducted in the noncomplexing medium of perchloric acid, sulfuric acid at the 6% level does not form any anionic species with titanium ($C \approx 1$ from Figure II). As the concentration of oxalate ion rises, which could be attained by either increasing the concentration of oxalic acid or decreasing the sulfuric acid percentage, complex anionic species such as $TiO(C_2O_4)_2^{=}$ are formed. These authors also determined the dissociation constants of both the titanylmono-oxalate and di-oxalate complexes:

$$TiOC_2O_4 \leftrightharpoons TiO^{++} + C_2O_4^{=} \qquad K = 2.5 \times 10^{-7}$$

$$TiO(C_2O_4)_2^{-2} \leftrightharpoons TiOC_2O_4 + C_2O_4^{=} \qquad K = 5 \times 10^{-4}$$

Pecsok also (59), using polarographic techniques, found that $TiO(C_2O_4)_2^{=}$ was formed in 0.1M oxalic-0.5M sulfuric acid solution.

The stability of zirconium complexes in an excess of oxalate ion indicates the formation of complexes with a strong metal-ligand bond. Depending mainly on the acidity of the solution either the zirconium ion or the zirconly is involved in the complexation. According to Zaitsev and Bochkarev (82) the complex ions $ZrC_2O_4^{+2}$, $ZrOC_2O_4$, $[ZrO(C_2O_4)(H_2O)_2]$, $[ZrO(C_2O_4)_2]^{-2}$ and $[(ZrO)_2(C_2O_4)]^{+2}$ have been found in oxalate solution. Here also an increase in the oxalate ion favors the formation of complex anions. Blumenthal (5, p. 324) reported that the formed complex anion is $[ZrO(C_2O_4)_2(H_2O)]^{-2}$.

The stability of the oxalate complexes of niobium and tantalum is intermediate between those of zirconium and molybdenum. Very little information is available on the structure of such compounds. Green (26) showed that up to 98% of niobium is removed from sulfuric acid solution containing small amounts of oxalic acid by one extraction with a liquid anion exchange resin. The extraction was also found to decrease with an increase in concentration of free acid. Using electrolytic migration techniques Nabivanets (58) studied the complex formation of Ta(V) ions in 0.5 N hydrochloric acid solution containing different complexing agents. He found that at $Ta:C_2O_4^{=}$ ratios of 1:1 and 1:2, electrically neutral complexes were formed. At higher oxalate concentrations, however, anionic complexes were formed. More than 90% of tantalum was in the anionic form in 0.025M oxalic-0.5M hydrochloric acid solution.

Molybdenum oxalato complexes, the most stable among all the complexes investigated, have been studied recently by Wendling and

Rohmer (76). Using polarographic and spectrophotometric techniques they showed that the predominant complex formed by molybdenum in oxalate solution, is $MoO_2(C_2O_4)^-$. The fact that this complex is formed by the coordination of the molybdenyl ion, MoO_2^+, with one oxalate ion, $C_2O_4^=$, readily explains why a larger fraction of the total molybdenum is complexed. All other metal ions require at least two oxalate ions to form the negatively charged complex.

The Effect of Methanol on the Exchange Adsorption

Water is by no means the only solvent which allows ion exchange to take place. Methanol, among other solvents with high dielectric constants, is a water-like solvent in which electrolytes can dissolve and dissociate, but not to the same extent as in water. Mainly because this investigation was carried out in mixed water-methanol media, no attempt is made to discuss the ion exchange phenomenon in pure nonaqueous solvents.

The replacement of a fraction of the water content of the solution in equilibrium with the resin by methanol can be expected to exert an influence, both in the solution and in the resin phase:

Resin Swelling

Due to the fact that a more polar solvent causes more swelling than a less polar solvent (30, p. 500) most resins have been found to swell less in pure methanol than in water. This can be readily understood by comparing the dipole moment of water (1.84 Debye) with that of methanol (1.68 Debye). This solvent uptake 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. It follows that water will be concentrated in the resinous phase 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 solvent 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 uptake by the resin becomes more profound with decreasing water content of the mixed solvent. Due to the comparatively small difference between the dipole moments of water and methanol this selective uptake is not very pronounced. The affinity of the functional groups of the quaternary amine type anion resins for alcohols partially compensates the contrary influence of the low polarity of methanol. It was noticed during the course of this research that Dowex 1-X8 resin swells about 9% less in solution containing 60% methanol than in pure aqueous eluents. Rückert and Samuelson (64) found that the sulfate form of Dowex 2-X8 swells about 18% less in solution containing 78% ethanol than in pure aqueous solution. Bonner and Moorefield (7) found that less swelling of a resin, like increased cross linkage, causes an increase of selectivity coefficients.

