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Chromatographic separations of niobium, tantalum, molybdenum, and tungsten

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CHROMATOGRAPHIC SEPARATIONS OF NIOBIUM
TANTALUM, MOLYBDENUM, AND TUNGSTEN.

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CHROMATOGRAPHIC SEPARATIONS OF NIOBIUM
TANTALUM, MOLYBDENUM, AND TUNGSTEN

by

Lionel Herbert Dahmer

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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1966

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INTRODUCTION

The analytical chemistry of tantalum, niobium, molybdenum, tungsten, and titanium has become of prime importance because of recent applications in super alloys for aircraft jet engines and turbine wheels, as alloying constituents for the aerospace effort, for fuel alloys in nuclear reactors, and as containers for molten metals and salts. Other, well-known uses are as alloying elements in tool steels, for surgical materials, and for rectifiers and magnets.

These applications place a great demand on the analytical chemist to develop reliable and versatile methods of separation and determination of these metals. The separation of mixtures of niobium, tantalum, molybdenum, tungsten, and titanium by classical methods is very lengthy and difficult. This is true partly because of the similarity between their chemical properties and partly because of the ease with which salts of these metals are hydrolyzed in acid solution.

It is not uncommon to find all of these metals present in an alloy. In addition, high temperature alloys usually contain cobalt, nickel, chromium, iron and others in varying proportions. The presence or absence of these other metals greatly affects the results obtained by classical methods for separating niobium, tantalum, molybdenum, tungsten, and titanium.

A once-popular classical method of separation is

Schoeller's salicylate procedure (1), for the separation of niobium and tantalum from titanium. In this method, the oxalates of these metal ions are decomposed with calcium chloride in the presence of sodium salicylate, and the earth acids are precipitated as salicylate complexes. The titanium-salicylate complex is soluble, but it coprecipitates. The niobium and tantalum recovery is often not complete and the precision is not very good.

Another procedure, described by Bedford (2), is over fifty years old but is still used. It involves a fusion of the earth acid oxides with potassium carbonate and precipitation of the niobium and tantalum by magnesium sulfate and ammonium chloride. The oxides of niobium, tantalum, titanium, and zirconium are precipitated but alkali tungstate remains in solution.

For about twenty-five years tannin, introduced by Schoeller, was in constant use for earth acid analysis. Schoeller and Powell (3), give detailed instructions for obtaining proper conditions for the separation of many metal ions.

The reagent, N-benzoyl-N-phenyl-hydroxylamine, has been used for obtaining precipitates of niobium, tantalum, and titanium that are virtually free from almost all other elements, including tungsten (4). Various precipitating conditions are used to precipitate consecutively niobium, tantalum, and titanium.

Dams and Hoste (5), were only moderately successful in an

attempt to separate niobium and tantalum by precipitation from homogeneous solution by thermal decomposition of their peroxy complexes in the presence of tannin and oxalate. The separation is improved by extracting the bisulfate melt with ammonium oxalate before adding hydrogen peroxide, hydrochloric acid, and tannin.

The combination of precipitation and separation is very time-consuming, but does give correct results for the metal contents of an alloy. Hague and Machlan (6), have determined niobium, tantalum, titanium, and zirconium in steels by precipitating these elements from solution with cupferron, igniting the precipitate to give mixed oxides, and separating the metal ions on an ion-exchange column.

In the methods discussed thus far, the fact that niobium and tantalum can exist in solution only as some kind of a complex has not been completely exploited. That is, this knowledge is only used to the extent that homogeneous solutions are prepared before a precipitant is added. However, newer techniques based on ion-exchange, cellulose chromatography, and liquid-liquid extraction are designed to take full advantage of the ability of niobium and tantalum to form various complexes which have varying acidities, tendencies to hydrolyze, and stabilities.

Some effective complexing agents which have been used in separations involving niobium, tantalum, molybdenum, and tungsten are hydrogen peroxide, organic acids, and hydro-

chloric-hydrofluoric acid solutions. The use of hydrogen peroxide in separation procedures, rather than hydrofluoric acid or organic acids, has the advantage that determinations or further separations are simplified.

Several cation exchange separations have been reported (7-11) which employ acidic solutions of hydrogen peroxide to elute niobium, tantalum, molybdenum, and tungsten as anionic complexes. However, only one or two of these metals are separated from a few other metals in the procedures reported, and elution conditions vary considerably. A method using a single eluent, that would separate niobium, tantalum, molybdenum, and tungsten as a group from a fairly large number of elements would have a definite advantage. The research of Part I of this thesis was intended to achieve this goal.

Anion exchange separations of niobium, tantalum, molybdenum, and tungsten are reported using organic acids or hydrofluoric-hydrochloric acid mixtures as eluents. An anion exchange separation of niobium, tantalum, molybdenum, tungsten, zirconium, and titanium from each other uses various combinations of organic acids, hydrochloric acid, and hydrogen peroxide as eluents (12). Good results are reported for analyses of the separated metals, but the separation time is long and elution volumes are very large.

A typical anion exchange separation procedure employing hydrochloric-hydrofluoric acid mixtures as eluents for niobium, tantalum, and associated elements, is reported by

Kallmann et al. (13). In this technique, niobium and tantalum are adsorbed by the resin from a hydrochloric-hydrofluoric acid solution, while a large group of other metals (including molybdenum, tungsten, and titanium) pass through the column. Niobium is subsequently separated from tantalum by elution with a solution of ammonium chloride-hydrofluoric acid. Tantalum is finally eluted with a solution of ammonium chloride-ammonium fluoride. Thus, the anion exchange separation procedure with hydrochloric-hydrofluoric acid mixtures is versatile, but long separation times and large volumes of effluent are limitations.

In one variation of the anion exchange procedure (14), niobium, tantalum, molybdenum, tungsten, titanium, and zirconium were separated from several other metals, using hydrofluoric acid, hydrochloric-hydrofluoric acid, and a solution of ammonium chloride-ammonium fluoride, as eluents. The total separation time is five hours. However, only micro quantities of metals were separated. Distribution ratio studies showed that the compositions of eluents are critical in some cases.

Hydrofluoric acid solutions are employed in the separation of niobium, tantalum, and associated elements, using cellulose as the support and ethyl methyl ketone as the eluent (15). In this method, a hydrofluoric acid solution of the metals is soaked up in cellulose pulp and transferred to the top of a cellulose column. Tantalum is eluted first with ethyl methyl ketone, saturated with water. Ethyl methyl

ketone, which contains a higher percentage of hydrofluoric acid, is then passed through the column to elute niobium. Provided that water is absent, or present in only very low concentration, metals other than niobium are not extracted (except tungsten, which is partially extracted) by the solvent used to elute niobium. Separation of niobium from tantalum is effected by this procedure, and both are separated from a large group of other metals. However, in addition to requiring long separation times and large effluent volumes, the separation by cellulose partition chromatography lacks versatility. The method is also less specific and more cumbersome than the anion exchange procedure.

The separation of niobium, tantalum, and associated elements using liquid-liquid extraction is a technique which is sometimes used. Solvent extraction systems can often be extended to a multistage column partition method. A convenient, quantitative separation is then possible in many cases.

Niobium and tantalum are separated by solvent extraction in the system cyclohexanone-0.4 N hydrofluoric acid, 4 N sulfuric acid (16). Co-extracted niobium is stripped from the solvent fraction by washing with water, and tantalum is re-extracted with a solution of ammonium oxalate and boric acid.

Another solvent extraction system that has been given considerable attention is the hydrofluoric acid, sulfuric acid-tributyl phosphate system (17). The extraction of niobium and tantalum was studied in this system as a function of hydro-

fluoric acid concentration, organic solvent ratio, sulfuric acid concentration, tributyl phosphate concentration, extraction frequency, and oxide concentration. A conclusion of the work is that this system has better extractability for tantalum and niobium than does the hydrofluoric acid, sulfuric acid-methyl isobutyl ketone system.

A particularly favorable solvent extraction separation of niobium and tantalum was reported by Werning et al. (18), using the 3 M hydrochloric acid, 1 M hydrofluoric acid-methyl isobutyl ketone system. After one extraction, tantalum is 99.2% extracted and niobium is only 1.6% extracted. We were very interested in trying to adapt this system to a reversed-phase chromatographic separation of niobium and tantalum since no such work has been reported. A faster separation, involving small effluent volumes, would overcome the limitations of presently available chromatographic methods. Since trace amounts of niobium, tantalum, molybdenum, and tungsten are of great interest, an investigation of the possibility of separating trace quantities of these metals was included in the research plan.

PART I. CATION EXCHANGE SEPARATION OF MOLYBDENUM, TUNGSTEN,
NIOBIUM, AND TANTALUM FROM OTHER METAL IONS

LITERATURE SURVEY

Hydrogen peroxide forms stable complexes in acidic aqueous solution with only a few metal ions. Most of these metal ions form anionic peroxy complexes although the titanium(IV)-peroxy complex is cationic. The compositions and structures of the peroxy complexes of niobium(V), tantalum(V), molybdenum(VI), tungsten(VI), vanadium(V), and titanium(IV) in acidic solution have been determined by several investigators (19-22).

Fritz and Abbink (23) used a dilute solution of hydrogen peroxide to elute vanadium from a cation exchange column and thus to separate it from a number of other metal ions. Strelow (24) used hydrogen peroxide and sulfuric acid to separate titanium from more than 20 cations by cation exchange.

Various authors have used solutions of hydrogen peroxide to elute molybdenum(VI), tungsten(VI), niobium(V), and tantalum(V) from cation exchange columns (7,8,9,10,11), but a very limited number of separations have been reported and the conditions for elution have varied considerably. Strelow (24) indicated a successful elution of molybdenum(VI) and niobium(V) from a cation exchange column with acidic hydrogen peroxide but stated that tungsten(VI) and tantalum(V) showed a tendency to hydrolyze.

The purpose of the present work was to study the cation exchange separation of molybdenum(VI), tungsten(VI), niobium(V), and tantalum(V) as a group from other metal ions.

EXPERIMENTAL

Apparatus

Ion-exchange columns

Conventional 1.2 cm. i.d. ion-exchange columns with coarse glass frits were used. A slurry of resin and eluting solution was added to the column until the bed had a height of 12 cm. Sample solutions and eluting solution were added dropwise from a separatory funnel inserted in the top of the column through a one-holed rubber stopper.

pH Meter

A Beckman Model G pH meter was used to control the pH in EDTA titrations. A Beckman 1190-72 glass electrode was used with a Beckman standard calomel electrode.

Reagents

Ion-exchange resin

Dowex 50W-X8 cation exchange resin, 100 to 200 mesh, was used in the hydrogen form. Backwashing of the commercial resin in a large column with distilled water effected removal of fine particles. The resin was then purified by washing with 3 liters of 10% ammonium citrate and 3 liters of 3 M hydrochloric acid. Finally, water was washed through the resin until the eluent gave a negative test for chloride with silver nitrate. Excess water was removed by aspirator suction and the resin was then air-dried.

Metal ion solutions

Except for the metal ion solutions listed, all metal ion stock solutions were 0.05 M solutions of the nitrate or perchlorate salt in dilute nitric or perchloric acid.

Chromium(III) was a 0.05 M solution of chromium chloride in dilute nitric acid.

Zirconium(IV) was a 0.05 M solution of zirconyl chloride in 0.3 M hydrochloric acid. The zirconium(IV) salt was dissolved in concentrated hydrochloric acid and diluted to volume.

Titanium(IV) was a 0.05 M solution of titanium tetrachloride in 0.2 M sulfuric acid and 0.3% hydrogen peroxide.

Tin(IV) was a 0.05 M solution of tin tetrachloride in 0.3 M hydrochloric acid.

