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SEPARATION OF TANTALUM AND NIOBIUM BY SOLVENT EXTRACTION

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November 12, 1952

Berkeley, California

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ABSTRACT

Tantalum and niobium are separated by extraction into di-isopropyl ketone from mineral acid -- hydrofluoric acid aqueous phases. Behavior of tantalum is presented in detail, although no conclusions as to species present is reached. Radiochemical separation procedures for tantalum and niobium are given.

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I. INTRODUCTION

Tantalum and niobium have been found to extract into certain polar organic solvents from aqueous solutions containing hydrofluoric and hydrochloric acids.(1) The dependence of extractability on extraction conditions has been studied to investigate the possibility of achieving a tantalum-niobium separation based on this phenomenon. Di-isopropyl ketone was chosed as a solvent for examination, since it was found not to extract significant amounts of hydrochloric acid.

Preliminary investigations indicated that a tantalum-niobium separation was indeed possible. In addition to the system tantalum-hydrochloric acid-hydrofluoric acid, the systems tantalum-sulfuric acid-hydrofluoric acid, tantalum-nitric acid-hydrofluoric acid, and tantalum-perchloric acid-hydrofluoric acid were investigated. The system sulfuric acid-hydrofluoric acid seemed to offer the most nearly specific solvent-extraction separation and purification of tantalum and niobium.

II. EXPERIMENTAL

Tantalum tracer was prepared by dissolving neutron-irradiated tantalum metal in nitric and hydrofluoric acids, adding a large volume of 6 M hydrochloric acid, and extracting twice into di-isopropyl ketone.

The ketone layers were combined and washed twice with an aqueous solution 6 M in hydrochloric acid and 1 M in hydrofluoric acid. The tantalum was then brought into aqueous medium by contacting the di-isopropyl ketone twice with water.

The resultant clear aqueous solution had a pH of 1.5 and no tantalum precipitated upon standing two or three weeks in a glass centrifuge cone. Aliquots (50λ) of the above solution containing about 1 mg. Ta_2O_5 were added to measured amounts of standardized acids and the total volume adjusted to 1 ml. in a glass centrifuge cone. One milliliter of Eastman technical grade di-isopropyl ketone was added to the cone, the mixture stirred well with a platinum stirring wire for one minute and centrifuged briefly; then equal aliquots were taken from each phase for counting. Care was taken to work rapidly and at room temperature to minimize the effects of the hydrofluoric acid on the glass. The rate of extraction was too rapid to measure. If the mineral acid was known to extract appreciably into di-isopropyl ketone, the ketone was pre-equilibrated with the same concentration of the mineral acid as used in the extraction. Hydrochloric and sulfuric acids did not extract appreciably while perchloric, hydrofluoric, and nitric acids did extract. For simplicity and ease of handling, results were based on initial concentration of the hydrofluoric acid in the aqueous phase because the hydrofluoric acid extracted appreciably into the ketone.

There was no attempt in this work to keep ionic strength constant, hence no conclusion could be made regarding species in solution.

The liquid aliquots from the extraction were transferred to machined teflon cups and the top covered with pressure sensitive tape

to prevent spilling. The gamma radiation from the Ta^{182} tracer in these samples was counted by means of a single channel scintillation pulse analyzer using a thallium-activated sodium iodide crystal. Samples of the organic and aqueous phases of a given extraction were counted consecutively in the same geometry to minimize errors. The results are shown in Figures 1, 2, and 3.

Niobium tracer was prepared by adding 15 mg. of niobium as the oxalate to a Zr^{95}-Nb^{95} mixture containing inactive zirconium. The oxalate was destroyed with nitric acid and potassium chlorate; Nb_2O_5 thereupon precipitated and was centrifuged, washed into a lusteroid cone, and dissolved in 1 ml. of concentrated hydrofluoric acid. The solution was adjusted to approximately 10 M in hydrofluoric acid and 6 M in hydrochloric acid, and transferred to a polyethylene bottle. This solution was extracted twice with equal volumes of di-isopropyl ketone, the organic layers being combined and washed with a solution of 6 M in hydrochloric acid and 10 M in hydrofluoric acid. The niobium was then extracted from the organic phase with water. The procedure was then the same as for the tantalum. Only check points were taken to show the large differences in extractibilities of tantalum and niobium (Table I), for accurate volume measurement with very high hydrofluoric acid concentrations did not seem feasible. However, in a solution about 6 M in sulfuric acid and 9 M in hydrofluoric acid, 90 percent of the niobium extracted into an equal volume of ketone and from about 3 M sulfuric acid and 4.5 M hydrofluoric acid, 40 percent extracted.

