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Radiochemistry of Zirconium and Hafnium

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Steinberg, Ellis P.; Subcommittee on Radiochemistry; Committee on Nuclear Science; National Research Council

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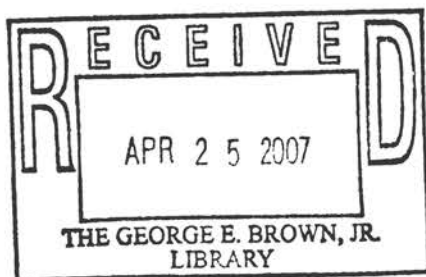University of California (Livermore)

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The Radiochemistry of Zirconium and Hafnium

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Argonne National Laboratory
Lemont, Illinois

January 1960

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 radio-chemically pure reagents, the problems of stockpiling uncontaminated materials, the 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

CONTENTS

I. General Reviews of the Inorganic and Analytical Chemistry of Zirconium and Hafnium.

"The Chemical Behavior of Zirconium," W. B. Blumenthal, D.
Van Nostrand Co., Inc. New York, 1958.

Pp. 628-653, "Chemical Elements and their Compounds," N. V.
Sidgwick, Oxford University Press, 1950.

Pp. 564-575, "Applied Inorganic Analysis," W. F. Hillebrand
et al., John Wiley and Sons, Inc., New York, 1953.

Chaps. 12 and 13, "Chapters in the Chemistry of the Less
Familiar Elements," B. S. Hopkins, Stipes Publishing Co.,
Champaign, Ill., 1939.

"Hafnium," Chap. IV in "Modern Advances in Inorganic Chemistry,"
E. B. Maxted, Oxford University Press, 1947.

R. L. Barnard and R. E. Telford, Chap. 20 in "Analytical
Chemistry of the Manhattan Project," C. J. Rodden, eds.,
McGraw-Hill Book Co., New York, 1950.

E. B. Read, Chap. 12 in "Metallurgy of Zirconium," B.
Lustman and F. Kerze, Jr., eds., McGraw-Hill Book Co.,
New York, 1955.

Gmelin's Handbuch der Anorganischem Chemie, Systems Nv. 43,
8th Edition (Ver̃ lag Chemie, Gmb H. Weinheim - Bergstrasse,
1958.)

"Zirconium," G. I. Miller, Academic Press (1957).

"Recent Advances in the Chemistry of Zirconium and Hafnium,"
E. M. Larsen, J. Chem. Ed. 28, 529 (1951).

1

"Solvent Extraction in Analytical Chemistry," G. H. Morrison
and H. Freiser, Wiley (1957).

"Ion-Exchangers in Analytical Chemistry," O. Samuelson, Wiley
(1955).

"Chemistry of the Metal Chelate Compounds," A. E. Martell
and M. Calvin, Prentice-Hall (1952).

II. General Reviews of the Radiochemistry of Zirconium and
Hafnium.

No general reviews have been published. D. N. Hume pre-
pared a preliminary review of the radiochemistry of some of
the major fission product elements in 1945, but it was not
published. Some materials from this review has been incor-
porated in the following presentation.

More complete information on the radiations of these isotopes
and references to the original literature may be found in "Table
of Isotopes," D. Strominger, J. M. Hollander, and G. T. Seaborg,
Revs. Mod. Phys. $\underline{30}$, No. 2, Part II, April 1958.

III. Table of Isotopes of Zirconium and Hafnium.

Isotope	Half-life	Type of Decay	Method of Preparation
Zr^{86}	17 hr	EC	$Ni(p,spall.)$; $As^{75}(N^{14},3n)$
Zr^{87}	94 min	β^+, EC	$Zr^{89}(\alpha,n)$
Zr^{88}	85 day	EC	$Ni(p,spall.)$
Zr^{89m}	4.4 min	It(93%),EC(5.6%),β^+(1.8%)	$Zr(X-ray)$
Zr^{89}	79.3 hr	EC($\sim$75%),β^+($\sim$25%)	$Y(d,2n)$
Zr^{90m}	0.83 sec	IT	$Zr^{90}(n,n')$
Zr^{93}	1.1×10^6 yr	β^-	Nuclear fission
Zr^{95}	65 day	β^-	Nuclear fission
Zr^{97}	17.0 hr	β^-	Nuclear fission
Zr^{98}	$\sim$1 min	β^-	Nuclear fission
Zr^{99}	35 sec	β^-	Nuclear fission
Hf^{170}	112 min	β^+	$Lu(p,6n)$
Hf^{171}	16.0 hr	EC	$Lu(p,5n),Yb(\alpha,3n)$
Hf^{172}	.5 yr	EC	$Lu(p,\gamma n)(\alpha,xn),Ta(d,2p9n)$
Hf^{173}	23.6 hr	EC	$Lu(p,3n)$; $Yb(\alpha,xn)$
Hf^{175}	70 day	EC	$Hf^{174}(n,\gamma)$
Hf^{178m}	4.8 sec	IT	daughter 2.1 hr Ta^{178}
Hf^{179m}	19 sec	IT	$Hf^{178}(n,\gamma)$
Hf^{180m}	5.5 hr	IT	$Hf^{179}(n,\gamma)$
Hf^{181}	44.6 day	β^-	$Hf^{180}(n,\gamma)$
Hf^{183}	64 min	β^-	$W(n,\alpha)$

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IV. <u>Review of those Features of Zirconium and Hafnium Chemistry of Chief Interest to Radiochemists.</u>*

1. The Metallic State

Zirconium and hafnium are difficult to prepare as pure metals. They are very infusible and react vigorously at high temperatures with carbon, oxygen, and nitrogen. When finely divided, the dry metal powders are pyrophoric and should be moistened for safe handling. In compact form and at low temperatures the metals are very inert chemically, being attacked appreciably only by HF, aqua regia, and fused KNO_3. The best method of preparation of the pure metals is probably the van Arkel-de Boer method of reducing the iodides on a hot filament. This produces the so-called "crystal bar" metal.

2. Soluble Salts

The solution chemistry of zirconium is not very well understood, and considerable confusion exists in the literature regarding the ionic species present in aqueous solutions. This results mainly from the formation of colloids and the fact that zirconium ions undergo extensive hydrolysis and polymerization, strongly dependent on pH and concentration.[1] The only important oxidation number is +4. The nitrate, chloride, bromide, iodide, perchlorate and sulfate of zirconium are soluble in acid solution.

3. Insoluble Salts

Among the more insoluble compounds is the very insoluble phosphate, $ZrO(H_2PO_4)_2$ (K_{sp}=2.28x10^{-18})[1a] which precipitates even

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*Zirconium and hafnium show a remarkable similarity in most of their chemical properties, and unless otherwise noted, any statements made concerning one generally will apply equally well to the other.

from 20% sulfuric acid. It has properties similar to those of ceric phosphate, but is dissolved by hydrofluoric acid. The iodate precipitates from 8 $\underline{M}$ HNO_3, and the arylsubstituted arsonates and cupferrate from acid solutions. The hydroxide (or hydrous oxide) is precipitated with ammonia or alkali hydroxide, and a peroxide with H_2O_2 from dilute acid. Of these, only the phosphate is soluble in excess reagent. Barium and hydrofluoric acid give slightly soluble barium fluorzirconate of uncertain composition, which is insoluble in excess fluoride and affords a good separation from niobium.

The customary weighing form in radiochemical and analytical procedures has been the ignited ZrO_2 following precipitation as phenyl arsonate, cupferrate or other organic precipitant.[2] However, a quantitative and well-defined precipitate of zirconium with mandelic acid and its derivatives[3] has proved more convenient and useful for mounting radioactive sources. Flavianic acid has also been suggested as a specific quantitative precipitant for zirconium and hafnium in 0.2-0.3 $\underline{N}$ HCl solution.[3a]

<div align="center">

4. Carrying of Tracer Zirconium
Activity on Other Precipitates

</div>

Zirconium tracer is strongly co-precipitated with most precipitates in acid solutions not containing complex-forming ions. The activity is easily carried on foreign matter and adheres to glassware. It is readily carried on many phosphates, such as those of bismuth and ceric cerium. In the absence of hold-back carrier, it is nearly completely carried on rare earth fluorides. Iron hydroxide is an effective carrier for zirconium tracer as is thorium iodate, but thorium oxalate is not. Titanium hypophosphate has also been suggested as a precipitant for tracer zirconium.[3b]

5. Complex Ions

In addition to the hydrolytic species referred to above, zirconium forms complex ions with many substances. As is the case with the hydrolysis products, the species present in solution are not well established. Connick and McVey[4] have studied the complexing ability of a number of substances, and their data is reproduced in Table I.

The fluoride is by far the most stable complex studied. Among the dicarboxylic acids, oxalic has a much greater complexing power than can be accounted for simply by a comparison of the acid dissociation constants.

Although similar data are not available for hafnium, the complex constants must differ significantly, as evidenced by differences in the ion-exchange behavior (see below).

6. Chelate Compounds

The formation of chelate complexes which are soluble in organic solvents is of great importance to the development of radiochemical separation procedures. Examples of such solvent extraction systems for zirconium and hafnium will be presented in detail later. In this section we shall review the various chelates formed by zirconium and hafnium.

Acetylacetone ($CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$). This β-diketone forms well-defined chelates with over 60 metals, many of them soluble in organic solvents. The solubilities of the acetylacetonates is such that macro-scale operations are feasible. Zirconium may be extracted to the extent of 73% with acetylacetone acting as both extracting agent and solvent at a pH of 2 to 3.[5]

Thenoyltrifluoroacetone (TTA), $[\overset{}{\underset{S}{\|}}\text{ }\| -C-CH_2-C-CF_3]$.