Molybdenum(VI) was a 0.05 M solution of molybdic acid which was made slightly basic (pH 8.3) with sodium hydroxide.

Tungsten(VI) was a 0.05 M solution of potassium tungstate in distilled water (pH 8.5). The potassium tungstate was prepared and purified in Ames Laboratory. It was analyzed for tungsten by the hydrogen reduction method and was found to be extremely pure.

The niobium(V) and tantalum(V) 0.05 M stock solutions were prepared as follows: Weighed amounts of the high purity metal (99.97%) were dissolved in hydrofluoric and nitric acids in tall plastic beakers provided with plastic covers. Dis-

solution was complete in about five minutes at room temperature. The resulting solution was evaporated to about 5-10 ml. in the plastic beaker and next was transferred to a platinum evaporating dish. After addition of 10 ml. of concentrated sulfuric acid, the solution was further evaporated to fumes of sulfur trioxide to remove traces of fluoride. The vessel was cooled and then diluted with approximately equal quantities of concentrated sulfuric acid and 30% hydrogen peroxide. The solution was transferred to a 500-ml. flask, a total of 30-55 ml. of concentrated sulfuric acid and 50-65 ml. of 30% hydrogen peroxide were added, and the solution was diluted to volume with distilled water. In all instances these stock solutions were stable for at least a month. In the fuming step it was found that if heating was continued much beyond the first appearance of sulfur trioxide fumes, it was difficult to dissolve the Nb_2O_5 and Ta_2O_5 which formed.

The eluting solution consisted of 0.25 M sulfuric, perchloric or nitric acid, containing 1% hydrogen peroxide.

Separation Procedure

Synthetic sample mixtures for separation were prepared by mixing known quantities of molybdenum (0.25 mmole), tungsten, niobium or tantalum (0.5 mmole for each of the last three) with approximately an equal quantity of a second metal ion. The mixture of niobium or tantalum and other metal ion was already 0.5-1 M in sulfuric acid and 1.5-2% in hydrogen

peroxide (from stock solutions, so that further addition of sulfuric acid and hydrogen peroxide was unnecessary.

The sample was added to a 12-cm. ion exchange column. Molybdenum was eluted with 100 to 150 ml. of 0.25 M sulfuric or perchloric acid containing 1% hydrogen peroxide. About 80 ml. of a 0.25 M nitric acid, 1% hydrogen peroxide solution was used to elute tungsten, niobium and tantalum. The use of nitric acid for the last three metals is desirable because recoveries in the gravimetric analytical method are reported to be slightly low (at least for tungsten), when much sulfuric acid is present in the precipitation medium (25). In each case, after elution the column was washed with about 25 ml. of distilled water. Then the other metal ion was stripped from the resin with the amount of eluting solution indicated in Table 1. The maximum flow rate obtainable was used in all of the elutions.

Table 1. Eluting solutions used for metal ions

Metal ions	Eluting solution
Y(III)	300 ml. of 4 <u>M</u> HCl
U(VI)	300 ml. of 2 <u>M</u> HCl
Zn(II), Mn(II), Co(II), Ni(II), Cu(II) Fe(III), Cr(III), Ti(IV), Sn(IV)	150 ml. of 3 <u>M</u> HCl
Pb(II)	250 ml. of 3 <u>M</u> HNO ₃
Al(III)	300 ml. of 3 <u>M</u> HCl
Zr(IV)	500 ml. of 3 <u>M</u> HCl

Analysis of Column Effluents

The column effluents containing the other metal ion were evaporated almost to dryness and then diluted to 100 ml. with distilled water for titration. The metal ions were titrated with 0.05 M EDTA by standard methods. Uranium was determined by the standard oxidation-reduction method of titrating with cerium(IV) after passing the uranium(VI) solution through a lead reductor. Chromium was determined by oxidation-reduction titration with iron(II).

Molybdenum in column effluents was determined gravimetrically as the oxinate according to the method of Balanescu (26). In order to destroy the molybdenum-peroxy complex, sulfur dioxide gas was bubbled through the solution, which was then gently boiled for about fifteen minutes. After addition of 10 ml. of 1 M ammonium acetate solution, the volume was adjusted to about 100 ml. Next, 1 ml. of 5% 8-hydroxyquinoline in 4 M acetic acid was added, and the sample was boiled for three minutes. The precipitate was collected in a medium frit, sintered glass crucible, washed with water, and dried at 135°C. overnight.

Tungsten, niobium and tantalum were determined by the homogeneous precipitation technique of Dams and Hoste (25, 5). The eluted solutions containing these metals as peroxy complexes were made about 5 M in nitric acid and then were heated at 60-90°C. After precipitation the hydrous oxides were

allowed to digest for at least two hours. In the present work it was found convenient to leave the solutions on a hot plate overnight and filter the precipitates the next morning. The precipitated oxides were collected on Selas No. 3010 porcelain filtering crucibles and then ignited in a muffle furnace for fifteen to thirty minutes. The temperatures used were 550°C. for WO_3 and 1000°C. for Nb_2O_5 and Ta_2O_5 . It is important that WO_3 not be heated above 700°C., because Carey, Raby and Banks (27) found that above this temperature volatilization becomes an important consideration. The crucibles were cooled in glass desiccators before weighing to obtain the amount of anhydrous oxide.

Results and Discussion

In the separation of molybdenum(VI) from other metal ions, the other metal ion is usually retained in a tight band at the top of the column, while molybdenum is rapidly eluted from the column as an anionic peroxy complex. Between 100 and 150 ml. of 1% hydrogen peroxide in 0.25 M sulfuric acid elutes molybdenum quantitatively from a 1.2x12-cm. column. Quantitative data for ion exchange separation of molybdenum (VI) from other metals are summarized in Table 2.

Using the color of tungsten blue as a qualitative test, it was found that tungsten(VI) is completely eluted from a 1.2x12-cm. cation exchange column by 80 to 90 ml. of 1% hydrogen peroxide in 0.25 M sulfuric or nitric acid. Further

Table 2. Ion-exchange separation of molybdenum(VI) from other metal ions. Results are the average of two or three determinations

Mo taken, mg.	Mo found, mg.	Diff., %	Other metal	Taken, ml. ^a	Found, ml. ^a	Diff., %
0.1173	0.1172	-0.1	Cu(II)	4.78	4.79	+0.2
0.1173	0.1174	+0.1	Fe(III)	4.22	4.225	+0.1
0.1173	0.1172	-0.1	Mn(II)	4.02	4.03	+0.2
0.1173	0.1173	+0.0	Ni(II)	3.97	3.99	+0.4
0.1173	0.1173	+0.0	U(VI)	16.78 ^b	16.78 ^b	+0.0
0.1179	0.1187	+0.7	Y(III)	4.93	4.93	+0.0

^aResults expressed in milliliters of 0.05 M EDTA required for titration.

^bMilliliters of 0.05 M cerium(IV) required for titration.

evidence for complete elution was provided by ashing some of the resin after elution and analyzing for tungsten by emission spectroscopy. No tungsten was detected in the resin. The recovery of tungsten eluted from the resin was also checked by gravimetric analysis and was found to be quantitative. The homogeneous precipitation method (25) of analysis for tungsten was compared to the standard hydrogen reduction method. The results of four determinations by the homogeneous precipitation method agree well with those obtained by Raby¹ on five determinations by hydrogen reduction: $56.33 \pm .03\%$

¹Raby, B. A., Ames Laboratory, Ames, Iowa, private communication, 1963.

(gravimetric- WO_3), compared to $56.34 \pm .05\%$ (hydrogen reduction-W). The analyses were done on the same sample of high purity potassium tungstate.

Results for the quantitative ion-exchange separation of tungsten(VI) from other metal ions are given in Table 3.

Table 3. Ion-exchange separation of tungsten(VI) from other metal ions. Results are the average of two determinations

WO_3 taken, mg.	WO_3 found, mg.	Diff., %	Other metal	Taken, ml. ^a	Found, ml. ^a	Diff., %
0.1197	0.1196	-0.1	Al(III)	9.90	9.88	-0.2
0.1153	0.1151	-0.2	Co(II)	8.92	8.92	± 0.0
0.1197	0.1196	-0.1	Cr(III)	29.72 ^b	29.70 ^b	-0.1
0.1159	0.1161	+0.2	Cu(II)	9.73	9.74	+0.1
0.1159	0.1158	-0.1	Fe(III)	9.44	9.44	± 0.0
0.1197	0.1195	-0.2	Mn(II)	10.48	10.49	+0.1
0.1197	0.1198	+0.1	Ni(II)	9.96	9.98	+0.2
0.1197	0.1195	-0.2	Pb(II)	10.02	10.02	± 0.0
0.1197	0.1197	± 0.0	Zn(II)	10.13	10.12	-0.1

^aResults expressed in milliliters of 0.05 M EDTA required for titration.

^bMilliliters of 0.05 M iron(II) required for titration after oxidation to chromium(VI).

As was the case with the tungsten separations, the resins used in the niobium and tantalum separations were submitted for spectrographic analysis after ashing. The reports consistently showed no evidence of niobium or tantalum. Quantitative recoveries of niobium and tantalum were obtained, as shown by gravimetric analysis of column effluents. About 80-90 ml. of 0.25 M nitric acid, 1% hydrogen peroxide solution was used as the eluent. Satisfactory separations of niobium and tantalum from various other metal ions were obtained except for niobium-tin (see Table 4).

Table 4. Ion-exchange separation of niobium(V) or tantalum(V) from other metal ions. Most results are the average of two determinations

M ₂ O ₅ taken, (g)	M ₂ O ₅ found, (g)	Diff., %	Other metal	Taken, ml. ^a	Found, ml. ^a	Diff., %
M = Nb						
0.0963	0.0960	-0.3	Al(III)	9.75	9.73	-0.2
0.0963	0.0962	-0.1	Cr(III)	18.55 ^b	18.52 ^b	-0.2
0.0963	0.0960	-0.3	Co(II)	9.74	9.72	-0.2
0.0963	0.0961	-0.2	Cu(II)	10.70	10.69	-0.1
0.0963	0.0965	+0.2	Fe(III)	10.54	10.61	+0.2

^aResults expressed in milliliters of 0.05 M EDTA required for titration.

^bMilliliters of 0.05 M iron(II) required for titration of chromium(VI).

Table 4. (Continued)

M ₂ O ₅ taken, (g)	M ₂ O ₅ found, (g)	Diff., %	Other metal	Taken, ml. ^a	Found, ml. ^a	Diff., %
M = Nb						
0.0963	0.0966	+0.3	Mn(II)	10.23	10.25	+0.2
0.0963	0.0964	+0.1	Ni(II)	10.05	10.06	+0.1
0.0663	0.0665	+0.3	Ti(IV) ^c	8.93	8.96	+0.3
0.0663	0.0662	-0.2	Ti(IV) ^d	2.06	2.05	-0.5
0.0663	0.0661	-0.3	Zr(IV) ^c	9.33	9.05	-3.0
0.0663	0.0662	-0.2	Zr(IV) ^d	1.90	1.91	+0.5
0.0663	0.1252	+89.0	Sn(IV) ^c	9.39	0.13	-99.0
0.0663	0.0756	+14.0	Sn(IV) ^d	1.39	0.37	-70.0
M = Ta						
0.1086	0.1089	+0.3	Al(III)	9.74	9.72	-0.2
0.1086	0.1086	+0.0	Cr(III)	18.57 ^b	18.53	-0.2
0.1086	0.1082	-0.4	Co(II)	9.78	9.80	+0.2
0.1086	0.1087	+0.1	Cu(II)	10.45	10.43	-0.2
0.1086	0.1082	-0.4	Fe(III)	9.32	9.30	-0.2
0.1086	0.1083	-0.3	Mn(II)	10.25	10.22	-0.3
0.1086	0.1083	-0.3	Ni(II)	9.45	9.46	+0.1

^c0.5 millimole.^d0.1 millimole.

