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The Radiochemistry of Niobium and Tantalum

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The Radiochemistry of Niobium and Tantalum

ELLIS P. STEINBERG

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois

August 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $0.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of niobium and tantalum is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of niobium and tantalum which might be included in a revised version of the monograph.

It is a pleasure to acknowledge the assistance of Miss Barbara Lore in a survey of the pertinent literature.

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ELLIS P. STEINBERG
Argonne National Laboratory *
9700 South Cass Avenue
Argonne, Illinois

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM

"The Analytical Chemistry of Tantalum and Niobium," W. R. Schoeller (Chapman and Hall, Ltd., London, 1937).

"Analysis of Minerals and Ores of the Rarer Elements," W. R. Schoeller and A. R. Powell (3rd ed. Griffin, London, 1955).

Chap. 15 in "Chapters in the Chemistry of the Less Familiar Elements," B. S. Hopkins (Stipes Publ. Co., 1940).

"Tantalum and Niobium," G. L. Miller (Academic Press, 1959).

"Analytical Chemistry of Niobium and Tantalum," R. H. Atkinson, J. Steigman, and C. F. Hiskey, Anal. Chem. 24, 477 (1952).

"Chemical Elements and their Compounds," H. V. Sidgwick (Oxford University Press, 1950), pp. 804-853.

"Annotated Bibliography of the Analytical Chemistry of Nb and Ta," Jan. 1935-June 1953, F. Cuttitta, Geol. Survey Bulletin 1029-A. (USGPO, 1957).

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*Operated by the University of Chicago under Contract W-31-109-eng-38.

"Research on the Compounds of Niobium and Tantalum," J. C. de Marignac, Ann. chim. (Phys.) **8**, 5 and **9**, 249 (1866).

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF NIOBIUM AND TANTALUM

D. N. Hume prepared a preliminary review of the radiochemistry of some of the major fission product elements in 1945, but it was not published. Some material from that review has been incorporated in the present survey. The following reviews contain information on radiochemical methods for a number of elements:

H. L. Finston and J. Miskel, "Radiochemical Separation Techniques," Annual Review of Nuclear Science **5**, 269 (1955).

W. W. Meinke, "Nucleonics" Anal. Chem. **32**, 104R (1960).

III. TABLE OF ISOTOPES OF NIOBIUM AND TANTALUM

Isotope	Half-life	Type of Decay	Method of Preparation
Nb^{89m}	0.8h	β^+	Nb(p,p4n); Zr(p,xn); $Br^{81}(C^{12},4n)$
Nb^{89}	1.9h	β^+	
Nb^{90m}	24s	IT	Mo^{90} decay
Nb^{90}	14.60h	β^+	$Zr^{90}(d,2n)$; $Mo^{92}(d.\alpha)$; $Mo(\gamma,pn)$
Nb^{91m}	64d	IT	$Zr^{90}(d,n)$; $Mo^{94}(d,\alpha n)$
Nb^{91}	long	EC	$Zr^{90}(d,n)$
Nb^{92m}	13h	EC	$Nb^{93}(p,pn)$
Nb^{92}	10.1d	EC, no β^-	$Y(\alpha,n)$;Zr(pn,);$Nb(\gamma,n)$; Nb(n,2n);Nb(d,T);Mo(n,p); $Mo^{94}(d,\alpha)$
Nb^{93m}	12y	IT	Zr^{93}decay; $Nb^{93}(n,n')$
Nb^{94m}	6.6m	IT 99+% β^-~0.1%	$Nb(n,\gamma)$; Nb(d,p)

TABLE OF ISOTOPES OF NIOBIUM AND TANTALUM (cont'd)

Isotope	Half-life	Type of Decay	Method of Preparation
Nb^{94}	1.8×10^{4}y sp act	β^-,no EC	Nb(n,γ)
Nb^{95m}	90h	IT	Nuclear fission; Mo^{97}(d,α); Zr^{95} decay
Nb^{95}	35d	β^-	nuclear fission; Mo(d,α) Zr^{95} decay
Nb^{96}	23.35h	β^-	Zr^{96}(p,n)
Nb^{97m}	60s	IT	Mo^{98}(γ,p); Zr^{97} decay
Nb^{97}	72.1m	β^-	Mo(n,p); Mo(γ,p); nuclear fission
Nb^{98}	51.5m	β^-	Mo^{98}(n,p); Mo^{100}(d,α); nuclear fission
Nb^{99}	2.4m	β^-	Mo^{100}(γ,p); nuclear fission
${}_{73}Ta^{176}$	8.0h	EC	Lu(α,3n); Ta spallation; W^{176} decay
Ta^{177}	53h	EC	Lu(α,2n); Lu(α,3n); Hf(p,n); Ta spallation; W^{177} decay
Ta^{178}	2.1h	EC ~ 97%, β^+~3%	Lu(α,n);Hf(p,n);Ta(p,p3n)
Ta^{178}	9.35m	EC 98%, β^+~2%	Hf(p,n); W^{178} decay
Ta^{179}	~600d	EC	Lu(α,n);Hf(p,n);Ta(p,p2n)
Ta^{180m}	8.15h	EC ~79%, β^- ~21%, no β^+	Ta^{181}(n,2n);Ta^{181}(γ,n)
Ta^{182m}	16.5m	IT	Ta(n,γ)
Ta^{182}	115.1d	β^-	Ta(n,γ);Ta(d,p);W(d,α); W(n, p)
Ta^{183}	5.0d	β^-	W(n,p);W(γ,p); W(n,pn)
Ta^{184}	8.7d	β^-	W^{184}(n,p)
Ta^{185}	50m	β^-	W^{186}(γ,p)
Ta^{186}	10.5m	β^-	W(n,p)

IV. REVIEW OF THOSE FEATURES OF NIOBIUM AND TANTALUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. The Metallic State

Niobium and tantalum are very similar in their chemical and physical properties. The metals are difficult to obtain. Niobium may be prepared by reducing the pentoxide with aluminum thermite and heating in *vacuo* to drive off excess aluminum. Tantalum is best prepared by reducing a fluorotantalate (e.g., K_2TaF_7) with an alkali metal and purified by heating in *vacuo* in an electric arc to volatilize impurities. Both are hard, grey metals with high melting points; niobium melting at 1950°C and tantalum at 2800°C. They absorb hydrogen and react with halogens, carbon, oxygen and nitrogen at high temperatures although niobium combines only slowly with oxygen. Both tantalum and niobium are very resistant to chemical attack, only HF among the acids having any action on them. Aqueous alkalies do not attack the metals, and fused alkalies do so only slowly.

2. Soluble Salts

Pentavalent Nb and Ta form no simple cations in aqueous solution and exist only in the form of complex ions. Niobic and tantalic acids are very weak and are readily hydrolyzed. The orthoniobates (e.g., Na_3NbO_4) and hexaniobates (e.g., $K_8Nb_6O_{19}$) are soluble in water. The alkaline hexatanlates are the only readily soluble tantalates known.

The only important valence of Nb and Ta is +5. Polarographic reduction to the +3 and +4 states in oxalate and tartrate solutions has been demonstrated by Elson.(1) The reduced Nb solutions exhibit a half-time for oxidation in air of 10-15 minutes, while the corresponding Ta solutions exhibit times of the order of hours.

3. Insoluble Salts

The most characteristic compound of both niobium and tantalum is the very insoluble pentoxide which is dissolved neither by acids nor bases in the absence of complex forming ions. The hydrated oxides are precipitated when acid is added to a solution of a niobate or tantalate.

Niobium and tantalum may be precipitated (along with titanium and some tungsten) by tannic acid from slightly acid tartrate or oxalate solution.(2) This precipitation was the standard method for the separation and estimation of Ta and Nb until the recent development of solvent extraction techniques. Milner, et al.(3) studied the pH dependence of the tannic precipitation from various complexing solutions. The optimum pH values for complete precipitation from the various solutions are given in the following table:

Solution	Acidity
Ammonium Acetate-HCl	0.1 - 0.25 N HCl(Nb)
Ammonium Oxalate	pH = 4.5
Ammonium Tartrate	pH $\geq$ 3(Nb)
	pH $\geq$ 4(Ta)
Ammonium Citrate	pH $\geq$ 5(Nb)
	pH $\geq$ 3.5(Ta)
Sulphosalicylic Acid	pH $\geq$ 0.5
Malic Acid	pH $\geq$ 4
Mandelic Acid	pH $\geq$ 2

The behavior of Ti with these solutions was also examined, and a possible separation from Nb and Ta was noted with sulphosalicylic acid solution in which only a small amount of titanium is precipitated with tannic at pH = 0.5. M. Sankar Das, et al.(4) used tannin in the presence of EDTA (ethylenediamine tetra-acetic acid) as a sequestering agent. However, Ti, Sn, Pb, and some W accompany the Nb and Ta tartrates.

A number of organic precipitants have been utilized for Nb and Ta, some affording a good separation between the two elements. Both Ta and Nb may be precipitated with cupferron from cold, acidic tartrate or oxalate solution(5) and with benzene arsonic acid from a solution containing excess tartaric acid.(6) Tantalum may be precipitated from hot acidic ammonium oxalate solution with n-propylarsonic acid(7) while Nb remains in solution. Moshier and Schwarberg(8) used tantalon (N-benzoyl-N-phenylhydroxylamine) for precipitation of Ta from HF-H_2SO_4 solution at pH 1.0. Under these conditions a good separation from Nb, Ti, and Zr is achieved. Niobium may be separated from Ta and most other elements except Sn by precipitation with cupferron from tartrate-ammonium acetate buffered solutions at pH 4.5 to 5.5.(9) Niobium may also be precipitated with tantalon from a tartrate solution at an acidity of 2.0 N.(10) At pH 3.5 -6.5 niobium is completely precipitated while tantalum remains in solution. The latter may be precipitated by lowering the pH to less than 1.5

The usual weighing and mounting form for Nb and Ta in radiochemical analyses is as ignited pentoxide following precipitation as hydrated oxide, tannate, or cupferrate. However, Majumdar and Mukherjee(11) have shown that a stable complex of Nb with tantalon of composition $NbO(C_{13}H_{10}NO_2)$ is formed and may be used for direct gravimetric estimation. This complex is highly soluble in $CHCl_3$, but insoluble in H_2O, acetone, CCl_4, C_6H_6, and ethyl and amylacetates. It is stable up to a temperature of 229°C and may be weighed directly after washing and drying at 110°C. The Ta complex is of indefinite composition and cannot be weighed directly. It may be ignited to the pentoxide for weighing.