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Table I

COMPLEXING ABILITY OF VARIOUS SUBSTANCES FOR ZIRCONIUM
(Tracer Zirconium, 2.00 $\underline{M}$ $HClO_4$, 25°C)

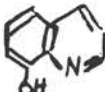| Substance	Concentration	Percent Zirconium Uncomplexed
Bisulfate ion, HSO_4^-	$\begin{cases} 0.0031\ \underline{M} \\ 0.272\ \underline{M} \end{cases}$	56 0.18
Hydrofluoric acid, HF	$\begin{cases} 10^{-5}\ \underline{M} \\ 0.008\ \underline{M} \end{cases}$	22 0.00012
Oxalic acid, $H_2C_2O_4$	0.001 $\underline{M}$	0.36
Malonic acid, $HOOC\text{-}CH_2\text{-}COOH$	0.01 $\underline{M}$	100
Succinic acid, $HOOC\text{-}(CH_2)_2\text{-}COOH$	0.005 $\underline{M}$	100
Glutaric acid, $HOOC\text{-}(CH_2)_3\text{-}COOH$	0.1 $\underline{M}$	94
Fumeric acid, HC-COOH // COOHCH	0.05 $\underline{M}$	88
Malpic acid HC-COOH ‖ HC-COOH	0.05 $\underline{M}$	74
Orthophosphoric acid, H_3PO_4	0.012 $\underline{M}$	68
Orthoboric acid, H_3BO_3	0.1 $\underline{M}$	100
Metasilicic acid, H_2SiO_3	0.01 $\underline{M}$	87
Acetic acid, CH_3COOH	1.0 $\underline{M}$	100
Trifluoroacetic acid, CF_3COOH	0.11 $\underline{M}$	51
Carbonic acid, H_2CO_3	1 atm. CO_2	90
Hydrogen peroxide, H_2O_2	0.015 $\underline{M}$	63
Chloride ion, Cl^-	$\begin{cases} 2.0\ \underline{M} \\ 1.2\ \underline{M} \end{cases}$	19 29
Nitrate ion, NO_3^-	$\begin{cases} 2.0\ \underline{M} \\ 1.2\ \underline{M} \end{cases}$	20 30

The presence of the trifluoromethyl group in this β-diketone in-
creases the acidity of the enol form and thus permits extractions
from solutions of very low pH. The TTA is generally used as a
0.02-0.5 $\underline{M}$ solution in benzene or toluene. At lower concentra-
tions the extraction rates become very slow. Connick and
McVey[4] have studied the behavior of zirconium -TTA complexes
and Moore[6] has developed a procedure for the separation of
zirconium from other elements utilizing TTA complexing. The
complex shows high extractability from 2-10 $\underline{M}$ HNO_3 or HCl solu-
tions into 0.5 $\underline{M}$ TTA in xylene. These conditions afford an ex-
cellent separation of zirconium from the fission products. A
small contamination with niobium can be reduced further by the
use of 0.9% H_2O_2 or 1.25 $\underline{M}$ $NH_2OH \cdot HCl$ as a sequestering agent.
Among the non-extractable ions are the alkalis, alkaline earths,
trivalent rare-earths, tin (II), nickel (II), cobalt (II), chro-
mium (III), uranyl, thorium (IV), iron (II), aluminum (III), and
bismuth (III). Zirconium and hafnium may be fractionated with
0.025 $\underline{M}$ TTA in benzene from 2 $\underline{M}$ $HClO_4$ acid.[7] The equilibrium
constants for zirconium and hafnium extractions were found to be
9.4×10^7 and 4.6×10^6 respectively.

Trifluoroacetylacetone (TFA), $[(CF_3CO)_2CH_2]$. Chelates
formed with this diketone are generally more soluble than those
with TTA. A zirconium hafnium separation may be achieved with
0 075 $\underline{M}$ TFA in benzene from 0.07 $\underline{N}$ HCl.[8]
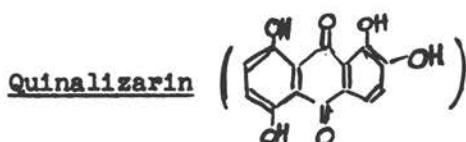
Quinalizarin forms complexes with a

number of metals, but only the complexes of Fe(III), Al, Sc, Ti,
Zr, and Th are extractable with isoamyl alcohol.[9] The re-
agent is generally used as 0.1% ethanolic solution.

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<u>8-quinolinol (oxine</u>), [structure]. Oxine forms slightly

soluble chelates with most metals, generally those that pre-
cipitate with aqueous ammonia. Zirconium forms a complex
soluble in chloroform from acetic acid-acetate buffered solu-
tions.[10]
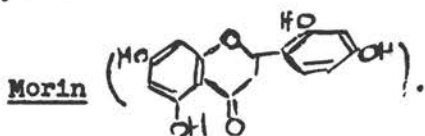
<u>Morin</u> [structure]. In acid medium,

morin reacts with a number of metals including Al, Be, Ce(III),
Ga, In, Sb(III), Sc, Sn, Th, Ti, and Zr to form complexes that
are extractable by butyl, amyl and cyclohexyl alcohols.[10]

<u>Ammonium Salt of N-Nitroso Phenylhydroxyl Amine (Cupferron)</u>

[structure]. Cupferron is well-known for its ability to
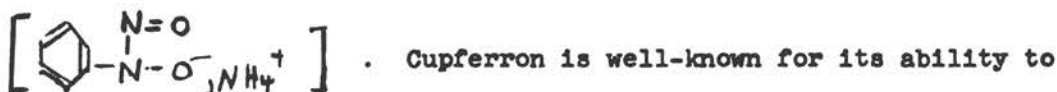
form slightly soluble chelates with many metals in mineral acid
solution. The cupferrates are generally soluble in a variety of
organic solvents such as chloroform, ether, ethyl, acetate, hex-
one, o-dichloro benzene, and benzene. Chloroform is the prefer-
red solvent. Zirconium cupferrate may be extracted from 1 $\underline{N}$
mineral acid solutions.[11]

7. Solvent Extraction Behavior

An excellent review of solvent extraction systems in analyt-
ical chemistry is given by Morrison and Freiser (see general refer-
ence list). The behavior of zirconium and hafnium in some of the
more important systems will be discussed here.

<u>Ethyl Ether</u>. This common solvent is effective for the ex-
traction of many elements from halide systems. Extraction of
zirconium, however, is not appreciable, the fluoride being ex-
tracted to the extent of 2.9% and the other halides even less.

The thiocyanate complexes of zirconium and hafnium exhibit differences in extractability into ethyl ether and a separation may be achieved.[12] From 8 $\underline{M}$ HNO$_3$, zirconium extracts only to the extent of 8% into ethyl ether.[13]

Methylisobutyl Ketone (Hexone). The distribution of Th(IV), U(VI), Pu(IV), Pu(VI), Zr(IV), Ca(II), and La(III) between aqueous HNO$_3$-Ca(NO$_3$)$_2$ solutions and hexone has been studied by Rydberg and Bernström.[14] Distribution ratios approaching unity are obtained for zirconium from solutions 3.5 - 4.0 $\underline{M}$ in Ca(NO$_3$)$_2$ and about 3 $\underline{M}$ in HNO$_3$.

Alkylphosphoric Acids. Scadden and Ballou[15] investigated di-n-butylester of phosphoric acid (DBPA), [(C$_4$H$_9$O)$_2$P$\overset{-OH}{\underset{O}{\nwarrow}}$], either alone or in a mixture with the monoester as in commercial "butylphosphoric acid," as an extractant for zirconium and niobium. Both tracer and macro levels of zirconium were found to extract quantitatively from aqueous solutions 1 $\underline{M}$ in HNO$_3$, HCl, HClO$_4$, or H$_2$SO$_4$. A 0.06 $\underline{M}$ solution of the dibutylphosphoric acid in di-n-butylether extracted > 95% of the Zr and < 5% of the Nb. The niobium extraction increased from 2 to 10% as the extraction time increased from 1 to 5 minutes, but zirconium was unaffected. Addition of 3% H$_2$O$_2$ reduced niobium extraction to less than 1% (even with a 10-minute extraction time) without affecting zirconium. More concentrated DBPA solutions extracted both zirconium and niobium 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. Tables II and III, taken from Scadden and Ballou, summarize the extraction behavior of a number of elements with DBPA.

Table II

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

Elements Extracted

Concn. of DBPA[a], $\underline{M}$	< 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.

Tri-n-butylphosphate (TBP) is an excellent solvent for
zirconium. It may be used pure or with an inert diluent such as
n-butylether, ether, kerosene, benzene, or CCl_4. The extracta-
bility increases with acid strength, and distribution ratio,
(organic/aqueous) of about 100 is observed from 8 $\underline{M}$ HCl and
1000 from 13 M HNO_3.[16]

A summary of zirconium extraction data from HNO_3 is given
in Figure 1, taken from Alcock et al.[17]

Table III

EXTRACTION PROPERTIES OF MACRO QUANTITIES OF FISSION PRODUCT
ELEMENTS WITH MIXED BUTYL PHOSPHORIC ACIDS CONDITIONS. AQUEOUS
PHASE 1 MG ELEMENT PER ML, 1 $\underline{M}$ H_2SO_4, 2.5 $\underline{M}$ $(NH_4)_3SO_4$, 0.004 $\underline{M}$
OXALIC ACID, 6% H_2O_2; VOLUME RATIO (ORG./ AQ.) 1 TO 1; MIXING
TIME, 15 MINUTES WITH 0.08 $\underline{M}$ DBPA AND 5 MINUTES WITH 0.6 $\underline{M}$ DBPA

Concn. of DBPA[a], $\underline{M}$	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.

When $Ca(NO_3)_2$ replaces HNO_3 the extraction of most other
elements increases, but that of zirconium remains about the
same. This may be the result of hydrolysis of zirconium which is
considerable even at acidities of 1-2 $\underline{M}$.[1,4]

Note: Commercial TBP often contains impurities of organic
pyrophosphates and mono and di-butyl phosphoric acids. These may
be removed by hydrolyzing the organic pyrophosphates with 8 $\underline{M}$
HCl and washing with aqueous Na_2CO_3(5%) and water.[16] This
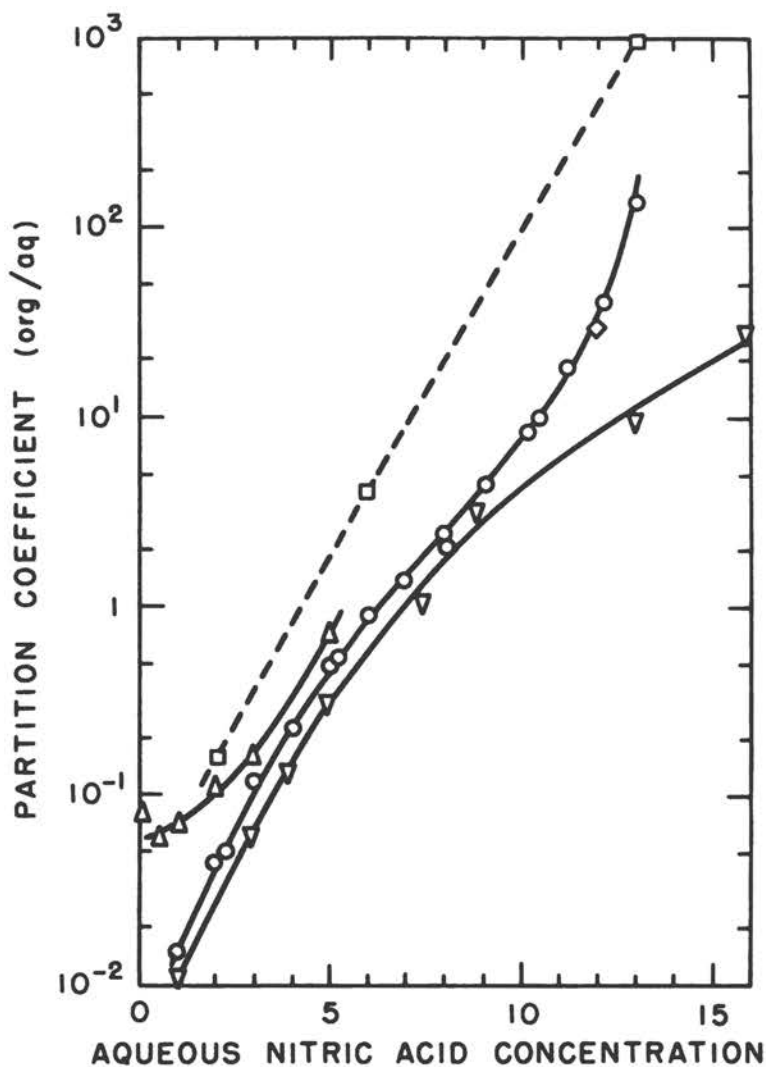
Figure 1

Extraction of zirconium from HNO$_3$ systems

o 19% TBP in kerosene (Alcock et al., J. Inorg. & Nucl. Chem. 4, 100 (1957))

▽ 30% TBP in CCl$_4$ (Murbach and McVey USAEC report LRL-115 (1954))

△ TBP in Varsol (Bruce, Peaceful Uses of Atomic Energy Vol. 7, paper 718, UN 1956)

□ 100% TBP (Peppard, Mason & Maier, J. Inorg. & Nucl. Chem. 3, 215 (1956))

◇ 25% TBP in benzene (Peppard, Mason, & Maier, ibid.)