Strelow (24) found that tantalum was not completely eluted due to its very pronounced tendency to hydrolyze. However, in the present work this difficulty has been eliminated perhaps because of the higher concentration of hydrogen peroxide and sulfuric acid in the stock solution aliquot which was introduced to the column. The use of a shorter column may have also helped to decrease hydrolytic tendencies.

Several alloys furnished by the Ames Laboratory's Metallurgy Department were also analyzed by the present procedure: niobium-nickel, tantalum-iron and tungsten-copper. After dissolution of these alloys in hydrofluoric and nitric acid and evaporation to sulfur trioxide fumes, several hours were spent in dissolving the hydrous oxides in sulfuric acid and hydrogen peroxide. Ta_2O_5 required the longest time to go into solution. For practical analyses it is recommended that evaporation be carried only to the point where all or most of the oxide has precipitated. By doing this with several trial tantalum and niobium solutions, it was found that the oxide dissolved within about fifteen minutes. The results of the alloy analyses are given in Table 5.

Since small amounts of zirconium(IV), titanium(IV) and tin(IV) are present in niobium and tantalum minerals, a study was made to determine the extent of interference of these metal ions in the gravimetric method used for niobium and tantalum. Beaker precipitations were carried out in which

Table 5. Analysis of alloys. Results are the average of four determinations

Alloy	Metal determined	Theory (%)	Found (%)	Difference (%)
Nb-Ni	Nb	40.16	40.15	-0.01
	Ni	59.84	59.72	-0.12
Ta-Fe	Ta	72.10	71.93	-0.17
	Fe	27.90	27.91	+0.01
W-Cu	W	40.09	40.02	-0.07
	Cu	59.91	59.91	+0.00

equimolar amounts of niobium and other metal ion were present. Results for niobium were high in all trials. In the case of zirconium results ranged from about 0.3% to 1.7% high when 0.1 millimole and 0.5 millimole amounts of zirconium were present, respectively. The degree of interference increased with titanium, results being from 2.5% to 10% high, while for tin the range was from 21% to 100% high.

Column separations of zirconium, titanium or tin from niobium were attempted. The total volume of solution added to the column was increased to 40 ml. in order to decrease the sulfate ion concentration (from 1 M to about 0.25 M), so that titanium and zirconium would not be eluted with niobium. In order to compensate for dilution the solution was made about 2% in hydrogen peroxide and 0.3 M in nitric acid by addition of appropriate amounts of each. A total of about 150 ml. of

eluting solution was used.

It can be seen in Table 4 that quantitative separations for both 0.5 millimole and 0.1 millimole amounts were achieved only for titanium. The separation of tin from niobium failed, but niobium can be separated from 0.1 millimole amounts of zirconium.

PART II. REVERSED-PHASE CHROMATOGRAPHIC SEPARATION OF
NIOBIUM, TANTALUM, MOLYBDENUM, AND TUNGSTEN
FROM EACH OTHER

LITERATURE SURVEY

The number of partition chromatographic methods available for the separation of niobium, tantalum, and associated metals is not large. One of the first separations of this type was the elution of tantalum, niobium, and other metals from a cellulose column with ketone solutions containing various concentrations of hydrofluoric acid (29).

Several paper chromatographic methods using ketones and hydrofluoric acid have been used to separate niobium and tantalum. Scott and Magee (29), used a mixture of methyl isobutyl ketone and hydrofluoric acid to separate niobium and tantalum in a steel sample. Several alcohols, alone, and in various proportions were tried, but they gave no separation. Ketones gave the best results.

Bruninx et al. (30), reported the separation of up to 50 μg of niobium and tantalum on paper by electrophoresis. The same authors also separated the oxalates of the metals using ethyl methyl ketone and 10 M hydrochloric acid. Microgram amounts were separated.

In another paper chromatographic technique (31), niobium, tantalum, and titanium were separated from each other. The solvent mixture found to be most effective is 2.2 M hydrofluoric acid-2 M nitric acid-diethyl ketone. The R_f values reported are: titanium - 0.00; niobium - 0.50; and tantalum - 0.95. The separation was accomplished in 30 minutes, followed

by spraying with 8-hydroxyquinoline to detect the location of the metal ion spots.

Some solvent extraction techniques have been reported for the separation of niobium, tantalum, and associated metals. One system that seemed to hold promise for column application, has the composition hydrochloric acid-hydrofluoric acid-methyl isobutyl ketone. Although Werning et al. (18), have thoroughly studied the extraction behavior of niobium and tantalum in this system, no attempt has been made to adapt the system to a column chromatographic procedure. The extraction efficiencies of various ketones were determined in this study, and methyl isobutyl ketone was found to be best for separation of niobium and tantalum. Cyclohexanone extracted a higher percentage of tantalum than did methyl isobutyl ketone, but the extraction of niobium was also significantly higher.

The separation of tantalum and niobium from hydrochloric-hydrofluoric acid solutions with methyl isobutyl ketone, was found to be a function of hydrofluoric and hydrochloric acid concentrations. Variable ratios of niobium to tantalum may be used with negligible influence on the efficiency of the separation. Equal volumes of 3 M hydrochloric acid, 1 M hydrofluoric acid solution and methyl isobutyl ketone gave optimum conditions for the separation. About 99.2% pure tantalum was recovered in the organic phase and 98.4% pure niobium remained in the aqueous phase (one stage).

Werning and Higbie (32), showed that tantalum is prefer-

entially extracted by 12 M hydrochloric acid from ketone solutions of the mixed anhydrous pentachlorides. Various ketone mixtures were tried, but the combination of methyl isobutyl ketone and diisopropyl ketone was found to be the best. This separation was applied to low grade ores but the authors do not believe that the procedure is limited to such ores.

The solvent extraction separation of niobium and tantalum was also investigated by Stevenson and Hicks (33). Tantalum and niobium were 81% and 4.5% extracted, respectively, by diisopropyl ketone, from a 3.7 M hydrochloric acid, 0.4 M hydrofluoric acid solution. In addition, niobium was found to be 90% extracted from a solution about 6 M in sulfuric acid, and 9 M in hydrofluoric acid. Since tantalum is highly extracted under these conditions, the separation of niobium and tantalum from many other metals is possible.

Milner et al. (34), have shown that niobium and tantalum are quantitatively extracted with methyl isobutyl ketone from a solution 6 M in sulfuric acid, 10 M in hydrofluoric acid, and 2.2 M in ammonium fluoride. Other metals associated with niobium and tantalum have very low distribution ratios in this system.

Nishimura (35), determined distribution ratios for niobium, tantalum, tin, titanium, and iron for extraction with methyl isobutyl ketone from the following mineral acids: hydrofluoric acid; hydrofluoric-hydrochloric acid; hydrofluoric-sulfuric acid; and hydrofluoric-nitric acid. Distri-

bution ratios were determined as a function of each acid concentration, and it was concluded that tin, titanium, and iron can be separated sufficiently from niobium and tantalum.

By using the previous solvent extraction data, one should be able to formulate a versatile separation procedure for niobium, tantalum, and associated metals. This was the aim of the second part of the research.

EXPERIMENTAL

Apparatus

Columns

Standard 1.2 cm. i.d. polyethylene tubing was held straight by tightly fitting glass tubing. A Teflon straight union reducer attachment, obtained from Beckman Instruments, Inc., Fullerton, California, was connected to the bottom of the polyethylene tubing. To the bottom of the reducer attachment was fitted a Nalgene stopcock, available from The Nalge Co., Inc., Rochester, N.Y. The resin was supported by a small plug of Dynel wool. A 125 ml. Nalgene separatory funnel, placed at the top of the column served as a reservoir for the eluent.

Stirrer

A Burrell shaker was used in the equilibration of samples for distribution studies.

Spectrophotometers

Most of the spectrophotometric measurements were made on a Beckman Model B Spectrophotometer. Silica cells with 1 cm. path length were used. A Cary Model 14 recording spectrophotometer was used for only a few experiments.

pH Meter

All pH measurements were made on a Beckman Model G pH meter equipped with a Beckman 1190-72 glass electrode and a Beckman standard calomel electrode.

Laboratory ware

Class A pipets and burets were used throughout the work. Nalgene ware and platinum evaporating dishes were used in work with hydrofluoric acid. For filtration of hydrous oxides of niobium, tantalum, and tungsten, Selas no. 3010 and 3001 porcelain filtering crucibles were employed.

Irradiation facilities and detection equipment

Irradiation of molybdenum and tungsten samples was made at the Ames Laboratory Research Reactor. At its rated maximum power, 5 megawatts, this produces a flux of 4×10^{13} n/cm² x sec. in the rabbit irradiation facility.

In this work, all counting was done using a 4x4 inch well-type NaI-(Tl) crystal in conjunction with a single channel gamma scintillation spectrometer composed of the following modules: RIDL model numbers 30-19; 33-10B; 40-12B; and 49-25. The window of the analyzer was set to measure the following gamma ray energies:

35d Nb ⁹⁵ -----	0.76 Mev	24h W ¹⁸⁷ -----	0.48 Mev
			0.68 Mev
182d Ta ¹⁸² -----	1.2 Mev	66h Mo ⁹⁹ -----	0.141 Mev
	1.1 Mev		

In the work involving radioactive molybdenum, it was best to allow time for Tc⁹⁹ to come to equilibrium with its parent Mo⁹⁹. The measured activity of a molybdenum solution then includes the 0.14 Mev peak of Tc⁹⁹.

Reagents

Column supports

Tee Six, an inert polytetrafluoroethylene support, was obtained from Analytical Engineering Laboratories, Inc., Hamden, Conn. The pre-sieved resin was available as 70/80 mesh or 160/170 mesh. Both mesh sizes were used in this work. Before use, the Tee Six powder was stirred with a mixture of hydrochloric acid, hydrofluoric acid, and methyl isobutyl ketone. The resin was then transferred with acetone to a Buchner funnel. Washing with anhydrous ether, followed by suction and air drying, made the Tee Six support ready for use.

Chromosorb W and Chromosorb P are available from F & M Scientific Corporation, New Castle, Delaware. These supports are supplied in pre-sieved 80/100 mesh size. They were both treated with dichloro dimethyl silane and dichloro diphenyl silane so that they would preferentially sorb the MIBK phase.

Cellulose powder is available from Reeve Angel Co., Clifton, New Jersey. The cellulose was slurried with a solution of petroleum jelly in benzene, followed by evaporation of the benzene.

Solvents

Methyl isobutyl ketone (MIBK) was obtained from Eastman Distillation Products Industries, Rochester, N.Y. This solvent was used without purification.

Metal ion solutions

Niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI) stock solutions were prepared by dissolution of each metal in a hydrofluoric-nitric acid mixture. The solution was evaporated to dryness, followed by addition of appropriate amounts of hydrofluoric acid and hydrochloric acid. The resulting solution was then transferred to Nalgene bottles for storage.

Solutions of radioactive Nb^{95} and Ta^{182} were prepared by transferring a portion of the solutions, obtained from Oak Ridge, Tenn., to a Nalgene bottle containing carrier in 7 M hydrochloric acid, 2 M hydrofluoric acid. The resulting solutions were stirred and allowed to stand a day to insure complete exchange.