4. Behavior of Tracer Quantities*

Tracer niobium is unstable in acid solution without complex forming anions and tends to deposit on glassware. It is strongly adsorbed by many precipitates (e.g., sulfides, hydroxides, zirconium phosphate, and bismuth phosphate) and by silica gel and soils. Precipitation of oxides from acid solution (e.g., manganese dioxide, tellurium dioxide) carries tracer niobium nearly completely. Any traces of dust or silica present in a clear solution results in marked losses. Frequently centrifugation of a clear solution leads to much activity being thrown down. In the absence of complex forming ions, tracer niobium seems to exist as a radiocolloid with the chemical properties of the oxide. Niobium is similar to zirconium in that it may exist as a negatively charged colloid in aqueous media. When irradiated uranium metal is dissolved, the fission product niobium is mostly present in the form of a radiocolloid very easily deposited on surfaces or coprecipitated with insoluble compounds. Addition of phosphoric or hydrofluoric acid to the metal solution converts the niobium into true solution. Carrier-free niobium tracer may be removed from glass surfaces by extraction with strong alkali hydroxide or dilute hydrofluoric acid. Niobium is volatilized when irradiated uranous oxide is treated with hydrogen fluoride at red heat. In the presence of complex-forming anions (tartrate, oxalate, fluoride), tracer niobium is stable in solution. Low concentrations of fluoride (from fluosilicate) prevent the carriage of niobium on bismuth phosphate. Niobium is not carried on lanthanum fluoride to any great extent, even in the absence of holdback carrier (distinction from zirconium).

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*Although the observations reported here refer to niobium, similar behavior may be expected for tantalum tracer.

5. Complex Ions

Complexes soluble in aqueous solution may be formed by treatment of the freshly precipitated pentoxides of Nb and Ta with oxalic, tartaric, HF, concentrated H_2SO_4, and concentrated H_3PO_4 acids, but not appreciably with HCl or HNO_3. With HF, niobium forms both normal ($NbF_7^{=}$) and oxy-fluoride ($NbOF_5^{=}$) complexes. Tantalum, on the other hand, forms only the normal complex ion with HF. The hydrated oxides are also soluble in alkaline solutions of catechol and pyrogallol. Fairbrother, Robinson, and Taylor(12) have shown that the freshly precipitated oxides also form water soluble complexes with a variety of α-hydroxy acids and amines. Pure niobic acid is much more readily soluble in these complexing agents than is tantalic acid. The dependence of the solubility on the method of preparation and the age of the hydrated oxides indicates that colloidal phenomena are probably involved.

A number of chelate complexes which are of particular importance in solvent extraction systems are discussed in the following section.

6. Solvent Extraction Behavior

Liquid-liquid extraction systems are effective in separating niobium and tantalum from other elements and offer the best method of separating these very similar elements from each other. An excellent treatment of solvent extraction systems is given by Morrison and Freiser.(13)

Fluorides. The fluoride complexes of Nb and Ta may be extracted into a variety of organic solvents. Ethyl ether extracts 65% of the Nb and 80% of the Ta from 20 M HF solutions.(14) Of a number of other elements studied, only Re(VII) extracted > 50%.

Milner and Wood(15) obtained complete extraction of Nb and Ta fluorides into methyl ethyl ketone. Tungsten extracted to the extent of 66%, Zr 22%, Cr 20%, Fe 17%, Mn 8.5%, Ga 2.4%, and V only a trace.

Methyl isobutyl ketone (hexone) has been used to extract Nb and Ta fluorides in the presence of H_2SO_4, HCl, and HNO_3. Nb and Ta are completely extracted from aqueous solutions 10 M in HF, 6 M in H_2SO_4 and 2.2 M in NH_4F.(16) The hexone-HF-H_2SO_4 system was also studied by Tews and May.(17) Complete extraction of both elements was obtained from aqueous solutions 5.6 N in HF and 9 N in H_2SO_4. The two elements can be separated by back-extracting the Nb with aqueous solutions of lower acidity in H_2SO_4 and HF. A number of combinations are suggested depending on the ratio of Nb/Ta. The extraction of Nb into hexone from 6.3 M H_2SO_4-1.6 M HF solutions was also shown to be effective by Waterbury and Bricker.(18) Higbie and Werning(19) made extensive studies of the hexone-HF-HCl system, particularly for industrial separations. Equal volumes of hexone and an aqueous solution of 1.1 N HF and 2.88 N HCl gave optimum conditions for the separation of Ta and Nb. 99.2% pure Ta was obtained in the organic phase and 98.4% pure Nb remained in the aqueous. Theodore(20) applied this method to the determination of Ta in Nb by a photometric technique. Faye and Inman(21) utilized a hexone-HF-HNO_3 system. At 7.0 M HF and 5.0 M HNO_3, Ta and Nb were extracted practically completely. The method gave high purity Nb and Ta in the presence of such elements as Si, Fe, Al, Ti, Mg, Ca, Pb, and Zr. Ta and Nb may be separated by hexone extraction of the Ta from 0.5 M HF + 1.0 M HNO_3. Under these conditions 98% of the Ta, but < 1% of the Nb extracts. The Ta and/or Nb may be stripped from the hexone phase by back-extraction with a dilute H_2O_2 solution (1 vol 30% H_2O_2 + 19 vol H_2O).

Diisopropyl ketone was shown by Stevenson and Hicks(22) to be an effective solvent for the separation of Nb and Ta from aqueous solutions of HF and mineral acids. The results are presented in Table 1. Niobium was found to extract to the extent of 90% from a solution 6 M in H_2SO_4 and 9 M in HF.

An effective separation of Nb from Pa was carried out by F. L. Moore(23) by extraction of the Nb into diisopropyl carbinol from aqueous solutions 6 M in H_2SO_4 and $\geq$ 2 M in HF. Pa did not extract, while > 97% of the Nb did. The Nb was readily stripped from the organic phase with distilled water.

Chernikov, Tramm and Pevzner(24) used cyclohexanone to separate Ta and Nb from HF-H_2SO_4 solutions. Ta was completely extracted from 2 M H_2SO_4-0.4 M HF. Nb extracts to a lesser degree and is removed by washing the organic layer with H_2O.

Table 1

EXTRACTION OF TANTALUM AND NIOBIUM INTO DIISOPROPYL KETONE

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

Chlorides. Niobium is readily extracted by diisopropyl ketone from 10 M HCl solutions. The Nb may be back-extracted in 6 M HCl.(25) Nb is effectively separated from Ta by extraction of the former from 6.5 M HCl with hexone.(26) The extraction behavior of the chloride complexes of Pa, Nb, and Ta into diisopropyl carbinol was studied by Casey and Maddock.(27) Their results are given in Fig. 1 which indicates that these elements may be effectively separated under appropriate pH conditions.

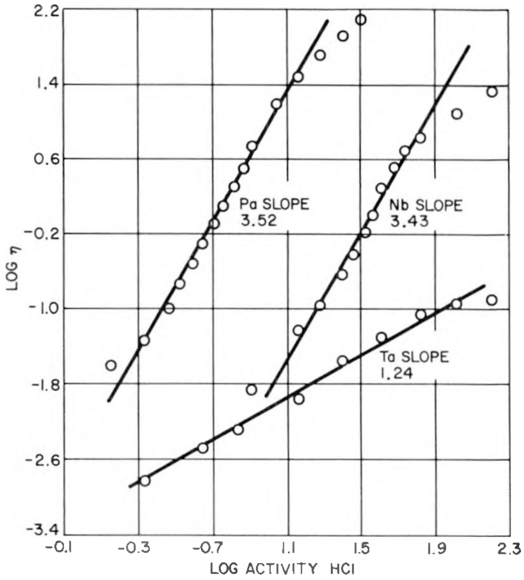

FIGURE 1
VARIATION OF THE LOGARITHM OF THE EXTRACTION COEFFICIENT
WITH THE LOGARITHM OF THE ACTIVITY OF
HYDROCHLORIC ACID IN THE AQUEOUS PHASE.
DATA FOR NIOBIUM, TANTALUM AND PROTACTINIUM

The addition of a small amount of HF greatly increased the extraction of Nb and Ta, but lowered that of Pa.

Scherff and Herrmann,(27A) showed that Ta and Nb could be extracted from 6 M HCl-(1-3)N HF with di-isobutyl carbinol. Pa and Zr remain in the aqueous phase. The Pa can be extracted after saturation of the aqueous phase with $AlCl_3$, leaving Zr.

Alkyl phosphoric acids. Scadden and Ballou(28) investigated di-n-butylester of phosphoric acid (DBPA) either alone or in a mixture with the monoester (as in commercial "butyl phosphoric acid") as an extractant for zirconium and niobium. A 0.06 M solution of DBPA in di-n-butyl ether extracted > 95% of the Zr and < 5% of the Nb. The Nb extraction increased from 2 to 10% as the extraction time increased from 1 to 5 minutes, but Zr was unaffected. Addition of 3% H_2O_2 reduced the Nb extraction to less than 1% (even with a 10-minute extraction time) without affecting Zr. More concentrated DBPA solutions extracted both Zr and Nb quantitatively. Precautions against emulsion formation must be taken with this reagent. Higher homologs, such as the octyl phosphoric acids are reported to be free of this difficulty, and are less soluble in H_2O. Tables 2 and 3, taken from Scadden and Ballou, summarize the extraction behavior of a number of elements with DBPA.

The extraction of Nb and Zr with dilute tributyl phosphate (TBP) (1% solution in toluene) from 8-10 N HCl serves as the basis for the separation of these elements from mixed fission products.(29) Both elements may be back-extracted with 0.5 N HCl. Hardy and Scargill(30) examined the extraction of Nb by TBP from HNO_3 solutions. Their results indicate that both extractable (ionic) and inextractable (complex polymeric) species are present. The extraction is low. The systems TBP-HF-HNO_3 and TBP-HF-H_2SO_4 were studied by Fletcher et al.(31) as a means of separating and purifying Nb and Ta from their ores. The extraction of both elements increases with acid concentration and is greater from H_2SO_4 than from HNO_3. An effective separation of Nb and Ta from Fe, Mn, Ti, and Sn is indicated using equal volumes of undiluted TBP and a 10 M HF-12 N H_2SO_4 aqueous solution. A counter current extraction system using 100% TBP and an 8 N HF-3 N HNO_3 aqueous feed is proposed for the separation of Nb and Ta. The Nb is back-extracted with 0.5 N HF and the Ta with Na_2CO_3.

Amines. Methyl dioctyl amine in xylene(32) and tribenzyl-

amine in $CHCl_3$ or CH_2Cl_2(33) extract Nb preferentially from Ta in concentrated HCl solutions.