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treatment is important if the results reported are to be reproduced.

Trialkylphosphine Oxides. $[(C_nH_{2n+1})_3P \rightarrow 0]$ Preliminary studies on the use of the phosphine oxides as extractants have been carried out.[17a] With a 0.1 $\underline{M}$ solution of tri-n-octylphosphine oxide in cyclohexane complete extraction from 1 $\underline{M}$ HCl was observed for Cr(VI), Au(I), Hf(IV), Zr(IV), Fe(III), Mo(VI), Sn(IV) and U(VI). Ions that were partially extracted include Sb(III), Bi(III), Cd(II), In(III), Hg(II), Pt(II), and Zn(II). The tri-2-ethyl-n-hexylphosphine oxide extracts fewer metals than the tri-n-octyl compound owing to the steric effect of the position of the ethyl group. From a 1 $\underline{M}$ HCl solution only Au(I), Sn(IV), and U(VI) are completely extracted. With 7 $\underline{M}$ HCl, Ga(III), Hf(IV), Zr(IV), Fe(III) Mo(VI), Sn(IV), and U(VI) are completely extracted.

8. Ion Exchange Behavior

In addition to their value in the separation of zirconium and hafnium from other elements, ion exchange techniques afford the most satisfactory means of separating hafnium and zirconium from each other.

Cation Exchange

Aqueous colloidal solutions of the hydrous oxides of zirconium and hafnium may be purified by contacting the solutions with a synthetic organic cation exchange resin (e.g. Amberlite IR-100) which retains impurities such as Be(II) and La(III), but has essentially no affinity for the colloids.[18] The removal of titanium and iron is not complete; about 80% and 95%, respectively, being removed in one passage through the column. The recovery can be as high as 99%. However, the metal content must be present in aqueous solution as hydrous oxide in

amounts greater than trace quantities, e.g., the order of 0.1 $\underline{M}$.
The amount of resin used must be considerably less than the
amount which would completely adsorb the solution.

Hafnium may be effectively separated from zirconium by
elution with HCl from a sulfuric acid resin (Dowex-50, e.g.).[19]
The elements are adsorbed from 2 $\underline{M}$ HClO$_4$ and eluted with 6 $\underline{M}$ HCl,
the hafnium eluting first. Other eluants may also be used to
effect a hafnium-zirconium separation in which the zirconium is
eluted first. Thus, a mixture of 0.45 $\underline{N}$ HNO$_3$ and 0.09 $\underline{M}$ citric
acid elutes zirconium from Dowex-50, but not hafnium.[20,21] The
hafnium may then be eluted with 5 $\underline{N}$ HNO$_3$. An excellent separa-
tion may be achieved with 1 $\underline{N}$ H$_2$SO$_4$ elution of zirconium from
Dowex-50. Hafnium is eluted with a 0.05 $\underline{M}$ oxalic - 0.2 $\underline{N}$ H$_2$SO$_4$
mixture,[22] or with 3 $\underline{N}$ H$_2$SO$_4$.[23]

The fluoride complexes of hafnium and zirconium may be
utilized to effect a separation of these elements from other non-
complexing ions, such as the rare earths, by passing an HCl-HF
solution of the elements through a cation exchange column.[24]
The negative fluoride complexes will not be adsorbed and will
pass through the column while the other ions will be retained.
Mixtures of zirconium hafnium, niobium, the rare earths, and
alkaline earths can be conveniently separated following adsorp-
tion on the top of a cation-exchange column by selective elu-
tion.[25] Thus, zirconium, hafnium and niobium can be eluted as
a group with 0.5% oxalic acid without appreciable movement of
the other ions down the column. At a pH of 3, a 5% citrate solu-
tion displaces the trivalent ions and at pH5 the remaining di-
valent and monovalent cations are removed in groups. Separations
within each group may then be carried out by readsorption and
chromatographic elution with citrate buffers.

Anion Exchange

Metals which form negatively charged complexes may be separated by ion exchange chromatography with anion exchange resins. This technique is particularly useful for the separation of zirconium and hafnium from each other and from other elements. A number of workers have made surveys of the anion exchange behavior of the elements. One of the most complete is that of Kraus and Nelson for HCl systems.[26] Other acid systems have been treated in a series of papers from the U. S. Naval Radiological Defense Laboratory.[27] Although no complete analytical procedure for zirconium and hafnium has been published as such, the adsorption and elution data from these papers may be used to devise a number of such separation schemes and a choice can be made depending on the needs of the experiment. The difficulties resulting from the hydrolytic polymerization of zirconium and hafnium can be effectively circumvented by the formation of the fluoride complexes, and HCl-HF mixtures are particularly advantageous for separations involving these elements.

Anion exchange techniques are especially valuable for zirconium-hafnium, zirconium-niobium, zirconium-protactinium, and zirconium-thorium separations. Thus, with Amberlite IRA-400 in the chloride form, zirconium and hafnium may be adsorbed from 0.64 $\underline{M}$ HF. Elution with a 0.2 $\underline{M}$ HCl - 0.01 $\underline{M}$ HF solution removes the zirconium first, and 69% of the original may be recovered with no hafnium.[28] Other systems have also been used for this separation.[29-31] The distribution coefficients for Zr, Hf, Nb, and Ta on Dowex-2 resin are shown as a function of HCl concentration in Figure 2, taken from Huffman, Iddings and Lilly.[30]

A Zr-Hf separation may be achieved by elution with 9.0 $\underline{M}$ HCl. In this case the Hf elutes first (Figure 3) in contrast to the behavior with the fluoride complexes.
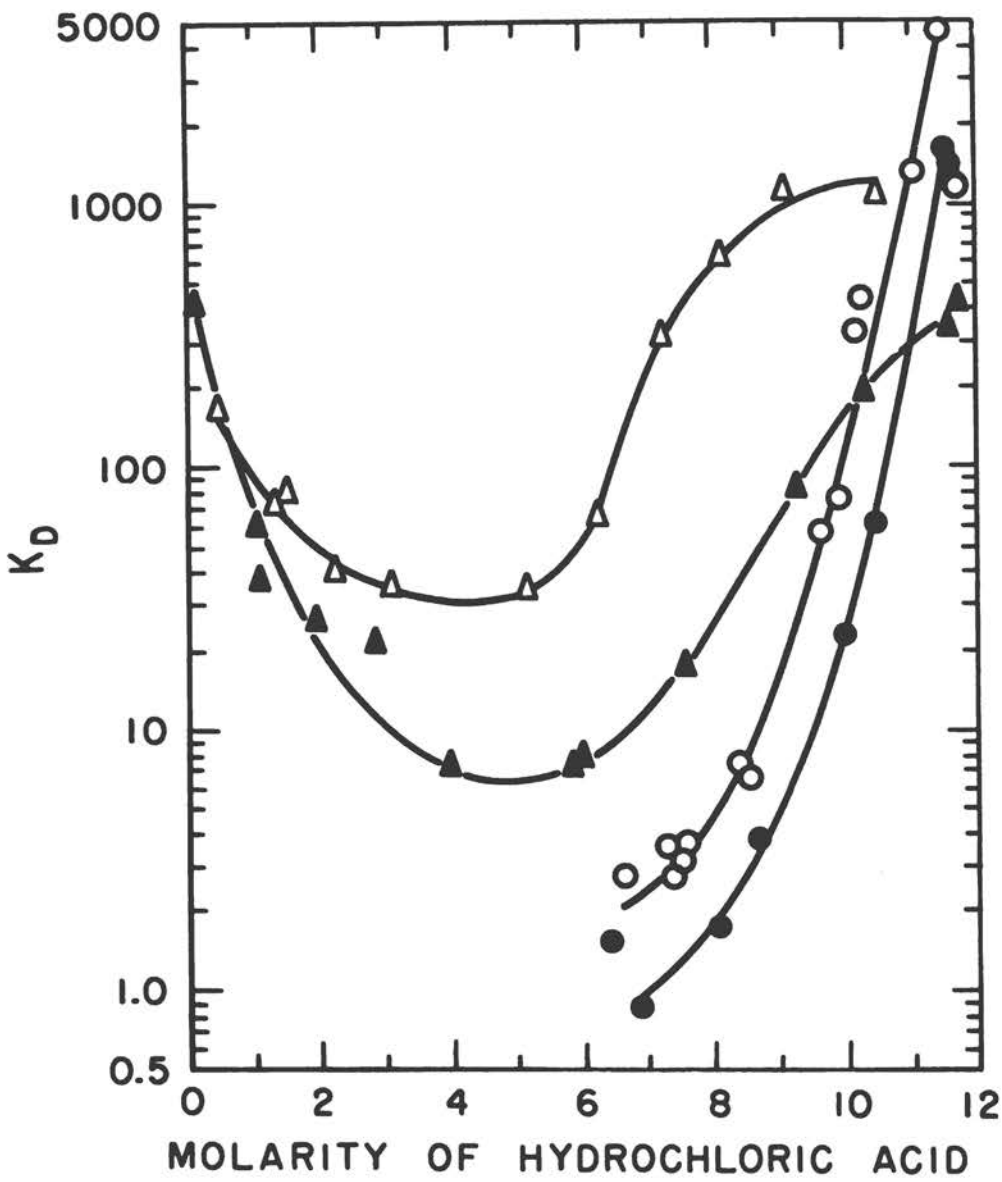
Figure 2
Dependence of the distribution coefficient at 25^0 on the hydrochloric acid concentration: △, niobium; ▲, tantalum; ○, zirconium; ●, hafnium.
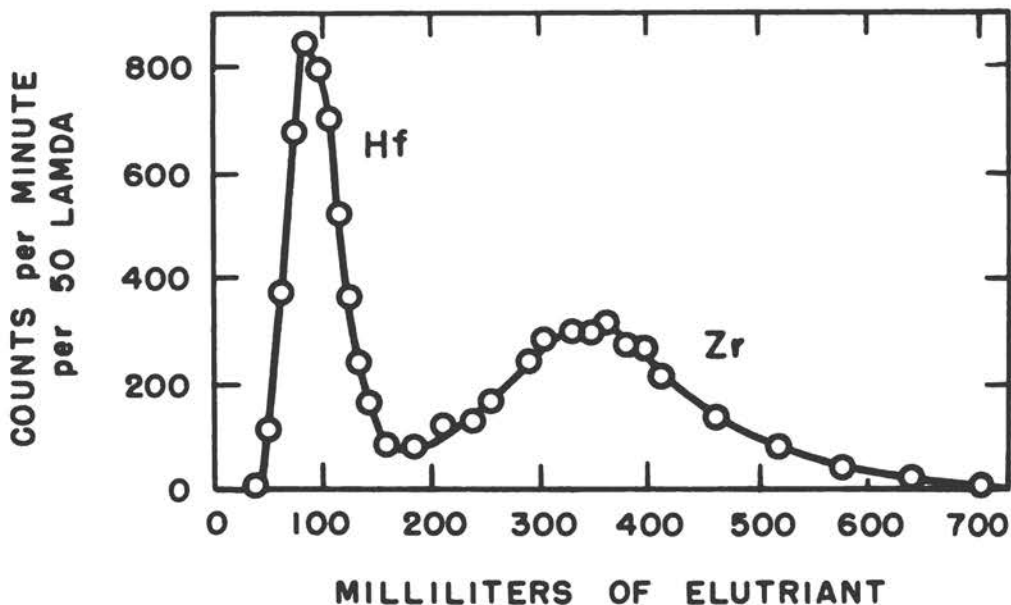
Figure 3
Elution of chlorozirconate and chlorohafniate
with 9.0 M hydrochloric acid.

