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**NUCLEAR SCIENCE SERIES**

**The Radiochemistry  
of Zirconium and Hafnium**



**U.S.  
Atomic  
Energy  
Commission**

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# **The Radiochemistry of Zirconium and Hafnium**

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Subcommittee on Radiochemistry  
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## 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, 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



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## INTRODUCTION

This volume which deals with the radiochemistry of zirconium and hafnium 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 zirconium and hafnium which might be included in a revised version of the monograph.

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 Anorganischen Chemie, Systems Nr. 43, 8th Edition (Verlag Chemie, GmbH 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).

"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 prepared 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 incorporated 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. 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 <sup>86</sup>   | 17 hr                  | EC                                       | Ni(p,spall.); As <sup>75</sup> (N <sup>14</sup> ,3n) |
| Zr <sup>87</sup>   | 94 min                 | $\beta^+$ , EC                           | Zr <sup>89</sup> ( $\alpha$ ,n)                      |
| Zr <sup>88</sup>   | 85 day                 | EC                                       | Ni(p,spall.)   |
| Zr <sup>89m</sup>  | 4.4 min                | It(93%),EC(5.6%), $\beta^+$ (1.8%)       | Zr(X-ray)  |
| Zr <sup>89</sup>   | 79.3 hr                | EC( $\sim$ 75%), $\beta^+$ ( $\sim$ 25%) | Y(d,2n)  |
| Zr <sup>90m</sup>  | 0.83 sec               | IT                                       | Zr <sup>90</sup> (n,n')                              |
| Zr <sup>93</sup>   | 1.1x10 <sup>6</sup> yr | $\beta^-$                                | Nuclear fission                                      |
| Zr <sup>95</sup>   | 65 day                 | $\beta^-$                                | Nuclear fission                                      |
| Zr <sup>97</sup>   | 17.0 hr                | $\beta^-$                                | Nuclear fission                                      |
| Zr <sup>98</sup>   | $\sim$ 1 min           | $\beta^-$                                | Nuclear fission                                      |
| Zr <sup>99</sup>   | 35 sec                 | $\beta^-$                                | Nuclear fission                                      |
| Hf <sup>170</sup>  | 112 min                | $\beta^+$                                | Lu(p,6n)   |
| Hf <sup>171</sup>  | 16.0 hr                | EC                                       | Lu(p,5n),Yb( $\alpha$ ,3n)                           |
| Hf <sup>172</sup>  | .5 yr                  | EC                                       | Lu(p, $\gamma$ h)( $\alpha$ ,xn),Ta(d,2p9n)          |
| Hf <sup>173</sup>  | 23.6 hr                | EC                                       | Lu(p,3n); Yb( $\alpha$ ,xn)                          |
| Hf <sup>175</sup>  | 70 day                 | EC                                       | Hf <sup>174</sup> (n, $\gamma$ )                     |
| Hf <sup>178m</sup> | 4.8 sec                | IT                                       | daughter 2.1 hr Ta <sup>178</sup>                    |
| Hf <sup>179m</sup> | 19 sec                 | IT                                       | Hf <sup>178</sup> (n, $\gamma$ )                     |
| Hf <sup>180m</sup> | 5.5 hr                 | IT                                       | Hf <sup>179</sup> (n, $\gamma$ )                     |
| Hf <sup>181</sup>  | 44.6 day               | $\beta^-$                                | Hf <sup>180</sup> (n, $\gamma$ )                     |
| Hf <sup>183</sup>  | 64 min                 | $\beta^-$                                | W(n, $\alpha$ )                                      |

#### IV. Review of those Features of Zirconium and Hafnium Chemistry of Chief Interest to Radiochemists.\*

##### 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  $\text{KNO}_3$ . 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.<sup>(1)</sup> 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,  $\text{ZrO}(\text{H}_2\text{PO}_4)_2$  ( $K_{sp}=2.28 \times 10^{-18}$ )<sup>(1a)</sup> 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 M  $\text{HNO}_3$ , 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  $\text{H}_2\text{O}_2$  from dilute acid. Of these, only the phosphate is soluble in excess reagent. Barium and hydrofluoric acid give slightly soluble barium fluorozirconate 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  $\text{ZrO}_2$  following precipitation as phenyl arsonate, cupferrate or other organic precipitant.<sup>(2)</sup> However, a quantitative and well-defined precipitate of zirconium with mandelic acid and its derivatives<sup>(3)</sup> 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 N  $\text{HCl}$  solution.<sup>(3a)</sup>

#### 4. Carrying of Tracer Zirconium Activity on Other Precipitates

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.<sup>(3b)</sup>

## 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<sup>(4)</sup> 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 ( $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ ). This  $\beta$ -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.<sup>(5)</sup>

Thenoyltrifluoroacetone (TTA),  $[\text{||} \text{---} \text{S} \text{---} \text{||}] \text{---} \overset{\text{O}}{\parallel}{\text{C}}\text{---}\text{CH}_2\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---}\text{CF}_3$ .

Table I

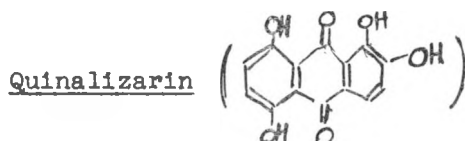
COMPLEXING ABILITY OF VARIOUS SUBSTANCES FOR ZIRCONIUM  
(Tracer Zirconium, 2.00 M HClO<sub>4</sub>, 25°C)