Dissociation

The comparatively low dielectric constant of methanol ($\epsilon = 32.6$ at 25°C) compared to water ($\epsilon = 78.5$ at 25°C) results in increasing ionic interaction and consequent repression of the dissociation of whatever electrolyte is present either in the resin phase or in the solution in equilibrium with the resin. The magnitude of this effect and its relation to the dielectric constant can be readily explained by Bjerrum's theory of ion pair formation (29, p. 70-74). Acetic acid has an ionization constant of 1.75×10^{-5} in water whereas it drops to 2×10^{-11} in ethanol where the dielectric constant is 24.2. Kolthoff and Brukenstien found that the dissociation constant of benzoic acid drops from 6.6×10^{-5} in water to 4×10^{-11} in methanol. This factor is highly important in the sulfuric-oxalic acid system due to the fact that oxalic acid is rather weak. It was concluded earlier (p. 90) that sulfuric acid in an oxalic acid solution serves only as a hydrogen ion reservoir which suppresses the dissociation of oxalic acid especially at the second ionization step $K_2 = 6.4 \times 10^{-5}$. Being strong, sulfuric acid is hardly affected by the presence of methanol but will continue to suppress the dissociation of oxalic acid. As a result, the dissociation of the weak hydrogen oxalate ion is repressed by both sulfuric acid and methanol, thus furnishing less oxalate ions necessary to complex the metal ion species. It should be pointed out that this investigation was not carried out in pure methanol but rather in a mixed water-methanol medium. The two ionization constants of oxalic acid ($K_1 = 5.9 \times 10^{-2}$ $K_2 = 6.4 \times 10^{-5}$) can be expected to decrease proportionally with the amount of methanol present in the solution. Apparently this is the main reason behind the gradual decrease of the distribution coefficients of molybdenum, niobium, tantalum and titanium (Figure VII) when increasing amounts of methanol are present in the 6% sulfuric-0.05M oxalic acid solution. There has been only one investigation where this same problem was encountered. In order to recover very small amounts of gold from a cyanide solution Burstall et al (9) used the strongly basic anion exchanger IRA-400 to absorb the gold and the other heavy metals cyanide complexes. To elute this gold they unsuccessfully tried different mineral acid solutions. Finally they found that gold can be easily eluted with an acetone solution containing 5% hydrochloric acid plus 5% water. As an explanation they rationalized that the presence of the mineral acid would bring about a partial ionization of the gold resin complex and that the complex gold ion would then be free to form, in the presence of the mineral acid, a nonionized covalent complex, with the solvent, which has little tendency to be readsorbed. Applying the interpretation proposed for the oxalate complexes a more reasonable explanation would be the suppression of the dissociation of the hydrogen cyanide and the consequent break of the gold cyanide complex. After all, gold is not known to form any complexes with acetone.

Solvation and Complex Formation

In all anion exchange studies, carried out in mixed solvents containing strong acids like hydrochloric (21), sulfuric (43) and nitric (18), the replacement of water by an organic solvent has been found to enhance the ion exchange absorbalities of ionorganic ions considerably. No significant repression of the acid dissociation constants is encountered here specially when the organic solvent is the water-like type but with lower dielectric constant. This will ensure the presence of a sufficiently high ligand concentration for the complexation of the metal ion. This is contrary to the situation just encountered where the weak oxalic acid is to furnish the oxalate ligands necessary for complexation. The enhancement of the absorbtion is due mainly to the role of the organic solvent in the solvation and complex formation of the metal ion species. There are many possible explanation for the increase of metal ion absorption by the resin. Yoshino and Kurimura (81) believe that the addition of the organic solvent favors the dehydration of the aquated metal ion and consequently favors the stepwise formation of negatively charged complexes. The fact that the resin phase is more concentrated in water than the outside solution explains why the hydrophilic electrolytes prefer the more aqueous pore liquid to the more organic liquid phase outside. Davies and Owen (15) found that potassium and sodium are tightly held by a cation exchange resin when they are absorbed from a 0. 7 N hydrochloric acid solution containing 80% acetone. Another possible factor is that the stability of the particular anionic complexes is enhanced by the introduction of the organic solvent. Korkisch and Tera (44) found that thorium forms negatively charged complexes with hydrochloric acid only if the solution contains high percentage of alcohol. No such complexes are formed in pure aqueous hydrochloric acid solution. Finally, neutral adsorption could be the reason behind the high absorbabilities. The lower the dielectric constant of the organic solvent the more association of electrolytes is obtained. Because there is no Donnan potential barrier against the adsorption of an uncharged species the entire salt might be extracted by the resin phase. The absorption of some metal chlorides from acid solution containing acetone was explained, by Katzin and Gebert, (34) on this basis.