The difference in behavior of zirconium and niobium leads
to a convenient separation. In 6-7 M HCl. zirconium passes
through the column, while the niobium is retained. The niobium
may then be eluted with 1.5 - 4.0 M HCl.[30,32] A variety of
conditions may also be utilized for a Zr-Nb separation in HCl-HF
mixtures.[32a] The oxalate complexes of Zr and Nb may also be
utilized for a separation.[33] Both are adsorbed on Dowex-1
resin from 0.1 - 0.4 M oxalic acid. The Zr is preferentially
eluted 1 M HCl - 0.01 M oxalic acid solution.

The differences in behavior of Zr and Pa with anion-exchange
resins are not great, both being strongly adsorbed from concen-
trated HCl solutions (> 9 M) and weakly adsorbed from dilute
acid (< 3 M). However, a separation may be effected by utiliz-
ing differences over the concentration range 6-8 M. Such separa-

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tions have been carried out using Dowex-2 and Amberlite IR-400[34] and Dowex-1[35] resins.

Since thorium does not form negative chloride complexes, it can easily be removed from ions that do, such as zirconium, by adsorbing the latter on an anion exchange resin. The fact that thorium does form complexes with HNO_3, while zirconium does not may also be utilized in a separations procedure.[36]

V. Problems of Sample Dissolution and Interchange with Carrier.

Zirconium and hafnium metals are dissolved by treatment with HF, a mixture of concentrated HCl and HNO_3, or concentrated H_2SO_4. The ores are more difficult to treat, and fusions with Na_2CO_3, $K_2S_2O_7$, Na_2O_2, or KHF_2 are necessary. When present as minor constituents or formed by nuclear reactions in a matrix of other elements or compounds, zirconium and hafnium offer no particular difficulty during dissolution of the major constituents. However, the tendency toward hydrolytic polymerization at low acidities must be borne in mind. Also, if phosphorus is present, the insoluble phosphates of zirconium and hafnium may be formed.

In any quantitative radiochemical analysis it is extremely important to carry out chemical steps to insure complete interchange of the radioactive species and any added inactive carrier or to insure that all the radioactive species are in the same chemical state before any separations are carried out. This is particularly true in the case of zirconium or hafnium where hydrolytic species and radiocolloid formation may cause difficulties. In general, the formation of the strong complex with fluoride or TTA is necessary. (Oxalate, e.g., does not effect complete interchange of fission produced zirconium species with added zirconyl carrier.)

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VI. Counting Techniques

The specific technique of counting any radioactive sample
will depend on the nature of the radioactivity and the needs of
the experiment. For many purposes an experiment can be designed
so that relative counting rates of samples of a particular nu-
clide will suffice. It is then only necessary to count under
nearly identical conditions to obtain precisions of the order of
one to two per cent. This criterion, in practice, is relatively
simple to meet and whenever possible, comparative counting is
therefore recommended. Of course, if it is necessary to compare
the activity of sources which differ in chemical or physical
nature or in the energy of their radiations, these differences
must be taken into account.

The determination of the absolute disintegration rate of a
radioactive source is a more difficult problem, and special tech-
niques must be employed. Such a determination involves a knowledge
of the decay scheme of the nuclide and the efficiency of the de-
tector for the particles or rays emitted from the source. It is
thus necessary to know the fraction of the radiation leaving the
source which enters the sensitive volume of the detector and the
intrinsic efficiency of the detector for the radiation. The inter-
actions of radiation with matter alter the simple geometric re-
lationship between the source and detector by processes of ab-
sorption and scattering in the material of the sample itself,
its support, any covering material, the space between the sample,
and detector, the detector window, and the housing of the de-
tector unit. These effects are complex and depend critically on
the size and material of the sample and its support and on the
energy and type of radiation. Much time and effort may be
saved by the judicious application of published correction
factors for the combined effects of backscattering, sample thick-

ness, etc. on counting determinations. However, it is extremely important to be aware of the sensitivity of the effects to experimental conditions. Where high accuracy is desired it is usually advisable for each investigator to determine the correction for his own conditions or employ techniques which minimize the effects.

In some cases the radioactivity of the nuclide of interest may be complicated by the presence of isotopic or genetically related species which are also radioactive. Corrections for the presence of these may be made, in general, by taking advantage of the differences in half-lives, energies, and, perhaps, types of radiation involved. Even in the case of a pure nuclide, different types of radiation may be emitted (e.g., β^-, e^-, x or γ-rays) and their contribution to the observed counting rates must be evaluated.

References on counting techniques should be consulted for details of the methods. A survey of counting methods for the assay of radioactive sources has been given by Steinberg.[37] Bayhurst and Prestwood[38] give a method for estimating beta counting efficiencies to about 3% using standard mounting and counting techniques. The use of gamma-ray scintillation spectrometry as an analytical tool has received considerable attention. This technique is described by Heath[39] and Olson.[40]

The most commonly encountered isotopes of zirconium and hafnium are Zr^{95}, Zr^{97}, and Hf^{181}. Beta counting techniques or the extremely useful gamma-scintillation counting technique may be utilized for measurement of these nuclides. Samples of Zr^{95} should be counted soon after isolation from niobium to minimize the contribution to the activity from the Nb^{95} daughter. Zr^{97} is generally counted in equilibrium with its 60s Nb^{97m} and 72 m Nb^{97} daughter. When both Zr^{95} and Zr^{97} are present, beta absorption and/or decay measurements may be utilized to analyze the components which differ considerably in both beta energy and half-life.

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VII. Collection of Detailed Radiochemical Procedures.

Procedure 1: Solvent Extraction Procedure for Zr.

Source: K. F. Flynn, L. E. Glendenin and E. P. Steinberg,
Argonne National Laboratory (unpublished).

Introduction

This procedure makes use of the formation of a benzene
soluble chelate of zirconium and TTA (α-thenoyl trifluoro
acetone). The organic phase is scrubbed to remove extraneous
activities, and the zirconium back-extracted with hydrofluoric
acid. A $BaZrF_6$ precipitation is made to concentrate the zirconium,
the barium is removed as sulfate, and the zirconium recovered
as the hydroxide. The zirconium is finally isolated and weighed
as the tetramandelate.

Interchange between carrier and radioactive species formed
in nuclear fission is as complete as with fluoride complexing.
A radiochemically pure product is obtained with about 75% chemical
yield. Two samples can be run in about one hour.

Procedure

1. To 1-5 ml aliquot of fission product solution add 5 mg
   Zr carrier (Note 1) and 1 ml conc. HNO_3. Dilute to 15
   ml and extract into 15 ml of 0.4 $\underline{M}$ TTA in benzene by
   stirring for 10 min. (Note 2.) Wash TTA phase 3 times
   with 10 ml of 1 $\underline{M}$ HNO_3.

2. Back extract Zr with 10 ml of 2 $\underline{N}$ HF by stirring for a
   few min. Add 1 ml of Ba^{++} (50 mg/ml) reagent, centrifuge
   and decant. Wash the Ba_2ZrF_6 precipitate with 10 ml of
   H_2O.

3. Dissolve ppt. in 3 ml 5% H_3PO_3, 1 ml conc. HNO_3 + 5 ml
   H_2O, (a clear solution should result). Add $\frac{1}{2}$ ml conc.

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H_2SO_4, centrifuge and discard ppt. Add conc. NH_4OH to supernate, centrifuge and decant. Wash ppt., dissolve in 3 ml conc. HCl, dilute to 15 ml and add 15 ml of 16% mandelic acid solution. Heat on a steam bath for 10 min. Centrifuge and decant. Wash ppt. with 10 ml of hot H_2O.

4. Filter ppt. through a weighed filter disc, wash with hot H_2O, alcohol and ether and dry at 110°C for 10 min. Cool and weigh as Zr tetramandelate.

Note 1

Zr carrier standardized as follows:

Pipet 3 ml of Zr carrier solution ($\sim$ 5 mg/ml) into a 40 ml centrifuge tube and add 1 ml of conc. HCl. Dilute to 10 ml, heat to boiling and add 20 ml of 16% mandelic acid solution. Heat on a steam bath for 10 min and filter through a weighed sintered glass crucible. Wash with hot H_2O, alcohol and ether and dry at 110°C for 10 min. Cool and weigh as Zr tetramandelate.

Zirconium tetramandelate $Zr(C_6H_5CHOHCOO)_4$

Gravimetric factor: 7.62

Note 2

If Pu is present it will extract with the Zr. To prevent extraction, the Pu must be reduced to the trivalent state. This may be accomplished by treatment with KI and $N_2H_4 \cdot 2HCl$ or, better, by reduction with H_2 using a Pt black wire as catalyst. The original solution should be converted to an HCl medium for the reduction of Pu. The extraction of Zr may be carried out from 1 $\underline{M}$ HCl solution.

Procedure 2: Determination of Zr^{95} in Fission
Product Mixtures.

Source: Richard B. Hahn and Richard F. Skonieczny,
          Nucleonics, Vol. 14, No. 2, p. 56 (Feb.1956).

The barium fluozirconate method [41] is commonly used for
determining radioactive zirconium (Zr^{95}) in fission products.   In
this procedure zirconium is separated from other activities by
precipitation as insoluble barium fluozirconate, followed by a
final precipitation with cupferron.   This is ignited to zirconium
dioxide, which is then weighed and counted.

    This method gives excellent separations from other activities.
The only disadvantage lies in the use of cupferron.   Cupferron [42]
(the ammonium salt of nitroso phenyl hydroxylamine) is unstable
in water, hence solutions must be prepared freshly before use,
or must be stored under refrigeration.   The cupferron-zirconium
precipitate is bulky and spatters badly upon ignition.   Because
of these disadvantages, other reagents were considered.   Man-
delic acid and its derivative_ seemed most promising.

    Kumins [43] showed that mandelic acid was a specific precip-
itant for zirconium.   He devised a procedure for determining
zirconium in the presence of various interfering elements.   Asta-
nina and Ostroumov [44] found that under controlled conditions,
the zirconium mandelate precipitate could be weighed directly
without ignition to the oxide.   Zirconium tetramandelate is a
dense, crystalline precipitate that is easily filtered and
washed.   It can be readily mounted and counted in radiometric
analysis.

Modified Procedure

    By substituting mandelic acid for cupferron, the following
modification of Hume's barium fluozirconate procedure was devised.