Chelates. Several chelate complexes of Nb, soluble in organic solvents, have been utilized for its separation and estimation, particularly by photometric methods. *Oxine* (8-quinolinol),(34) cupferron,(35) and sodium diethyl dithiocarbamate,(36) are useful for this purpose. 5,7-dichloro-8-quinolinol complexes Nb, and the complex may be extracted from solutions at pH 10 with nitrobenzene, amyl acetate, or bis(2-chloroethyl) ether.(26) Ta does not extract. Glycolic acid was used

Table 2

EXTRACTION PROPERTIES OF CARRIER-FREE CONCENTRATIONS OF FISSION PRODUCT ELEMENTS WITH MIXED BUTYL PHOSPHORIC ACIDS.
(AQUEOUS PHASE, 1 *M* HNO_3, 3% H_2O_2; 5-MINUTE MIXING; VOLUME RATIO (ORG./AQ.) 1 TO 1)

	Elements Extracted		
Concn. of DBPA[a], *M*	< 5% by DBPA	5-95% by DBPA	> 95% by DBPA
0.06	Cs, Sr, La, Ce(III), Ag[b], Cd, Ge, Se(IV), Te(IV), Sb(III)[c], Sb(V), As(V), Pd[b], Ru, Rh, Nb	Y 15%, Sn(IV)[b] 50%, Mo[b] 15%	Zr, In
0.6	Cs, Sr, La, Ag[b], Cd, Ge, Se(IV), Te(IV), Sb(III)[c], Sb(V), As(V), Pd[b] Ru, Rh	Mo[b] 23%, Nb 60%, Ta[c] 85%	Zr, Nb[c], Y, In, Sn(IV)[b]

[a] Di-*n*-butyl phosphoric acid solutions in which mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid is 4.5 to 1.

[b] Ag, Sn, Pd, and Mo not carrier-free; their concentrations were 0.5, 3, 8, and 8 γ/ml, respectively.

[c] No hydrogen peroxide present.

Table 3

EXTRACTION PROPERTIES OF MACRO QUANTITIES OF FISSION PRODUCT ELEMENTS WITH MIXED BUTYL PHOSPHORIC ACIDS. (AQUEOUS PHASE 1 MG ELEMENT PER ML, 1 *M* H_2SO_4, 2.5 *M* $(NH_4)_2SO_4$, 0.004 *M* OXALIC ACID, 6% H_2O_2; VOLUME RATIO (ORG./ AQ.) 1 TO 1; MIXING TIME, 15 MINUTES WITH 0.06 *M* DBPA AND 5 MINUTES WITH 0.6 *M* DBPA)

Concn. of DBPA[a] *M*	Elements Extracted		
	< 5% by DBPA	5-95% by DBPA	> 95% by DBPA
0.06	Cs, Sr, Y, La, Ce(III), Ag, Cd, Ge, Se(IV), Te(IV), Sb(III)[b], Sb(V), As(V), Pd, Ru, Rh, Mo, Nb	Sn(IV) 15%, In 85%	Zr, I_2
0.6	Cs, Sr, La, Ce(III), Ag, Cd, Ge, Se(IV), Te(IV), Sb(III)[b], Sb(V), As(V), Pd, Ru, Rh, Mo	Sn(IV) 50%, Ta 35%	Zr, Nb[b], Y, Ho, In, I_2

[a] Di-*n*-butyl phosphoric acid solution in which mole ratio of di-*n*-butyl phosphoric acid to mono-*n*-butyl phosphoric acid is 4.5 to 1.

[b] No hydrogen peroxide present.

as a chelating agent and furfural as a solvent in a separation of Ta from Nb.(37) Extraction of Ti, Nb, and Ta cupferrates was studied by Alimarin and Gibalo.(38) Mixed oxides of these elements were fused with potassium pyrosulfate and the melt dissolved in a 2% ammonium bitartrate solution. The solution was adjusted to the desired pH with dilute NH_4OH, an equal volume of isoamyl alcohol, and a 4% aqueous cupferron solution added. The pH dependence of the extraction is shown in Fig. 2. The data are the result of three successive extractions with isoamyl alcohol. A complete separation of Ti from Nb and Ta is possible at pH 5.

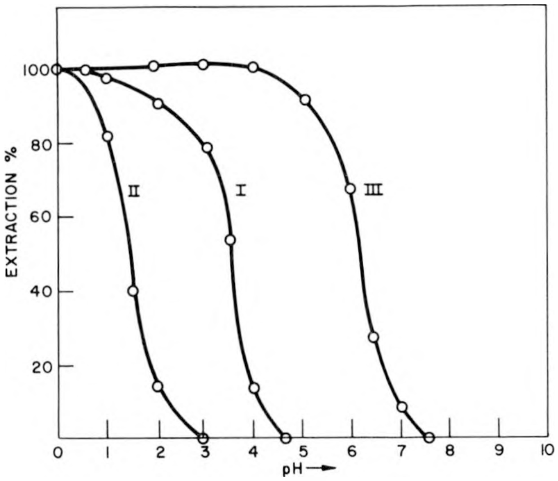

FIGURE 2
RELATIONSHIP BETWEEN THE DEGREE OF EXTRACTION OF NIOBIUM (I), TANTALUM (II) AND TITANIUM (III) CUPFERRATES BY ISOAMYL ALCOHOL AND THE pH

7. Ion Exchange Behavior

Since Nb and Ta exhibit strong tendencies toward radiocolloid formation, it is generally advisable to ensure true solutions by the use of strong complexing agents. The negatively charged complexes formed with F^- or $C_2O_4^=$ ion, for example, are particularly well suited to separations of Nb and Ta from each other, as well as from other elements, with anion exchange resins.

Several systematic studies of the application of anion exchange resins to the separation of the elements have been made.(39,40) The work of Krause and Moore, in particular, has demonstrated the excellent separation of Zr, Pa, Nb, and Ta using Dowex-1 resin with HCl-HF solutions. Their data is reproduced in Figs. 3, 4, and 5. Huffman, Iddings and Lilly(41) determined the distribution coefficients for Nb, Ta, Zr, and Hf on Dowex-2 resin. These data are reproduced in Fig. 6 and in-

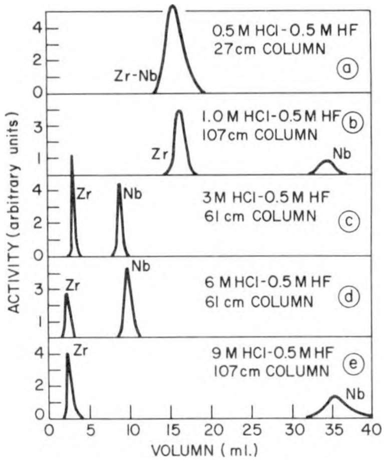

FIGURE 3
SEPARATION OF Zr AND Nb WITH DOWEX-1 ANION EXCHANGE COLUMNS: AVERAGE FLOW RATE ca. 0.3 ml./sq.cm./minute; CROSS-SECTION OF COLUMN: 0.0226 sq.cm

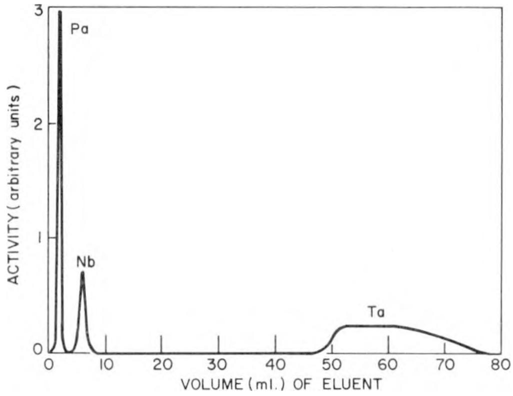

FIGURE 4
SEPARATION OF PROTACTINIUM (V), NIOBIUM(V) AND TANTALUM(V) BY ANION EXCHANGE: 12.5 cm. DOWEX-1 COLUMN, 0.0226 sq. cm. CROSS-SECTION, 0.3 ml. minute^{-1} FLOW RATE, ELUENT 9 M HCl-0.05 M HF

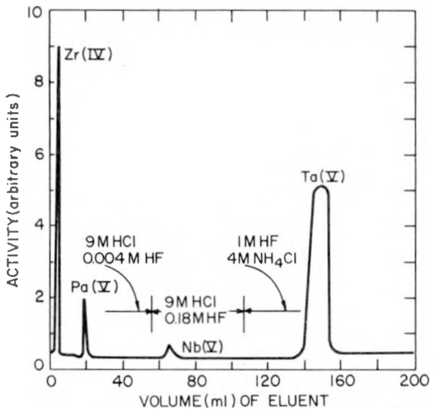

FIGURE 5
SEPARATION OF ZIRCONIUM (IV), PROTACTINIUM(V) NIOBIUM(V), AND TANTALUM (V) BY ANION EXCHANGE: 6-cm. DOWEX-1 COLUMN, 0.32 sq. cm. CROSS-SECTIONAL AREA, AVERAGE FLOW RATE 0.2 ml. minute^{-1} cm.$^{-2}$

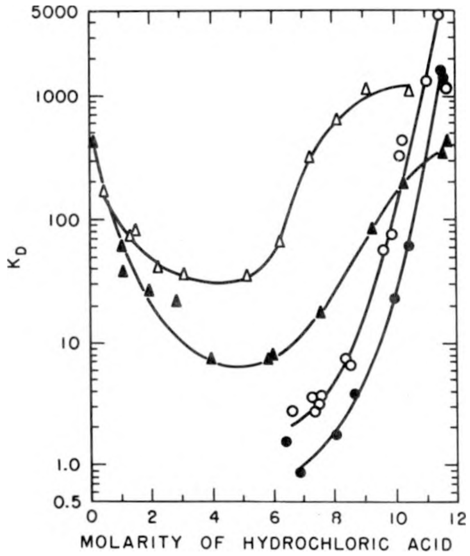

Figure 6
Dependence of the distribution coefficient at 25° on the hydrochloric acid concentration: △, niobium; ▲, tantalum; ○, zirconium; ●, hafnium.

dicate an excellent separation of Nb and Ta from Zr and Hf. Ta and Nb may be adsorbed from 9 M HCl and stripped with dilute HCl, the Ta eluting first.

The separation of Nb, Ti, Mo, and W was investigated by Hague, Brown and Bright(42) using Dowex-1 and HCl-HF solutions. Niobium was easily separable under a wide range of acid conditions from 5% HF-10% HCl to 20% HF-25% HCl, the separation increasing with HF concentration.

Oxalic acid was used as a complexing agent for the separation of Nb from Ta with Dowex-2 resin.(43) Solutions of 1 M HCl and 0.5 M $H_2C_2O_4$ yielded Ta-free Nb with a recovery of 95%. The Ta was recovered in 85-90% yield, but contained about 1% Nb.

Cation exchange separations of Zr, Hf, Nb, the rare earths, and alkaline earths were investigated by Tompkins et al.(44) and Cohn et al.(45) The cations are adsorbed on Amberlite IR-1 in the H-form from 0.01-0.1 N acid solution. The Nb, Zr, and Hf may be selectively eluted as a group with 0.5% oxalic acid without appreciable movement of the other ions down the column.