Table I. Relative Extractabilities of Tantalum and Niobium into Di-isopropyl Ketone

Acid Concentrations	Element	Percent Extracted	Extraction Coefficient	Ratio of Extraction Coefficients, Ta/Nb
HCl 3.70 M and HF 0.40 M	Ta	81	4.3	91
	Nb	4.5	0.047	
HNO_3 3.92 M and HF 0.40 M	Ta	79	3.8	880
	Nb	0.43	0.0043	
H_2SO_4 4.50 M and HF 0.40 M	Ta	95	19	160
	Nb	11	0.12	
$HClO_4$ 4.61 M and HF 0.40 M	Ta	90	9.0	290
	Nb	3.0	0.031	

The ratio of extraction coefficients in Table I show that separation of tantalum and niobium by this method is possible.

A mixture of 10 mg. (as metals) each of tantalum and niobium were put into 5 ml. of a solution adjusted to 3 M in hydrochloric acid and 0.4 M in hydrofluoric acid. This solution was extracted with 5 ml. of di-isopropyl ketone for one minute. The phases were separated, the aqueous phase extracted again, and the organic phase washed with 3 M hydrochloric acid and 0.4 M hydrofluoric acid. The washing and second extraction were discarded.

Boric acid was added to the aqueous phase to complex any fluoride present. Then ammonium hydroxide was added to precipitate the hydrated

oxides which were washed with a dilute ammonium nitrate solution. The organic phase was contacted twice with water, the water layers combined, boric acid added, and the hydrated oxides precipitated with ammonium hydroxide and washed with a dilute ammonium nitrate solution. The precipitates were analyzed spectrographically. The composition of the precipitate from the aqueous layer was 98 percent niobium and 2 percent tantalum, and the composition of the precipitate from the organic layer was 99.5 percent tantalum and 0.5 percent niobium.

The extractabilities of other elements into the ketone were examined briefly. In the 6 M hydrochloric acid-hydrofluoric acid system elemental halogens, iron(III), gallium(III), antimony(V), arsenic(III), selenium(VI) and tellurium(VI) apparently extract very well, and all but antimony(V) back-extract into water. Antimony(III) extracts slightly and arsenic(V) and tellurium(IV) somewhat better, while selenium(IV) does not extract appreciably. It is significant that silicon(IV), tin(IV), titanium(IV), manganese(II), zirconium(IV), and hafnium(IV) do not extract. In the 6 M sulfuric acid-0.4 M hydrofluoric acid system, only elemental halogens, selenium(VI) and tellurium(VI) tend to follow. A radiochemical separation procedure has been designed and tested for tantalum which gives decontamination factors of at least 10^5 from all fission products. The steps appear below:

1. Dissolve uranium target in hydrochloric acid and make a clear solution with hydrogen peroxide in a polyethylene cone (avoid contact between hydrofluoric acid solutions and glass).

2. Add tantalum in hydrochloric acid and hydrofluoric acid to target solution and selenium and tellurium holdbacks (add sufficient hydrofluoric acid to make final solution at least 0.6 M in hydrofluoric acid, final volume of 15 ml.).

3. Extract three times for five minutes with 5 ml. di-isopropyl ketone (remove ketone with saran pipet).

4. Combine and wash organic layers in polyethylene three times with 5 ml. of a solution 6 M in sulfuric acid and 0.4 M in hydrofluoric acid.

5. Back extract tantalum three times for one minute with 5 ml. portions of 6 M hydrochloric acid containing boric acid and combine in glass.

6. Wash equeous phase once for one minute with 10 ml. di-isopropyl ketone, discard organic phase.

7. Add 1 drop phenolphthalein to aqueous phase, make basic with ammonium hydroxide, add 1 drop 2 percent aerosol, digest hot, centrifuge.

8. Wash with slightly basic ammonium nitrate solution.

9. Wash twice with fuming nitric acid, digest, centrifuge.

10. Transfer to lusteroid cone, dissolve precipitate in a solution 6 M in sulfuric acid and 0.6 M in hydrofluoric acid.

11. Transfer to polyethylene cone and repeat steps 3 through 9.

12. Transfer tantalum precipitate to platinum crucible, ignite, weigh as Ta_2O_5.

A fission product separation procedure has been devised for niobium to give decontamination factors of 10^6 for all other fission

products. Tantalum, however, is probably not separated from niobium. The steps appear below:

1. Dissolve uranium target in concentrated hydrochloric acid to which niobium carrier has been added in oxalate form (lusteroid tube).