PROCEDURE 2 (Cont'd.)

The first five steps are essentially the same as those given by
Hume, with the exception that the volume and weights of reagents
are only about one-fourth as large. This modification was neces-
sary to minimize self-absorption of the beta particles by the
final precipitate of zirconium tetramandelate. Five milligrams
of zirconium carrier gave optimum results. (See Table 1.)

TABLE 1—Effect of Carrier Weight on Self-Absorption of Beta Activity

Zirconium carrier (mg)	Zirconium tetramandelate (mg)	Zirconium yield (%)	Activity* (cpm/ml)
4.68	22.4	62.67	3.27×10^5
4.68	21.1	59.04	3.43×10^5
9.36	43.2	60.53	2.68×10^5
9.36	37.2	52.12	2.75×10^5
18.72	96.2	67.41	1.60×10^5
18.72	96.3	67.48	1.59×10^5

*3.50×10^5 cpm of Zr activity added to each sample.

The procedure is as follows:

1. Add 5 mg of zirconium carrier (in zirconyl nitrate solu-
tion) to 1 ml of 6$\underline{N}$ nitric acid in a Lusteroid centrifuge tube.
Add a known amount of the radioactive solution to be analyzed,
0.5 ml of 27$\underline{N}$ (conc.) hydrofluoric acid and mix thoroughly.

2. Add 0.25 ml of lanthanum nitrate solution (10 mg
La^{3+}/ml), stir thoroughly, centrifuge, add a second 0.25 ml of
lanthanum nitrate carrier, and centrifuge the precipitate down on

top of the first precipitate. Decant the supernate to a clean Lusteroid tube and discard the precipitate.

3. Add 1 ml of barium nitrate carrier solution. Stir thoroughly, centrifuge, and discard the supernate.

4. Suspend the precipitate in 2 ml water, add 1 ml of saturated boric acid solution, dissolve by adding 0.25 ml of 15N (conc.) nitric acid and stirring until a clear solution is obtained. Add 0.5 ml of barium nitrate carrier solution and 0.25 ml of conc. hydrofluoric acid to the clear solution. Stir, then centrifuge down the precipitate and discard the supernate.

5. Repeat step 4.

6. Suspend the precipitate in 2 ml of water and 0.5 ml of boric acid. Dissolve by adding 2 ml of 6$\underline{N}$ hydrochloric acid. Add 6$\underline{N}$ sodium hydroxide while stirring to the above solution until it is basic. Centrifuge and discard the supernate.

7. Dissolve the precipitate of zirconium hydroxide by adding 3 ml of 12$\underline{N}$ (conc.) hydrochloric acid and 3 ml of water. Transfer this solution to a glass centrifuge tube. Rinse the Lusteroid tube twice with 1-ml portions of water and add these washings to the solution in the glass tube. Add 10 ml of saturated (15%) mandelic acid solution. Stir and heat in a water bath at 80°-90°C for about 20 min.

8. Filter the hot solution using weighed 1-cm filter paper disks in a Hirsch funnel. Wash with 10 ml of 5% mandelic acid-2% hydrochloric acid mixture, then with three 5-ml portions of 95% ethyl alcohol and finally with two 5-ml portions of ethyl ether. Transfer the precipitate and filter paper to a tared watch glass and dry under a heat lamp for about 5 min. Weigh, then mount for counting.

Reagents

Zirconyl nitrate, lanthanum nitrate, barium nitrate, and boric acid are prepared as in Hume's procedure [41]. Mandelic acid (saturated): 160 gm of solid mandelic acid dissolved in 1 liter of water.

5% mandelic acid-2% hydrochloric acid wash solution: 50 gm of solid mandelic acid and 48.5 ml of concentrated hydrochloric acid (37%) are dissolved in enough distilled water to make 1 liter of solution.

Sodium hydroxide (6$\underline{N}$): 240 gm of solid NaOH dissolved in distilled water to make 1 liter of solution.

Discussion

The procedure was tested by analyzing identical samples of zirconium-niobium tracer by Hume's cupferron method and by the mandelic acid method given previously. A mica end-window (2.3 mg/cm^2) G-M tube and scaler were used for beta counting.

The data in Table 2 show the mandelic acid method gives results comparable to those obtained in the cupferron method.

A second series of samples were run in which the gamma activity was counted (see Table 3). A bismuth-wall G-M tube and scaler were used.

The gamma counts obtained by the mandelic acid method were 6-14% lower than those obtained by the cupferron method. No suitable explanation can be offered for this discrepancy. The mandelic acid method, therefore, is not recommended for analyses made by gamma count.

Separation from F.P. Activities

To study the effectiveness of separation of zirconium activity from other fission products, the mandelic acid procedure was

TABLE 2—Zr^{95} Determination by Cupferron and Mandelic Acid Methods (Beta Count[*])

Sample	Cupferron (cpm)	Mandelic acid (cpm)
1	699 778	748 761
2	791 788	766 779
3	3.63×10^5	3.50×10^5 3.87×10^5
4	2.74×10^5 2.73×10^5	2.61×10^5 2.71×10^5
5	2.40×10^5 2.44×10^5	2.39×10^5 2.40×10^5

[*]Accuracy is ±3%.

TABLE 3—Zr^{95} Determination by Cupferron and Mandelic Acid Methods (Gamma Count)

Sample	Cupferron (cpm)	Mandelic acid (cpm)
1	8,432 8,296	7,327 7,385
2	7,641 7,517	6,900 6,625
3	8,609 8,332	7,829 7,782
4	7,671 7,532	7,119 6,703

repeated with samples containing approximately 10^4 beta counts per minute of Ce^{144}-Pr^{144}, Nb^{95}, and Sr^{90}-Y^{90}. In all cases less than 100 cpm was obtained. Thus the method can be used for determining zirconium in the presence of these activities.

p-Bromomandelic Acid

Experiments were conducted using p-bromomandelic acid (45) in place of mandelic acid. The precipitates of zirconium tetra-p-bromomandelate were much larger in weight and in volume than those obtained with mandelic acid. The analytical results were poor owing to self-absorption of the beta particles by the precipitate. Since this reagent has no particular advantage over mandelic acid, it is not recommended.

* * *

Procedure 3: Zirconium.

Source: G. M. Iddings in Radiochemical Procedures in Use at the University of California Radiation Laboratory (Livermore) Report UCRL-4377, Aug. 10, 1954.

Purification: 5×10^{13} Atoms of Zr^{97} isolated from a 1-day-old mixture containing 10^{15} fissions exhibited no contaminating activity when decay was followed through six half lives. (See Note at end of procedure.)

Yield: ~ 50 per cent.

Separation time: About four hours.

1. To a solution of the activity, at least 2$\underline{N}$ in HCl, add 10 mg Zr carrier and several mg of La carrier. Make the solution 0.5$\underline{M}$ in HF. Centrifuge and discard the precipitate.

2. Add three drops of saturated $BaCl_2$ solution to the supernatant. Centrifuge and discard supernatant. Wash precipitate with water.

3. To the precipitate add 4 ml of saturated H_3BO_3 solution, 10 ml of water and 2 ml conc. HNO_3. To the clear solution add several drops of conc. H_2SO_4 and a few drops of two percent aerosol. Centrifuge and discard the precipitate.

4. To the supernatant add NH_4OH in excess. Centrifuge precipitate and discard supernatant. Wash precipitate twice with dilute ammonia.

5. Add 10 ml conc. HCl to the precipitate. Dilute the solution to $2\underline{N}$ HCl.

6. Transfer solution to a 125-ml, open top, cylindrical separatory funnel (with stem detached immediately below the stopcock). Add 30 ml of $0.4\underline{M}$ thenoyltrifluoroacetone (TTA) solution in benzene and equilibrate layers for 30-40 minutes by rapid stirring with a motor-driven glass stirring rod (paddle).

7. Allow layers to separate. Drain and discard aqueous layer. Wash organic phase four times with 15 ml of conc. HCl, allowing ten minutes for each wash.

8. Evaporate the organic layer in a No. 1 porcelain crucible under a lamp.

9. When the benzene has evaporated and only the Zr-TTA compound remains, moisten the solid with a few drops of conc. H_2SO_4 and heat very gently, at first (to minimize spattering).

10. Ignite to ZrO_2 at 800°C. Pulverize the solid and transfer to a tared aluminum hat.

NOTE: The above procedure will not separate from protactinium isotopes if these are present in the original solution.

In this case, either one of the following procedures can
be interposed between steps 4 and 5:

A. Pass the solution (12$\underline{N}$ in HCl) through a Dowex-1 anion
exchange resin column (50-100 mesh), 6 mm i.d. x 8 cm in
length. Pass 5 ml conc. HCl through column. Discard
effluents. Pass 15-20 ml of 7$\underline{N}$ HCl through column.
Collect effluent and dilute to 2$\underline{N}$ HCl. Proceed with
step 5. (Elution with 7$\underline{N}$ HCl elutes zirconium,
leaves protactinium on column.)

B. Make solution $\sim$7$\underline{N}$ in HCl. Add an equal volume of di-
isopropyl ketone and equilibrate layers for a few
minutes. Discard organic layer. Repeat DIPK extrac-
tion twice.

Procedure 4: Zirconium.

Source: Goeckerman, in "Chemical Procedures used in
Bombardment Work at Berkeley," W. W. Meinke
(UCRL-432, Aug. 1948).

Target material: $\sim$ 1 g Bi metal   Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles   Equipment required: Centri-
fuge, tubes, lusteroid
cones, ice, small porcelain
crucible.

Yield: $\sim$ 60%

Degree of purification: Decontamination factor $\sim$ 10^4 from fis-
sion and spallation products (no Th & negligible Hf activ-
ity present).

Advantages: Good yield of pure Zr, if no Hf activity present.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Zr, make sample up to ~ 5 ml of 5 $\underline{N}$ HNO_3 in a lusteroid cone. Add 2 ml conc. HF & 10 mg La. Repeat LaF_3 pptn.

(2) Add 50 mg Ba to supn. Wash $BaZrF_6$ ppt.

(3) Dissolve ppt in 2 ml 5% H_3BO_3, add 1 ml conc. HNO_3 & 5 ml H_2O, repeat LaF_3 pptn twice (as in (1) and (2)).

(4) Repeat $BaZrF_6$ pptn.

(5) Dissolve with 2 ml H_3BO_3, 2 ml conc. HCl, & 5 ml H_2O. Add 1 drop conc H_2SO_4 & cont out $BaSO_4$.

(6) Dil supn to 20 ml & add 2 ml 6% cupferron in ice bath, filter, wash with cold 1 $\underline{N}$ HCl containing cupferron, ignite in a porcelain crucible. Weigh as ZrO_2 (13.5 mg per 10 mg Zr).

Remarks: This procedure probably effects no separation from Hf.Th I don't know about. Zr can be separated from Hf by the use of TTA or anion exchange resins.

Procedure 5: Zirconium.

Source: Newton, in "Chemical Procedures used in Bombardment work at Berkeley," W. W. Meinke (UCRL-432, Aug. 1948).

Target material: Thorium metal (.1-1 gm)   Time for sep'n: 1-2 hrs.

