RADIOCHEMISTRY OF ZIRCONIUM AND NIOBIUM

BY

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(Based largely on an unpublished
review by D. N. Hume)

ZIRCONIUM

Macro Chemistry

The only important oxidation number is +4. The normal
state in aqueous solution is the zirconyl ion (ZrO^{++}); the
tetrapositive ion is not capable of existence in dilute acid
solutions. Alkali hydroxides and ammonia precipitate zirconyl
salts as $ZrO(OH)_2$, insoluble in excess base but soluble in
mineral acids. The precipitation is hindered by much ammonium
fluoride. On heating or drying, the hydroxide is converted
to the much more insoluble oxide, ZrO_2. Ignited zirconium
oxide is soluble only in hydrofluoric acid. Hydrogen sulfide
has no effect on solutions of zirconium salts. Alkali sulfides
precipitate the hydroxide. Zirconyl nitrate, chloride, and
sulfate are soluble in acid solution. Zirconyl fluoride is
insoluble but readily dissolves in hydrofluoric acid. Reduction
to the metal is very difficult. Commercial zirconium contains
an appreciable amount of hafnium impurity.

Among the more important insoluble compounds is the very
insoluble phosphate, $ZrO(H_2PO_4)_2$, K_{sp} = 2.28 x 10^{-18} which

precipitates even 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 aryl-substituted arsonates and cupferride precipitate from acid solutions; none are appreciably soluble in excess reagent. Oxalic acid and alkali carbonates give precipitates soluble in excess reagent. Barium and hydrofluoric acid give slightly soluble barium fluozirconate of uncertain composition, insoluble in excess and affording a good separation from niobium. The customary weighing form is ignited ZrO_2. A quantitative and well-defined precipitate of zirconium tetra-mandelate, $Zr(C_6H_5CHOHCO_2)_4$, is a more convenient and useful form for weighing and mounting radioactive Zr sources.

Soluble complexes are readily formed with hydrofluoric and oxalic acids. Tartaric acid gives complexes stable also in basic solution. Sulfates form complexes which are less stable but sufficiently strong to prevent precipitation on addition of oxalate ion in acid solution. The solubility of $ZrO(H_2PO_4)_2$ in excess phosphoric acid indicates the formation of a complex ion $ZrO(H_2PO_4)_4^=$ with a dissociation constant equal to about 10^{-16}. Zirconium cupferride is insoluble in water and dilute mineral acids but is readily soluble in chloroform and may be extracted from 3 to 6 $\underline{M}$ hydrochloric acid solution, separating zirconium from other fission products except niobium. Anhydrous zirconium halides are

volatile at high temperatures.

The radiochemical determination of zirconium activity in fission material is accomplished, after first scavenging rare earths and alkaline earths with lanthanum fluoride and repeated precipitation of barium fluozirconate to separate from niobium and other fission products, by precipitation as the mandelate.

Tracer Chemistry

The interchange of zirconium activity in fission material with added zirconyl carrier is quite incomplete, especially in the presence of phosphate. It is necessary to use strong complexing agents, preferably fluoride, to gain complete interchange. Oxalate medium is inferior for effecting exchange, and phosphate is quite poor. TTA extraction has been found to effect complete interchange.

Zirconium tracer is strongly coprecipitated with most precipitates in acid solutions not containing complex-forming ions. The activity is easily carried on "crud" and adheres to glassware. Tracer zirconium is carried readily on many phosphates, such as those of bismuth and ceric cerium. In the absence of holdback carrier, it is carried nearly completely on rare earth fluorides. It is carried fairly well by thorium iodate, but not by thorium oxalate. It is carried effectively by iron oxide when the sol is flocculated. Zirconium activity is very poorly decontaminated by sodium uranyl acetate cycles.

It exists in UNH partially as a colloid and partially in the form of ions. Pure, carrier free zirconium tracer (source unspecified) was shown to be a negatively charged colloid by electrophoresis experiments.

Zirconium is strongly adsorbed from UNH solution by Amberlite resin and may be selectively eluted, along with niobium, by one-half per cent oxalic acid. When complexed with ferron, it is not adsorbed on Amberlite. The adsorption of zirconium on silica gel is appreciable.