Solutions of radioactive Mo^{99} and W^{187} were prepared as follows: One mg. of the metal was sealed inside a 2 mm. i.d. fused quartz tube. Primary containers of 1 mm. diameter surgical polyethylene tubing were also used. The primary tube was then sealed inside a polyethylene tube to avoid breakage or loss. All tubes and metal samples were washed with distilled water and ether to avoid sodium contamination. Tweezers and tongs were used to handle the materials. After irradiation of the samples, the metal ion solutions were prepared in the usual way by dissolution of the metal in a hydrofluoric-nitric acid mixture. A lead brick shield was needed during the preparation of radioactive solutions, especially

in the case of molybdenum and tungsten where short half lives and high activities were involved.

Except for the metal ion solutions listed, all other metal ion solutions were 0.02 M to 0.05 M solutions of the nitrate or perchlorate salt in dilute nitric - or perchloric acid.

Chromium(III) was a 0.05 M solution of chromium chloride in dilute nitric acid.

Zirconium(IV) was a 0.05 M solution of zirconyl chloride in 0.3 M hydrochloric acid. The zirconium(IV) salt was dissolved in concentrated hydrochloric acid and diluted to volume.

Titanium(IV) was a 0.025 M solution of titanium tetrachloride in 5 M hydrochloric acid.

Eluents

The eluents used in some of the column separations were:

- A) 7 M hydrochloric acid, 2 M hydrofluoric acid
- B) 4 M hydrochloric acid, 8 M hydrofluoric acid
- C) 2 M hydrochloric acid, 1 M hydrofluoric acid
- D) MIBK

This sequence of eluents is considered to be optimum for the separation of tungsten, molybdenum, niobium, and tantalum. However, other slightly different eluent compositions were used with success and these are given with each table of data. The aqueous solutions were equilibrated with MIBK before use by shaking for about five minutes in a separatory funnel. Eluents were used on the same day that they were prepared.

Analytical Procedures

Gravimetric procedures

Molybdenum(VI) was precipitated with 8-hydroxyquinoline according to the method of Balanescu (26). The column effluents containing molybdenum(VI) were heated to fumes with sulfuric acid to destroy organic matter. The solution was then diluted to about 100 ml. with water and treated as described in Part I of this thesis.

Niobium(V), tantalum(V), and tungsten(VI) were analyzed according to the homogeneous precipitation technique of Dams and Hoste (5). The details of this method are described in Part I of this thesis.

Volumetric procedures

The titration of most metal ions was done with 0.05 M EDTA by standard methods. Chromium was determined by oxidation-reduction titration with iron(II).

An interesting volumetric method for determining niobium(V) is presented by Lassner (36). This is a chelatometric method using nitrilotriacetic acid which forms a 1:1 complex with the niobium(V)-peroxy ion. Nitrioloacetic acid was added in excess, and the excess was titrated with copper (II) at pH 5.0-5.15 by using the metallofluorescent indicator, methylcalcein, under ultraviolet illumination. For small amounts of niobium(V) (about 10 mg.), the method was found to give an error of about 0.3-0.7%. The error was about 1.0%

for larger amounts of niobium(V). The method of end point detection was somewhat inconvenient, and the change at the end point was not very marked at times. The gravimetric method was at least as accurate and more reliable than the volumetric method, and was used in preference to the latter method.

Spectrophotometric procedures

Molybdenum(VI) and tungsten(VI) were determined spectrophotometrically by the thiocyanate method (37).

The absorbance of the niobium(V)-peroxy complex in concentrated sulfuric acid was measured in the spectrophotometric method (38) used for niobium(V). Solutions were fumed with sulfuric acid and diluted to the mark in 10 ml. volumetric flasks with concentrated sulfuric acid. The absorbance was then measured at 360 m μ .

A method developed by Belcher, et al. (39) was also used to determine niobium(V) spectrophotometrically. Niobium(V) solutions are heated to fumes with sulfuric acid to eliminate fluoride. A solution containing between 9-70 μ g. of niobium (V) is adjusted to pH 6.0 and is transferred to 100 ml. volumetric flasks. Next, 10 ml. of 0.02 M EDTA, 10 ml. of 10^{-3} M 4-(2-Pyridylazo-resorcinol) solution, and 5 ml. of an acetate buffer solution are added. The absorbance of the solution is measured at 550 m μ after 45 minutes. The absorptivity of the complex is as high as that recorded for the

thiocyanate method, and the stability is superior. Most interfering ions can be masked with EDTA and cyanide. Interference from tantalum(V) is avoided if enough tartrate is added.

Tantalum(V) was determined spectrophotometrically by the method reported in the compilation edited by Vinogradov and Ryabchikov (40). A solution containing tantalum(V) is heated to fumes with sulfuric acid. If the solution is not clear and transparent, ammonium persulfate solution is added and heating is continued. The solution is then mixed with 10 ml. of 10% tartaric acid solution and is transferred to a 100 ml. volumetric flask. An aliquot of the resulting solution is added to 10 ml. of 0.5% Arsenazo I solution and 25 ml. of 6 M hydrochloric acid, contained in a 100 ml. volumetric flask. The absorbance of the solution is determined immediately at 570 m μ .

Radiochemical procedures

Column effluents were collected in Nalgene graduated cylinders and transferred to platinum dishes. Oxalic, citric, or tartaric acid was added to keep the metal ions in solution. The solutions were evaporated to about 4 ml., and then were transferred to 18x150 mm. Pyrex test tubes for counting. A standard (reference) solution consisted of radioactive tracer solution, which was taken with the same pipet that was used for synthetic mixture preparation. Standard solutions were

evaporated and transferred in the same manner as for column effluents. Niobium(V), tantalum(V), and tungsten(VI) solutions were analyzed immediately after column separations were achieved. However, counting of activities of molybdenum(VI) solutions was not done until 15 hours after performing separations. This allowed Mo^{99} and Tc^{99} to reach transient equilibrium.

Elution curves

In early stages of this work, the progress of elution of metal ions from the column was followed qualitatively by using various spot tests. Most of the tests used are described by Feigl (41).

Evaporation of column fractions containing molybdenum (VI) resulted in formation of molybdenum blue oxide. A more sensitive test used for molybdenum(VI) was the reaction with thiocyanate and tin(II) chloride to produce red, soluble $\text{H}_3\text{MoO}(\text{CNS})_5$. Interference from tungsten(VI) was avoided by performing the test on filter paper moistened with hydrochloric acid.

Evaporation of fractions containing tungsten(VI) resulted in formation of yellow WO_3 . The reaction of tungsten(VI) with tin(II) chloride and concentrated hydrochloric acid on filter paper to form a bluish green spot was also used to detect tungsten(VI) (42).

The formation of white hydrous oxides of niobium(V) and

tantalum(V) served as fair tests for the presence of these metal ions. The best spot test for tantalum(V) seems to be the reaction of tantalum(V) with methylene blue to give a purple precipitate (42). The test is carried out in dilute fluoride solution. Fairly high concentrations of niobium(V), molybdenum(VI), tungsten(VI), and other metal ions were tested and found not to interfere. The yellow color produced in the reaction of niobium(V) with hydrogen peroxide was used to test for niobium(V). Zinc in hydrochloric acid reduces niobium(V) to blue or brown niobium(III). Molybdenum(VI) and tungsten(VI) are also reduced and produce colored solutions. However, tantalum(V) is not reduced and the test was somewhat useful for niobium(V).

Qualitative analyses of column fractions by emission spectroscopy also provided information with which to select proper elution conditions.

Quantitative measurements of the activities of fractions were made in order to construct Figures 3 and 4. Fractions were collected in 5 ml. increments and were counted in Pyrex tubes.

Distribution ratio methods

Distribution ratio data were obtained by determining the amount of solute in the MIBK phase, and in the aqueous phase. Many of the analyses were performed radiochemically, and the phase volumes were usually equal. In a typical determination,

1 ml. of the tracer was added to a measured volume of inactive metal ion solution in a separatory funnel. The solution was stirred and allowed to stand 1 hour to allow complete exchange to occur. Appropriate volumes of pre-equilibrated acid solutions were then added. After addition of an equal volume of pre-equilibrated MIBK, the mixture was shaken for about 10 minutes. Then it was allowed to settle for 15 minutes before separating the phases. The phases were transferred to graduated cylinders for volume measurement, followed by another transfer to tubes for counting.

Gravimetric and spectrophotometric methods were also used to analyze phases. In these analyses, the phases were heated to fumes with sulfuric acid, and then a determination was made according to procedures previously described.

Column procedure

Tea Six powder was stirred with enough pre-equilibrated MIBK to form a free flowing slurry. This mixture was allowed to stand for about 10 minutes before transferring it to the column. Additional MIBK was used to complete the transfer. The level of the MIBK was allowed to settle to the top of the resin, and then pre-equilibrated aqueous phase was passed through. A graduated cylinder was placed at the bottom of the column to collect the effluent.

When the MIBK phase had been completely displaced by aqueous phase, the volume of MIBK was measured and noted as

V_M , the volume of mobile phase (interstitial volume). After allowing the level of the aqueous phase to settle to the top of the resin, a sample was carefully introduced by means of a separatory funnel. This sorption step was done at a flow rate of 0.25 ml./min., about half as fast as for elution of metal ions. Sequential elution of metal ions in the sample mixture was then carried out using pre-equilibrated acid solutions. Fractions were collected and analyzed according to procedures described previously.

The total volume (V_T) of MIBK associated with the resin column was obtained by pipeting MIBK into a graduated cylinder containing the resin. The volume of excess MIBK above the top of the resin was then measured. This value was subtracted from the amount added by pipet, giving the value of V_T . The difference between V_T and V_M gives V_S , the volume of MIBK sorbed to the resin (volume of stationary phase).

RESULTS AND DISCUSSION

Distribution Ratios

The determination of batch distribution ratios is usually the first step in determining optimum conditions for elution of a mixture of metal ions, e.g., from a column. A relationship derived from plate theory, which includes the distribution ratio, can be used to obtain information about column behavior. This will be illustrated in the next section.

Distribution ratios were determined for extraction of niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI) from 1 M hydrofluoric acid, 1 M nitric acid into methyl isobutyl ketone (Table 6). This system was investigated briefly because a successful paper chromatographic separation of niobium(V) from tantalum(V) was reported using the same aqueous phase and diethyl ketone (32). The distribution ratios in Table 6 do not suggest a separation scheme for all four metals.

Table 6. Distribution ratios for niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI)

1 <u>M</u> HNO ₃	-MIBK system
1 <u>M</u> HF	

Metal ion	D_{M+n}
Nb(V)	0.5
Ta(V)	41
Mo(VI)	0.6
W(VI)	0.07

Further investigation of the above system might have proved promising but a different solvent extraction system, reported by Werning et al. (18) looked very good and appeared to be adaptable to a multistage column separation. Figure 1 shows the per cent extraction of tantalum(V) and niobium(V) from solutions of variable hydrochloric and hydrofluoric acid concentrations into methyl isobutyl ketone. From 3 M hydrochloric, 1 M hydrofluoric acid, tantalum(V) is 99.2% extracted into methyl isobutyl ketone, while niobium(V) is only 1.6% extracted (single stage).

Since a separation scheme including molybdenum(VI) and tungsten(VI) was desired, the distribution ratios of these metal ions were determined. Earlier investigators had found that molybdenum(VI) extracted appreciably into methyl isobutyl ketone from about 3 M to 7 M hydrochloric acid (43). However, the presence of hydrofluoric acid greatly decreased the extraction of molybdenum(VI) (44). If sulfuric acid was then added, however, the extraction of molybdenum(VI) increased again. Thus, distribution ratios were determined for the four metal ions, with sulfuric acid present in the aqueous phase in some experiments.

Table 7 shows the effect of hydrochloric and hydrofluoric acid concentrations on the distribution ratios. Reading this table from right to left also gives the order of elution for a separation scheme developed in this work.