Type of bbdt: 60" alphas   Equipment required:

                                             Standard

Yield: ~ 60%

Procedure: The Th metal is dissolved in conc HCl plus a few drops of .2 $\underline{M}$ $(NH_4)_2SiF_6$ to clear up the black residue. The HCl is diluted to 2 $\underline{N}$ and an aliquot taken.

(1) Use a lusteroid tube, add HNO_3 to make 5 ml of soln 4 to 5 molar in HNO_3. Add 20 mg Zr carrier, 2 ml conc HF and mix well. Centrifuge off ThF_4.

(2) Add 10 mg La^{+++} carrier. Mix well and centrifuge. Add a second 10 mg La^{+++} and centrifuge down on top of 1st ppt. Decant.

(3) Add 50 mg Ba^{++} to supn. Mix and let stand 1 min. Centrifuge.

(4) Dissolve ppt by adding 2 ml 5% H_3BO_3 and stirring. Add 1 ml conc HNO_3 and 5 ml H_2O. Add 2 ml 27N HF and 50 mg Ba^{++}. Stir until ppt forms and let stand 1 minute longer.

(5) Repeat (4).

(6) Dissolve with 2 ml H_3BO_3, 2 ml conc HCl and 5 ml H_2O. Add 1 drop conc H_2SO_4 and centrifuge off $BaSO_4$.

(7) Transfer supernate. Dilute to 20 ml and ppt Zr at ice temp with 2 ml 6% cupferron reagent. Centrifuge. Wash ppt with 1 ml cold HCl containing a few drops of cupferron. Filter at once.

(8) Ignite ppt to ZrO_2 in porcelain crucible. Weigh.

Remarks: This procedure has been described previously. (Phys. Rev. $\underline{75}$, 17 (1949)).

Preparation of carrier solutions: Dissolve 29.40 gms $ZrO(NO_3)_2 \cdot 2H_2O$ in water, adding a few drops of HNO_3 if necessary to clarify the solution. Dilute to 1 liter.

Standardization: Take 5 ml carrier. Make 2 $\underline{M}$ in HCl and cool
in ice bath to 10° C. Add a slight excess of 6% cupferron solu-
tion. Filter and ignite in a porcelain crucible with care to
prevent splattering of oils distilled from cupferron. Final ig-
nition temperature 600° C. Weigh as ZrO_2. (6% cupferron solu-
tion: 6 gms cupferron and pinch of $(NH_4)_2CO_3$ in 100 ml H_2O.
Solution slowly decomposes.)

Procedure 6. Carrier-Free Zirconium from Proton Bombard-
ment of Nb.

Source: E. K. Hyde and G. D. O'Kelley, Phys. Rev. $\underline{82}$, 944
(1951).

Thin strips of spectrographically pure niobium metal were
bombarded for periods of from 5 to 20 minutes with 100-Mev pro-
tons in the 184-inch cyclotron. Such bombardments produced $\sim 10^9$
disintegrations per minute of total zirconium activity. Numerous
bombardments were carried out in the course of the research.

The niobium target foils were dissolved immediately by drop-
ping them into a mixture of concentrated HNO_3 and concentrated HF.
Ten milligrams of lanthanum nitrate were added, with stirring to
precipitate LaF_3. All the zirconium activities in solution were
coprecipitated with the LaF_3 and cleanly separated from the niobium,
a separation which has been studied by Ballou[46] and by Gest, Burgus,
and Davies[47] The co-separation is believed to be caused by the
surface adsorption of $ZrF_6^=$ ion on LaF_3. The LaF_3 precipitate was
contacted with strong KOH to metathesize the fluoride to the hy-
droxide compound. Then the hydroxide was dissolved in $2\underline{M}$ $HClO_4$.
In order to scavenge out any traces of niobium which might remain,

manganese dioxide was precipitated from the resulting solution by adding in turn Mn^{++} and $KMnO_4$.

The zirconium was extracted from the $HClO_4$ solution by contacting it intimately for 15 minutes with an equal volume of a 0.2$\underline{M}$ solution of α-thenoyltrifluoroacetone (hereinafter referred to as TTA) in benzene. Aluminum nitrate was added to the aqueous phase to complex any traces of fluoride ion which might remain from the metathesis step, since the fluoride ion interferes with the TTA extraction. The work of Connick and McVey[48] and of Huffman and Beaufait[49] was used as a guide in this purification step. The Zirconium-TTA complex in benzene solution was thoroughly scrubbed of possible traces of extraneous activities by contact with 2$\underline{M}$ $HClO_4$ wash solution. Then the benzene solution was diluted 10-fold and contacted with one-tenth its volume of concentrated HCl to effect the return of the zirconium to an aqueous medium.

This zirconium fraction was quite pure both chemically and radioactively; but to be absolutely certain of its purity, it was subjected to an additional purification step, capable in itself of effecting excellent decontamination from most other elements. The HCl solution was slowly passed through a short column (2 cm x 4 mm) of Dowex-1 anion exchange resin[50] which had been pre-equilibrated with concentrated HCl. Unpublished research results of this laboratory[51] have shown that from solutions 10$\underline{M}$ or higher in HCl concentration, negatively charged chloride complex ions of zirconium adsorb strongly on Dowex anion resin. From solutions of concentration less than 6$\underline{M}$, they do not adsorb. Niobium forms even stronger complexes, but the other elements which could possibly be present are not adsorbed. Hence, by passing the concentrated HCl solution

through the resin column and rinsing it well with more concentrated
HCl solution, the zirconium was quantitatively and cleanly ad-
sorbed. The zirconium could be immediately desorbed by passing
a 4M HCl solution through the column. In some
experiments, the zirconium activity was left on the column and
periodically milked of its yttrium daughter activity by rinsing
the column with 10-12M HCl at the proper time. The zirconium
was retained quantitatively and the yttrium quantitatively removed
by this step.

This isolation procedure has several advantages over some
previous methods commonly used for radiochemical isolation of zir-
conium such as co-precipitation on barium fluozirconate. A prin-
cipal one is that the zirconium is isolated in a carrier free
state.

Procedure 7: Preparation of Carrier-free Zirconium Tracer .

Source: N. E. Ballou, Radiochem. Studies: The Fission
         Products, C. D. Coryell and N. Sugarman, eds.,
         NNES, Vol. 9, Paper 249.

A procedure is presented for the preparation of carrier-
free zirconium tracer. The procedure makes use of the co-separa-
tion of zirconium activity from fission material on thorium iodate.
The method is rapid, and the radiochemical yield is about 80 per
cent. The purity of the final product is satisfactory.

INTRODUCTION

A rapid method for the isolation of zirconium activity from
ether-extracted uranyl nitrate has been developed. Zirconium

is co-precipitated with $Th(IO_3)_4$ from $4\ \underline{M}\ HNO_3$ containing H_2O_2 to keep niobium (columbium) in solution and to ensure the trivalency of cerium. The precipitation of thorium oxalate removes the thorium and UX_1 (Th^{234}), leaving carrier-free zirconium in an oxalate solution.

PROCEDURE

To 1 ml of the aqueous concentrate of ether-extracted uranyl nitrate are added 5 mg of thorium carrier, 1 ml of 3 per cent H_2O_2, 8 ml of conc. HNO_3, and 20 ml of $0.35\ \underline{M}\ HIO_3$. The solution and precipitate are cooled and allowed to stand for 5 min. The precipitate is removed by centrifugation and dissolved in HCl and SO_2. Thorium hydroxide is precipitated with NH_4OH, and this precipitate is dissolved in 8 ml of conc. HNO_3. After the addition of 1 ml of 3 per cent H_2O_2 the thorium is precipitated with 20 ml of $0.35\ \underline{M}\ HIO_3$ and allowed to stand for 5 min. The precipitate of $Th(IO_3)_4$ is dissolved in HCl and SO_2, and $Th(OH)_4$ is precipiated from this solution with NH_4OH.

After the $Th(OH)_4$ precipitate is dissolved in 1 ml of $6\ \underline{N}$ HCl and 15 ml of H_2O, the solution is heated to boiling and 5 ml of sat. $H_2C_2O_4$ solution is added. The solution is cooled and allowed to stand for 10 min, and the $Th(C_2O_4)_2$ precipitate is centrifuged off. A second precipitation of $Th(C_2O_4)_2$ from the solution is made by adding 5 mg of thorium carrier and letting it stand for 30 min. The $Th(C_2O_4)_2$ precipitate is then centrifuged off, leaving a solution of zirconium activity. If a zirconium tracer solution free of oxalic acid is desired, $Fe(OH)_3$ can be precipitated from the solution. This carries the zirconium activity. The iron can then be removed by extraction into isopropyl ether from $8\ \underline{N}$ HCl solution in the usual manner.

DISCUSSION

A representative zirconium preparation was analyzed for niobium contamination by adding niobium carrier as the oxalate complex and then precipitating Nb_2O_5 by the destruction of the oxalate complex with MnO_4^-. After the removal of the co-precipitated MnO_2 with SO_2, the Nb_2O_5 was dissolved in oxalic acid and reprecipitated. This precipitate was found to contain about 4 per cent of the original activity, about one-half of which could be attributed to growth of the 35d Nb^{95} daughter since the preparation of the 65d Zr^{95} tracer.

A preparation was made which used 0.5 ml of 30 per cent H_2O_2 instead of 1 ml of 3 per cent H_2O_2. The niobium decontamination was not improved. In the absence of H_2O_2, niobium precipitates with $Th(IO_3)_4$ about as efficiently as zirconium does.

The zirconium in solution after the removal of the niobium was precipitated on $Fe(OH)_3$. An aluminum absorption curve of the activity was identical with the aluminum absorption curve of 65d Zr^{95} isolated with carrier and carefully purified from radiochemical impurities.

A sample of the zirconium tracer was subjected to the complete isolation procedure, and 78 per cent recovery was attained. The time required is about 2 hrs. If the tracer is to be used under conditions requiring the absence of niobium activity, it should be prepared just before use in order to avoid contamination from the growth of the 35d Nb^{95} daughter of 65d Zr^{95}.

Procedure 8: Carrier-free Zr^{89} from the $Y^{89}(d,2n)$ Reaction.

Source: A. N. Murin, V. D. Nefedov, I. A. Yutlandov,
"The Production and the Separation of Carrier-
free Radioactive Isotopes," Uspeckhi Khimii, 24,
527 (1955). (AERE Lit Trans. 722, Harwell, 1956.)

<u>Zirconium</u>. Zr_{40}^{89}; T = 79.3 hours; K (75%) β^+ (25%);
E_{β}^+ = 0.910 Mev; γ; E_{γ} = 0.92 Mev.

Production reaction: $Y^{89}(d,2n)Zr^{89}$.

Irradiated Y_2O_3 was dissolved in hydrochloric acid and the
solution was evaporated almost to dryness and was diluted with
water   . The yttrium was separated in the form of YF_3 by pre-
cipitation with HF. The excess HF was removed by evaporation
with a few millilitres of concentrated H_2SO_4. After dilution,
$FeCl_3$ was introduced into the solution and was precipitated in
the form of $Fe(OH)_3$ with the help of NH_4OH. Thus the radio-zirco-
nium was quantitatively adsorbed by the precipitate of $Fe(OH)_3$.
After dissolving the precipitate of $Fe(OH)_3$ in 6$\underline{N}$ HCl the carrier
was removed by extraction with ether.

Procedure 9: Preparation of Carrier-free Zirconium-Niobium
Tracer.