The increase of the distribution coefficients of both hafnium and zirconium in Figure VII is, apparently, attributed to one or more of the preceding factors. Assuming that the methanol content of the solution suppresses the dissociation constants of oxalic acid and brings the oxalate ion concentration to a minimum, only the zirconium and hafnium metal ions are then present in a 6% sulfuric-acid-60% methanol. Like any other absorption from a strong acid solution the resin uptake of the metal species increases on increasing the amount of the organic solvent in the solution. This was confirmed by the determination of the distribution coefficients of both hafnium and zirconium in 6% sulfuric-60% methanol solution with no oxalic acid present (Figure IX).

A very small amount of oxalate is present in 6% sulfuric-0.050M oxalic-60% methanol. Its effect on the variation of the distribution coefficients, when increasing amounts of methanol are present, can be detected by carefully comparing the hafnium and zirconium curves in Figures VII and IX. In 6% sulfuric-0. 05 M oxalic the distribution coefficient of hafnium increases by a factor of 1. 9 on replacing 60% of the water content of the solution with methanol. In 6% sulfuric acid the factor is about 7. The same thing can be said about zirconium where the factors are 2. 1 and 8. Again, this leads to the conclusion that the presence of methanol influences the absorption of the metal species in two opposite directions depending on whether the complex is formed by a weak acid like the axalic or a strong acid like the sulfuric.

It was already pointed out (p. 87) that the formation of a titanium anionic complex requires a comparatively high level of sulfate ion. No matter how high or low the sulfuric acid concentration may be, anionic species can not be formed in sulfuric acid solution. Only in a solution with high concentration of a sulfate salt and low acidity can such anionic species exist. The addition of methanol to 6% sulfuric acid solution does not fulfill such requirement. This is apparently the reason behind the almost complete lack of absorption of titanium by the resin, a phenomenon evident in Figure IX.

The behavior of molybdenum in 6% sulfuric-60% methanol can not be explained according to any one of the previous patterns. If molybdenum forms stable sulfate complexes, like those of hafnium and zirconium, it would be expected to be absorbed more tightly on the addition of methanol and the distribution coefficients should increase instead of decreasing as illustrated in Figure IX. This odd behavior and the premature elution already observed, (p. 46) appear to confirm the assumption made earlier that the anionic molybdenum sulfate species are involved in a slow equilibrium with some neutral or positively charged species. The presence of methanol appears to favor the break of those anionic species and promote their transfer into an unabsorbable form by the resin. The fact that molybdenum is largely present in a polymerized form in solution might have a great effect upon this odd behavior also. It is also possible that methanol promotes the formation of large polymers which can not go through the small pores of the Dowex 1-X8. Further kinetic and complexometric studies are necessary to establish the nature of molybdenum in sulfuric acid solution and the effect of methanol on the species formed.

BIBLIOGRAPHY

1. Babko, A. K. and L. I. Dubovenko. Oxalate complexes of titanium (IV). Russian Journal of Inorganic Chemistry 4:165-168. 1959.

2. Bandi, W. R. et al. Anion exchange separation of zirconium, titanium, niobium, tantalum, tungsten and molybdenum. Analytical Chemistry 33:1275-1278. 1961.

3. Beukenkamp, John and Kermit D. Herrington. Ion-exchange investigation of the nature of titanium (IV) in sulfuric acid and perchloric acid. Journal of the American Chemical Society 82:3025-3031. 1960.

4. Bhatnagar, S. S., A. N. Kapur and M. L. Puri. Adsorption properties of synthetic resins. Journal of the Indian Chemical Society 13:679-688. 1936.

5. Blumenthal, Warren B. The chemical behavior of zirconium. Princeton, New Jersey, Van Nostrand, 1958. 398 p.

6. Bonner, O. D. Use of ion exchange resins with nonaqueous and mixed solvents. Journal of Chemical Education 34:174-177. 1957.