| Substance  | Concentration  | Percent<br>Zirconium<br>Uncomplexed         |
|--|--|---|
| Bisulfate ion, HSO <sub>4</sub> <sup>-</sup>                                       | $\begin{cases} 0.0031 \text{ M} \\ 0.272 \text{ M} \end{cases}$  | $\begin{matrix} 56 \\ 0.18 \end{matrix}$    |
| Hydrofluoric acid, HF  | $\begin{cases} 10^{-5} \text{ M} \\ 0.008 \text{ M} \end{cases}$ | $\begin{matrix} 22 \\ 0.00012 \end{matrix}$ |
| Oxalic acid, H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>                          | 0.001 <u>M</u>   | 0.36  |
| Malonic acid, HOOC-CH <sub>2</sub> -COOH   | 0.01 <u>M</u>  | 100   |
| Succinic acid, HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH                          | 0.005 <u>M</u>   | 100   |
| Glutaric acid, HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH                          | 0.1 <u>M</u>   | 94  |
| Fumaric acid, $\begin{array}{c} \text{HC-COOH} \\ // \\ \text{COOHCH} \end{array}$ | 0.05 <u>M</u>  | 88  |
| Malpic acid $\begin{array}{c} \text{HC-COOH} \\    \\ \text{HC-COOH} \end{array}$  | 0.05 <u>M</u>  | 74  |
| Orthophosphoric acid, H <sub>3</sub> PO <sub>4</sub>                               | 0.012 <u>M</u>   | 68  |
| Orthoboric acid, H <sub>3</sub> BO <sub>3</sub>                                    | 0.1 <u>M</u>   | 100   |
| Metasilicic acid, H <sub>2</sub> SiO <sub>3</sub>                                  | 0.01 <u>M</u>  | 87  |
| Acetic acid, CH <sub>3</sub> COOH  | 1.0 <u>M</u>   | 100   |
| Trifluoroacetic acid, CF <sub>3</sub> COOH   | 0.11 <u>M</u>  | 51  |
| Carbonic acid, H <sub>2</sub> CO <sub>3</sub>                                      | 1 atm. CO <sub>2</sub>   | 90  |
| Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub>                                   | 0.015 <u>M</u>   | 63  |
| Chloride ion, Cl <sup>-</sup>  | $\begin{cases} 2.0 \text{ M} \\ 1.2 \text{ M} \end{cases}$       | $\begin{matrix} 19 \\ 29 \end{matrix}$      |
| Nitrate ion, NO <sub>3</sub> <sup>-</sup>  | $\begin{cases} 2.0 \text{ M} \\ 1.2 \text{ M} \end{cases}$       | $\begin{matrix} 20 \\ 30 \end{matrix}$      |



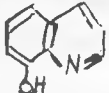
The presence of the trifluoromethyl group in this  $\beta$ -diketone increases the acidity of the enol form and thus permits extractions from solutions of very low pH. The TTA is generally used as a 0.02-0.5 M solution in benzene or toluene. At lower concentrations the extraction rates become very slow. Connick and McVey<sup>(4)</sup> have studied the behavior of zirconium -TTA complexes and Moore<sup>(6)</sup> has developed a procedure for the separation of zirconium from other elements utilizing TTA complexing. The complex shows high extractability from 2-10 M  $\text{HNO}_3$  or HCl solutions into 0.5 M TTA in xylene. These conditions afford an excellent separation of zirconium from the fission products. A small contamination with niobium can be reduced further by the use of 0.9%  $\text{H}_2\text{O}_2$  or 1.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  as a sequestering agent. Among the non-extractable ions are the alkalis, alkaline earths, trivalent rare-earth, tin (II), nickel (II), cobalt (II), chromium (III), uranyl, thorium (IV), iron (II), aluminum (III), and bismuth (III). Zirconium and hafnium may be fractionated with 0.025 M TTA in benzene from 2 M  $\text{HClO}_4$  acid.<sup>(7)</sup> The equilibrium constants for zirconium and hafnium extractions were found to be  $9.4 \times 10^7$  and  $4.6 \times 10^6$  respectively.

Trifluoroacetylacetone (TFA),  $[(\text{CF}_3\text{CO})_2\text{CH}_2]$ . Chelates formed with this diketone are generally more soluble than those with TTA. A zirconium hafnium separation may be achieved with 0.075 M TFA in benzene from 0.07 N HCl.<sup>(8)</sup>

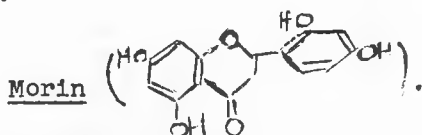


forms complexes with a

number of metals, but only the complexes of Fe(III), Al, Sc, Ti, Zr, and Th are extractable with isoamyl alcohol.<sup>(9)</sup> The reagent is generally used as 0.1% ethanolic solution.

8-quinolinol (oxine), . Oxine forms slightly

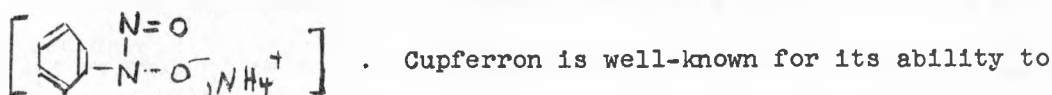
soluble chelates with most metals, generally those that precipitate with aqueous ammonia. Zirconium forms a complex soluble in chloroform from acetic acid-acetate buffered solutions. (10)



In acid medium,

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

Ammonium Salt of N-Nitroso Phenylhydroxyl Amine (Cupferron)



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, hexone, o-dichloro benzene, and benzene. Chloroform is the preferred solvent. Zirconium cupferrate may be extracted from 1 N mineral acid solutions. (11)

## 7. Solvent Extraction Behavior

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

Ethyl Ether. This common solvent is effective for the extraction of many elements from halide systems. Extraction of zirconium, however, is not appreciable, the fluoride being extracted 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.<sup>(12)</sup> From 8 M  $\text{HNO}_3$ , zirconium extracts only to the extent of 8% into ethyl ether.<sup>(13)</sup>

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

Alkylphosphoric Acids. Scadden and Ballou<sup>(15)</sup> investigated di-n-butylester of phosphoric acid (DBPA),  $[(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{OH})_2]$ , 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 M in  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ , or  $\text{H}_2\text{SO}_4$ . A 0.06 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%  $\text{H}_2\text{O}_2$  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 M  $\text{HNO}_3$ , 3%  $\text{H}_2\text{O}_2$ : 5-MINUTE MIXING; VOLUME RATIO  
(ORG./AQ.) 1 TO 1

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

<sup>a</sup>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.

<sup>b</sup>Ag, Sn, Pd, and Mo not carrier-free: their concentrations were  
0.5, 3, 8, and 8  $\gamma$ /ml, respectively.

<sup>c</sup>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  $\text{CCl}_4$ . The extracta-  
bility increases with acid strength, and distribution ratio,  
(organic/aqueous) of about 100 is observed from 8 M  $\text{HCl}$  and  
1000 from 13 M  $\text{HNO}_3$ .<sup>(16)</sup>

A summary of zirconium extraction data from  $\text{HNO}_3$  is given  
in Figure 1, taken from Alcock et al.<sup>(17)</sup>

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 M  $H_2SO_4$ , 2.5 M  $(NH_4)_3SO_4$ , 0.004 M  
OXALIC ACID, 6%  $H_2O_2$ ; VOLUME RATIO (ORG./AQ.) 1 TO 1; MIXING  
TIME, 15 MINUTES WITH 0.08 M DBPA AND 5 MINUTES WITH 0.6 M DBPA

| Concn. of<br>DBPA <sup>a</sup> ,<br><br><u>M</u> | Elements Extracted   |                       |  |
|--|--|-----------------------|--|
|  | < 5% by DBPA   | 5-95% by DBPA         | > 95% by<br>DBPA                                 |
| 0.06   | Cs, Sr, Y, La, Ce(III),<br>Ag, Cd, Ge, Se(IV),<br>Te(IV), Sb(III), <sup>b</sup> Sb(V)<br>As(V), Pd, Ru, Rh, Mo, Nb | Sn(IV) 15%, In<br>85% | Zr, I <sub>2</sub>                               |
| 0.6  | Cs, Sr, La, Ce(III), Ag, Cd,<br>Ge, Se(IV), Te(IV), Sb(III) <sup>b</sup><br>Sb(V), As(V), Pd, Ru, Rh, Mo           | Sn(IV) 50%, Ta<br>35% | Zr, Nb, <sup>b</sup> Y, Ho<br>In, I <sub>2</sub> |

<sup>a</sup>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.