2. Add a drop of concentrated hydrofluoric acid, clear solution with a few drops of concentrated nitric acid and digestion.

3. Transfer to polyethylene cone, adjust to 6 M in hydrochloric acid, and extract three times with half volumes of di-isopropyl ketone. Discard organic layer.

4. Add sufficient concentrated hydrochloric acid and hydrofluoric acid to make the solution 6 M in hydrochloric acid and 9 M in hydrofluoric acid.

5. Extract three times with half volumes of di-isopropyl ketone, combine ketone layers.

6. Wash combined organic layers three times with a solution 6 M in sulfuric acid and 9 M in hydrofluoric acid.

7. Extract niobium from ketone three times with half volumes water. Water layers are collected in a tube containing saturated boric acid solution.

8. Add phenolphthalein, make just basic with ammonium hydroxide, digest.

9. Wash niobium precipitate twice with slightly basic ammonium nitrate solution, then twice with concentrated nitric acid.

10. Transfer precipitate to polyethylene cone and dissolve in a solution 6 M in sulfuric acid and 9 M in hydrofluoric acid.

11. Repeat steps 5 through 9.

12. Transfer precipitate to platinum crucible, ignite and weigh as Nb_2O_5.

III. CONCLUSIONS

Tantalum and niobium can be separated by preferential extraction of the tantalum into di-isopropyl ketone from mineral acid-hydrofluoric acid aqueous systems. Niobium may also be separated from nearly all other elements by extraction from solutions substantially higher in acidity and hydrofluoric acid concentration.

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(1) Walter E. Nervik, private communication.

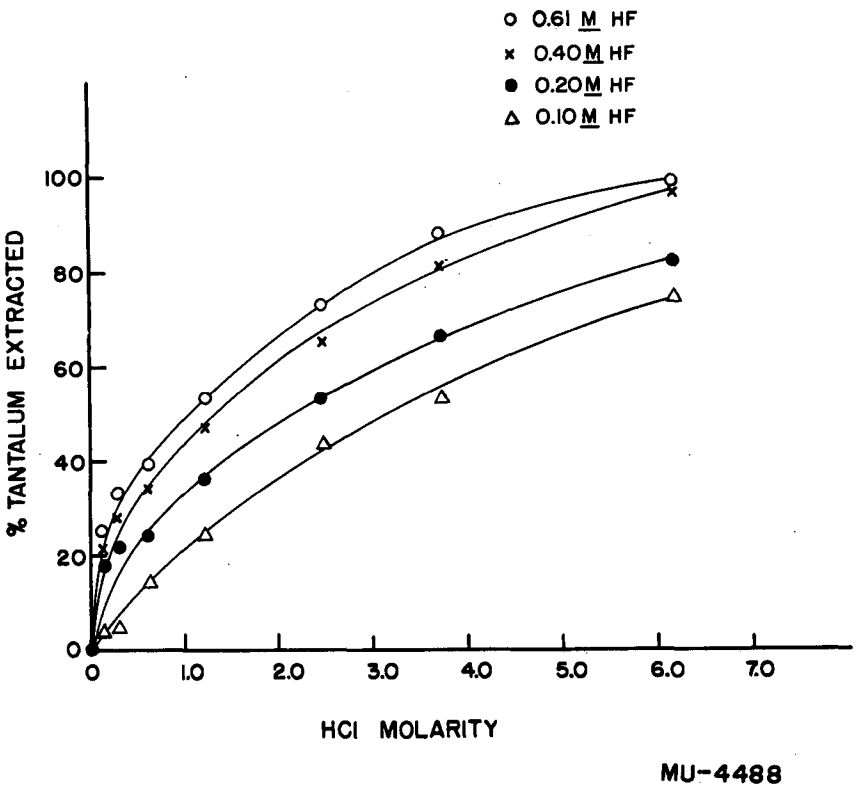

Figure 1. Extractability of Tantalum in the System Hydrochloric Acid - Hydrofluoric Acid - Diisopropyl Ketone as a Function of Hydrochloric Acid Concentration.