Negative complexes of Nb and Ta are not adsorbed on cation exchange resins, and thus, they may be conveniently separated from many cations that are readily adsorbed. The colloidal nature of Nb, Ta, Zr, Hf, and Pa may be exploited by the fact that the colloids are not adsorbed on cation exchangers whereas ionic impurities are.(46) The radio colloidal behavior of Zr and Nb has been extensively studied by Schubert et al.(47)

Chromatographic adsorption methods for the separation of Nb and Ta have been developed utilizing several extractants in the presence of adsorption beds such as cellulose or alumina. A quantitative separation of combined Ta and Nb was achieved by Wood(48) by the extraction of the fluorides with methyl ethyl ketone containing HF in the presence of activated cellulose. The extraction of a number of other elements was inhibited by ammonium fluoride, and the Ta and Nb were finally recovered by precipitation with tannin. An improved separation was made by Burstall, et al.(49) in which the Ta is extracted first with methyl ethyl ketone saturated with H_2O. The Nb is then extracted with the same solvent containing 40% HF.

Activated alumina was used by Tikhomiroff(50) as the adsorption medium for Nb and Ta in oxalate solution. Ta may be eluted with ammonium oxalate at pH 7, leaving the Nb unaffected on the column. Niobium is eluted with ammonium oxalate containing H_2SO_4.

V. SAMPLE DISSOLUTION AND INTERCHANGE WITH CARRIER

Niobium and tantalum metals are dissolved in HNO_3-HF solution or by alkali fusion. Concentrated H_2SO_4 or HF alone acts slowly on the metals. The minerals of these metals are best treated by fusions with NaOH, KOH, Na_2O_2, $K_2S_2O_7$ or KHF_2. Acid mixtures, such as HNO_3-HF, dissolve most samples, but generally leave some residue which must be treated by fusion.

The most important consideration in dealing with solutions of Nb and Ta is the problem of deposition of the hydrated oxides from solution. Complexing agents such as F^- or $C_2O_4^=$ should be present to ensure true solution of these elements.

Since Nb and Ta are essentially monovalent, there are no particular problems in the interchange of radioactive and carrier species.

VI. COUNTING TECHNIQUES

The most important radioactive isotopes of Nb and Ta are 35-day Nb^{95} (formed in nuclear fission) and 111-day Ta^{182} (formed by neutron capture in Ta^{181}). Both nuclides may be counted with standard beta or gamma counting apparatus. However, the energy of the Nb^{95} beta is rather low (0.15 Mev), and corrections for sample self-absorption and scattering, may be large and uncertain.

One of the most significant advances in radioactivity assay has been the introduction of the NaI scintillation spectrometer for γ-ray measurements. Catalogs of the γ-ray spectra of many nuclides are available(51) and may be conveniently used to identify the radioactivities. With suitable calibration, gamma-ray spectrometers may be used for absolute disintegration rate determinations.

Figures 7 and 8 give the γ-ray spectra obtained by Heath(51) for Nb^{95} and Ta^{181}.

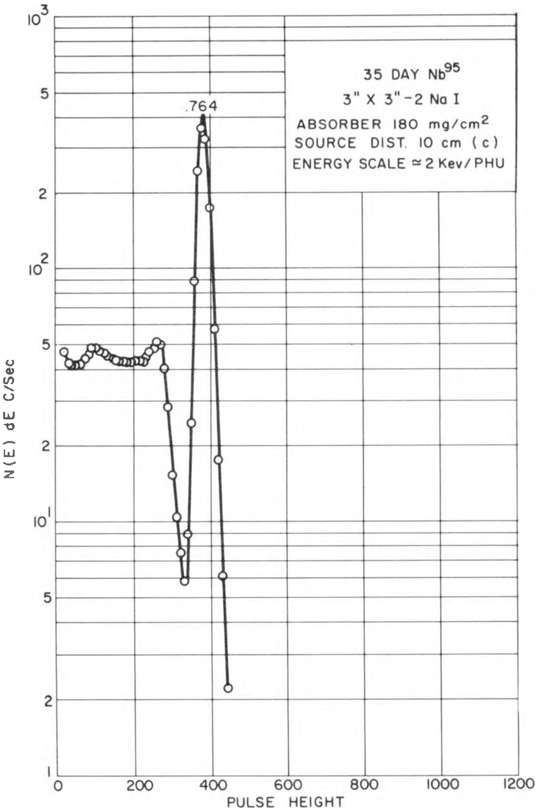

FIGURE 7
GAMMA-RAY SPECTRUM OF Nb^{95}

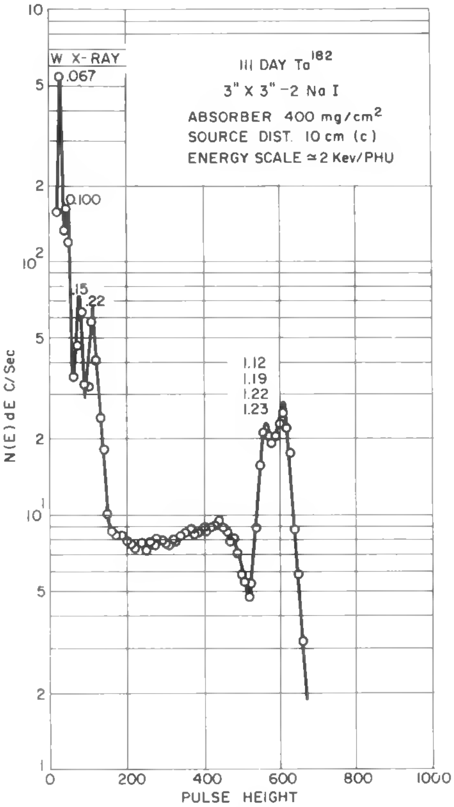

FIGURE 8
GAMMA-RAY SPECTRUM OF Ta^{181}

VII. COLLECTED PROCEDURES

A. Solvent extraction procedures for Nb

B. Solvent extraction procedures for Ta

C. Precipitation procedures for Nb

D. Carrier-free separations

Procedure #1 (Diisopropyl ketone method for Nb)

Source: P. C. Stevenson and H. G Hicks, Anal. Chem. 25, 1517 (1953).

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

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, and 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 diisopropyl 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 diisopropyl ketone, and 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 of water. Collect water layers in a tube containing saturated boric acid solution.

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

Procedure #2 (TBP method for Nb)

Source: D. F. C. Morris and D. Scargill, Anal. Chim. Acta. 14, 57 (1956).

Preparation and standardization of carrier

Dissolve 26.0 g of potassium niobate in *ca.* 200 ml of water, heat the solution nearly to boiling and add 15 ml of concentrated HNO_3 slowly with stirring. Continue heating and stirring for two to three minutes and centrifuge Wash the precipitate three times with centrifugation, with 50 ml of hot 2% NH_4NO_3 solution. Add 200 ml of saturated oxalic acid, and heat with stirring until the niobic acid dissolves. Cool and dilute to 1 litre. Filter the solution if it is not clear.

Pipette exactly 5 ml of the carrier solution into a 100 ml beaker. Add 30 ml of 6 M HNO_3 and *ca.* 1 g. of $KClO_3$ and carefully heat the solution to boiling. Boil gently with occasional stirring for *ca.* 5 minutes. Cool the mixture and add conc. NH_4OH with stirring to make the pH value 8 to 10 (*ca.* 15 ml). Filter quantitatively on a Whatman No. 42 filter paper through a 2 inch 60° funnel, returning the first portion of the filtrate if it is not clear, and wash with hot water. Ignite in a porcelain crucible at *ca.* 800° C for 15 minutes and weigh as Nb_2O_5.

Procedure (for uranyl nitrate solutions)

Step 1. Place the sample solution (1 to 10 ml volume) in a 50 ml glass centrifuge tube. Add 10 mg zirconium carrier (10 mg Zr/ml prepared from zirconyl nitrate and 1 M nitric acid).

Procedure 2 (Continued)

Step 2. Add to the solution an equal volume of concentrated HNO_3; 1 ml of saturated oxalic acid, and 2 ml of niobium carrier. Gently stir for 10 minutes (Note 1). Heat the solution nearly to boiling and add 0.5 g of $KBrO_3$ in small portions, boiling for a few seconds after each addition. Evaporate the solution to low bulk and centrifuge the precipitated niobic acid (Note 2). Decant and discard the supernate. Wash the precipitate in 10 ml of hot 2% NH_4NO_3 solution (Note 3).

Step 3. Transfer the precipitate to a polythene tube. Dissolve in 2.5 ml of 40% HF, add 2 ml of 12 M H_2SO_4 and 4-5 ml of pure TBP. Stir mechanically for 2 minutes using a polythene stirring rod. Centrifuge, transfer the organic layer to a clean polythene tube, and discard the aqueous phase. Add 5 ml of petroleum ether to the TBP phase and then 4 ml of 6 M NH_4OH. Stir the phases for 1 minute. Centrifuge at high speed for 1 minute and separate and discard the organic layer. Wash the aqueous phase with 5 ml of petroleum ether (Note 4). Centrifuge at high speed for 1 minute, decant and discard the organic and aqueous supernate.

Step 4. Wash the niobic acid precipitate with 10 ml of hot 2% NH_4NO_3 solution. Transfer to a crucible with 2 ml of distilled water, heat to dryness, and ignite at 800° C for *ca.* 15 minutes. Allow to cool in a desiccator, and break up the Nb_2O_5 to a fine powder with a flat-ended glass rod. Slurry the Nb_2O_5 with a little ethyl alcohol on to a weighed aluminum counting tray. Dry under a radiant heater lamp taking care to ensure that the resulting deposit on the tray is uniform. Weigh the tray and Nb_2O_5 to establish the chemical yield. Count on a γ-scintillation counter through a standard aluminum-lead sandwich.

Notes

1. For exchange of Nb activity and carrier, oxalic acid must be present, and it is advisable to stir the solution for at least 10 minutes.
2. If $[SiF_6]^{-2}$ or F^- is present niobic acid will not be precipitated. Addition of an excess of H_3BO_3 to the sample eliminates this difficulty.
3. The washing is done with 2% NH_4NO_3 solution to prevent peptization.
4. The washing with petroleum ether is designed to remove any traces of TBP.

Reagents

Conc. nitric acid.

Saturated oxalic acid.

Potassium bromate.

2% Ammonium nitrate (slightly acidified with nitric acid).

40% Hydrofluoric acid.

12 M Sulphuric acid.

Tri n-butyl phosphate.

Petroleum ether

Ethyl alcohol.

DISCUSSION

The procedure was tested for separation from different possible interfering activities by using the following radioactive tracers: caesium 137 - barium 137 (equilibrium mixture), cerium 144 - praseodymium 144 (equilibrium mixture), ruthenium 106 - rhodium 106 (equilibrium mixture), molybdenum 99- technetium 99m (equilibrium mixture), and zirconium 95. The results of these experiments are summarized in Table 1. These data indicate that separation from caesium, cerium, praseodymium, ruthenium, rhodium, molybdenum, technetium, and zirconium is adequate for fission product mixtures normally encountered.

Analyses by the procedure of four uranyl nitrate solutions prepared from neutron irradiated uranium which had cooled various lengths of time were carried out. Results are given in Table 2.