<sup>b</sup>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 M.<sup>(1,4)</sup>

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 M HCl and washing with aqueous  $Na_2CO_3$  (5%) and water.<sup>(16)</sup> This

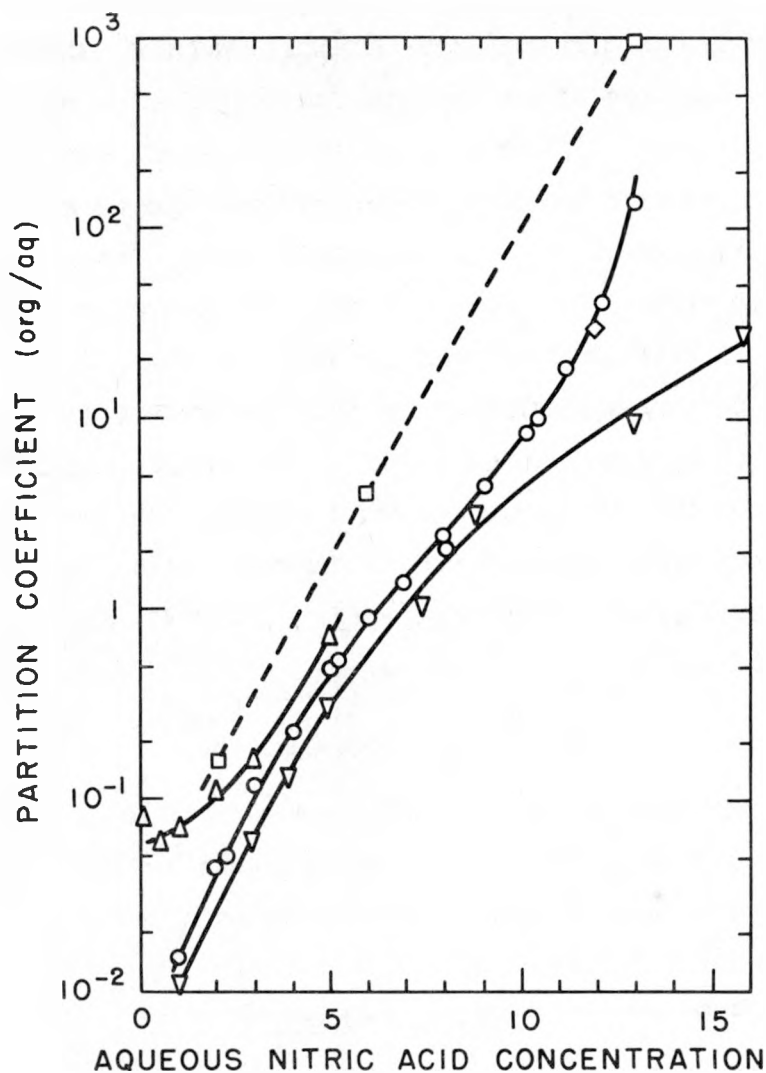


Figure 1

Extraction of zirconium from  $\text{HNO}_3$  systems

- 19% TBP in kerosene (Alcock *et al.*, J. Inorg. & Nucl. Chem. 4, 100 (1957))
- ▽ 30% TBP in  $\text{CCl}_4$  (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.*)

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

Trialkylphosphine Oxides. [ $(C_nH_{2n+1})_3P \rightarrow O$ ] Preliminary studies on the use of the phosphine oxides as extractants have been carried out.<sup>(17a)</sup> With a 0.1 M solution of tri-n-octylphosphine oxide in cyclohexane complete extraction from 1 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 M HCl solution only Au(I), Sn(IV), and U(VI) are completely extracted. With 7 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.<sup>(18)</sup> 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 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.).<sup>(19)</sup> The elements are adsorbed from 2 M  $\text{HClO}_4$  and eluted with 6 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 N  $\text{HNO}_3$  and 0.09 M citric acid elutes zirconium from Dowex-50, but not hafnium.<sup>(20,21)</sup> The hafnium may then be eluted with 5 N  $\text{HNO}_3$ . An excellent separation may be achieved with 1 N  $\text{H}_2\text{SO}_4$  elution of zirconium from Dowex-50. Hafnium is eluted with a 0.05 M oxalic - 0.2 N  $\text{H}_2\text{SO}_4$  mixture,<sup>(22)</sup> or with 3 N  $\text{H}_2\text{SO}_4$ .<sup>(23)</sup>

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.<sup>(24)</sup> 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 adsorption on the top of a cation-exchange column by selective elution.<sup>(25)</sup> 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 solution displaces the trivalent ions and at pH5 the remaining divalent 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.<sup>(26)</sup> Other acid systems have been treated in a series of papers from the U. S. Naval Radiological Defense Laboratory.<sup>(27)</sup> 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 M HF. Elution with a 0.2 M HCl - 0.01 M HF solution removes the zirconium first, and 69% of the original may be recovered with no hafnium.<sup>(28)</sup> Other systems have also been used for this separation.<sup>(29-31)</sup> 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.<sup>(30)</sup>

A Zr-Hf separation may be achieved by elution with 9.0 M HCl. In this case the Hf elutes first (Figure 3) in contrast to the behavior with the fluoride complexes.