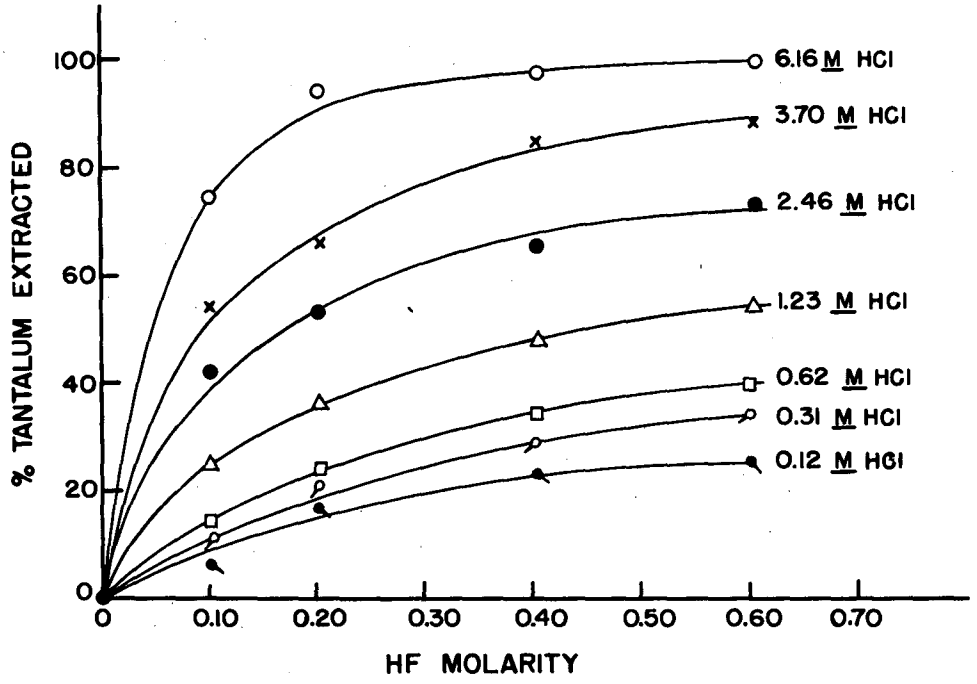

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Figure 2. Extractability of Tantalum in the System Hydrochloric Acid - Hydrofluoric Acid - Diisopropyl Ketone as a Function of Hydrofluoric Acid Concentration.

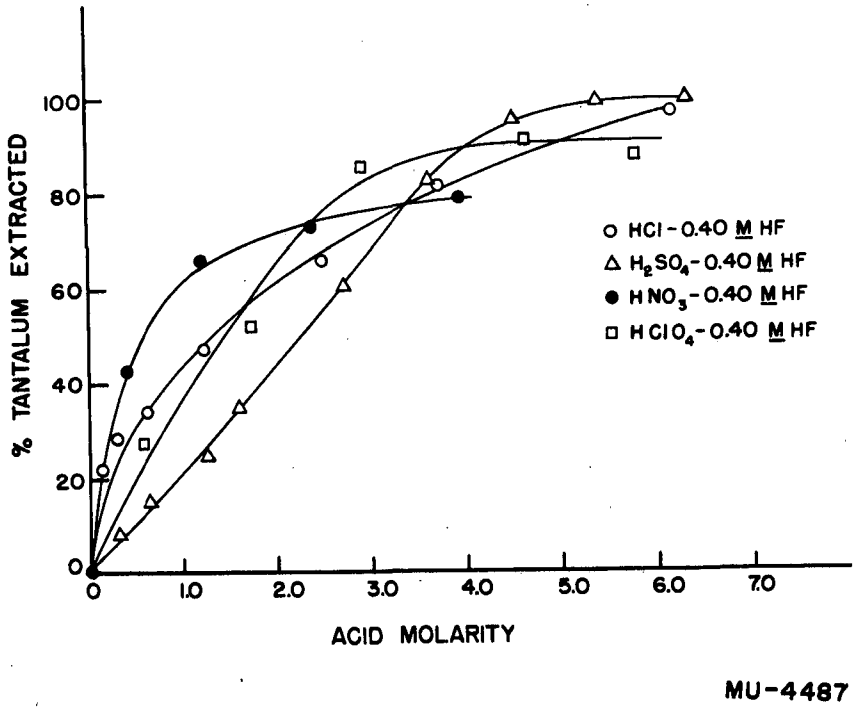

Figure 3. Extractability of Tantalum in the System Mineral Acid - Hydrofluoric Acid - Diisopropyl Ketone as a Function of Mineral Acid Concentration.