Zirconium forms negative complexes in strong HCl or mixed HCl-HF solutions, and these are strongly adsorbed by anion exchange resins. Under proper conditions zirconium may be effectively separated from niobium and hafnium. Cation exchange resins are also effective for zirconium separations, and an excellent zirconium-hafnium separation may be made with $1N-H_2SO_4$ elution of Dowex-50. Carrier free zirconium tracer may be made by adsorption on Amberlite resin and selective elution by oxalic acid, followed by separation from niobium through removal of the latter on manganese dioxide in 10 $\underline{M}$ nitric acid. Alternatively, niobium may be separated first by coprecipitation in MnO_2, Zr adsorbed on Dowex-50 from strong HCl, and eluted with dilute acid.

Zirconium is slightly, but appreciably extracted from aqueous nitrate media by oxygenated organic solvents. Differences in extractibility with hexone have been attributed

to the presence of zirconium tracer in more than one ionic or
molecular species. In nitric acid-thiocyanate solutions,
zirconium tracer is readily extracted with hexone. The extraction
of zirconium with TFA (tetrafluoro acetyl acetone) and benzene,
with TTA (α-thenoyl trifluoro acetone) in benzene or with TBP
(tri-n-butyl phosphate) in di-n-butyl ether is very efficient.
These solvents are especially useful in radiochemical separations.
The cupferron extraction is also satisfactory in the absence of
carrier. The diffusion of zirconium from uranium when the latter
is heated near its melting point is fairly extensive. Zirconium
is volatilized when UO_2 is treated with hydrogen fluoride at
red heat but is not volatilized from uranium tetrafluoride with
hydrogen fluoride.

NIOBIUM

Macro Chemistry

The only important oxidation state of niobium is the +5.
The +3 exists in aqueous solutions in strongly reducing media
(zinc and acid) but is rapidly oxidized in air and is therefore
not ordinarily encountered. Pentavalent niobium forms no simple
cations in aqueous solution but exists only in the form of
complex ions.

The most characteristic compound of niobium is the very
insoluble oxide, Nb_2O_5, which is dissolved neither by acids nor
bases in the absence of complex forming ions. From acid

solutions of not too stable niobium complexes (fluoride, sulfate, oxalate), alkalies and ammonia precipitate the flocculent hydrous oxide, insoluble in excess and insoluble in mineral acids but soluble in complex forming acids. The fresh precipitate is soluble in hydrogen peroxide and acid, and it is then stable to the addition of base. Ignition leads to the very insoluble anhydrous oxide which requires treatment with hydrofluoric acid or fusion with alkali carbonate to effect solution. Acid tartrate or oxalate solutions of niobium are not affected by hydrogen sulfide.

Complexes soluble in acid are formed by a treatment of fresh Nb_2O_5 with oxalic, tartaric, hydrofluoric, concentrated sulfuric, and concentrated phosphoric acids but not appreciably by hydrochloric or nitric acids. Niobium pentoxide is dissolved by digestion with a mixture of concentrated sulfuric acid and selenium oxydichloride. With hydrofluoric acid, both normal (NbF_7^{--}) and oxyfluoride ($NbOF_5^{--}$) complexes are formed. Little is known about the constitution of other complexes, but there is some evidence that niobium, like molybdenum and tungsten, may form heteropoly acids.

The oxide is the most important of the insoluble compounds, being precipitated completely from strong nitric acid upon destruction of organic complex forming ions present. An orange precipitate is obtained with tannin in acid solutions. Cupferron precipitates niobium, even from oxalic acid, and the

precipitate may be ignited to the oxide for weighing. Niobium pentoxide may be made soluble by fusion with alkali carbonates, yielding polycarbonates stable in neutral or alkali solutions but which precipitate as the oxide on the addition of acid.