Source: J. A. Marinsky, D. N. Hume, and N. E. Ballou in
NNES, Vol. 9, Paper 250.

A rapid procedure for the preparation of very pure carrier-
free zirconium-niobium tracer involves the chloroform extraction
of the cupferrides of zirconium and niobium activities from an
irradiated uranyl nitrate solution.

1. INTRODUCTION

This procedure makes use of the fact that zirconium and niobium form, at tracer concentrations, very stable chloroform-soluble cupferrides[52] in acid solutions. The two activities are separated from the other fission elements almost quantitatively to yield a mixture of pure zirconium-niobium tracer.

To a uranyl nitrate solution made 6$\underline{M}$ in HCl and 0.05$\underline{M}$ in SO_2 are added $CHCl_3$ and a freshly prepared 6 per cent solution of cupferron. The final uranyl nitrate concentration is about 8 per cent. The zirconium and niobium activities are extracted by the $CHCl_3$. A second extraction is performed on the solution again with $CHCl_3$ and cupferron. The $CHCl_3$ extracts are combined, and the small amount of contaminating activities is almost completely removed by a wash with 6$\underline{M}$ HCl. This wash also serves to remove considerable amounts of excess cupferron and its decomposition products. The $CHCl_3$ layer is then treated with a portion of dil. HCl to which a few drops of bromine are added. The cupferrides are decomposed, and zirconium and niobium activities enter the aqueous phase. Boiling this solution helps to remove traces of organic matter from the decomposed cupferron, and the niobium and zirconium activities are available in dil. HCl with a trace of HBr.

2. PROCEDURE

A 5-ml sample of 32 per cent uranyl nitrate in a separatory funnel is made 6$\underline{M}$ in HCl and 0.05$\underline{M}$ in SO_2 (in a volume of about 20 ml). A 10-ml portion of $CHCl_3$ is added. The funnel is cooled for 5 to 10 min in an ice bath. A 1.2-ml sample of cold 6 per cent cupferron (Note 1) is added, and the funnel is shaken vigorously for 30 sec. After separation the $CHCl_3$ layer is

drained off. Another portion of $CHCl_3$ and cold 6 per cent cup-ferron is added to the aqueous layer, and the funnel is again shaken vigorously for about 30 sec. The $CHCl_3$ layer is again drained off. The two $CHCl_3$ layers are combined, and the aque-ous layer is discarded.

Both the $CHCl_3$ layer (in the separatory funnel) and a 10-ml wash solution $6\underline{M}$ in HCl and $0.05\underline{M}$ in SO_2 are cooled in an ice bath for about 5 min. The two solutions are then combined, and 1.2 ml of cold cupferron is added. After vigorous shaking for 30 sec the layers are separated and the aqueous phase is discarded.

To the $CHCl_3$ layer in a separatory funnel is added 5 ml of $6\underline{M}$ HCl. Several drops of Br_2 are added, and the funnel is shaken vigorously for several minutes at 10-min intervals. After 1 hr the layers are separated and the $CHCl_3$ layer is discarded (Note 2). The aqueous layer is boiled until the solution is only slightly colored (Note 3).

Notes. 1. Because of the instability of the cupferron it is necessary to perform the extraction as rapidly as possible when oxidizing materials are present in the solution (e.g., nitrites and nitrates). In solutions containing no oxidant, cooling is un-necessary and SO_2 addition can be neglected.

2. The separation of the two layers can be accomplished efficiently by drawing off most of the original $CHCl_3$ layer, add-ing fresh $CHCl_3$, and repeating the withdrawal. This may be done three or four times so that, when the aqueous phase is finally collected, very little organic material from the original $CHCl_3$ phase will be present to contaminate the product.

3. If the presence of oxalic acid in the tracer solution is not objectionable, the solution may be made 0.5 per cent in

$H_2C_2O_4$ before boiling. The presence of oxalic acid prevents the strong adsorption of the activities on the glass walls. Both zirconium and niobium are readily adsorbed on glassware from the $CHCl_3$-cupferron solution. It is good practice to store niobium tracer as an oxalate solution and to destroy oxalic acid by fuming with conc. HNO_3 immediately before use.

3. DISCUSSION

The yield of zirconium is 55 to 60 per cent; the yield of niobium is 30 to 35 per cent. Analyses for possible contaminating activities indicated the following upper limits: lanthanum, 0.03 per cent; barium, 0.06 per cent; ruthenium, 0.07 per cent; and tellurium, 0.004 per cent.

Procedure 10: Preparation of Carrier-free Zirconium and Niobium Tracers.

Source: R. Overstreet and L. Jacobson in NNES, Vol. 9, Paper 251.

A procedure is presented for the simultaneous preparation of carrier-free zirconium and niobium activities from irradiated uranyl nitrate. The procedure makes use of the carrying of zirconium and niobium on thorium iodate to isolate these elements from most of the other fission products. The separation of niobium and zirconium from each other is based on the formation of a soluble complex oxide of niobium by K_2CO_3 fusion.

1. INTRODUCTION

In the present procedure for preparing carrier-free zirconium and niobium activities from irradiated uranyl nitrate, the

bulk of the uranyl nitrate is removed by ether extraction. Zirconium, niobium, and other ammonia-insoluble fission products are separated from the remaining uranyl nitrate by complexing the uranium with hydroxylamine in ammoniacal solution and carrying the insoluble fission products on $Fe(OH)_3$. Zirconium, niobium, and cerium are then separated as the iodates by the use of thorium carrier,[*] and the zirconium and niobium are separated from the cerium and thorium by means of HF. The niobium is removed from the zirconium by repeated fusions with K_2CO_3, thorium holdback carrier being used for the zirconium. The thorium is finally separated from the zirconium by precipitation with HF. Each of the purified activities is carried on $Fe(OH)_3$, and the iron is then removed by ether extraction.

2. PROCEDURE

Reduce the amount of uranyl nitrate to about 5 g by means of repeated ether extractions. Treat the concentrated solution with 100 mg of iron carrier and 15 g of $NH_2OH \cdot HCl$, and make strongly alkaline with NH_4OH. Heat to boiling, cool, and centrifuge the $Fe(OH)_3$ precipitate. Dissolve the precipitate in HCl and reprecipitate twice more in the presence of $NH_2OH \cdot HCl$. Dissolve the final $Fe(OH)_3$ precipitate in HNO_3, add 25 mg of thorium carrier, and make 5$\underline{N}$ in HNO_3. Precipitate the thorium as $Th(IO_3)_4$ by the addition of an equal volume of 0.35$\underline{M}$ KIO_3 reagent. Centrifuge, and wash the precipitate with dil. KIO_3 solution. Decompose the precipitate by repeated evaporations with conc. HCl and evaporate to dryness.

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[*]Editors' Note: Thorium iodate in the presence of H_2O_2 was used by N. E. Ballou (Paper 249, this volume) to prepare carrier-free zirconium activity.

Dissolve the residue in 20 ml of $5\underline{N}$ HNO_3 and add 5 mg each of barium, strontium, yttrium, tellurium, ruthenium, cesium, and lanthanum carriers. Precipitate the thorium as before by the addition of 20 ml of KIO_3 reagent. Centrifuge, wash the precipitate, and decompose with HCl as before. Dissolve the final residue in $1\underline{N}$ HCl and add 10 mg of cerium carrier. Make the solution $2\underline{N}$ in HF, centrifuge, wash, and discard the precipitate. Combine the centrifugate and washings, and evaporate to fuming with 1 ml of conc. H_2SO_4.

Dilute the solution to about 40 ml and add 10 mg of thorium carrier. Make basic with NH_4OH, centrifuge, and wash the precipitate of $Th(OH)_4$. Evaporate to dryness, fuse with 4 g of K_2CO_3, cool, and extract the mass with 10 ml of H_2O. Centrifuge the suspension, and wash the residue with 10 ml of 30 per cent K_2CO_3 solution. Combine the supernatant solution and washings, and set aside for the separation of niobium.

Fume the ThO_2 residue from the K_2CO_3 fusion with 2 ml of conc. H_2SO_4 for about 15 min. Cool and dilute to 30 ml with H_2O. Add 5 mg of niobium carrier, make basic with NH_4OH, centrifuge, and wash the resulting precipitate. Dry and again subject the precipitate to the zirconium-niobium separation by means of K_2CO_3 fusion. Repeat the fusion on the ThO_2 residue, but do not add niobium carrier. Dissolve the final ThO_2 residue with H_2SO_4 as described previously, and dilute to 40 ml. Make the solution $2\underline{N}$ in HF, centrifuge, and wash the ThF_4 precipitate with dil. HF.

Combine the supernatant solution and washings from the fluoride precipitate, evaporate to fuming, and dilute. Add 10 mg of iron carrier and make the solution basic with NH_4OH. Centrifuge, wash the precipitate, and dissolve in 15 ml of $9\underline{N}$ HCl. Ex-

tract the iron with isopropyl ether, leaving a carrier-free solution of zirconium activity.

Acidify the solution that was set aside for niobium separation, and precipitate $Th(OH)_4$ with NH_4OH. Centrifuge, wash the precipitate, and dissolve in HNO_3. Precipitate $Th(IO_3)_4$ as before, decompose with HCl, and dilute to 50 ml. Make the solution 1$\underline{N}$ in HCl and 2$\underline{N}$ in HF, and centrifuge the ThF_4 precipitate. Wash with 1$\underline{N}$ HF and discard the precipitate.

Add 2 ml of conc. H_2SO_4 and 10 mg of zirconium carrier to the combined supernatant solution and washings, and evaporate to fuming. Cool, dilute with H_2O; and precipitate $Zr(OH)_4$ with NH_4OH. Fuse the precipitate with 3 g of anhydrous K_2CO_3, and extract the melt with 10 ml of H_2O. Centrifuge the residue, and wash with 10 ml of 30 per cent K_2CO_3 solution. Set aside the filtrate and washings, and fuse and extract the residue twice more. Combine the filtrates and washings from all three fusions,[*] and acidify. Add 10 mg of iron carrier, and precipitate $Fe(OH)_3$ with NH_4OH. Centrifuge, wash the precipitate, and dissolve in 9$\underline{N}$ HCl. Remove the iron by repeated extractions with isopropyl ether, leaving a carrier-free solution of niobium activity.

3. DISCUSSION

An analysis for zirconium and niobium from an aliquot of the pure zirconium tracer solution was carried out 24 hrs after the completion of the zirconium preparation. Of the total activity, 3.3 per cent was found in the niobium fraction.

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[*]Previous experiments with radiozirconium showed that no zirconium passes into the filtrate from carbonate fusions.

An aliquot of the final zirconium solution was taken for
a test of radioactive purity. Ten milligrams each of zirconium,
strontium, barium, thorium, yttrium, cerium, lanthanum, ruthenium,
and tellurium carriers was added to the aliquot. The solution was
made $3\underline{N}$ in HCl in a volume of 50 ml. One milliliter of 85 per
cent H_3PO_4 was added, and the mixture was boiled for 30 min. The
precipitate of zirconium phosphate carrying zirconium and niobium
was centrifuged out and washed. Another 10 mg of zirconium
carrier was added to the combined supernatant solution and wash-
ings, and the mixture was again boiled. The second zirconium
phosphate precipitate was centrifuged out and washed. The com-
bined supernatant solution and washings were evaporated to dry-
ness in a porcelain dish. The zirconium phosphate precipitates
were combined and also taken to dryness in a porcelain dish. The
activities of the two fractions were measured with a thin-window
Lauritsen electroscope. It was found that 99.8 per cent of the
total activity was in the zirconium-niobium fraction.