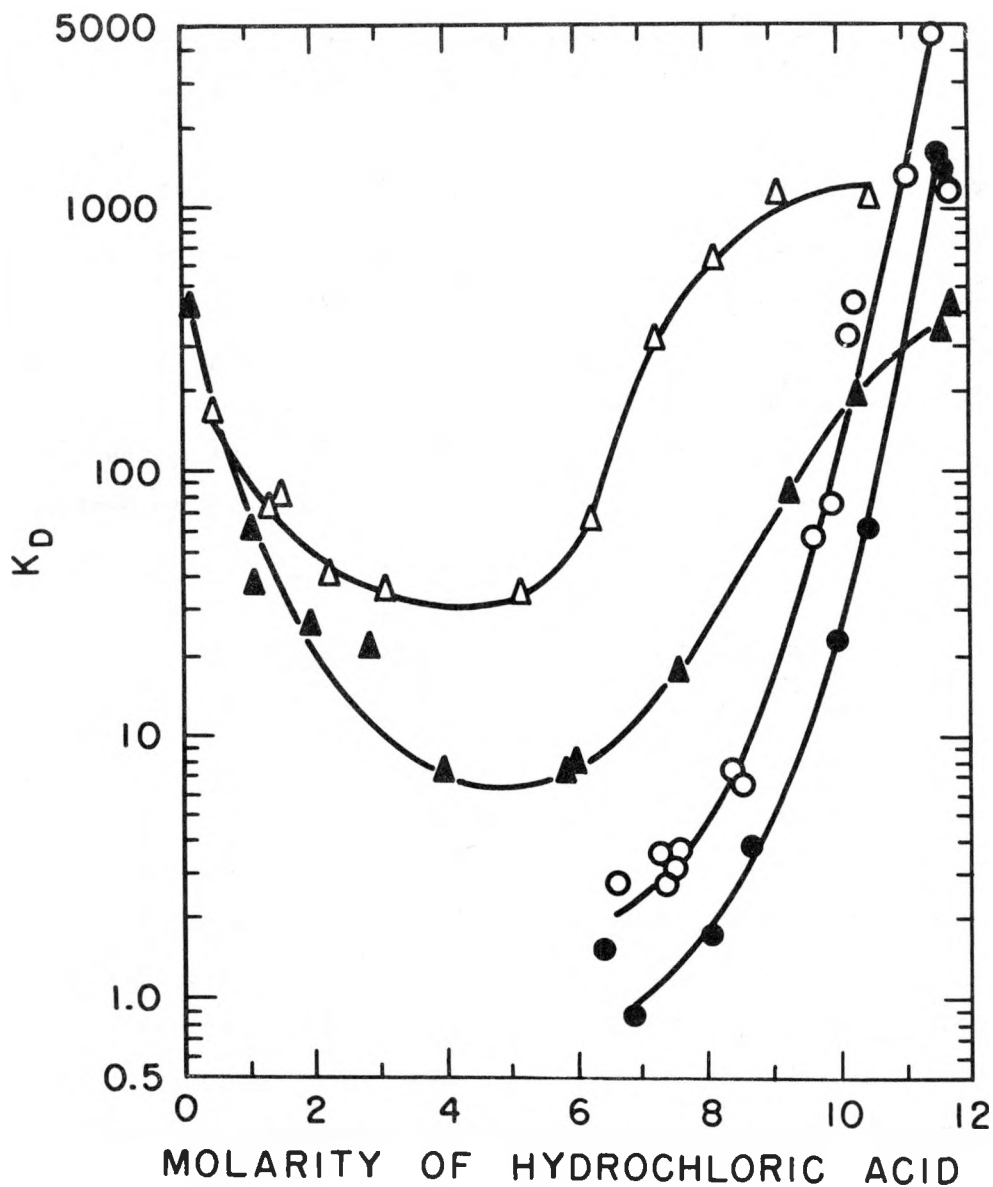


Figure 2  
Dependence of the distribution coefficient at 25° on the hydrochloric acid concentration:  $\Delta$ , niobium;  $\blacktriangle$ , tantalum;  $\circ$ , zirconium;  $\bullet$ , hafnium.

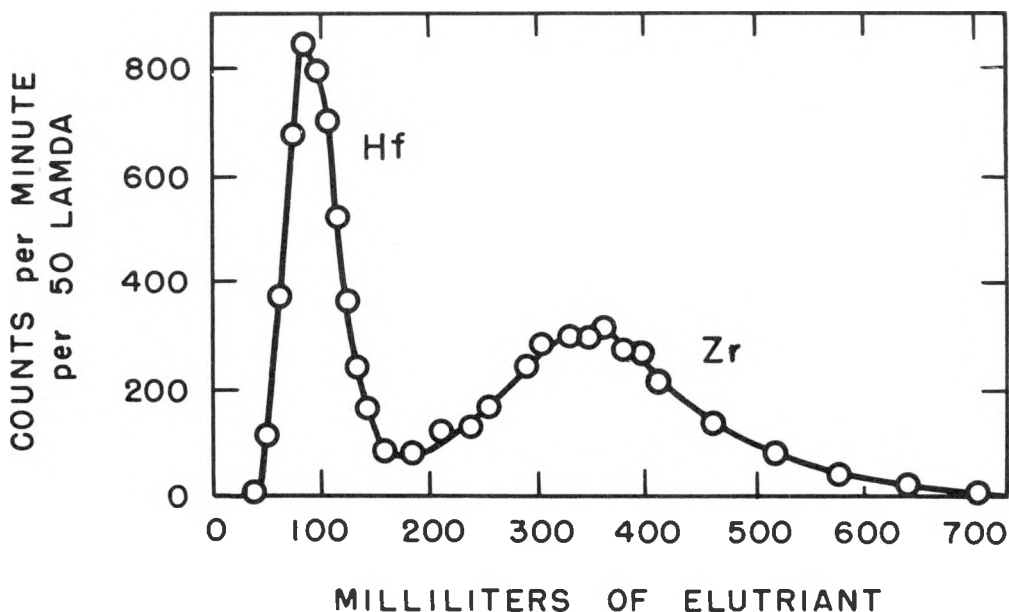


Figure 3  
Elution of chlorozirconate and chlorohafniate  
with 9.0 M hydrochloric acid.

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.<sup>(30,32)</sup> A variety of conditions may also be utilized for a Zr-Nb separation in HCl-HF mixtures.<sup>(32a)</sup> The oxalate complexes of Zr and Nb may also be utilized for a separation.<sup>(33)</sup> 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 concentrated HCl solutions (> 9 M) and weakly adsorbed from dilute acid (< 3 M). However, a separation may be effected by utilizing differences over the concentration range 6-8 M. Such separa-

tions have been carried out using Dowex-2 and Amberlite IR-400<sup>(34)</sup> and Dowex-1<sup>(35)</sup> 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  $\text{HNO}_3$ , while zirconium does not may also be utilized in a separations procedure.<sup>(36)</sup>

#### 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  $\text{HNO}_3$ , or concentrated  $\text{H}_2\text{SO}_4$ . The ores are more difficult to treat, and fusions with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_7$ ,  $\text{Na}_2\text{O}_2$ , or  $\text{KHF}_2$  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.)