Niobium halides, except the complex fluorides, are unstable in aqueous solutions. The pentachloride, volatile at 240°, is formed from the oxide and carbon tetrachloride vapor at high temperatures. Both the pentachloride and oxytrichloride decompose violently in the presence of water, precipitating the oxide. Niobium cupferride is extracted from acid solution with chloroform. Alkali and alkaline earth salts of fluoniobic acid are fairly soluble in acid solution, enabling a separation from zirconium. Many reactions characteristic of pure niobium compounds do not hold in the presence of other elements, especially zirconium, which very readily coprecipitates with niobium in nearly all its insoluble compounds. The radio-chemical determination of niobium activity customarily involves precipitation of Nb_2O_5 from strongly acid solution, dissolution of the oxide in oxalic acid, and reprecipitation by destruction of oxalate. A barium fluozirconate scavenging of zirconium is desirable if phosphate is present. The chemical yield is determined by weighing the ignited oxide. Tellurium is poorly decontaminated, but if only gamma activity is to be counted there is negligible interference. A clean separation from tellurium and minor fission products is obtained by

adsorption on Amberlite resin, followed by elution with oxalic acid or cupferron-chloroform extraction.

Tracer Chemistry

There appears to be no difficulty with the interchange between niobium carrier and tracer. Tracer niobium is unstable in acid solution without complex forming anions and tends to deposit on glassware. It is strongly adsorbed by many precipitates, e.g. sulfides, zirconium phosphate, and bismuth phosphate. Precipitation of oxides from acid solution (e.g. manganese dioxide, tellurium dioxide) carries tracer niobium nearly completely. Any traces of dust or silica present in a clear solution results in marked losses. Frequently centrifugation of a clear solution leads to much activity being thrown down. In the absence of complex forming ions, tracer niobium seems to exist as a radio colloid with the chemical properties of the oxide. Niobium is similar to zirconium in that it may exist as a negatively charged colloid in aqueous medium. Dissolved metal contains most if not all of the niobium in the form of a radio colloid very easily deposited on surfaces or coprecipitated with insoluble compounds. Addition of phosphoric or hydrofluoric acid to metal solution converts the niobium into true solution. Carrier-free niobium tracer may be removed from glass surfaces by extraction with strong alkali hydroxide or dilute hydrofluoric acid. Niobium is volatilized when irradiated

uranous oxide is treated with hydrogen fluoride at red heat. Niobium is readily adsorbed on Amberlite resin and may be selectively eluted (with zirconium) by 0.5% oxalic acid. Niobium and tantalum may be separated on anion exchange resins. Niobium is strongly adsorbed by silica gel and by soils. In the presence of complex-forming anions (tartrate, oxalate, fluoride), tracer niobium is stable in solution. Low concentrations of fluoride (from fluosilicate) prevent the carriage of niobium on bismuth phosphate. Niobium is not carried on lanthanum fluoride to any great extent, even in the absence of holdback carrier, (distinction from zirconium). Niobium tracer is carried effectively by iron oxide when the sol is flocculated. Extraction of niobium with hexone is negligible and with tetrafluoro acetyl acetone under conditions where zirconium is extensively extracted, only a few per cent of the niobium passes into the benzene phase. Niobium may be extracted from concentrated HCl into di-isopropyl ketone affording a separation from zirconium. Tantalum may be separated from niobium in mineral acid-HF solutions by di-isopropyl ketone extraction. Niobium extracts from 8 M HCl into a solution of methyldioctylamine in xylene; tantalum does not.

SOLVENT EXTRACTION PROCEDURE FOR Zr

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_3BO_3, 1 ml conc. HNO_3 + 5 ml H_2O, (a clear solution should result). Add ½ ml conc. 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 (~ 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 Pu extraction, it 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.

ZIRCONIUM

(This procedure is a modification by C. W. Stanley, G. P. Ford, and E. J. Lang of one described by D. N. Hume, CN-1312, May 15, 1945.)

Introduction

In the procedure described below exchange between carrier and Zr^{97} is effected by the formation of the fluorozirconate complex $ZrF_6^=$. Rare-earth and alkaline-earth activities are removed by lanthanum fluoride scavenging, and then zirconium is separated by three barium fluorozirconate precipitations. These precipitations give excellent decontamination from niobium, the fluoro complex of which is soluble. Zirconium is finally precipitated with mandelic acid from hydrochloric acid medium and ignited to the oxide, ZrO_2, in which form it is weighed and counted. The chemical yield is about 75% and a set of eight analyses can be performed in about 7 hours.

Reagents

Zr carrier: 10 mg Zr/ml [added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1 $\underline{M}$ HNO_3] - standardized

La carrier: 10 mg La/ml [added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O]

HCl: 1 $\underline{M}$; conc.

HNO_3: 1 $\underline{M}$; conc.