7. Bonner, O. D. and Jane C. Moorefield. Ion exchange in mixed solvents. Journal of Physical Chemistry 58:555-557. 1954.

8. Brake, Loren D., Wallace M. McNabb and J. Fred Hazel. A spectrophotometric method for the determination of nickel. Analytica Chimica Acta 19:39-42. 1958.

9. Burstall, F. H. et al. Ion exchange process for recovery of gold from cynide solution. Industrial and Engineering Chemistry 45:1648-1658. 1953.

10. Cheng, K. L. Analytical applications of Xylenol Orange-I. Determination of traces of zirconium. Talanta 2:61-66. 1959.

11. ________________. Determination of zirconium and hafnium with Xylenol Orange and Methylthymol Blue. Analytica Chimica Acta 28:41-53. 1963.

12. Connick, Robert E. and William H. McVey. The aqueous chemistry of zirconium. Journal of the American Chemical Society 71:3182-3191. 1949.

13. Cornish, F. W. The practical application of chromatographic theory to analytical and preparative separations by ion-exchange elution. Analyst 83:634-642. 1958.

14. Cotton, Albert F. and G. Wilkinson. Advanced inorganic chemistry. New York, Interscience, 1962. 959 p.

15. Davies, C. W. and B. D. R. Owen. The behavior of ion-exchange resins with mixed solvents. Journal of the Chemical Society, 1956. p. 1676-1680.

16. Edge, R. A. The adsorption of yttrium, neodymium and lanthanum on a strong base anion exchange resin from dilute hydrochloric acid solutions containing ethanol. Journal of Chromatography 5:539-540. 1961.

17. ________________. Anion exchange behavior of some rare earths in dulute sulphuric acid solutions containing ethanol. Journal of Chromatography 6:452-454. 1961.

18. Faris, John P. and Joseph W. Warton. Anion exchange resin separation of the rare earths, yttrium and scandium in nitric acid - methanol mixtures. Analytical Chemistry 34:1077-1080. 1962.

19. Freund, Harry and Frend John Miner. Determination of aluminum in zirconium. Analytical Chemistry 25:564-567. 1953.

20. Fritz, James S. and Richard G. Greene. Separation of rare earths from other metal ions by anion exchange. Analytical Chemistry 36:1095-1097. 1964.

21. Fritz, James S. and Donald J. Pietrzyk. Non-aqueous solvents in anion-exchange separations. Talanta 8:143-162. 1961.

22. Fritz, James S. and Thomas A. Rettig. Separation of metals by cation exchange in acetone-water-hydrochloric acid. Analytical Chemistry 34:1562-1566. 1962.

23. Fritz, James S. and Hirohiko Waki. Anion exchange separation of magnesium and calcium with alcohol-nitric acid. Analytical Chemistry 35:1079-1083. 1963.

24. Fritz, James S., Hirohiko Waki and Barbara B. Garralda. Anion exchange separation of calcium and strontium. Analytical Chemistry 36:900-903. 1964.

25. Glueckauf, E. Theory of chromatography. Transactions of the Faraday Society 51:34-44. 1955.

26. Green, H. The application of liquid ion exchange resins in analysis. Part III. The reaction of niobium and uranium. Metallurgia 68:143-145. 1963.

27. Hague, John L., Eric D. Brown and Harry A. Bright. Separation of titanium, tungsten, molybdenum and niobium by anion exchange. Journal of Research of the National Bureau of Standards 53:261-262. 1954.

28. Hague, John L. and Lawrence A. Machlan. Determination of titanium, zirconium, niobium and tantalum in steels: Separations by anion exchange. Journal of Research of the National Bureau of Standards 62:11-19. 1959.

29. Harned, H. S. and B. B. Owen. Physical chemistry of electrolytic solutions, 3d ed. New York, Reinhold, 1958. 803 p.

30. Helfferich, Friedrich. Ion exchange. New York, McGraw-Hill, 1962. 624 p.

31. Hillebrand, W. F. et al. Applied inorganic analysis. 3d ed. New York, John Wiley, 1959. 1034 p.

32. Huffman, E. H. and R. C. Lilly. The anion exchange separation of zirconium and hafnium. Journal of the American Chemical Society 71:4147. 1949.

33. Kakita, Yachiyo and Hidehiro Goto. Spectrophotometric determination of tantalum in iron, steel and niobium metal. Analytical Chemistry 34:618-621. 1962.

34. Katzin, Leonard and Elizabeth Gebert. Absorption of inorganic salts from organic solvents onto anion exchange resins. Journal of the American Chemical Society 75:801-803. 1953.