Aluminum absorption curve measurements and γ-scintillation spectrometer measurements indicated the presence of a β-particle of ca. 0.15 Mev. and a γ-ray of 0.77 Mev. in each case. These results agree well with the values of 0.160, 0.159, 0.148, 0.146, and 0.15 Mev. quoted for the 35d. niobium-95 β-particle and the values of 0.745, 0.758. 0.77 and 0.75 Mev. quoted for the energy of the niobium-95 γ-ray. No other β or γ activities could be detected in samples from Solutions 2, 3 and 4, save a trace of a β component of energy ca. 0.7 Mev.[*] In the case of samples obtained

Table 1

SEPARATION OF VARIOUS ELEMENTS IN THE PROCEDURE

Element	γ activity added		γ activity above background in counted samples		
Cs-Ba	176000	cts/min.	15	34	cts/min.
Ce-Pr	75000		1	0	
Ru-Rh	356000		20	19	
Mo-Tc	68600		45	121	
Zr	79100		120	69	(values uncorrected for growth of Nb activity during the experiment).

---

[*] It should be noted that the Al absorption curve of pure 35 d ^{95}Nb is not obtained until about two weeks after the last step in any radiochemical procedure for the activity analysis of niobium in mixed fission products. This is due to the presence of conversion electrons from the decay of 90 h 95^{m} Nb.

Table 2

RADIOCHEMICAL NIOBIUM ANALYSES OF URANYL NITRATE SOLUTIONS PREPARED FROM IRRADIATED URANIUM COOLED FOR VARIOUS LENGTHS OF TIME

Solution	Days since end of irradiation	Niobium activity γ cts/min/ml		
1	10		1894	
			1900	
			1976	
			1864	
		mean	1909	s=2.5%
2	99		5867	
			6019	
			5898	
			5898	
		mean	5920	s=1.1%
3	146		3540	
			3510	
			3510	
			3660	
		mean	3555	s = 2.0%
4	150		3505	
			3444	
			3496	
			3466	
		mean	3478	s = 0.8%

$s = \sqrt{\frac{\Sigma d^2}{n-1}}$ = standard deviation, where d = deviation from the mean of single measurements.
n = number of measurements.

on Solution 1 in which the uranium had had only 10d cooling, aluminum absorption curve measurements and γ-scintillation spectrometer measurements indicated the presence of contamination due to tellurium activity. γ-scintillation counter measurements of the decay curves of the samples indicated a maximum contamination of ca. 5%.

It can be stated from the above results that the procedure provides satisfactory radiochemical purity with γ-scintillation counting using a standard Al-Pb sandwich, and also a standard deviation of 2% or less, in the analysis of material with a cooling time of greater than 30 days (Te interference is then negligible).

The procedure is quick, requiring about 1.5 h for a complete analysis. Chemical yields generally obtained have been of the order of 60%.

The interchange between tracer and carrier under the conditions of the procedure has been tested by taking a portion of pure niobium-95 tracer in 1 M nitric acid solution, which was evaporated on a tray and γ counted; the same quantity of tracer was analyzed by the radiochemical procedure. The results shown in Table 3 indicate that satisfactory exchange occurs.

Table 3

ANALYSIS OF CARRIER FREE NIOBIUM TRACER BY THE METHOD

	TBP procedure	evaporated sample
γ activity of niobium	4018 cts/min	3925 cts/min
corrected for 100% yield	4052	

Procedure #3 (Cupferron extraction method for Nb)

Source: J. S. Gilmore, US AEC Report La-1721 (2nd ed.), Jan. 1958.

1. Introduction

In the separation of niobium from other fission activities, zirconium is removed as barium fluozirconate; any +4 uranium present, as well as rare-earth activities, are carried down as the fluorides at this stage. Niobium is then converted to its cupferron derivative which is extracted into chloroform. This step gives an effective separation from +6 uranium. The cupferron complex is destroyed and the niobium precipitated as the hydrous oxide, $Nb_2O_5 \cdot XH_2O$, by means of ammonia water; molybdenum remains in solution as a molybdate. The oxide is dissolved in sulfuric acid and decontamination from tin and antimony effected by means of a sulfide precipitation. Further decontamination is obtained by additional precipitations of the oxide, extractions of the cupferron derivative, and acid sulfide scavengings. Niobium is finally precipitated as the hydrous oxide and ignited to the oxide, in which form it is weighed and counted. The chemical yield is 40 to 50% and duplicate samples can be analyzed in about 4 hours. If the sample solution contains large quantities of uranium the chemical yields are likely to be low; at present there is no explanation for this.

2. Reagents

Nb carrier: 10 mg Nb/ml (added as Nb (V) in oxalic acid solution-standardized)

Zr carrier: 10 mg Zr/ml (added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1 <u>M</u> HNO_3)

Cu carrier: 10 mg Cu/ml (added as $CuCl_2 \cdot 2H_2O$ in H_2O)

HCl: 6 <u>M</u>

HCl: conc.

HNO_3: 6 <u>M</u>

HNO_3: conc.

H_2SO_4: conc.

HF: conc.

Tartaric acid: 25% aqueous solution

H_3BO_3: saturated aqueous solution

NH_4OH: 6 <u>M</u>

NH_4OH: conc.

$(NH_4)_2C_4H_4O_6$: saturated aqueous solution

$BaCl_2$: 50 mg/ml

$KClO_3$: solid (for standardization)

H_2S: gas

Cupferron reagent: 6% aqueous solution (kept in refrigerator)

Methyl red indicator solution: 0.1% in 90% ethanol

Chloroform.

3. Equipment

Muffle furnace

Fisher burner

Centrifuge

Block for holding centrifuge tubes

Mounting plates (Note 2)

Forceps

Tongs for holding Erlenmeyer flasks

Pipets: assorted sizes

Wash bottle

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)

Filter flasks

100-ml beaker (one per standardization)

2", 60° funnels (one per standardization; three per sample)

125-ml separatory funnels (three per sample)

125-ml Erlenmeyer flasks (three per sample)

No. 42 Whatman filter paper (9 cm)

No. 42 Whatman filter circles: 7/8" diameter

40-ml Lusteroid centrifuge tubes (four per sample)

40-ml conical centrifuge tubes: Pyrex 8320 (nine per sample)

Crucibles: Coors 000 (one per sample)

Crucibles: Coors 00 (one per standardization)

Steam bath

Ice bath

Stirring rods.

4. Preparation and Standardization of Carrier

(Taken from Radiochemical Studies: The Fission Products, Book 3, pp 1524-5)

Dissolve 26.0 gm of potassium hexaniobate, $K_8Nb_6O_{19} \cdot 16H_2O$, (Fan-steel Metallurgical Corp.) in about 200 ml of H_2O, heat the solution nearly to boiling, and add 15 ml of conc. HNO_3 slowly with stirring. Continue heating and stirring for 2 to 3 min and centrifuge. Wash the precipitate three times, with centrifugation, with 50 ml of hot 2% NH_4NO_3 solution. Add 200 ml of saturated $H_2C_2O_4$, and heat with stirring until Nb_2O_5 dissolves. Cool and dilute to 1 liter. Filter the solution if it is not clear.

Pipet exactly 5 ml of the carrier solution into a 100-ml beaker. Add 30 ml of 6 M HNO_3 and about 1 gm of $KClO_3$ and carefully heat the solution to boiling. Boil gently with occasional stirring for about 5 min. Cool the mixture and add conc. NH_4OH with stirring to make the pH value 8 to 10 (about 15 ml). Filter quantitatively on a No. 42 Whatman filter paper through a 2", 60° funnel, returning the first portion of the filtrate if it is not clear, and wash with hot H_2O. Ignite in a Coors 00 crucible at about 800° for 15 to 20 min and weigh as Nb_2O_5.

Four standardizations performed as described above gave results agreeing within 0.5%.

5. Procedure

Step 1. To exactly 4 ml of Nb carrier in a 40-ml Lusteroid centrifuge tube, add 3 ml of conc. HF, 10 ml of the sample in 4 M HCl, 1 ml of Zr carrier, and 4 ml of $BaCl_2$ solution (50 mg/ml). Centrifuge the $BaZrF_6$ precipitate, transfer the supernate to a clean 40-ml Lusteroid tube, and discard the precipitate. Repeat the $BaZrF_6$ precipitation three times, the third time transferring the supernate to a 125-ml separatory funnel.

Step 2. To the supernate add 30 ml of a saturated H_3BO_3 to destroy the Nb-fluoride complex and make the solution 1 M in HCl. Add 4 ml of cold 6% cupferron reagent and let the mixture stand for 1 min. Extract the Nb-cupferron complex into 20 ml of $CHCl_3$ and transfer the $CHCl_3$ layer into a 125-ml Erlenmeyer flask.

Step 3. To the aqueous phase, still in the separatory funnel, add 2 ml of cupferron reagent, extract with 10 ml of $CHCl_3$, and combine the extract with the previous one. Wash the aqueous phase with 10 ml of $CHCl_3$ and combine the washings with the previous extracts.

Step 4. Heat the $CHCl_3$-extract with 3 ml of conc. H_2SO_4 and about 20 ml of HNO_3 to destroy organic matter.

Step 5. Transfer the solution to a 40-ml conical centrifuge tube and make the solution basic by the addition of conc. NH_4OH. Centrifuge and discard the supernate. Dissolve the precipitate ($Nb_2O_5 \cdot XH_2O$) in 3.3 ml of conc. H_2SO_4 and dilute the solution to 20 ml with H_2O. Add 1 ml of Cu carrier and saturate the solution with H_2S. Centrifuge and filter into a clean 40-ml conical centrifuge tube, using a 2", 60° funnel and No. 42 Whatman filter paper.

Step 6. Make the supernate basic by addition of conc. NH_4OH to precipitate $Nb_2O_5 \cdot XH_2O$. Centrifuge, discard the supernate, and wash the precipitate with a mixture of 5 ml of 6 M NH_4OH, 3 ml of 6 M HNO_3, and 5 ml of H_2O (Note 1). Dissolve the precipitate by warming in 0.5 ml of 25% tartaric acid solution. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard any residue.

Step 7. Add 10 ml of conc. HNO_3 to the supernate and heat the mixture on a steam bath for about 15 min. Centrifuge, discard the supernate, and dissolve the $Nb_2O_5 \cdot XH_2O$ precipitate in 1 ml of conc. HF and 3 drops of 6 M HCl.

Step 8. Transfer the solution to a 125-ml separatory funnel, add 10 ml of saturated H_3BO_3, and make the solution 1 M in HCl. Add 4 ml of cold cupferron reagent and extract the solution with 20 ml of $CHCl_3$. Transfer the $CHCl_3$ layer to a 125-ml Erlenmeyer flask.

Step 9. Repeat Steps 3, 4, 5, 6, and 7.

Step 10. Repeat Steps 8, 3, 4, 5, 6, and 7, but dissolve the $Nb_2O_5 \cdot XH_2O$ precipitate formed in Step 7 in 5 ml of saturated $(NH_4)_2C_4H_4O_6$ solution and sufficient conc. NH_4OH to make the solution alkaline.