H_2SO_4: conc.

HF: conc.

H_3BO_3: saturated aqueous solution

NH_4OH: conc.

$NH_2OH \cdot HCl$: solid

$Ba(NO_3)_2$: 50 mg Ba/ml

Cupferron: 6% aqueous solution (freshly prepared and kept
in refrigerator)

Mandelic acid: 16% aqueous solution

Aerosol: 1% aqueous solution

Ethanol: 95%

Equipment

Ice bath

Centrifuge

Fisher burner

Block for holding centrifuge tubes

Forceps

Porcelain crucibles: Coors 0 or 00 and Coors 1 or 2

Ground-off Hirsch funnels: Coors 0000

Stainless steel filter chimneys (i.d. 3/4")

Filter flasks

No. 42 Whatman filter circles: 1" diameter, tared

No. 42 Whatman filter paper: 11 cm

100-ml beakers

2", 60° funnels

Pipets: assorted sizes

50-ml Lusteroid test tubes

40-ml conical centrifuge tubes: Pyrex 8320
Stirring rods

Preparation and Standardization of Carrier

Dissolve 30.0 g of $ZrO(NO_3)_2 \cdot 2H_2O$ in H_2O and add sufficient conc. HNO_3 to make the solution 1 $\underline{M}$ in HNO_3. Filter and make the filtrate up to 1 liter with 1 $\underline{M}$ HNO_3.

Pipet 10.0 ml of the solution into a 100-ml beaker, make the solution 2 $\underline{M}$ in HCl, and cool in an ice bath. Add a slight excess of 6% cupferron solution and filter. Wash the precipitate with 1 $\underline{M}$ HCl containing a little cupferron. (Keep all solutions and the cupferron derivative of Zr cold.) Transfer the precipitate to a porcelain crucible (Coors 1 or 2) and ignite for 1 hr at 600 to 800°. Cool and weigh as ZrO_2.

Procedure

Step 1. Place the sample in a 50-ml Lusteroid tube and add 4 ml of Zr carrier. Adjust to 4 to 5 $\underline{M}$ in HNO_3 and to a volume of about 12 ml (Note 1). Add solid $NH_2OH \cdot$ HCl so that the solution is 2 to 3% in NH_2OH (Note 2). Make the solution about 5 $\underline{M}$ in HF. Allow to stand for a minute to insure exchange between radiozirconium and carrier.

Step 2. Add 10 drops of La carrier and centrifuge for a short time. Add another 10 drops of La carrier on top of the previous precipitate and centrifuge thoroughly. Decant the supernate into another Lusteroid tube and discard the precipitate.

Step 3. Repeat Step 2 twice.

Step 4. After a total of six LaF$_3$ scavengings, add 1 ml
of Ba(NO$_3$)$_2$ solution per 5 ml of the supernate. Let stand for
1 min and centrifuge. Discard the supernate.

Step 5. To the precipitate add 4 ml of saturated H$_3$BO$_3$
(Note 3) and slurry. Add 2 ml of conc. HNO$_3$ and slurry again.
Add 10 to 12 ml of H$_2$O and mix well. If the precipitate does
not dissolve completely, centrifuge and decant the supernate
into another Lusteroid tube.

Step 6. Precipitate BaZrF$_6$ by the addition of 2 ml of
Ba(NO$_3$)$_2$ solution and 2 ml of conc. HF. Centrifuge and dissolve
as before (Step 5).

Step 7. Precipitate BaZrF$_6$ as before (Step 6) and dissolve
the precipitate in 4 ml of saturated H$_3$BO$_3$, 4 ml of conc. HCl,
and 10 ml of H$_2$O. Add 3 drops of conc. H$_2$SO$_4$ diluted with 5 ml
of H$_2$O. Add 3 drops of conc. H$_2$SO$_4$ diluted with 5 ml of
H$_2$O and let stand for 15 min. Add a drop or two of aerosol
solution and centrifuge. Transfer the supernate to a 40-ml
glass centrifuge tube and discard the BaSO$_4$ precipitate.