## 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 nuclide 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 techniques must be employed. Such a determination involves a knowledge of the decay scheme of the nuclide and the efficiency of the detector 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 interactions of radiation with matter alter the simple geometric relationship between the source and detector by processes of absorption 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 detector 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.,  $\beta^-$ ,  $e^-$ ,  $x$  or  $\gamma$ -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.<sup>(37)</sup> Bayhurst and Prestwood<sup>(38)</sup> 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<sup>(39)</sup> and Olson.<sup>(40)</sup>

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.

## 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 ( $\alpha$ -thenoyl trifluoro acetone). The organic phase is scrubbed to remove extraneous activities, and the zirconium back-extracted with hydrofluoric acid. A  $\text{BaZrF}_6$  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.  $\text{HNO}_3$ . Dilute to 15 ml and extract into 15 ml of 0.4 M TTA in benzene by stirring for 10 min. (Note 2.) Wash TTA phase 3 times with 10 ml of 1 M  $\text{HNO}_3$ .
2. Back extract Zr with 10 ml of 2 N HF by stirring for a few min. Add 1 ml of  $\text{Ba}^{++}$  (50 mg/ml) reagent, centrifuge and decant. Wash the  $\text{Ba}_2\text{ZrF}_6$  precipitate with 10 ml of  $\text{H}_2\text{O}$ .
3. Dissolve ppt. in 3 ml 5%  $\text{H}_3\text{PO}_3$ , 1 ml conc.  $\text{HNO}_3$  + 5 ml  $\text{H}_2\text{O}$ , (a clear solution should result). Add  $\frac{1}{2}$  ml conc.

PROCEDURE 1 (Cont'd.)

- $\text{H}_2\text{SO}_4$ , centrifuge and discard ppt. Add conc.  $\text{NH}_4\text{OH}$  to supernate, centrifuge and decant. Wash ppt., dissolve in 3 ml conc.  $\text{HCl}$ , 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  $\text{H}_2\text{O}$ .
4. Filter ppt. through a weighed filter disc, wash with hot  $\text{H}_2\text{O}$ , alcohol and ether and dry at  $110^\circ\text{C}$  for 10 min. Cool and weigh as Zr tetramandellate.

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.  $\text{HCl}$ . 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  $\text{H}_2\text{O}$ , alcohol and ether and dry at  $110^\circ\text{C}$  for 10 min. Cool and weigh as Zr tetramandellate.

Zirconium tetramandellate  $\text{Zr}(\text{C}_6\text{H}_5\text{CHOHCOO})_4$

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  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  or, better, by reduction with  $\text{H}_2$  using a Pt black wire as catalyst. The original solution should be converted to an  $\text{HCl}$  medium for the reduction of Pu. The extraction of Zr may be carried out from 1 M  $\text{HCl}$  solution.



Procedure 2: Determination of  $\text{Zr}^{95}$  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 <sup>(41)</sup> is commonly used for determining radioactive zirconium ( $\text{Zr}^{95}$ ) 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 <sup>(42)</sup> (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. Mandelic acid and its derivative seemed most promising.

Kumins <sup>(43)</sup> showed that mandelic acid was a specific precipitant for zirconium. He devised a procedure for determining zirconium in the presence of various interfering elements. Astanina and Ostroumov <sup>(44)</sup> 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 necessary to minimize self-absorption of the beta particles by the final precipitate of zirconium tetramandate. 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 tetramandate (mg) | Zirconium yield (%) | Activity* (cpm/ml) |
|------------------------|-----------------------------|---------------------|--------------------|
| 4.68                   | 22.4                        | 62.67               | $3.27 \times 10^5$ |
| 4.68                   | 21.1                        | 59.04               | $3.43 \times 10^5$ |
| 9.36                   | 43.2                        | 60.53               | $2.68 \times 10^5$ |
| 9.36                   | 37.2                        | 52.12               | $2.75 \times 10^5$ |
| 18.72                  | 96.2                        | 67.41               | $1.60 \times 10^5$ |
| 18.72                  | 96.3                        | 67.48               | $1.59 \times 10^5$ |

\*  $3.50 \times 10^5$  cpm of Zr activity added to each sample.

The procedure is as follows:

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

2. Add 0.25 ml of lanthanum nitrate solution (10 mg  $\text{La}^{3+}$ /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 6N hydrochloric acid. Add 6N 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 12N (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

Zircoryl 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 (6N): 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 ( $2.3 \text{ mg/cm}^2$ ) 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<sup>95</sup> Determination by Cupferron and Mandelic Acid Methods (Beta Count\*)

| Sample | Cupferron<br>(cpm)                       | Mandelic acid<br>(cpm)                   |
|--------|--|--|
| 1      | 699                                      | 748                                      |
| 2      | 772<br>779<br>791<br>788                 | 761<br>766<br>779                        |
| 3      | $3.63 \times 10^5$                       | $3.50 \times 10^5$<br>$3.87 \times 10^5$ |
| 4      | $2.74 \times 10^5$<br>$2.73 \times 10^5$ | $2.61 \times 10^5$<br>$2.71 \times 10^5$ |
| 5      | $2.40 \times 10^5$<br>$2.44 \times 10^5$ | $2.39 \times 10^5$<br>$2.40 \times 10^5$ |

\* Accuracy is  $\pm 3\%$ .TABLE 3—Zr<sup>95</sup> Determination by Cupferron and Mandelic Acid Methods (Gamma Count)

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

repeated with samples containing approximately  $10^4$  beta counts per minute of Ce<sup>144</sup>-Pr<sup>144</sup>, Nb<sup>95</sup>, and Sr<sup>90</sup>-Y<sup>90</sup>. 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.

\* \* \*

This work was supported in part by a grant (AT-11-1) 213 from the Atomic Energy Commission.

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:  $5 \times 10^{13}$  Atoms of  $\text{Zr}^{97}$  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  $2N$  in  $\text{HCl}$ , add 10 mg Zr carrier and several mg of La carrier. Make the solution  $0.5M$  in  $\text{HF}$ . Centrifuge and discard the precipitate.

PROCEDURE 3 (Cont'd.)