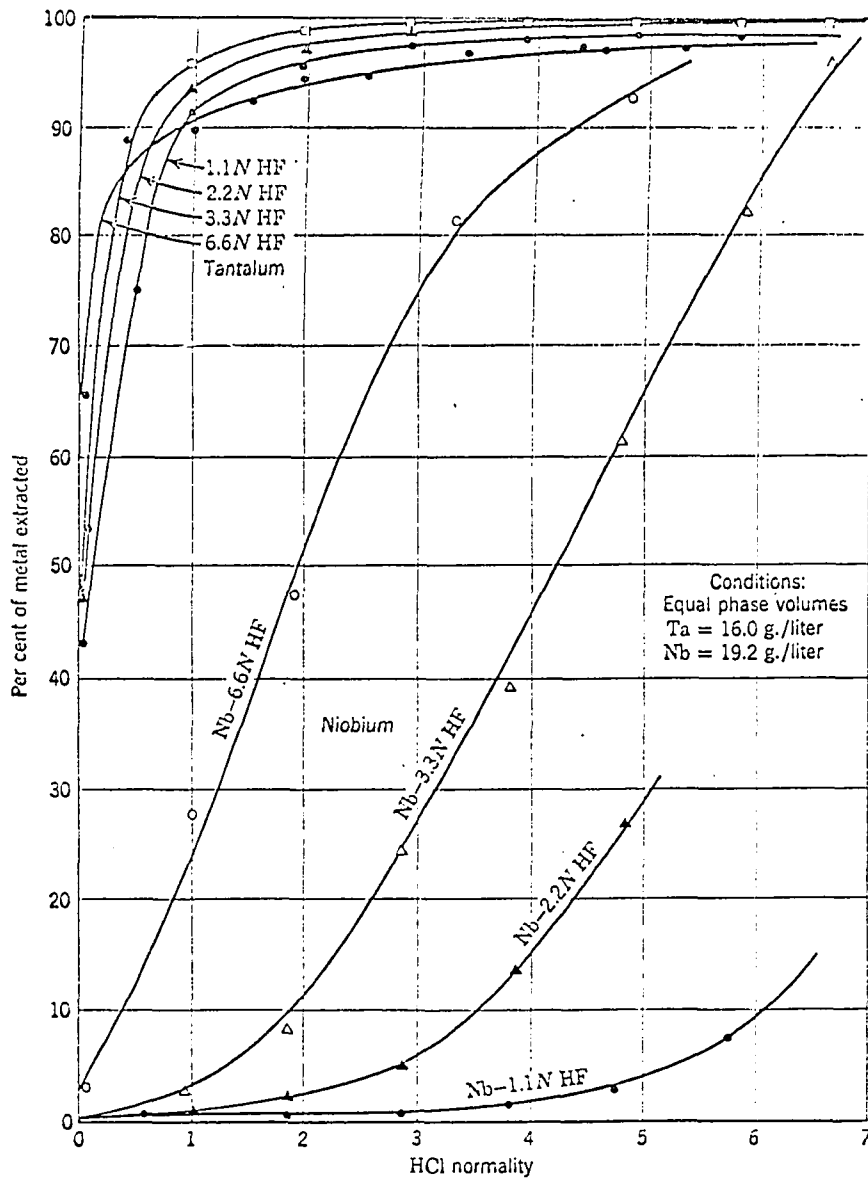


Figure 1. Extraction of niobium and tantalum from HCl-HF into MIBK (18)

Table 7. Variation of distribution ratio with hydrochloric and hydrofluoric acid concentrations

$$M^{+n} = 0.025 \text{ M}$$

HCl	HF	D_{Ta}	D_{Nb}	D_{Mo}	D_W
7	2	392	64	6.2	0.1
4	8	---	33	0.4	
2	1	106	0.2		

Table 8 shows the effect of sulfuric acid concentration on the distribution ratios for the four metal ions. The results show that the extraction of molybdenum(VI) and tungsten(VI) into methyl isobutyl ketone is significantly increased by an increase in the sulfuric acid concentration. However, for tungsten(VI) the absolute value of the distribution ratio is still low.

Table 8. Variation of distribution ratio with sulfuric acid concentration

$$HCl = 7 \text{ M} \quad HF = 2 \text{ M} \quad M^{+n} \text{ aq.} = 0.025 \text{ M}$$

Metal ion	H_2SO_4 aq.	$D_{M^{+n}}$
Ta(V)	0.0 M	392
Ta(V)	0.5 M	438
Nb(V)	0.0 M	39.5
Nb(V)	0.5 M	46
Nb(V)	1.0 M	49
Mo(VI)	0.0 M	6.2
Mo(VI)	0.5 M	9.6
Mo(VI)	1.0 M	12.0
W(VI)	0.0 M	0.10
W(VI)	0.5 M	0.16
W(VI)	1.0 M	0.32

The trend for niobium(V) and tantalum(V) extraction seems to be a small increase in extractability with increasing sulfuric acid concentration.

Table 9 contains additional metal ion distribution ratios which were obtained using slightly different aqueous acid concentrations.

Table 9. Distribution ratios for metal ions between methyl isobutyl ketone and the aqueous phase indicated

Metal ion	HCl (<u>M</u>)	HF (<u>M</u>)	H ₂ SO ₄ (<u>M</u>)	D	M ⁺ⁿ aq. (<u>M</u>)
W(VI)	6	2	0.1	0.03	0.025
W(VI)	6	2	0.5	0.07	0.025
W(VI)	6	2	1.0	0.1	0.025
W(VI)	6	3	1.0	0.2	0.025
Nb(V)	3	1	0	0.4	0.025
Nb(V)	7	2	0	18	0.2
Nb(V)	7	2	0	48	1x10 ⁻⁸ and 0.05 M each in Ta(V), Mo(VI), W(VI)
Mo(VI)	6	2	0.1	3.3	0.025
Mo(VI)	6	2	0.5	5.5	0.025
Mo(VI)	6	2	1.0	9.3	0.025
Mo(VI)	6	3	1.0	7.4	0.025
Mo(VI)	6	5	0	1.6	0.025

Some of the same general trends were observed. The extraction of tungsten(VI) and molybdenum(VI) into methyl isobutyl ketone increases with increasing sulfuric acid concentration, the increase for molybdenum(VI) being more pronounced than that for tungsten(VI). An increase in hydrofluoric acid concentration in the aqueous phase is again seen to decrease the

extractability of molybdenum(VI), probably owing to formation of more of the less extractable fluoro complex.

The distribution ratios of several other metal ions were determined between 7 M hydrochloric acid, 2 M hydrofluoric acid and methyl isobutyl ketone (Table 10). Most of these metals are alloyed with niobium, tantalum, molybdenum, and tungsten commercially. All of these metal ions except iron (III) either do not readily form chloro complexes or are not much extracted by methyl isobutyl ketone. The data indicate that only iron(III) is highly extracted. The extractabilities of the rest of the metal ions range from 0-17%.

Table 10. Distribution ratios of some other metal ions

7 M HCl, 2 M HF-MIBK system

concentration of metal ion = 0.02 M to 0.05 M

Metal ion	D_{M+n}
Fe(III)	59
Co(II)	0.1
Ni(II)	0.02
Cu(II)	0.05
Mn(II)	0.07
Al(III)	0.09
Cr(III)	0.07
V(IV)	0.19
Zr(IV)	0.04
Ti(IV)	0.0

It is useful to know if the distribution ratio of a metal ion remains constant or changes over a range of metal ion concentrations. The data of Table 11 were used to construct

Table 11. Variation of distribution ratio with metal ion concentration (data for construction of Figure 2)

7 M HCl, 2 M HF-MIBK system

Equal phase volumes unless otherwise indicated

MIBK and aqueous phases analyzed in each D determination

Metal ion	M ⁺ⁿ aq.	Log M ⁺ⁿ aq.	D _{M+n}	Log D _{M+n}
Mo (VI)	1.0x10 ⁻⁵ <u>M</u>	-5.000	6.4	0.806
Mo (VI)	2.5x10 ⁻²	-1.602	7.2,6.6,4.7 (Ave.6.2)	0.792
Mo (VI)	2.5x10 ⁻¹	-0.602	6.2,6.2	0.792
Mo (VI)	5.0x10 ⁻¹	-0.301	3.9,4.3,4.6* (Ave. 4.3)	0.634
Mo (VI)	1.0	0.000	2.2	0.343
Mo (VI)	1.5	0.176	1.6	0.204
Nb (V)	1.0x10 ⁻³ <u>M</u>	-8.000	64,65	1.810
Nb (V)	4x10 ⁻⁴	-3.400	59	1.771
Nb (V)	1.25x10 ⁻²	-1.903	57	1.756
Nb (V)	2.5x10 ⁻²	-1.602	52	1.716
Nb (V)	5.0x10 ⁻²	-1.301	45	1.654
Nb (V)	1.0x10 ⁻¹	-1.000	42	1.623
Nb (V)	1.6x10 ⁻¹	-0.796	17	1.231
Nb (V)	2.0x10 ⁻¹	-0.699	16	1.204
Nb (V)	3.0x10 ⁻¹	-0.523	7,13	1.114

*MIBK phase = 20 ml., aqueous phase = 10 ml.

Table 11. (Continued)

Metal ion	M^{+n} aq.	Log M^{+n} aq.	D_{M+n}	Log D_{M+n}
Ta(V)	$1.0 \times 10^{-8} \underline{M}$	-8.000	422	2.625
Ta(V)	1.0×10^{-7}	-7.000	354	2.549
Ta(V)	1.0×10^{-6}	-6.000	445	2.649
Ta(V)	2.5×10^{-2}	-1.602	392	2.593
Ta(V)	5.0×10^{-2}	-1.301	396	2.598
Ta(V)	1.0×10^{-1}	-1.000	249	2.396
Ta(V)	2.0×10^{-1}	-0.699	202	2.306
W(VI)	$1.0 \times 10^{-6} \underline{M}$	-6.000	0.1	-1.00
W(VI)	2.5×10^{-2}	-1.602	0.1	-1.00

Figure 2, in which the logarithm of the distribution ratio is plotted against the logarithm of metal ion concentration (aqueous phase, before equilibration). From $10^{-8} \underline{M}$ to about $0.05 \underline{M}$ tantalum(V), the distribution ratio is fairly constant at about 400. Over this same concentration range, the distribution ratio for niobium(V) changes from 64 to 45, with almost all of the decrease occurring above $0.01 \underline{M}$ niobium(V). As the concentration of tantalum(V) or niobium(V) is increased above about $0.025 \underline{M}$, the distribution ratio begins to decrease fairly rapidly. The distribution ratio for molybdenum(VI)