Step 8. To the supernate add conc. NH$_4$OH until the
solution is basic. Centrifuge down the Zr(OH)$_4$ and discard
the supernate. Dissolve the precipitate in 2 ml of conc.
HCl, 4 ml of saturated H$_3$BO$_3$, and 10 ml of H$_2$O. Centrifuge
and, if a precipitate is formed, transfer the supernate to
a 40-ml centrifuge tube, discarding the precipitate.
Reprecipitate Zr(OH)$_4$ with conc. NH$_4$OH. Centrifuge and

dissolve as before. Precipitate a third time and dissolve the precipitate in 2 ml of conc. HCl and 15 ml of H_2O (Note 4).

Step 9. Heat the solution to boiling and add 10 ml of 16% mandelic acid. Bring to a boil again and filter onto No. 42 Whatman filter paper (11 cm), using suction. Transfer the paper and precipitate to a porcelain crucible (Coors 0 or 00), and ignite for 1 hr at 800°. Powder the ZrO_2 with the fire polished end of a stirring rod. Add 2 drops of ethanol, slurry, and grind again. Add 10 ml of ethanol, stir, and filter onto a previously washed, dried, and tared No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Wash the ZrO_2 and chimney with 5 ml of ethanol. Dry at 110° for 10 to 15 min., cool, weigh and mount, and count (Notes 5 and 6).

Notes

1. With this volume of solution, the chemical yield is good since the loss of Zr with the LaF_3 scavengings is small.

2. NH_2OH reduces Np(VI) and Pu(VI) so that these will be carried on the LaF_3 and thus not interfere in the Zr separation. NH_2OH may decompose on the addition of HF, causing the solution to effervesce.

3. H_3BO_3 removes F^- ion by conversion to BF_4^- and thus aids in the dissolution of $BaZrF_6$ by HNO_3.

4. This step of the procedure is not essential, but its performance probably completes the separation of Ba^{++} and lessens the possibility of the formation of $ZrOSO_4$. For rough work this step could very well be eliminated.

5. The samples are mounted on Al plates with two-sided Scotch tape and covered with Mylar film. Four drops of Zapon Solution (1% in ethanol) are used to keep the ZrO_2 under the Mylar film.

6. To eliminate the tail resulting from decay of 65d Zr^{95} to 37d Nb^{95}, 17h Zr^{97} is counted through a 112-mg Al/cm^2 absorber and a correction is made for self-absorption.

NIOBIUM

J. S. Gilmore

Introduction

In the separation of niobium from other fission activities, zirconium is removed as barium fluozirconate; any +4 uranium present, as well as rare-earth activities, are carried down as the fluorides at this stage. Niobium is then converted to its cupferron derivative which is extracted into chloroform. This step gives an effective separation from +6 uranium. The cupferron complex is destroyed and the niobium precipitated as the hydrous oxide, $Nb_2O_5 \cdot XH_2O$, by means of ammonia water; molybdenum remains in solution as a molybdate. The oxide is dissolved in sulfuric acid and decontamination from tin and antimony effected by means of a sulfide precipitation.

Further decontamination is obtained by additional precipitations of the oxide, extractions of the cupferron derivative, and acid sulfide scavengings. Niobium is finally precipitated as the hydrous oxide and ignited to the oxide, in which form it is weighed and counted. The chemical yield is 40 to 50% and duplicate samples can be analyzed in about 4 hours. If the sample solution contains large quantities of uranium the chemical yields are likely to be low; at present there is no explanation for this.

Reagents

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

Zr carrier: 10 mg Zr/ml (added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1 $\underline{M}$ HNO_3)

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

HCl: 6 $\underline{M}$

HCl: conc.

HNO_3: 6 $\underline{M}$

HNO_3: conc.

H_2SO_4: conc.

HF: conc.

Tartaric acid: 25% aqueous solution

H_3BO_3: saturated aqueous solution

NH_4OH: 6 $\underline{M}$

NH_4OH: conc.