2. Add three drops of saturated  $\text{BaCl}_2$  solution to the supernatant. Centrifuge and discard supernatant. Wash precipitate with water.
3. To the precipitate add 4 ml of saturated  $\text{H}_3\text{BO}_3$  solution, 10 ml of water and 2 ml conc.  $\text{HNO}_3$ . To the clear solution add several drops of conc.  $\text{H}_2\text{SO}_4$  and a few drops of two percent aerosol. Centrifuge and discard the precipitate.
4. To the supernatant add  $\text{NH}_4\text{OH}$  in excess. Centrifuge precipitate and discard supernatant. Wash precipitate twice with dilute ammonia.
5. Add 10 ml conc.  $\text{HCl}$  to the precipitate. Dilute the solution to  $2\text{N}$   $\text{HCl}$ .
6. Transfer solution to a 125-ml, open top, cylindrical separatory funnel (with stem detached immediately below the stopcock). Add 30 ml of  $0.4\text{M}$  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.  $\text{HCl}$ , 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.  $\text{H}_2\text{SO}_4$  and heat very gently, at first (to minimize spattering).
10. Ignite to  $\text{ZrO}_2$  at  $800^\circ\text{C}$ . 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.

PROCEDURE 3 (Cont'd.)

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

- A. Pass the solution ( $12\text{N}$  in  $\text{HCl}$ ) through a Dowex-1 anion exchange resin column (50-100 mesh), 6 mm i.d.  $\times$  8 cm in length. Pass 5 ml conc.  $\text{HCl}$  through column. Discard effluents. Pass 15-20 ml of  $7\text{N}$   $\text{HCl}$  through column. Collect effluent and dilute to  $2\text{N}$   $\text{HCl}$ . Proceed with step 5. (Elution with  $7\text{N}$   $\text{HCl}$  elutes zirconium, leaves protactinium on column.)
- B. Make solution  $\sim 7\text{N}$  in  $\text{HCl}$ . Add an equal volume of diisopropyl ketone and equilibrate layers for a few minutes. Discard organic layer. Repeat DIPK extraction 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 bddt: $184^{\text{m}}$ all particles | Equipment required: Centrifuge, tubes, lusteroid cones, ice, small porcelain crucible. |

Yield:  $\sim 60\%$

Degree of purification: Decontamination factor  $\sim 10^4$  from fission and spallation products (no Th & negligible Hf activity present).



PROCEDURE 4 (Cont'd.)

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

Procedure:

- (1) To aliquot of  $\text{HNO}_3$  soln of target, add 10 mg Zr, make sample up to ~ 5 ml of 5 N  $\text{HNO}_3$  in a lusteroid cone. Add 2 ml conc. HF & 10 mg La. Repeat  $\text{LaF}_3$  pptn.
- (2) Add 50 mg Ba to supn. Wash  $\text{BaZrF}_6$  ppt.
- (3) Dissolve ppt in 2 ml 5%  $\text{H}_3\text{BO}_3$ , add 1 ml conc.  $\text{HNO}_3$  & 5 ml  $\text{H}_2\text{O}$ , repeat  $\text{LaF}_3$  pptn twice (as in (1) and (2)).
- (4) Repeat  $\text{BaZrF}_6$  pptn.
- (5) Dissolve with 2 ml  $\text{H}_3\text{BO}_3$ , 2 ml conc. HCl, & 5 ml  $\text{H}_2\text{O}$ . Add 1 drop conc  $\text{H}_2\text{SO}_4$  & cont out  $\text{BaSO}_4$ .
- (6) Dil supn to 20 ml & add 2 ml 6% cupferron in ice bath, filter, wash with cold 1 N HCl containing cupferron, ignite in a porcelain crucible. Weigh as  $\text{ZrO}_2$  (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 bddt: 60" alphas

Equipment required:

Standard

Yield: ~ 60%

PROCEDURE 5 (Cont'd.)

Procedure: The Th metal is dissolved in conc HCl plus a few drops of .2 M  $(\text{NH}_4)_2\text{SiF}_6$  to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken.

- (1) Use a lusteroid tube, add  $\text{HNO}_3$  to make 5 ml of soln 4 to 5 molar in  $\text{HNO}_3$ . Add 20 mg Zr carrier, 2 ml conc HF and mix well. Centrifuge off  $\text{ThF}_4$ .
- (2) Add 10 mg  $\text{La}^{+++}$  carrier. Mix well and centrifuge. Add a second 10 mg  $\text{La}^{+++}$  and centrifuge down on top of 1st ppt. Decant.
- (3) Add 50 mg  $\text{Ba}^{++}$  to supn. Mix and let stand 1 min. Centrifuge.
- (4) Dissolve ppt by adding 2 ml 5%  $\text{H}_3\text{BO}_3$  and stirring. Add 1 ml conc  $\text{HNO}_3$  and 5 ml  $\text{H}_2\text{O}$ . Add 2 ml 27N HF and 50 mg  $\text{Ba}^{++}$ . Stir until ppt forms and let stand 1 minute longer.
- (5) Repeat (4).
- (6) Dissolve with 2 ml  $\text{H}_3\text{BO}_3$ , 2 ml conc HCl and 5 ml  $\text{H}_2\text{O}$ . Add 1 drop conc  $\text{H}_2\text{SO}_4$  and centrifuge off  $\text{BaSO}_4$ .
- (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  $\text{ZrO}_2$  in porcelain crucible. Weigh.

Remarks: This procedure has been described previously. (Phys. Rev. 75, 17 (1949)).

Preparation of carrier solutions: Dissolve 29.40 gms  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in water, adding a few drops of  $\text{HNO}_3$  if necessary to clarify the solution. Dilute to 1 liter.

Standardization: Take 5 ml carrier. Make 2 M in HCl and cool in ice bath to 10° C. Add a slight excess of 6% cupferron solution. Filter and ignite in a porcelain crucible with care to prevent splattering of oils distilled from cupferron. Final ignition temperature 600° C. Weigh as  $\text{ZrO}_2$ . (6% cupferron solution: 6 gms cupferron and pinch of  $(\text{NH}_4)_2\text{CO}_3$  in 100 ml  $\text{H}_2\text{O}$ . Solution slowly decomposes.)

Procedure 6. Carrier-Free Zirconium from Proton Bombardment of Nb.

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

Thin strips of spectrographically pure niobium metal were bombarded for periods of from 5 to 20 minutes with 100-Mev protons 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 dropping them into a mixture of concentrated  $\text{HNO}_3$  and concentrated  $\text{HF}$ . Ten milligrams of lanthanum nitrate were added, with stirring to precipitate  $\text{LaF}_3$ . All the zirconium activities in solution were coprecipitated with the  $\text{LaF}_3$  and cleanly separated from the niobium, a separation which has been studied by Ballou<sup>(46)</sup> and by Gest, Burgess, and Davies.<sup>(47)</sup> The co-separation is believed to be caused by the surface adsorption of  $\text{ZrF}_6^-$  ion on  $\text{LaF}_3$ . The  $\text{LaF}_3$  precipitate was contacted with strong KOH to metathesize the fluoride to the hydroxide compound. Then the hydroxide was dissolved in 2M  $\text{HClO}_4$ . In order to scavenge out any traces of niobium which might remain,

manganese dioxide was precipitated from the resulting solution by adding in turn  $\text{Mn}^{++}$  and  $\text{KMnO}_4$ .