To a suitable aliquot of the purified niobium solution, 100
mg of niobium carrier and 10 mg each of strontium, yttrium, zir-
conium, tellurium, cesium, barium, lanthanum, cerium, and thorium
carriers were added and treated for the quantitative removal of
the niobium alone as Nb_2O_5. The solution was treated with a few
milliliters of HF and then was evaporated to fumes with $HClO_4$.
The material was fumed to a volume of 3 ml, cooled, and boiled
for 15 min with 10 ml of $12\underline{N}$ HCOOH. The solution was then filtered,
and the paper was washed. The filtrate and washings from the
Nb_2O_5 separation were combined and evaporated to dryness, and the
activity was measured. When corrected for self-absorption in the
sample, the activity of this fraction was 5 per cent of the activity

of the aliquot taken. Its absorption curve, however, was very similar to the absorption curve of niobium; this indicated that the purity of the solution was considerably higher than the minimum value of 95 per cent obtained.

Procedure 11: Hafnium.

Source: J. R. Grover, "The Reactions of Ta with 5.7 Bev Protons," (Report UCRL-3932, Berkeley, Sept. 1957).

Barium fluohafnate and barium fluozirconate were precipitated together when ice-cold, saturated barium nitrate solution was added to the chilled target solution. The precipitate was quickly washed with ice water and then slurried for several minutes with an ice-cold mixture of concentrated nitric acid and saturated boric acid. The slurry was diluted with water, to dissolve the sediment, and made basic with ammonium hydroxide. The precipitated hydroxides were washed with water and dissolved in 1 $\underline{M}$ hydrofluoric acid. Cerium carrier was added, and the precipitated fluoride was removed by centrifugation. The solution was chilled in an ice bath, and ice-cold saturated barium nitrate was added to precipitate the hafnium and zirconium. The precipitate was dissolved and the hydroxides were precipitated in the manner described above. This time the hydroxide precipitate was dissolved in 3 $\underline{M}$ perchloric acid. The zirconium and hafnium were extracted from this solution into 0.4 $\underline{M}$ thenoyltrifluoroacetone in benzene, and back-extracted into 5 percent ammonium bifluoride. Boric acid was added to complex the fluoride, and the solution was made basic with ammonium hydroxide. The precipitated hy-

droxides were washed with water and dissolved in 3 $\underline{M}$ perchloric acid. The solution was heated in the hot water bath and 1/2 ml of wet Dowex-50 cation-exchange resin was introduced. The hot suspension was allowed to stand with occasional stirring for a few minutes, then allowed to settle, and the resin was transferred to the top of a Dowex-50 resin bed contained in a column 7 mm by 55 cm. This was done in the same way as is described in the rare earth section. Zirconium was eluted by passing 0.5 $\underline{M}$ sulfuric acid through the column. After the zirconium was completely eluted, that is, after the eluate failed to show a precipitate when made basic with ammonium hydroxide, the hafnium was eluted with 3 $\underline{M}$ sulfuric acid. The hydroxides were precipitated by making the respective eluates basic with excess ammonium hydroxide. The hydroxides were washed with water, slurried with more water, and mounted for counting employing the filter-chimney setup.

This separation is very clean. No trace of the very prominent K x-rays occurring in the decay of hafnium could be found in the zirconium, and spectrographic analysis of the hafnium sample proved the absence of zirconium.

REFERENCES

1. A. J. Zielen and R. E. Connick, J. Am. Chem. Soc. $\underline{78}$, 5785 (1956); E. H. Dewell and A. V. Voight, USAEC Report 15C-146 (1957); J. Schubert and E. E. Conn, Nucleonics $\underline{4}$, No. 6, 2 (1949).

1a. W. H. Burgus, USAEC Report CN-2560, January 1945 (unpublished).

2. See e.g., F. J. Welcher, "Organic Analytical Reagents," (D. Van Nostrand Co., N. Y. 1947) and R. Betcher and C. L. Wilson, "New Methods in Analytical Chemistry," (Reichold, N. Y. (1955)).

3. R. E. Oesper and J. J. Klingenberg, Anal. Chem. $\underline{21}$, 1509 (1949); R. B. Hahn and R. F. Skonieczny, USAEC Report AECU-2908 (1954).

3a. T. Nascutire, Proc. 2nd Geneva Conf. $\underline{28}$, 664 (1958).

3b. L. Kosta and L. Ravnile, Proc. 2nd Geneva Conf. $\underline{28}$, 143 (1958).

4. R. E. Connick and W. H. McVey, J. Am. Chem. Soc. $\underline{71}$, 3182 (1949).

5. J. F. Steinbach, Ph. D. Thesis, University of Pittsburgh, (1953); UCAEC Report NYO-6347.

6. F. L. Moore, Anal. Chem. $\underline{28}$, 997 (1956).

7. E. H. Huffman and L. J. Beaufait, J. Am. Chem. Soc. $\underline{71}$, 3179 (1949).

8. B. G. Schultz and E. M. Larsen, J. Am. Chem. Soc. $\underline{72}$, 3610 (1950).

9. G. Beck, Mikrochim. Acta $\underline{34}$, 282 (1949).

10. E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed. (Interscience (1959).)

11. N. H. Furman, W. B. Mason, and J. S. Pekola, Anal. Chem. 21, 1325 (1949); C. C. Miller and R. A. Chalmers, Analyst. 78, 686 (1953).

12. W. Fischer and W. Chalybaeus, Z. anorg. u. allgem. Chem. 254, 79 (1947); ibid., 255, 277 (1948).

13. R. Bock and E. Bock, Z. anorg. u. allgem. Chem. 263, 146 (1950).

14. J. Rydberg and B. Bernström, Acta Chem. Scand. 11, 86 (1957).

15. E. M. Scadden and N. E. Ballou, Anal. Chem. 25, 1602 (1953).

16. D. F. Peppard, G. W. Mason, and J. L. Maier, J. INC 3, 215 (1956).

17. K. Alcock, et al. J. INC 4, 100 (1957).

17a. C. A. Blake, Jr., et al., Proc. 2nd Geneva Conf. 28, 289 (1958); J. C. White and W. J. Ross, USAEC Report ORNL-2443 (Jan. 7, 1958).

18. A. J. Ayres, J. Am. Chem. Soc. 69, 28 (1947); U S. Patent 2, 567, 661 (Sept. 11, 1951).

19. K. Street, Jr., and G. T. Seaborg, J. Am. Chem. Soc. 70, 4268 (1948); J. E. Neunhan, ibid., 73, 5899 (1951).

20. J. T. Benedict, W. C. Schumb, and C. D. Coryell, J. Am. Chem. Soc. 76, 2036 (1954).

21. Z. Dizder, Bull. Inst. Nuclear Sci., Boris Kidrich (Belgrade) 2, 85 (1953).

22. B. A. J. Lister, J. Chem. Soc. London, 3123 (1951).

23. B. A. J. Lister and T. M. Hutcheon, Research, (London) 5, 291 (1952).

24. H. J. Hettel and V. A. Farsel, Anal. Chem. 27, 1311 (1955).

25. E. R. Tompkins, J. X. Kheper, and W. E. Cohn, J. Am. Chem. Soc. 69, 2769 (1947); W. E. Cohn, G. W. Parker, and E. R.

Tompkins, Nucleonics 3, No. 5 22 (1948); W. E. Brown and W. Riemer III, J. Am. Chem. Soc. 74, 1278 (1952).

26. K. A. Kraus and F. Nelson, Peaceful Uses of Atomic Energy, Vol. 7, Paper P/837 (UN 1956).

27. L. R. Bunney, et al., Anal. Chem. 31, 324 (1959); L. Wish, ibid., 326 (1959); E. C. Freiling, J. Pascual, and A. A. Delucchi, ibid., 330 (1959).

28. E. H. Huffman and R. C. Lilly, J. Am. Chem. Soc. 71, 4147 (1949); ibid., 73, 2902 (1959).

29. K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. 71, 3263 (1949).

30. E. H. Huffman, G. N. Iddings, and R. C. Lilly, J. Am. Chem. Soc. 73, 4474 (1951).

31. W. Forsling, Arkiv. of Kemi 5, 503 (1952).

32. E. K. Hyde and U. D. O'Kelley, Phys. Rev. 82, 944 (1951)

32a. K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. 73, 9 (1951).

33. R. E. Wacker and W. H. Baldwin, USAEC Report ORNL 637 (March 23, 1950).

34. A. G. Maddock and W. Pugh, J. INC 2, 114 (1955).

35. S. Kahn and D. E. Hawkinson, J. INC 3, 155 (1956).

36. E. K. Hyde, USAEC Report UCRL-8703 (April, 1959).

37. E. P. Steinberg, Chap. IV in "Handbook of Instruments and Techniques," (to be published by NRC Subcommittee on Instruments and Techniques; also issued as AEC Report ANL-5622, revised Jan. 1958).

38. B. P. Bayhurst and R. J. Prestwood, Nucleonics 17, 82 (1959).

39. R. L. Heath, AEC Report IDO-16408 (July, 1957).

40. D. G. Olson, AEC Report IDO-14495 (Nov. 1959).

41. D. N. Hume. Determination of zirconium activity in fission by the barium fluozirconate method, in "Radiochemical Studies: The Fission Products," National Nuclear Energy

Series IV-9, Book 3, p. 1499, C. Coryell and N. Sugarman, ed. (McGraw-Hill Book Co., Inc., New York, 1951)

42. G. F. Smith, "Cupferron and Neo-Cupferron," p. 12(G. F. Smith Chemical Co., Columbus, Ohio, 1938)

43. C. A. Kumins, Anal. Chem. 19, 376 (1947)

44. A. A. Astanina, E. A. Ostroumov, Zhur. Anal. Khim. 6, 27 (1951); Chem. Abstracts 45, 6121 (1951)

45. R. E. Oesper, J. J. Klingenberg, Anal. Chem. 21, 1509 (1949)

46. N. Ballou, National Nuclear Energy Series, Plutonium Project Record, "Radiochemical Studies: The Fission Products," (McGraw-Hill Book Co., Inc., New York, to be published 1951), Vol 9B, Paper No. 824.4.

47. Gest, Burgus, and Davies, U. S. Atomic Energy Commission Declassified Document, AECD-2560 (April 18, 1949) (unpublished).

48. R. E. Connick and W. H. McVey, J. Am. Chem. Soc. 71, 3182 (1949).

49. E. H. Huffman and L. J Beaufait, J. Am. Chem. Soc. 71, 3179 (1949).

50. Manufactured by Dow Chemical Company, Midland, Michigan; purchased from Microchemical Specialties Company, Berkeley, California.

51. D. A. Orth and K. Street, Jr., preliminary report on unpublished work, University of California Radiation Laboratory Memorandum MB-IP-451 (January 27, 1950).

52. G. A. Cowan, R. E. Fryell, and H. A. Potratz, Report CK-993, Oct. 9, 1943.