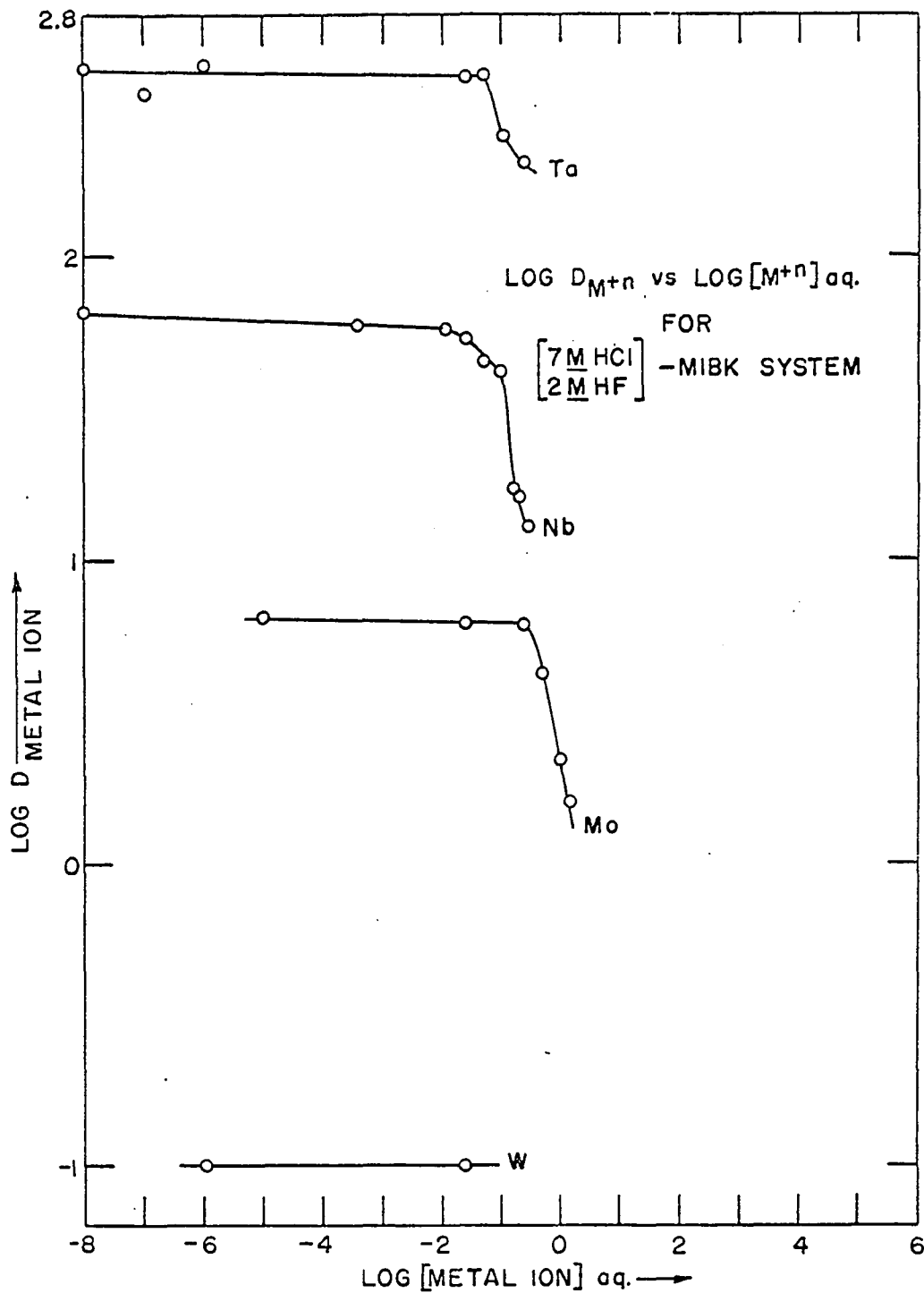


Figure 2. Variation of distribution ratio with metal ion concentration (initial)
Equal phase volumes in most cases

is constant between 10^{-5} M and 0.25 M, and then it decreases rapidly at higher molybdenum(VI) concentrations. The distribution ratio for tungsten(VI) appears to remain constant at the low value of 0.1.

One observation that can be made from Figure 2 is that separation factors for metal ions in this system are obtained directly by subtraction of the logarithms of the distribution ratios. Another use for the plot is the prediction of elution behavior of the metal ions. For instance, consider the separation of a mixture of niobium(V), 0.20 M, and small concentrations of tantalum(V), molybdenum(VI), and tungsten(VI). When the mixture is sorbed to the top of a Tee Six column, impregnated with methyl isobutyl ketone, niobium(V) is retained (along with tantalum(V) and molybdenum(VI)), since niobium(V) is 94% extracted under these conditions. Then, if the metal ions are eluted with 7 M hydrochloric acid, 2 M hydrofluoric acid, molybdenum(VI) would be eluted first, and niobium(V) would appear somewhat later. The course of this elution can be described by plotting the concentration of niobium(V) against milliliters of eluate. The curve that would result would be roughly bell-shaped but with a "tail" on the trailing edge. This is due to the fact that niobium (V) in the leading and trailing edges of the niobium(V) band move slower down the column than does the center of the band. The concentration of niobium(V) in the center of the band is

higher than that in the trailing edges. Thus the niobium(V) peak is eluted relatively rapidly, and the niobium(V) remaining in the trailing edge of the band is held more tightly (higher distribution ratio). More mobile phase than might be anticipated would be required to elute last traces of niobium(V).

Difficulty would follow if the mixture contained a metal ion with a distribution ratio just enough higher than that for niobium(V) theoretically to permit a separation. The tailing of niobium(V) would result in contamination of the other metal ion fraction. Thus initial concentrations of metal ions should be adjusted to correspond to the plateau of the curve.

Beyond the level portion of the curve in Figure 2, a decrease in distribution ratio was observed for molybdenum (VI), niobium(V), and tantalum(V). Overloading of the organic phase was not the cause of the decrease because approximately the same distribution ratios were obtained when organic phase volumes were doubled. The decrease in distribution ratios with increasing metal ion concentrations was probably the result of formation of aqueous phase polymers, or some other metal ion species which was not extracted.

Theory of Chromatographic Separations

Separations based on partition chromatography have a definite advantage over batch type solvent extraction methods in that only a significant difference in the extractability

of the sample components is needed. This is true for partition chromatography in which the stationary phase is a polar substance, and reversed-phase chromatography where phases are reversed and the stationary phase is a non-polar substance. Although a countercurrent distribution apparatus can be employed to make a solvent extraction procedure quantitative, a single column with controlled eluent supply seems advantageous for many cases, especially if the column loading is no problem.

If a chromatographic separation involves only a partitioning effect (i.e. no adsorption or ion-exchange interaction of the solute with the support), then the following relationship exists between D , the batch distribution ratio, and V_R , the retention volume:

$$V_R = DV_S + V_M \quad (1)$$

where, V_R = volume of eluent required to elute the solute to its maximum concentration in the effluent,

D = batch distribution ratio for the extraction of solute from aqueous into organic phase,

V_M = volume of mobile phase (interstitial volume),

V_S = volume of stationary phase.

In order to test Equation 1, 1×10^{-8} mmole of radioactive niobium(V) was introduced to a 11.3 x 1.2 cm. Tee Six column impregnated with methyl isobutyl ketone. Elution was carried out with a 7 M hydrochloric acid-2 M hydrofluoric

acid solution, and 5 ml. fractions were collected for counting. An elution curve of net counts per minute vs milliliters of effluent is shown in Figure 3. In this experiment, the flow rate was 0.3 ml./min., V_M was 5.0 ml., V_S was 3.3 ml., and D was 64. The theoretical V_R , calculated from Equation 1, was 216 ml. as compared to the experimental V_R of 223 ml. This good agreement illustrates how a knowledge of an equilibrium value (D) can be used to predict approximately the volume of eluent needed to elute a solute to its maximum concentration in the effluent.

The number of theoretical plates, N , was calculated for this column by using the relationship given by Samuelson (45).

$$N = 8 \left(\frac{V_R}{B} \right)^2 \quad (2)$$

where, V_R = retention volume,

B = width of the elution curve (in milliliters in this case), at a solute concentration of
 $c = c_{\max}/e = 0.368 c_{\max}$.

N was calculated to be 124, which corresponds to a height equivalent to a theoretical plate of 0.09 cm. Gas chromatographic columns generally have low HETP values (of the order of fractions of a mm.), so the value obtained in this experiment is considered good.

The shape of the elution curve in Figure 3 is bell-shaped and shows little, if any tailing. Tee Six was selected in the beginning of the work primarily because tetrafluoroethylene

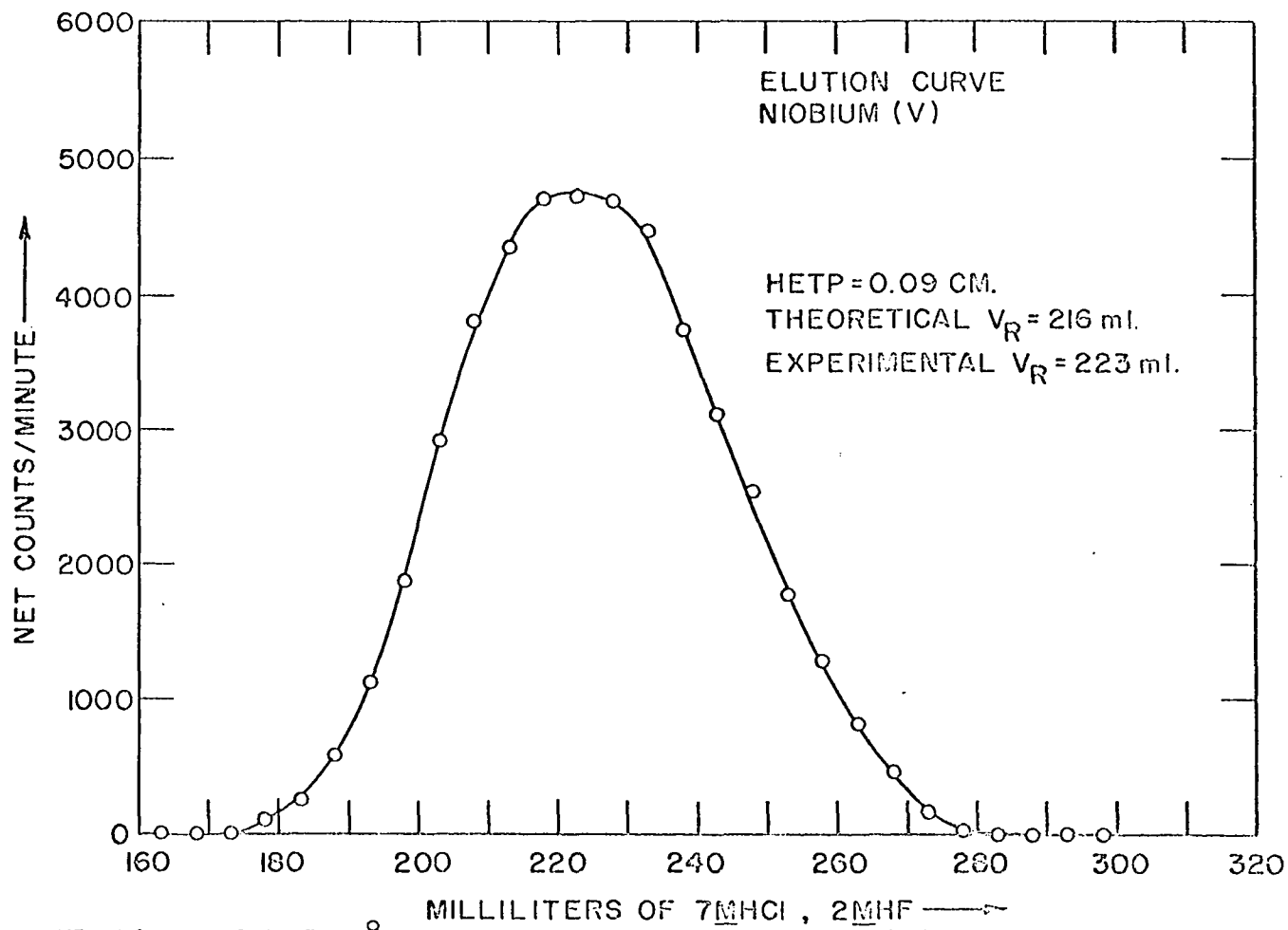


Figure 3. Elution of 1×10^{-8} mmole radioactive niobium(V) from a 11.3×1.2 cm. column of 170 mesh Tee Six. The stationary phase is MIBK and the eluent is 7 M hydrochloric acid, 2 M hydrofluoric acid. Fractions were collected in 5 ml. increments

polymers are the most inert of all supports. Thus interaction of solute with support, which can cause tailing, was not expected to occur. The solvent capacity of Tee Six is fairly good. Chromosorb W and Chromosorb P were tested as supports (both coated with dichlorodimethylsilane and dichlorodiphenylsilane), but hydrofluoric acid reacted significantly with these materials. Cellulose was also tried (coated with petroleum jelly), but retention of an iron(III) solution was poor so cellulose was abandoned.