Step 11. Cool the solution in an ice bath and add 4 ml of cupferron reagent. Add 6 M HCl dropwise to acidify (2 drops past a methyl red end point). Filter the Nb-cupferron complex onto a No. 42 Whatman filter circle, 7/8" diameter, using the standard ground-off Hirsch funnel and filter chimney equipment. Ignite at 800° for 15 to 20 min. Cool the Nb_2O_5, mount, and count (Note 2).

Notes

1. The $Nb_2O_5 \cdot XH_2O$ precipitate is washed with NH_4NO_3 solution to prevent peptization.
2. The ignited Nb_2O_5 is mounted on an Al plate, 2-1/2" x 3-1/4", which has a depression 5/8" in diameter and 1/32" deep in the center of one side. A dilute solution of Zapon in

ethanol is used to spread and fasten the oxide to the plate. The precipitate is covered with rubber hydrochloride.

The sample is counted in a beta counter with no absorber. The isotopes counted are 68m Nb^{97}, 23.3h Nb^{96}, and 37d Nb^{95}.

Procedure #4 (Cupferron extraction method for Nb)

Source: R. H. Goeckermann, US AEC Report UCRL-432 (Aug. 1949).

Element separated: Niobium

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, lustoroid cones, crucible

Yield: approx. 50%

Degree of purification: Decontamination factor $> 10^3$ from fission & spallation products.

Advantages: Fair yield of pure Nb

Procedure:

1. Add equal volume of concentrated HNO_3 to aliquot of HNO_3 soln of target, 1 ml 6 N HCl, 1 ml saturated $H_2C_2O_4$, 20 mg Nb, and 10 mg Zr. Heat and add 0.5 g $KBrO_3$ in small portions. Digest 5 min, and centrifuge Nb_2O_5. Wash precipitate hot with 3 ml 6 N HNO_3, 2 ml 6 N NH_4OH, and 5 ml H_2O.
2. Dissolve in 1-2 ml saturated $H_2C_2O_4$ + 10 drops 6 N HCl. Make up to 20 ml of 6 N HCl, 0.05 M H_2SO_3, and add 10 ml $CHCl_3$. Cool in ice bath, add 2 ml fresh 6% cupferron and shake well. Extract a second time with more $CHCl_3$ and cupferron. Wash $CHCl_3$ with 20 ml cold 6 N HCl and 0.05 M H_2SO_3 containing more cupferron.

3. Boil with 10 ml concentrated HNO_3, adding $KBrO_3$ until $CHCl_3$ is gone, solution is pale yellow and Nb_2O_5 has precipitated.
4. Transfer to lusteroid with dil. HNO_3. Dissolve by adding 1 ml concentrated HF. Add 2 ml 6 N HNO_3, 10 mg Zr, and 5 ml H_2O. Add 50 mg Ba dropwise and centrifuge $BaZrF_6$.
5. Add 6 ml concentrated NH_4OH to supernatant (to pH 8-10). Centrifuge Nb_2O_5, and wash with 3 ml 6 N NH_4OH, 1 ml 6 N HNO_3, and 5 ml H_2O. Use a second wash to transfer precipitate back to glass.
6. Dissolve hot in 2 ml saturated $H_2C_2O_4$ plus 10 drops 6 N HNO_3. Add 3 ml H_2O, 5 ml concentrated HNO_3, heat, add 0.5 g $KBrO_3$ slowly, digest 5 min., centrifuge. Stir precipitate up with 3 ml 6 N HNO_3, 2 ml 6 N NH_4OH, and 5 ml H_2O, heat, filter, ignite in a crucible 15 min.

   Weigh as Nb_2O_5 (14.30 mg per 10 mg Nb).

Remarks: The extrn is supposed to separate Nb from Zr, Te, & Mo.

The extrn separation was substituted for heavy metal sulfide scav. to remove Te and Mo. The extrn procedure can possibly be combined with carrying of the Nb tracer on MnO_2 pptd from 10 N HNO_3 for a carrier free procedure.

Procedure #5. (Diisopropyl ketone extraction method for Ta)

Source: M. Lindner, US AEC Report UCRL-4377 (Aug. 1954).

Purification: 10^{10} Atoms of Ta^{182} isolated from a 3-day-old solution containing 10^{15} fissions showed no evidence of contamination by foreign radionuclides when decay was followed through one half life.

Yield: 30 to 60 per cent.

Separation time: Four hours.

Reagents: Diisopropylketone and a solution of 12 N H_2SO_4- 0.4 N HF.

Remarks: The procedure is in essence that of Stevenson and Hicks (Anal. Chem. 25, 1517 (1953)). The use of glass equipment through the entire procedure is permissible because of the low HF_2^- concentration. The only equipment necessary is 12-ml centrifuge cones.

1. To the solution, which should be at least 1 N in either HCl or HNO_3, add 10 milligrams of Ta carrier.* Bring to a boil and digest for ten minutes while the solution boils. Add 6 M acid if necessary to replenish volume. Centrifuge precipitate and wash twice with conc. HNO_3, bringing to a boil each time. On the last wash, transfer slurry to a 12-ml centrifuge cone.
2. Dissolve the precipitate in 2 ml of 12 N H_2SO_4-0.4 N HF. Ignore any small quantities of undissolved foreign material.
3. Add 2 ml of diisopropylketone and equilibrate layers for about one-half minute with a platinum stirring wire. Centri-

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*Fluoride-free tantalum carrier can be made by dissolving freshly precipitated and washed hydrated tantalum oxide in hot saturated oxalic acid. Rather concentrated solutions of tantalum may be made in this manner and may be diluted to any desired concentration with water.

fuge the layers and transfer the ketone layer to a clean 12-ml cone. Repeat the equilibration twice, combining the organic layers.

4. Wash the combined ketone fraction with 2 ml 12 N H_2SO_4-0.4 N HF. Discard the aqueous layer.
5. To the ketone layer, add 2 ml water, equilibrating layers for about 30 seconds with a platinum stirring wire. Centrifuge layers. It may be necessary to centrifuge for five to ten minutes at this point because the organic layer often exhibits emulsification. Repeat the treatment twice with 2-ml portions of water.
6. To the combined water layers add one drop of phenolphthalein and sufficient conc. NH_4OH to make the solution barely alkaline. If necessary, "back-titrate" by dropwise addition of 4 N HNO_3 to a faint pink. Centrifuge the resultant precipitate and wash once with 5 ml conc. HNO_3 or with 5 ml of a solution of 1 M NH_4OH nearly saturated with NH_4NO_3.
7. Repeat the cycle (steps 2 through 6) twice.
8. Wash the final precipitate with 5 ml acetone. Discard the wash. With vigorous stirring motion of a platinum wire in the precipitate, place the cone in a boiling water bath and continue stirring until the precipitate appears dry and the acetone has evaporated from the cone.
9. Slowly place the cone over an open bunsen flame, finally heating the bottom of the cone strongly. At this point the precipitate usually turns black. Cool.
10. Cautiously shake the black powder out of the cone onto a weighed platinum disc. Ignite the platinum disc over a Meker burner until the precipitate appears white. Cool and weigh as Ta_2O_5.

Procedure #6. (Diisopropyl ketone method for Ta)

Source: F. F. Felber, Jr., UCRL (unpublished).

Separated from: HfO_2 Cyclotron target.

Procedure

1. The target (~ 350 mg is dissolved with 6 M HCl - 1 M HF in a Pt dish, and evaporated to 0.5 - 0.75 ml.
2. The precipitate is centrifuged, and reserved for Hf recovery.
3. The supernatant liquid is cooled in an ice bath, and centrifuged to remove any Hf that precipitates. The Hf precipitates are combined.
4. The clear supernatant solution is extracted with an equal volume of diisopropyl ketone which had been previously equilibrated with 6 M HCl - 1 M HF. (Note 1.)
5. The organic phase is washed with an equal volume of 6 M HCl - 1 M HF and the washing discarded.
6. The Ta is back extracted into an equal volume of H_2O.
7. 30 - 50 mg solid $(NH_4)_2 C_2O_4$ is added to the solution, and Ta electroplated.

Notes

1. If larger volumes can be tolerated, two extractions may be performed.
2. A high concentration of F^- results in a low plating yield.

Procedure #7. (Precipitation method for Nb)

Source: L. E. Glendenin, Paper 253 in "Radiochemical Studies: The Fission Products," NNES, Vol. 9, ed. by C.D.Coryell and N. Sugarmane (McGraw-Hill, 1951)

PREPARATION AND STANDARDIZATION OF CARRIER

Preparation. (a) From Niobium Metal. Niobium carrier solution can be prepared from niobium metal as follows: Place 10.0 g of pure niobium metal in a platinum dish and dissolve in a few milliliters of 27 M HF containing a little conc. HNO_3. Transfer to a bakelite beaker, dilute to about 200 ml, and add conc. NH_4OH to make the pH value 8 to 10. Wash the Nb_2O_5 three or four times by centrifugation with about 50 ml of hot 1 M NH_4OH (containing 1 g of NH_4NO_3 to prevent peptization). Stir the precipitate of Nb_2O_5 with 5 ml of 6 M HNO_3, and transfer to a 500-ml beaker with about 200 ml of saturated oxalic acid. Heat just to boiling and continue heating until the Nb_2O_5 is dissolved. Cool, and dilute to 1 liter. Filter the solution if it is not clear.

(b) From Potassium Hexaniobate. Niobium carrier solution can be prepared more conveniently from the water-soluble salt potassium hexaniobate ($K_8Nb_6O_{19}.16H_2O$), commercially available as "potassium niobate " from the Fansteel Metallurgical Corp., as follows: Dissolve 26.0 g of the pure salt in about 200 ml of H_2O, heat the solution nearly to boiling, and add 15 ml of conc. HNO_3 slowly with stirring. Continue heating and stirring for 2 or 3 min and centrifuge. Wash three times, with centrifugation, with 50 ml of hot 2 per cent NH_4NO_3 solution. Add 200 ml of saturated oxalic acid, and heat with stirring until the Nb_2O_5 dissolves. Cool and dilute to 1 liter. Filter the solution if it is not clear.

Standardization. Pipet 5 ml of the carrier solution into a beaker. Add 30 ml of 6 M HNO_3 and about 1 g of $KClO_3$ and carefully heat the solution to boiling. Boil gently with occasional stirring for about 5 min. Cool the mixture and add conc. NH_4OH with stirring to make the pH value 8 to 10 (about 15 ml). Filter quantitatively on Whatman No. 42 filter paper, returning the first portion of filtrate if it is not clear, and wash with hot water. Ignite at about 800°C for 15 to 20 min and weigh as Nb_2O_5.

PROCEDURE

Step 1. (a) Uranyl Nitrate Solutions. Add 10 mg of zirconium holdback carrier and proceed as in (b), but do not transfer to lusteroid tube (Note 1). Omit steps 2 and 3; proceed immediately to step 4.