35. Kember, N. F., Patricia J. Macdonald and R. A. Wells. The selective elution of metals adsorbed on cation-exchange resins by organic solvents. Part I. Journal of the Chemical Society, 1955. p. 2273-2280.

36. Khopkar, Shripad M. and Anil K. De. Anion exchange studies of zirconium (IV) in citrate solution. Analytica Chimica Acta 24:134-137. 1961.

37. Kojima, M. Japan Analyst: The Journal of Japanese Society for Analytical Chemistry 6:369. 1957.

38. Korkisch, J. Methode zur bestimmung von titan in natürlichen wässern. Zeitschrift für Analytische Chemie 178:39-42. 1960.

39. Korkisch, J. and A. Farag. Beiträge zur analytischen chemie des zirkoniums. Zeitschrift für Analytische Chemie 166: 81-88. 1959.

40. Korkisch, Johann and Isidor Hazan. Anion exchange separation of gallium, induim and aluminum. Analytical Chemistry 36:2308-2311. 1964.

41. Korkisch, J., I. Hazan and G. Arrhenius. Ion exchange in mixed solvents. Talanta 10:865-877. 1963.

42. Korkisch, J. and G. E. Janauer. The distribution of vanadium between alcoholic-hydrochloric acid solutions and the strongly basic anion-exchanger Dowex-1. Talanta 8:569-574. 1961.

43. Korkisch, J. and G. E. Janauer. Ion exchange in mixed solvents. Talanta 9:957-985. 1962.

44. Korkisch, Johann and Fouad Tera. Separation of thorium by anion exchange. Analytical Chemistry 33:1264-1266. 1961.

45. Kraus, Kurt A. and George E. Moore. Anion exchange studies. III. Protactinium in some HCl-HF mixtures: separation of niobium, tantalum and protactinium. Journal of the American Chemical Society 73:2900-2902. 1951.

46. Kraus, Kurt A. and George E. Moore. Separation of columbium and tantalum with anion exchange resins. Journal of the American Chemical Society 71:3855. 1949.

47. ________________. Separation of zirconium and hafnium with anion exchange resins. Journal of the American Chemical Society 71:3263. 1949.

48. ________________. Separation of zirconium and niobium in HCl-HF mixtures. Journal of the American Chemical Society 73:9-13. 1951.

49. Kraus, Kurt A. and Frederick Nelson. Anion exchange studies. VIII. Separation of iron and aluminum in sulfate solutions. Journal of the American Chemical Society 75:3273-3274. 1953.

50. ________________. Anion exchange studies of the fission products. I. Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955. New York, United Nations 1956. Vol. 7, p. 113-125.

51. Kraus, Kurt A., Frederick Nelson and George Moore. Anion exchange studies. XVII. Molybdenum (VI), tungsten (VI) and uranium (VI) in HCl and HCl-HF solutions. Journal of the American Chemical Society 77:3972-3977. 1955.

52. Kressman, R. E. and J. A. Kitchener. Cation exchange with a synthetic phenolsulphonate resin. Journal of the Chemical Society, 1949. p. 1211-1213.

53. Machlan, Lawrence A. and John L. Hague. Separation of hafnium from zirconium and their determination:Separation by anion exchange. Journal of Research of the National Bureau of Standards. 66A:517-520. 1962.

54. Marple, L. W. The sorption of rare earths on anion exchange resins from nitric acid-mixed solvent systems. Journal of Inorganic and Nuclear Chemistry 26:859-864. 1964.

55. Martin, A. J. P. and R. L. M. Synge. A new form of chromatogram employing two liquid phases, a theory of chromatography. Biochemical Journal 35:1358-1364. 1941.

56. Mayer, Stanley W. and Edward R. Tompkins. Ion exchange as a separation method. IV. A theoretical analysis of the column separations process. Journal of the American Chemical Society 69:2866-2874. 1947.

57. Nabivanets, B.I. Determination of the composition and stability of sulphato-complexes of the titanyl ion by ion-exchange chromatography. Russian Journal of Inorganic Chemistry 7:352-354. 1962.

58. ________________. State of tantalum (V) in solutions of oxalic, tartaric, and hydrofluoric acids and hydrogen peroxide. Russian Journal of Inorganic Chemistry 8:1205-1209. 1963.

59. Pecsok, Robert L. A polarographic study of the oxalato complexes of titanium. Journal of the American Chemical Society 73:1304-1309. 1951.