Another experiment was performed to test the validity of Equation 1 for a mixture of metal ions. About 0.25 mmole each of inactive tantalum(V), molybdenum(VI), and tungsten(VI) was mixed with 1×10^{-8} mmole of active niobium(V), and separated on a 29.5 x 1.2 cm. Tee Six column impregnated with methyl isobutyl ketone. The initial sample volume was 4 ml. and the flow rate was 0.5 ml./min. Elution was performed with a 7 M hydrochloric-2 M hydrofluoric acid solution, and fractions were collected at 5 ml. intervals for counting. A batch distribution ratio of 48 was found for niobium(V) under conditions identical with those for the column separation. In this experiment, V_M and V_S were 12 ml. and 8 ml., respectively. The V_R calculated from Equation 1 was 396, compared to an experimental V_R value of 345. This is not very good agreement but it should be noted that the measurement of V_S is critical when high distribution ratios are involved. For example, the theoretical V_R would be 336 if V_S was found to be 7 ml.

instead of 8 ml. The number of theoretical plates was calculated to be 325, giving a height equivalent to a theoretical plate of 0.10.

According to the theoretical plate concept, a solute peak moves down a column at a constant velocity, and the elution curve can be approximated by a Gaussian curve. The number of theoretical plates does not affect the rate at which a peak travels, but it does determine the sharpness of the band. A high number of theoretical plates will result in a steep, narrow solute band, while a low number of plates will cause the band to be diffuse.

The number of theoretical plates depends upon the nature of the solute, the support and the solvent system. For a given solute, inert support, and solvent system, the number of plates is determined largely by the particle size of the support, and by the flow rate. The use of a support with large surface area will enable the solute to come to equilibrium faster in both phases. Thus, the number of theoretical plates tends to increase with a decrease in particle size.

A flow rate that is too fast or too slow can cause a reduction in the number of theoretical plates. Solute may move to another plate before complete equilibration has occurred in the first plate if the flow rate is too fast. Since more plates are then needed for the solute to reach equilibrium, the number of theoretical plates for the column is reduced. If the flow rate is extremely slow it is possible

that solute will diffuse from one plate to another before equilibrium is reached in the first plate. However, this is not likely to occur in practical separations, since a reasonably fast rate of flow is usually used.

In the early stages of movement down a column, the solute is distributed in plates following the Poisson distribution. After passage of more than 25 theoretical plates, the shape of the elution curve is approximately Gaussian, and can be calculated according to an expression given by Samuelson (45, p. 126).

$$c = c_{\max.} \exp \left[- \frac{N(V_R - V)^2}{2V_R V} \right] \quad (3)$$

$$\text{where, } c_{\max.} = \frac{m}{V_R} \left(\frac{N}{2\pi} \right)^{\frac{1}{2}} \quad (4)$$

and, N = number of theoretical plates

V_R = peak retention volume

V = eluent volume

m = meq. solute.

Thus, a knowledge of the number of theoretical plates and the retention volume enables one to construct a complete elution curve. In practice, the number of theoretical plates is calculated from an elution curve from a preliminary experiment. The peak retention volume is also determined for the same column. Then elution curves can be constructed for columns having other dimensions as well as for the particular column used in the preliminary experiment. Factors such as

particle size, flow rate, and eluent concentration must be held constant when a change in column dimension is made. The number of theoretical plates can be obtained from Equation 2.

If we assume a pure partitioning process, the elution curve will be bell-shaped. However, if the solute loading of a particular column is very high, the number of theoretical plates available will be less than that used to construct the elution curve. Channelling would also reduce the number of theoretical plates since equilibrium in every plate would not be attained.

According to plate theory, a calculation of conditions required for the quantitative separation of two solutes can be made if both distribution ratios are known, and the number of theoretical plates is known for one of the solutes. The number of theoretical plates is assumed to be approximately the same for solutes with similar properties. The sharpness of separation depends on the overlap of the two elution bands. The impurity content of the first solute band (band 1) may be defined as $\Delta m_2/m_1 - \Delta m_1$ (where m = meq. solute on the column), or approximately as $\Delta m_2/m_1$. A chart is given by Samuelson (43, p. 131), which gives the relationship between cross-contamination of two elution bands as a function of the number of theoretical plates for various values of the ratio V_{R2}/V_{R1} . The number subscripts refer to band 1 and band 2. The use of this chart can be illustrated as follows: If the

ratio $V_{R2}/V_{R1} = 1.3$ for two solutes present in equal amounts, the intersection of lines on the chart shows that 540 plates are required to obtain a purity (for each solute) of 0.1%. Under the same conditions, where the ratio is 2.0, only 80 plates are necessary for 0.1% purity. Thus, in the latter instance the column could be shortened by a factor of about 1/6.

It may be useful to know the peak concentration (c_{max}) in order to select the proper method of analysis after separation of the two solutes. Equation 4 can be used for this. The calculation of the band width, β , can be made from Equation 2, and is useful for selecting the size of effluent fractions to collect for analysis.

Separations

Separation of niobium(V) and tantalum(V)

Figure 1 shows that the most favorable separation of niobium and tantalum is obtained using an aqueous phase which is about 3 M in hydrochloric acid and 1.1 M in hydrofluoric acid. Niobium and tantalum, in equal and variable molar ratios, were separated on a 16 x 1.2 cm. Tee Six column impregnated with methyl isobutyl ketone. About 50 ml. of 3 M hydrochloric acid-1.1 M hydrofluoric acid eluted niobium at a flow rate of 0.5 ml./min. Tantalum was stripped from the column with 100 ml. of 15% hydrogen peroxide, at maximum rate of flow (about 2 ml./min.). Data for quantitative

separations are given in Table 12.

Table 12. Separation of niobium(V) from tantalum(V)

16x1.2 cm. Tee Six column (70mesh)
 flow rate 0.5 mole/min.
 50 ml. of 3 M HCl, 1.1 M HF elutes niobium
 100 ml. of 15% H₂O₂ elutes tantalum

Ratio Ta:Nb	Nb ₂ O ₅			Ta ₂ O ₅		
	Taken mg.	Found mg.	Diff. mg.	Taken mg.	Found mg.	Diff. mg.
0.1 to 1	654.0	649.3	-4.7	110.5	111.2	+0.7
1 to 1	67.0	66.5	-0.5	110.7	111.3	+0.6
1 to 1	67.0	66.2	-0.8	110.7	110.9	+0.2
1 to 1	67.0	66.6	-0.4	110.7	111.2	+0.5
1 to 1	67.0	66.4	-0.6	110.7	112.0	+1.3
1 to 1	67.0	66.6	-0.4	110.7	110.3	-0.4
1 to 1	67.0	66.6	-0.4	110.7	111.0	+0.3
1 to 1	67.0	66.8	-0.2	---	---	---
5 to 1	12.1	12.6	+0.5	110.5	111.3	+0.8
10 to 1	12.1	11.7	-0.4	221.0	221.9	+0.9

Separation of molybdenum(VI) and tungsten(VI)

The distribution ratios for molybdenum and tungsten for extraction from 6 M hydrochloric acid-3 M hydrofluoric acid-1 M sulfuric acid into methyl isobutyl ketone are given in Table 9. The low distribution ratio for tungsten, 0.2, and a distribution ratio of 7.4 for molybdenum in this system suggests that a separation of the two metal ions should be possible. The results of a quantitative separation of molybdenum and tungsten on a 26x1.2 cm. Tee Six column are shown in Table 13. Spot tests and spectroscopic analyses indicated that tungsten was completely eluted with 15-20 ml. of 6 M hydro-

Table 13. Separation of molybdenum(VI), tungsten(VI) and niobiumV

26x1.2 cm. Tee Six column (170 mesh)

flow rate 0.5 ml./min.

Metal	Eluent		Taken mg. oxide	Found mg. oxide	Diff. mg. oxide
	Volume	Composition			
W	20 ml.	6M HCl, 1M H ₂ SO ₄ , 3M HF	59.1	58.7	-0.4
Mo	50 ml.	3M HCl, 1M H ₂ SO ₄ , 10M HF	38.3	38.5	+0.2
W	20 ml.	6M HCl, 1M H ₂ SO ₄ , 3M HF	59.1	59.6	+0.5
Mo	50 ml.	3M HCl, 1M H ₂ SO ₄ , 10M HF	38.3	38.2	-0.1
Nb	50 ml.	3M HCl, 1M HF	29.0	28.7	-0.3

chloric acid-3 M hydrofluoric acid-1 M sulfuric acid. For the separation in Table 13, 20 ml. of the aqueous eluent was used. Next, molybdenum was stripped from the column with 3 M hydrochloric acid - 10 M hydrofluoric acid-1 M sulfuric acid at maximum flow rate. The reduction in hydrochloric acid concentration and the large increase in hydrofluoric acid

concentration causes molybdenum to be rapidly eluted. Spot tests showed that molybdenum was eluted with 40-50 ml. of the preceding eluent.

Separation of molybdenum(VI), tungsten(VI), and niobium(V)

Figure 1 shows that niobium is highly extracted from 6 M hydrochloric-3 M hydrofluoric acid solution into methyl isobutyl ketone. High extraction is also indicated for niobium from 3 M hydrochloric-10 M hydrofluoric acid solution. The addition of some sulfuric acid enhances the extraction of niobium primarily by providing more hydronium ions.

Molybdenum, tungsten, and niobium were retained by the column from a solution 6 M in hydrochloric acid, 3 M in hydrofluoric acid, and 1 M in sulfuric acid. Tungsten was eluted with 20 ml. of a solution of the preceding composition, and molybdenum was quantitatively removed from the column with 50 ml. of 3 M hydrochloric acid-10 M hydrofluoric acid-1 M sulfuric acid. Finally, rapid elution of niobium was carried out with 50 ml. of 3 M hydrochloric acid-1 M hydrofluoric acid. The results of the quantitative separations are given in Table 13. Column dimensions were the same as those used for the separation of the molybdenum-tungsten mixture.

Separation of niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI)

Reference to Figure 1 shows that tantalum is very highly extracted by methyl isobutyl ketone from all of the solutions

that were used to elute tungsten, molybdenum, and niobium in the preceding separations. Thus, all four metal ions were separated on a 26x1.2 cm., Tee Six column, using the same eluents as described in the separation of molybdenum, tungsten, and niobium. Tantalum was last to be eluted, using 50 ml. of methyl isobutyl ketone at maximum flow rate. Spot tests and emission spectroscopic analyses indicated that Ta was quantitatively removed with 40-50 ml. of methyl isobutyl ketone. Results for separations are given in Table 14.

Another separation of all four metal ions was performed in which the system was simplified by omitting sulfuric acid. The distribution ratios for the metal ions in the system 7 M hydrochloric acid-2 M hydrofluoric acid-methyl isobutyl ketone, are given in Table 7. All of the metal ions except tungsten (VI) are extracted into methyl isobutyl ketone to a considerable extent. The distribution ratio for tungsten was lower in this system (0.1 as compared to 0.2 for the system containing sulfuric acid). Tungsten was first to be eluted with 20 ml. of 7 M hydrochloric acid-2 M hydrofluoric acid. Molybdenum was eluted next with 50 ml. of 6 M hydrochloric acid-6 M hydrofluoric acid ($D = 1.6$). Elution with 50 ml. of 3 M hydrochloric acid-1 M hydrofluoric acid removed niobium, and tantalum was stripped at maximum flow rate with 50 ml. of methyl isobutyl ketone. Column conditions were the same as for the preceding separation of the four metal ions. Spectroscopic analyses showed that the separations were clean.