(b) Phosphate Solutions. To the sample (Note 1) in a 50-ml glass centrifuge tube, add an equal volume of conc. HNO_3, 1 ml of 6 M HCl, 1 ml of saturated oxalic acid, and 2 ml of niobium carrier. Heat the solution nearly to boiling and add 0.5 g of $KClO_3$ in small portions, boiling for a few seconds after each addition. Centrifuge the Nb_2O_5 (Note 2), decant the supernatant solution, and stir in 3 ml of 6 M HNO_3, 2 ml of 6 M NH_4OH, and 5 ml of H_2O (Note 3). Heat the mixture nearly to boiling, transfer to a 50-ml lusteroid tube, and centrifuge.

Step 2. Dissolve the Nb_2O_5 in 1 ml of 27 M HF and add 2 ml of 6 M HNO_3, 1 ml of zirconium carrier, and 5 ml of H_2O. Add 1 ml of $Ba(NO_3)_2$ solution (50 mg/ml) drop by drop, stir for 1 min, and centrifuge out the $BaZrF_6$. Decant the supernatant solution into a lusteroid tube, add 1 ml of zirconium carrier, and centrifuge.

Step 3. Decant the supernatant solution into a lusteroid tube, add conc. NH_4OH (about 7 ml) to make the pH value 8 to 10 (phenolphthalein indicator), and centrifuge the Nb_2O_5. Wash the precipitate by stirring up in 3 ml of 6 M NH_4OH, 1 ml of 6 M HNO_3, and 5 ml of H_2O, and centrifuge (Note 4). Repeat the washing, using the wash solution to transfer the precipitate to a 50-ml glass centrifuge tube. Heat nearly to boiling and centrifuge. Add about 10 drops of 6 M HNO_3 to the precipitate and proceed immediately to the next step (Note 5).

Step 4. Dissolve the precipitate of Nb_2O_5 by heating with 2 ml of saturated oxalic acid. Add about 3 ml of H_2O and 5 ml of conc. HNO_3, and heat nearly to boiling. Add 0.5 g of $KClO_3$ in small portions, boil for a few seconds after each addition, and centrifuge. Wash the Nb_2O_5 in a mixture of 3 ml of 6 M HNO_3, 2 ml of 6 M NH_4OH, and 5 ml of H_2O (Note 3). Heat nearly to boiling, and filter (Note 6). Transfer to a crucible, burn off the filter paper, and ignite in a muffle furnace at 800°C for about 15 min. Cool, weigh the crucible and its contents, transfer the ignited precipitate to the mounting card, and reweigh the crucible to find the weight of Nb_2O_5 mounted.

Notes

1. The volume of the sample should not exceed 10 ml.
2. If SiF_6^{--} or F^- is present, Nb_2O_5 will not precipitate. An excess of H_3BO_3 added to the sample eliminates this difficulty. If the original sample is turoid or of doubtful composition, use step 1b.
3. The washing is done with HNO_3 containing NH_4NO_3 to prevent peptization.
4. The washing is done with NH_4OH containing NH_4NO_3 to prevent peptization.
5. Freshly precipitated Nb_2O_5 dissolves readily in hot oxalic acid. If the precipitate is allowed to stand, however, it may become very difficult to dissolve. If the precipitate will not dissolve, transfer to a lusteroid tube with 5 ml of water, dissolve with 1 ml of HF, and repeat step 3, beginning with the addition of the NH_4OH.
6. If the first portion of the filtrate is not clear, return it to the filter.

Procedure #8. (Precipitation method for Nb)

Source: A. S. Newton, USAEC Report UCRL-432 (Aug. 1949).

Element separated: niobium

Target material: thorium metal (.1-1 gm)

Type of bbdt: 60" α's

Procedure:

1. The Th metal is dissolved in conc. HCl plus a few drops of .2 M NH_4LiF_6 solution to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken. Add 10 mg Zr holdback carrier. Add an equal volume conc. HNO_3, 1 ml 6 M HCl, 1 ml saturated $H_2C_2O_4$, and 20 mg Nb carrier. Heat solution nearly to boiling, add 0.5 gm $KBrO_3$ in small portions digesting and boiling a few minutes after each addition. Digest 5 minutes and centrifuge off pptd Nb_2O_5. Stir up ppt with 3 ml 6 M HNO_3, 2 ml 6% NH_4OH and 5 ml H_2O. Heat mixture nearly to boiling and transfer to a 50-ml lusteroid tube and centrifuge.
2. Dissolve ppt with 1 ml 27 N HF. Add 2 ml 6 M HNO_3, 10 mg Zr holdback carrier, and 5 ml H_2O. Add 50 mg $Ba(NO_3)_2$ in solution dropwise. Centrifuge out $BaZrF_6$. Decant into another lusteroid tube, add 10 mg Zr carrier and centrifuge.
3. To supernate in lusteroid, add about 6 ml conc. NH_4OH (to pH 8-10). Centrifuge the Nb_2O_5. Wash ppt by stirring up in 3 ml of 6 M NH_4OH, 1 ml 6 M HNO_3, 5 ml H_2O. Centrifuge. Repeat washing and use wash solution to transfer ppt to a glass tube. Heat nearly to boiling and centrifuge. Add about 10 drops of 6% HNO_3 to ppt and immediately proceed on 4.
4. Dissolve the precipitate by heating with 2 ml saturated $H_2C_2O_4$. Add about 3 ml H_2O, 5 ml conc. HNO_3 and heat nearly to boiling. Add 0.5 gm $KBrO_3$ in small portions, boil a few minutes after each addition. Digest 5 minutes and centri-

fuge. Wash Nb_2O_5 in mixture of 3 ml 6 M HNO_3, 2 ml 6 M NH_4OH and 5 ml H_2O. Heat nearly to boiling and filter. Transfer to a crucible, burn off filter paper and ignite in muffle 15 min. Weigh on watchglass as Nb_2O_5 and count.

Preparation of carrier solution:

Dissolve 26.0 gms of pure potassium hexaniobate ($K_8Nb_6O_{19}\cdot 16H_2O$ available from Fansteel Corporation as potassium niobate) in 200 ml H_2O. Heat nearly to boiling and add 15 ml conc. HNO_3 slowly with stirring. Heat 2-3 min and centrifuge off ppt'd Nb_2O_5. Wash three times by centrifugation with 50 ml hot 2% NH_4NO_3 solution.

Add 200 ml saturated oxalic acid solution to the Nb_2O_5. Heat with stirring until the Nb_2O_5 dissolves. Cool and dilute to 1 liter. Filter if solution is not clear.

Standardization:

Take 5 ml carrier, add 30 ml 6 N HNO_3. Add 1 gm $KBrO_3$ and heat solution to boiling. Boil 5 minutes with occasional stirring. Cool, add about 15 ml conc. NH_4OH to a pH of 8-10. Filter on to Whatman #42. Refilter if not clear. Wash with hot H_2O. Ignite at 800°C for 15-20 min. Weigh as Nb_2O_5.

Procedure #9. (Carrier-free separation of Nb by precipitation)

Source: J. M. Siegel, W. P. Bigler and D. N. Hume, Paper 255 in "Radiochemical Studies: The Fission Products," NNES Vol. 9, ed. by Coryell and Sugarman (McGraw-Hill, 1951).

CHEMICAL PROCEDURE

Step 1. To a suitable volume (5 to 100 ml) of fission-product concentrate (Note 1) or zirconium-niobium tracer concentrate (Note 2) are added 10 mg of tellurium carrier (as H_2TeO_3) and 10 ml of conc. HCl, and the solution is evaporated to approximately 2 ml (Note 3). A second 10-ml portion of conc. HCl is added, and the solution is again evaporated to about 2 ml. To the residual solution are added 20 ml of 3 $\underline{M}$ HCl and 2 ml of saturated oxalic acid, and the solution is heated to boiling. Sulfur dioxide is bubbled through the hot solution until the tellurium precipitate is well coagulated (Note 4). The solution is filtered through a sintered-glass filter stick, and the precipitate is discarded.

Step 2. The supernatant liquid is evaporated to about 2 ml in order to expel most of the HCl (Note 5). Twenty milliliters of 10 $\underline{M}$ HNO_3, 10 mg of Mn^{++} carrier, and 1.5 g of $KClO_3$ are added either by slurrying with the HNO_3 or by the addition of small portions of the solid. After the initial evolution of Cl_2 has subsided, the mixture is heated cautiously to boiling. The boiling is continued for 2 to 3 min to coagulate MnO_2, and the supernatant liquid is filtered off through a sintered-glass filter stick. The precipitate is dissolved in 10 ml of 10 $\underline{M}$ HNO_3 containing 2 to 3 drops of 30 per cent H_2O_2 and boiled for a few minutes to decompose the excess H_2O_2. Ten milliliters of 10 $\underline{M}$ HNO_3 and 1 g of $KClO_3$ are then added, and the mixture is boiled for 2 to 3 min to reprecipitate MnO_2. The supernatant solution is filtered off, and the MnO_2 is dissolved and reprecipitated a third time by the above procedure.

Step 3. The third MnO_2 precipitate is dissolved in 20 ml of H_2O containing 0.5 ml of 5 M HNO_3 and 2 drops of 30 per cent H_2O_2. Ten milligrams of Fe^{++} carrier is added, and the solution is boiled with 2 drops of saturated bromine water. A solution of 6 M NH_4OH is added drop by drop until $Fe(OH)_3$ almost precipitates (Note 6), the solution is heated to boiling, and about 0.5 ml of 3 M $NH_4C_2H_3O_2$ is added drop by drop to precipitate basic ferric acetate [probably $FeOH(C_2H_3O_2)_2$]. The supernatant liquid is filtered off through a sintered-glass filter stick, and the precipitate is dissolved in 20 ml of H_2O containing 0.5 ml of 6 M HNO_3. Basic ferric acetate is reprecipitated by the above procedure, filtered, and dissolved in 20 ml of 8 M HCl. This solution is then extracted three or four times with 20-ml portions of isopropyl ether. The aqueous phase is then evaporated to approximately 2 ml (Note 3) to expel ether and HCl and is diluted to the desired volume.

Notes

1. The fission-product concentrate is the aqueous phase obtained by the exhaustive ether extraction of uranyl nitrate and filtered to remove silica. Less than 1 g of uranyl nitrate per 50 ml of solution should be present. The starting material must be free of SiO_2 to prevent the loss of niobium by adsorption.
2. If the zirconium-niobium mixture is isolated by the cupferron-chloroform method, it will be free of tellurium, and step 1 may be omitted.
3. Niobium is lost on the walls of the container if the solution is evaporated to dryness. The activity may be removed by boiling with 1 M KOH or 0.01 M oxalic acid, giving stable solutions of tracer as the niobate or as the oxalate complex, re-

spectively. The oxalate may be removed before use by treating with aqua regia and fuming with HNO_3 to give a solution in HNO_3. Niobium tracer in HNO_3 or HCl loses activity rather quickly owing to adsorption on the walls of the glass container.