60. Rajan, K.S. and J. Gupta. Separation of zirconium and hafnium using anion-exchange resins:part III - Resolution of hafnia concentrates. Journal of Scientific and Industrial Research 18B:460-463. 1959.

61. Rieman, William and Roger Sargent. Ion exchange. In: Physical methods in chemical analysis. Vol. IV. New York, Academic Press, 1960. p. 133-222.

62. Robinson, David A. and G.F. Mills. Adsorption of fatty acids from solvents. Industrial and Engineering Chemistry 41:2221-2224. 1949.

63. Ruch, R.R., F. Tera and G.H. Morrison. Anion exchange behavior of alkali and alkaline earth elements in dioxane-mineral acid media. Analytical Chemistry 36:2311-2315. 1964.

64. Rüchert, Heinz and Olaf Samuelson. Die verteilung von athylalkohol und wasser bei ionenaustauschern auf harzbasis. Acta Chemica Scandinavic 11:303-314. 1957.

65. Ryabchikov, D.I. et al. Ion exchange study of complex formation by zirconium and hafnium with sulfate ions. Russian Journal of Inorganic Chemistry 7:34-37. 1962.

66. Samuelson, Olof and Eero Sjöström. Ion exchange method for determination of alkali metals in presence of calcium an magnesium. Analytical Chemistry 26:1908-1910. 1954.

67. Sandell, E. B. Colorimetric metal analysis. 3d ed. New York, Interscience, 1959. 1032 p.

68. Shukla, R. P. and R. P. Bhatnagar. Kinetics of cation exchange reaction in solvent other than water. Part II. Effect of water on exchange of copper ion on Amberlite IRC-50. Journal of the Indian Chemical Society 32:782-784. 1955.

69. Snell, F. D. and Cornelia T. Snell. Colorimetric methods of analysis. Vol. II A. Princeton, New Jersey, Van Nostrand, 1959. 703 p.

70. Speeke, A. and J. Hoste. La separation niobium-tantale en milieu chloro-oxalique sur echangeur d'anions. Talanta 2:332-340. 1959.

71. Sugawara, Ken F. Spectrophotometric determination of trace amounts of zirconium, titanium and molybdenum in tungsten using anion exchange separations. Analytical Chemistry 36:1373-1374. 1964.

72. Tompkins, Edward R., Joseph X. Khym and Waldo E. Cohn. Ion exchange as a separations method. I. The separation of fission-produced radioisotopes, including individual rare earths, by complexing elution from Amberlite resin. Journal of the American Chemical Society 69:2769-2777. 1947.

73. Van Erkelens, P. C. On the concentration and separation of the trace-elements Fe, Cu, Zn, Mn, Pb, Mo and Co. Analytica Chimica Acta 25:226-232. 1961.

74. Van Santin R., J. H. Schlewitz and C. H. Toy. The spectrophotometric determination of zirconium with 8-hydroxyquinoline. Unpublished results. Wah Chang Corp. Albany, Oregon. 1965.

75. Wacker, R. E. and W. H. Baldwin. The separation of Zr and Nb oxalato complexes by anionic exchange. 1950. 6 p. (U. S. Atomic Energy Commission. ORNL-637)

76. Wendling, Edgar and Raymond Rohmer. Complexes oxalique due molybdene pentavalent. Bulletin de la Société Chimique de France. 1963. 2550-2555.

77. Wilkins, D. H. The separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium and tantalum in a high temperature alloy by anion-exchange. Talanta 2:355-360. 1959.

78. Wilkins, D. H. and G. E. Smith. Ethanol-water-hydrochloric acid eluents in anion exchange separations. Talanta 8: 138-142. 1961.

79. Wood, D. F. and I. R. Scholes. Determination of niobium and tantalum in binary alloys and zirconium alloys. Analytical Chimica Acta 21:121-135. 1959.

80. Yoe, John H. and Alfred R. Armstrong. Colorimetric determination of titanium with disodium-1, 2-dihydroxybenzene-3, 5-disulfonate. Industrial and Engineering Chemistry, Analytical Edition 19:100-102. 1947.

81. Yoshino, Yukichi and Yoshimi Kurimura. Anion exchange adsorption of some metals from mixed solvents. Bulletin of the Chemical Society of Japan 30:563-566. 1957.

82. Zaitsev, L. M. and G. S. Bochkarev. Preparation of some oxalato compounds of zirconyl. Russian Journal of Inorganic Chemistry 7:802-805. 1962.