The zirconium was extracted from the  $\text{HClO}_4$  solution by contacting it intimately for 15 minutes with an equal volume of a 0.2M solution of  $\alpha$ -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<sup>(48)</sup> and of Huffman and Beaufait<sup>(49)</sup> 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 2M  $\text{HClO}_4$  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<sup>(50)</sup> which had been pre-equilibrated with concentrated HCl. Unpublished research results of this laboratory<sup>(51)</sup> have shown that from solutions 10M or higher in HCl concentration, negatively charged chloride complex ions of zirconium adsorb strongly on Dowex anion resin. From solutions of concentration less than 6M, 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 adsorbed. 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 zirconium such as co-precipitation on barium fluozirconate. A principal 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-separation 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  $\text{Th}(\text{IO}_3)_4$  from 4 M  $\text{HNO}_3$  containing  $\text{H}_2\text{O}_2$  to keep niobium (columbium) in solution and to ensure the trivalency of cerium. The precipitation of thorium oxalate removes the thorium and  $\text{UX}_1$  ( $\text{Th}^{234}$ ), 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  $\text{H}_2\text{O}_2$ , 8 ml of conc.  $\text{HNO}_3$ , and 20 ml of 0.35 M  $\text{HIO}_3$ . The solution and precipitate are cooled and allowed to stand for 5 min. The precipitate is removed by centrifugation and dissolved in  $\text{HCl}$  and  $\text{SO}_2$ . Thorium hydroxide is precipitated with  $\text{NH}_4\text{OH}$ , and this precipitate is dissolved in 8 ml of conc.  $\text{HNO}_3$ . After the addition of 1 ml of 3 per cent  $\text{H}_2\text{O}_2$  the thorium is precipitated with 20 ml of 0.35 M  $\text{HIO}_3$  and allowed to stand for 5 min. The precipitate of  $\text{Th}(\text{IO}_3)_4$  is dissolved in  $\text{HCl}$  and  $\text{SO}_2$ , and  $\text{Th}(\text{OH})_4$  is precipitated from this solution with  $\text{NH}_4\text{OH}$ .

After the  $\text{Th}(\text{OH})_4$  precipitate is dissolved in 1 ml of 6 N  $\text{HCl}$  and 15 ml of  $\text{H}_2\text{O}$ , the solution is heated to boiling and 5 ml of sat.  $\text{H}_2\text{C}_2\text{O}_4$  solution is added. The solution is cooled and allowed to stand for 10 min, and the  $\text{Th}(\text{C}_2\text{O}_4)_2$  precipitate is centrifuged off. A second precipitation of  $\text{Th}(\text{C}_2\text{O}_4)_2$  from the solution is made by adding 5 mg of thorium carrier and letting it stand for 30 min. The  $\text{Th}(\text{C}_2\text{O}_4)_2$  precipitate is then centrifuged off, leaving a solution of zirconium activity. If a zirconium tracer solution free of oxalic acid is desired,  $\text{Fe}(\text{OH})_3$  can be precipitated from the solution. This carries the zirconium activity. The iron can then be removed by extraction into isopropyl ether from 8 N  $\text{HCl}$  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  $\text{Nb}_2\text{O}_5$  by the destruction of the oxalate complex with  $\text{MnO}_4^-$ . After the removal of the co-precipitated  $\text{MnO}_2$  with  $\text{SO}_2$ , the  $\text{Nb}_2\text{O}_5$  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  $\text{Nb}^{95}$  daughter since the preparation of the 65d  $\text{Zr}^{95}$  tracer.

A preparation was made which used 0.5 ml of 30 per cent  $\text{H}_2\text{O}_2$  instead of 1 ml of 3 per cent  $\text{H}_2\text{O}_2$ . The niobium decontamination was not improved. In the absence of  $\text{H}_2\text{O}_2$ , niobium precipitates with  $\text{Th}(\text{IO}_3)_4$  about as efficiently as zirconium does.

The zirconium in solution after the removal of the niobium was precipitated on  $\text{Fe}(\text{OH})_3$ . An aluminum absorption curve of the activity was identical with the aluminum absorption curve of 65d  $\text{Zr}^{95}$  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  $\text{Nb}^{95}$  daughter of 65d  $\text{Zr}^{95}$ .

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

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

Zirconium.  $\text{Zr}_{40}^{89}$ ;  $T = 79.3$  hours;  $K$  (75%)  $\beta^+$  (25%);  
 $E_{\beta^+} = 0.910$  Mev;  $\gamma$ ;  $E_{\gamma} = 0.92$  Mev.

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

Irradiated  $\text{Y}_2\text{O}_3$  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  $\text{YF}_3$  by precipitation with HF. The excess HF was removed by evaporation with a few millilitres of concentrated  $\text{H}_2\text{SO}_4$ . After dilution,  $\text{FeCl}_3$  was introduced into the solution and was precipitated in the form of  $\text{Fe}(\text{OH})_3$  with the help of  $\text{NH}_4\text{OH}$ . Thus the radio-zirconium was quantitatively adsorbed by the precipitate of  $\text{Fe}(\text{OH})_3$ . After dissolving the precipitate of  $\text{Fe}(\text{OH})_3$  in 6N 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<sup>(52)</sup> 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  $6M$  in  $HCl$  and  $0.05M$  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  $6M$   $HCl$ . 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  $6M$  in  $HCl$  and  $0.05M$  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  $\text{CHCl}_3$  and cold 6 per cent cupferron is added to the aqueous layer, and the funnel is again shaken vigorously for about 30 sec. The  $\text{CHCl}_3$  layer is again drained off. The two  $\text{CHCl}_3$  layers are combined, and the aqueous layer is discarded.

Both the  $\text{CHCl}_3$  layer (in the separatory funnel) and a 10-ml wash solution  $6\text{M}$  in  $\text{HCl}$  and  $0.05\text{M}$  in  $\text{SO}_2$  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  $\text{CHCl}_3$  layer in a separatory funnel is added 5 ml of  $6\text{M}$   $\text{HCl}$ . Several drops of  $\text{Br}_2$  are added, and the funnel is shaken vigorously for several minutes at 10-min intervals. After 1 hr the layers are separated and the  $\text{CHCl}_3$  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 unnecessary and  $\text{SO}_2$  addition can be neglected.