4. Any hexavalent tellurium activity initially present will be reduced to the tetravalent state by the HCl treatment, and from this state the reduction to the metal occurs readily with SO_2.
5. The presence of large amounts of HCl requires the addition of excessive quantities of $KClO_3$. This tends to interfere with the carrying of niobium on MnO_2.
6. It is usually necessary to add 1 drop in excess and then to dissolve the $Fe(OH)_3$ with a drop of 6 M HNO_3.

TESTS AND ANALYSES

In the development of this procedure four small-scale preparations of less than 0.5 millicurie and one large-scale preparation of 50 millicuries were made. In the four small-scale preparations the recovery yield ranged from 80 to 95 per cent, but in the large-scale preparation it was only 40 per cent. This low yield was largely the result of losses caused by the mechanical difficulties involved in remote-control operations.

Absorption curves of all the preparations were determined; except for the first run they showed very little β contamination. An analysis of the large-scale preparation for tellurium indicated that less than 0.2 per cent of the total β and γ activity was due to tellurium.

The sodium bismuthate test for manganese and the potassium thiocyanate test for iron indicate that both of these elements are present in very small amounts in the final tracer solution.

The tellurium precipitate was tested for niobium activity.

The precipitation of tellurium was carried out in the presence of niobium activity under the same conditions as in the tracer isolation. The loss on the tellurium precipitate was 0.8 per cent.

Procedure #10. (Carrier-free separation of Ta by solvent extraction)

Source: F. F. Felber, Jr., (UCRL, unpublished)

Separated from: Lu_2O_3 Cyclotron Target

Procedure

1. The target (~ 100 mg) is dissolved in 20 - 25 ml 6 M HCl, and any insoluble residue is centrifuged down, and reserved for Lu recovery.
2. Five mg HfO_2 is dissolved in 1 ml conc. HF and added to the clear supernatant liquid, precipitating LuF_3 (Note 1).
3. The precipitate is centrifuged, and reserved for Lu recovery, and the supernatant solution is evaporated to 0.5 - 0.75 ml.
4. The solution is diluted to a convenient volume with 6 M HCl, and cooled in an ice bath, and any precipitate which appears is centrifuged and combined with the previous precipitate.
5. The clear solution is extracted with an equal volume of di-isopropyl ketone which had previously been equilibrated with 6 M HCl (Note 2).
6. The organic phase is washed with an equal volume of 6 M HCl and the washing discarded.
7. The Ta is back extracted into an equal volume of H_2O, and 30 - 50 mg of solid $(NH_4)_2C_2O_4$ is added to ready the solution for plating.

Notes

1. Hf acts as a holdback carrier.
2. Two extractions may be performed if larger volumes can be tolerated.

Procedure #11. (Carrier-free separation of Nb by ion-exchange)

Source: C. E. Mellish, UKAEA Report A.E.R.E. 1/M 39 (1955).

A source of Nb was required containing no zirconium and as large a ratio as possible of Nb^{95m} to Nb^{95}. This was required in a solution containing less than ½ mg of total solid which could be evaporated on a thin polystyrene foil. Thus the Zr^{95} available, about 20 mCs., had to be stripped of all the niobium it contained, left for a while for the niobium to grow, and then stripped of niobium again before the short lived isomer could decay appreciably. This was achieved by the use of an anion exchange column, after two other separation procedures had been tried and rejected.

First, a method of separation due to Fudge (A. J. Fudge, A.E.R.E. Report C/R 1502) was attempted. This involved a chromatographic separation of Zr and Nb on a cellulose column, in a solution of methyl ethyl ketone/HF. The method was abandoned for two reasons; (a) because the column appeared to behave erratically with the carrier-free material, and (b) because of the difficulty of obtaining less than ½ mg of total solid when evaporating down the 400 ml of liquid required to elute the niobium.

Secondly a solvent extraction method was attempted, in which Zr was extracted from the Zr/Nb mixture into n-butyl ether in the presence of di-butyl phosphate (J. M. Baker, et al. Proc. Phys. Soc. 66, 305, 1953). This method was unsatisfactory because of a glass-like residue in the final source material resembling phosphoric acid. This may have arisen by hydrolysis of the DBP under the acid conditions employed.

Anion Resin Column Method

The Zr/Nb mixture was evaporated to dryness, taken up in a solution 9 N in HCl and 2 N in HF and added to the resin column. Eluting with this mixture removes the Zr fairly quickly; the niobium is left on the column and is difficult to remove. The first time the process was carried out, in fact, the niobium had grown in a HNO_3/Oxalic acid mixture and proved impossible to elute. The column of resin, which was 20 cm long and 1.0 cm in diameter, and held in a polythene tube, was therefore cut up, and a niobium source obtained by destroying the resin holding the Nb with concentrated nitric and sulphuric acids and 100-vol hydrogen peroxide. This gave a source which was satisfactory with regard to total solid, and this could be used as a method for obtaining the niobium.

In subsequent experiments, the Nb^{95} was allowed to grow in the HCl/HF mixture, and it was found possible to elute it with acid 3 N in HCl and 0.05 N in HF. These concentrations were arrived at by extrapolating the figures of Kraus and Moore (K. A. Kraus and G. E. Moore, J. Am. Chem. Soc., 75, 1460, 1953; ibid., 73, 9, 1951) to obtain as large an elution constant for Nb as possible.

Monitoring in the separation is performed by counting samples of effluent with an end window Geiger tube. The samples are counted with and without an absorber in front of the counter to absorb all β-particles, when niobium can be distinguished by its higher γ-β ratio.

The final source was prepared by evaporating the niobium solution to dryness and taking it up in a few drops of 40% HF; this was evaporated on a polystyrene foil without damage to it. The source contained less than 2% zirconium, and was supplied about 30 hours after the Zr-Nb separation.

Procedure #12. (Carrier-free separation of Ta by precipitation and ion-exchange)

Source: A. N. Murin, V. D. Nefedov, I. A. Yutlandov, Uspeckhi Khimii 24, 527 (1955).

Irradiated oxide of Hf (HfO_2) was dissolved in a mixture of HNO_3 and HF. Excess HF was removed by evaporation with 10 N HNO_3. To the solution was added $KMnO_4$, and MnO_2 was precipitated. The MnO_2 quantitatively carried down the radio-tantalum. The precipitate was dissolved in oxalic acid and the Mn^{+2} was removed by adsorption on a cation exchange resin (Amberlite lR-1 or Dowex-50).

Procedure #13. (Chromatographic extraction method for Nb)

Source: A. J. Fudge, UKAEA Report A.E.R.E. C/R 1502 (Dec. 1954).

SPECIAL REAGENTS

Niobium Carrier (5 mg Nb_2O_5/ml)

2.5 g of Specpure niobium pentoxide was dissolved by warming with 20 ml of 40% w/v hydrofluoric acid under an infrared lamp. If solution was slow more hydrofluoric acid solution was added until a clear solution has been obtained. This solution was then washed quickly into a 500 ml graduated glass flask or polythene bottle and made up to 500 ml with 2% hydrofluoric acid solution. The solution was stored in stopped polythene bottles.

Zirconium Carrier (10 mg Zr/ml)

4.7 g of zirconium nitrate [$Zr(NO_3)_4 \cdot 5H_2O$] was dissolved in 6.3 ml of concentrated nitric acid and 5 mls of water with gentle warming. When a clear solution had been obtained, the solution was diluted carefully to 100 ml , allowed to stand overnight and filtered if turbid.

Hydrofluoric Acid solution (1:3)

100 g of A.R. hydrofluoric acid (40% w/v) solution was weighed into a polythene beaker and diluted with 300 ml of redistilled water. The mixture was stored in screw-capped polythene bottles.

Developing solution

100 g of A.R. hydrofluoric acid (40% w/v) solution was weighed into a polythene bottle, and 400 ml of redistilled methyl ethyl ketone added. This solution was again stored in screw-capped bottles and keeps almost indefinitely if well secured.

Tannin solution (2%)

2 g of tannin was dissolved in 100 ml of redistilled water, and the solution filtered to remove the residue.

Preparation of standardized 95-Niobium tracer solution

(1) 5 millicuries of 95-niobium tracer (as supplied by R.C.C. Amersham) was washed into a Pt basin and evaporated to dryness.

(2) The residue was fused with 1.0 g of powdered potassium bisulphate and cooled. 5 ml of niobium carrier, and 1.0 ml of zirconium carrier solutions were added with 10 ml of hydrofluoric acid (40% w/v) and the mixture evaporated to dryness.

(3) The residue was dissolved, by warming under an infrared lamp,

in the minimum quantity of diluted (1:3) hydrofluoric acid solution and 1.0 g of A.R. ammonium fluoride.

(4) Sufficient Whatman cellulose powder was then added to the solution to give a powdery mixture.

(5) A cellulose column was prepared by adding Whatman cellulose powder to a polythene column 12" x 1" containing 20% hydrofluoric acid/methyl ethyl ketone solution until a column 8" high has been obtained.

(6) The niobium tracer on the cellulose pulp was then added to the column, and 400 ml of 20% hydrofluoric acid/ methyl ethyl ketone allowed to flow through the column.

(7) The eluent was evaporated to dryness in a platinum basin under an I.R. lamp and the residue ignited to 500°C to remove carbonaceous matter.

(8) The residue was dissolved in dilute hydrofluoric acid (1:3) solution and made up to 100 ml . Standardization was carried out by D. At. En. method 1013.

Analysis of fission product solution

(1) A suitable aliquot of fission product solution was pipetted into a Pt basin, together with one ml of hydrofluoric acid (40% w/v), and the mixture evaporated to dryness under an I.R. lamp.

(2) Add 1 ml (a) of hydrofluoric acid (40% w/v) and 1 ml of Nb carrier solution and repeat the evaporation to dryness.

(3) Add 1 ml (b) of hydrofluoric acid (1:3) and stir with a polythene rod for a few minutes. Allow to stand for 15 minutes.

(4) Take 0.01 ml of solution and deliver in as narrow a band as possible to one end of a Whatman No. 1. filter paper C.R.L.1

(5) Add the 95-niobium standard solution to the adjacent strip.

(6) Allow the strip to dry for one hour over saturated potassium carbonate solution.

(7) Pour developing solution (25 ml) into 600 ml polythene beaker, and place strip into solvent,[c] with the sample spots lowermost. Allow the solvent to diffuse upwards for 20 min.

(8) Expose the strips to ammonia vapor in a dessicator, then dry using hot air. Spray with 2% tannin solution from a glass atomizer, and dry again with hot air.

(9) Remove the colored portions at the top of the strip and mount for counting between two pieces of Sellotape and place across a counting tray.

(10) γ count the sample and standard [d] and determine the disintegration rate from the efficiency of counting obtained from the 95-niobium standard.

[a] Use a polythene pipette.

[b] Use a glass pipette.

[c] Care must be taken to prevent the strip touching the sides of the beaker.

[d] Counting is done in all cases through a lead sandwich which consists of Al sheet (1800 mg/sq. cm.), Pb sheet (3.5 g/sq. cm.), Al sheet (200 mg/sq. cm.).

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