Table 14. Separation of niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI)

26x1.2 cm. Tee Six column (170 mesh)

flow rate 0.5 ml./min.

Metal	Eluent		Taken mg. oxide	Found mg. oxide	Diff. mg. oxide
	Volume	Composition			
W	20 ml.	6M HCl, 1M H ₂ SO ₄ 3M HF	59.1	59.4	+0.3
Mo	50 ml.	3M HCl, 1M H ₂ SO ₄ 10M HF	38.3	38.2	-0.1
Nb	50 ml.	3M HCl, 1M HF	29.0	28.6	-0.4
Ta	50 ml.	MIBK	54.2	53.4	-0.8
W	20 ml.	7M HCl, 2M HF	57.8	57.1	-0.7
Mo	50 ml.	6M HCl, 6M HF	38.5	38.4	-0.1
Nb	50 ml.	3M HCl, 1M HF	33.1	32.0	-1.1
Ta	50 ml.	MIBK	56.6	56.3	-0.3

The relative standard deviation for 29 chemical analyses for molybdenum, tungsten, niobium, and tantalum was $\pm 1.34\%$.

Separation of niobium(V) and tantalum(V)-spectrophotometric determination of niobium(V)

A mixture of 1 part niobium and 1000 parts tantalum was separated on a 26x1.2 cm. Tee Six column. The amount of niobium taken was 1×10^{-4} mmole. Niobium was separated from tantalum with 50 ml. of 3 M hydrochloric acid-1 M hydrofluoric acid and was analyzed for spectrophotometrically.

A mixture of 1 part niobium and 1000 parts each of tantalum, molybdenum, and tungsten was also separated on a 26x 1.2 cm. Tee Six column. Elution conditions and results of the separations are given in Table 15.

Table 15. Separation and spectrophotometric determination of niobium(V)

26x1.2 cm. Tee Six column (170 mesh)
flow rate 0.5 ml./min.

20 ml. of 7 M HCl, 2 M HF elutes tungsten
50 ml. of 6 M HCl, 6 M HF elutes molybdenum
50 ml. of 3 M HCl, 1 M HF elutes niobium

Mixture, metal ion ratio	Taken mmole Nb	Found mmole Nb	% Error
Ta:Nb 1000:1	4.00×10^{-4}	3.85×10^{-4}	-3.7
Ta, Mo, W:Nb 1000:1	4.00×10^{-4}	3.82×10^{-4}	-4.5

Separation and radiochemical determination of niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI)

The results of separations of very small amounts of radioactive isotopes from large amounts of one or more inactive metal ions are listed in Table 16. One part of active niobium was separated from 10^4 parts of inactive tantalum. One part of active niobium was also separated from 10^5 , 10^6 , and 10^7 parts each of inactive molybdenum, tungsten, and tantalum in three different mixtures. The amount of inactive metal ion was 0.25 mmole in every case.

One part of active tantalum was separated from 10^4 parts of inactive niobium. One part of active tantalum was also separated from 10^4 and 10^7 parts each of inactive molybdenum, tungsten, and niobium. The amount of each inactive metal ion was 0.25 mmole.

A separation of 1 part active tungsten from 10^7 parts inactive molybdenum, niobium, and tantalum (0.25 mmole each), was successfully performed. One separation, involving 1 part active molybdenum and 10^6 parts inactive tungsten, niobium, and tantalum (0.25 mmole each), was also carried out.

The results of radiochemical separations are listed in Table 16, together with percentage recovery of the active metal ions.

In all the radiochemical separations involving active niobium, a relatively constant percentage of the total activ-

Table 16. Separation and radiochemical determination of niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI)

26x1.2 cm. Tee Six column (170 mesh)

flow rate 0.5 ml./min.

20 ml. of 7 M HCl, 2 M HF elutes tungsten

50 ml. of 6 M HCl, 6 M HF elutes molybdenum

50 ml. of 3 M HCl, 1 M HF elutes niobium

50 ml. of MIBK elutes tantalum

Mixture metal ion ratio active ion	Fraction analyzed	Counts/min.	Active ion recovery, %
Ta:Nb 10 ⁴ :1 Nb(V)	Nb standard Nb	53,064 52,763	99.4
Mo,W,Ta:Nb 10 ⁵ :1 Nb(V)	Nb standard Nb W Mo Ta background	4,549 4,576 356 341 334 337	100
Mo,W,Ta:Nb 10 ⁶ :1 Nb(V)	Nb standard Nb W Mo Ta background	114,837 114,140 871 327 348 333	99.4
Mo,W,Ta:Nb 10 ⁷ :1 Nb(V)	Nb standard Nb W Mo Ta background	11,232 11,109 399 356 336 338	99.0

Table 16. (Continued)

Mixture metal ion ratio active ion	Fraction analyzed	Counts/min.	Active ion recovery, %
Nb:Ta 10 ⁴ :1 Ta(V)	Ta standard	26,398	99.9
	Ta	26,866	
	Nb	420	
	background	424	
Mo,W,Nb:Ta 10 ⁴ :1 Ta(V)	Ta standard	19,429	99.3
	Ta	19,288	
	W	274	
	Mo	279	
	Nb background	274 269	
Mo,W,Nb:Ta 10 ⁷ :1 Ta(V)	Ta standard	7,036	99.7
	Ta	7,018	
	W	437	
	Mo*	437	
	Nb**	435	
	background	444	
Mo,Nb,Ta:W 10 ⁷ :1 W(VI)	W standard	1,077	99.9
	W	1,076	
	column stripping	647	
	background	638	
W,Nb,Ta:Mo 10 ⁶ :1 Mo(VI)	Mo standard	2,104	98.9
	Mo*	2,059	
	W	1,674	
	column stripping	1,626	
	background	1,648	

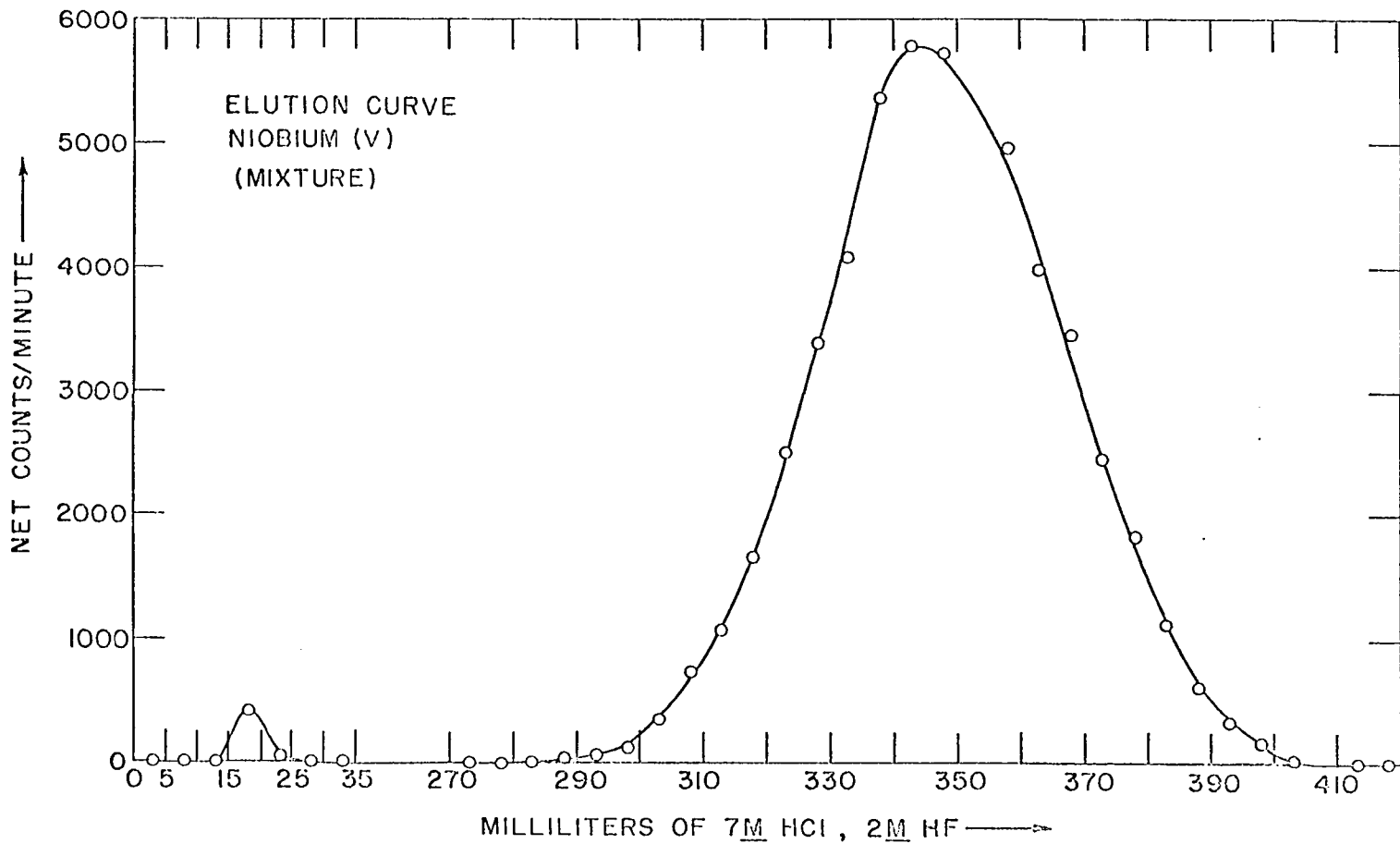
* 50 ml. of 4 M HCl, 8 M HF used to elute molybdenum.

**50 ml. of 2 M HCl, 1 M HF used to elute niobium.

ity always appeared in the tungsten fractions (see Table 16). This activity is shown also as a small peak in the elution curve (refer to Figure 4). Figure 4 shows the small peak of activity occurring shortly after a column volume of eluent was passed through. Since niobium(V) was the only active metal ion added to the column, this initial activity came from some species in the niobium(V) stock solution. A gamma ray spectrum of the niobium(V) stock solution was obtained on a multichannel analyzer but it revealed no other metal ion trace impurities. Since the interfering species was eluted immediately after one column volume was passed through, we believed the species to be non-extractable, radiocolloidal niobium(V). To prove this, some niobium(V) stock solution, 7 M in hydrochloric acid and 2 M in hydrofluoric acid, was equilibrated with methyl isobutyl ketone, followed by back-extraction of the niobium(V) into a solution of 2 M hydrochloric acid-1 M hydrofluoric acid. Appropriate amounts of concentrated hydrofluoric and hydrochloric acids were added in order to give a niobium(V) solution which was 7 M in hydrochloric acid, and 2 M in hydrofluoric acid. This solution was then introduced to a column and elution was carried out with equilibrated 7 M hydrochloric acid-2 M hydrofluoric acid. After one column volume and four 5 ml. fractions were collected there was no activity observed, so the conclusion about the source of the activity was apparently correct.

Figure 4. Elution of a mixture of 1×10^{-8} mmole radioactive niobium(V) and 0.25 mmole each of inactive tantalum(V), molybdenum(VI), and tungsten(VI) from a 29.5x1.2 cm. column of 170 mesh Tee Six

The stationary phase is MIBK and the eluent is 7 M hydrochloric acid, 2 M hydrofluoric acid. Fractions were collected in 5 ml. increments



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