2. The separation of the two layers can be accomplished efficiently by drawing off most of the original  $\text{CHCl}_3$  layer, adding fresh  $\text{CHCl}_3$ , 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  $\text{CHCl}_3$  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

$\text{H}_2\text{C}_2\text{O}_4$  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  $\text{CHCl}_3$ -cupferron solution. It is good practice to store niobium tracer as an oxalate solution and to destroy oxalic acid by fuming with conc.  $\text{HNO}_3$  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  $\text{K}_2\text{CO}_3$  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  $\text{Fe}(\text{OH})_3$ . 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  $\text{HF}$ . The niobium is removed from the zirconium by repeated fusions with  $\text{K}_2\text{CO}_3$ , thorium holdback carrier being used for the zirconium. The thorium is finally separated from the zirconium by precipitation with  $\text{HF}$ . Each of the purified activities is carried on  $\text{Fe}(\text{OH})_3$ , 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  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and make strongly alkaline with  $\text{NH}_4\text{OH}$ . Heat to boiling, cool, and centrifuge the  $\text{Fe}(\text{OH})_3$  precipitate. Dissolve the precipitate in  $\text{HCl}$  and reprecipitate twice more in the presence of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . Dissolve the final  $\text{Fe}(\text{OH})_3$  precipitate in  $\text{HNO}_3$ , add 25 mg of thorium carrier, and make 5N in  $\text{HNO}_3$ . Precipitate the thorium as  $\text{Th}(\text{IO}_3)_4$  by the addition of an equal volume of 0.35M  $\text{KIO}_3$  reagent. Centrifuge, and wash the precipitate with dil.  $\text{KIO}_3$  solution. Decompose the precipitate by repeated evaporations with conc.  $\text{HCl}$  and evaporate to dryness.

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\* Editors' Note: Thorium iodate in the presence of  $\text{H}_2\text{O}_2$  was used by N. E. Ballou (Paper 249, this volume) to prepare carrier-free zirconium activity.

Dissolve the residue in 20 ml of  $5\text{N}$   $\text{HNO}_3$  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  $\text{KIO}_3$  reagent. Centrifuge, wash the precipitate, and decompose with  $\text{HCl}$  as before. Dissolve the final residue in  $1\text{N}$   $\text{HCl}$  and add 10 mg of cerium carrier. Make the solution  $2\text{N}$  in  $\text{HF}$ , centrifuge, wash, and discard the precipitate. Combine the centrifugate and washings, and evaporate to fuming with 1 ml of conc.  $\text{H}_2\text{SO}_4$ .

Dilute the solution to about 40 ml and add 10 mg of thorium carrier. Make basic with  $\text{NH}_4\text{OH}$ , centrifuge, and wash the precipitate of  $\text{Th}(\text{OH})_4$ . Evaporate to dryness, fuse with 4 g of  $\text{K}_2\text{CO}_3$ , cool, and extract the mass with 10 ml of  $\text{H}_2\text{O}$ . Centrifuge the suspension, and wash the residue with 10 ml of 30 per cent  $\text{K}_2\text{CO}_3$  solution. Combine the supernatant solution and washings, and set aside for the separation of niobium.

Fume the  $\text{ThO}_2$  residue from the  $\text{K}_2\text{CO}_3$  fusion with 2 ml of conc.  $\text{H}_2\text{SO}_4$  for about 15 min. Cool and dilute to 30 ml with  $\text{H}_2\text{O}$ . Add 5 mg of niobium carrier, make basic with  $\text{NH}_4\text{OH}$ , centrifuge, and wash the resulting precipitate. Dry and again subject the precipitate to the zirconium-niobium separation by means of  $\text{K}_2\text{CO}_3$  fusion. Repeat the fusion on the  $\text{ThO}_2$  residue, but do not add niobium carrier. Dissolve the final  $\text{ThO}_2$  residue with  $\text{H}_2\text{SO}_4$  as described previously, and dilute to 40 ml. Make the solution  $2\text{N}$  in  $\text{HF}$ , centrifuge, and wash the  $\text{ThF}_4$  precipitate with dil.  $\text{HF}$ .

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  $\text{NH}_4\text{OH}$ . Centrifuge, wash the precipitate, and dissolve in 15 ml of  $9\text{N}$   $\text{HCl}$ . 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  $\text{Th}(\text{OH})_4$  with  $\text{NH}_4\text{OH}$ . Centrifuge, wash the precipitate, and dissolve in  $\text{HNO}_3$ . Precipitate  $\text{Th}(\text{IO}_3)_4$  as before, decompose with  $\text{HCl}$ , and dilute to 50 ml. Make the solution 1N in  $\text{HCl}$  and 2N in  $\text{HF}$ , and centrifuge the  $\text{ThF}_4$  precipitate. Wash with 1N  $\text{HF}$  and discard the precipitate.

Add 2 ml of conc.  $\text{H}_2\text{SO}_4$  and 10 mg of zirconium carrier to the combined supernatant solution and washings, and evaporate to fuming. Cool, dilute with  $\text{H}_2\text{O}$ ; and precipitate  $\text{Zr}(\text{OH})_4$  with  $\text{NH}_4\text{OH}$ . Fuse the precipitate with 3 g of anhydrous  $\text{K}_2\text{CO}_3$ , and extract the melt with 10 ml of  $\text{H}_2\text{O}$ . Centrifuge the residue, and wash with 10 ml of 30 per cent  $\text{K}_2\text{CO}_3$  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  $\text{Fe}(\text{OH})_3$  with  $\text{NH}_4\text{OH}$ . Centrifuge, wash the precipitate, and dissolve in 9N  $\text{HCl}$ . 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 3N in HCl in a volume of 50 ml. One milliliter of 85 per cent  $\text{H}_3\text{PO}_4$  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 washings, and the mixture was again boiled. The second zirconium phosphate precipitate was centrifuged out and washed. The combined supernatant solution and washings were evaporated to dryness 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, zirconium, tellurium, cesium, barium, lanthanum, cerium, and thorium carriers were added and treated for the quantitative removal of the niobium alone as  $\text{Nb}_2\text{O}_5$ . The solution was treated with a few milliliters of HF and then was evaporated to fumes with  $\text{HClO}_4$ . The material was fumed to a volume of 3 ml, cooled, and boiled for 15 min with 10 ml of 12N  $\text{HCOOH}$ . The solution was then filtered, and the paper was washed. The filtrate and washings from the  $\text{Nb}_2\text{O}_5$  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 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 M perchloric acid. The zirconium and hafnium were extracted from this solution into 0.4 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-



hydroxides were washed with water and dissolved in 3 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 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 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.

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