$(NH_4)_2C_4H_4O_6$: saturated aqueous solution

$BaCl_2$: 50 mg/ml

$KClO_3$: solid (for standardization)

H_2S: gas

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

Methyl red indicator solution: 0.1% in 90% ethanol

Chloroform

Equipment

Muffle furnace

Fisher burner

Centrifuge

Block for holding centrifuge tubes

Mounting plates (Note 2)

Forceps

Tongs for holding Erlenmeyer flasks

Pipets: assorted sizes

Wash bottle

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

Filter chimneys (one per sample)

Filter flasks

100-ml beaker (one per standardization)

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

125-ml separatory funnels (three per sample)

125-ml Erlenmeyer flasks (three per sample)

No. 42 Whatman filter paper (9 cm)

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

40-ml Lusteroid centrifuge tubes (four per sample)

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

Crucibles: Coors 000 (one per sample)

Crucibles: Coors 00 (one per standardization)

Steam bath

Ice bath

Stirring rods

Preparation and Standardization of Carrier

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

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

Pipet exactly 5 ml of the carrier solution into a 100-ml
beaker. Add 30 ml of 6 M HNO_3 and about 1 gm of $KClO_3$ and
carefully heat the solution to boiling. Boil gently with
occasional stirring for about 5 min. Cool the mixture and
add conc. NH_4OH with stirring to make the pH value 8 to 10
(about 15 ml). Filter quantitatively on a No. 42 Whatman
filter paper through a 2", 60° funnel, returning the first

portion of the filtrate if it is not clear, and wash with hot H_2O. Ignite in a Coors 00 crucible at about 800° for 15 to 20 min and weigh as Nb_2O_5.

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

Procedure

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

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

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

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

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

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

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

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

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

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

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

Notes

1. The $Nb_2O_5 \cdot XH_2O$ precipitate is washed with NH_4NO_3 solution to prevent peptization.

2. The ignited Nb_2O_5 is mounted on an Al plate, 2-1/2" x 3-1/4", which has a depression 5/8" in diameter and 1/32" deep in the center of one side. A dilute solution of Zapon in ethanol is used to spread and fasten the oxide to the plate. The precipitate is covered with rubber hydrochloride.

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

PREPARATION OF CARRIER-FREE ZIRCONIUM TRACER

By N. E. Ballou

A procedure is presented for the preparation of carrier-free zirconium tracer. The procedure makes use of the coseparation 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 coprecipitated 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 precipitated 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
coprecipitated 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 hr. 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}.

PREPARATION OF CARRIER-FREE ZIRCONIUM-NIOBIUM TRACER

By J. A. Marinsky, D. N. Hume, and N. E. Ballou

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.

INTRODUCTION

This procedure makes use of the fact that zirconium and niobium form, at tracer concentrations, very stable chloroform-soluble cupferrides 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.

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 cupferron 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 aqueous 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 unnecessary 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, adding 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.

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.

IMPROVED PREPARATION OF CARRIER-FREE NIOBIUM
TRACER WITH MANGANESE DIOXIDE

By J. M. Siegel, W. P. Bigler, and
D. N. Hume

The MnO_2 procedure for the preparation of carrier-free niobium tracer from fission material has been modified to improve the yield and purity of the final product. The principal change is in the method of tellurium decontamination. The tellurium is removed by the reduction of tellurium with SO_2 in 3 $\underline{M}$ HCl rather than by the reduction of H_2TeO_4 with zinc metal, since Zn^{++} interferes with the carrying of niobium on MnO_2.

INTRODUCTION

The procedure of Glendenin and Gest for the preparation of carrier-free niobium tracer on MnO_2 has been revised according to suggestions by Glendenin. The principal change is in the method by which the necessary decontamination from tellurium is carried out. The removal of tellurium by the reduction of H_2TeO_4 with zinc metal has been eliminated. Instead, the starting material containing added tellurium (IV) carrier is fumed twice with conc. HCl, and the tellurium is precipitated by SO_2 in the presence of 3 $\underline{M}$ HCl and oxalic acid. The zinc reduction method was descarded because (1) without oxalic acid, niobium is lost on precipitated tellurium, (2) in the presence of oxalic acid, tellurium is incompletely reduced by zinc, and (3) in either case Zn^{++} interferes with the carrying of niobium on MnO_2.

The revised method consists in the metathesis of the original fission mixture with conc. HCl, the removal of the tellurium with carrier from oxalic and hydrochloric acids, the carrying of niobium on MnO_2 from 10 $\underline{M}$ HNO_3 (three times), separation from manganese by coprecipitation with basic ferric acetate, and the removal of the iron by extraction with isopropyl ether.

CHEMICAL PROCEDURE

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

Step 2. The supernatant liquid is evaporated to about 2 ml in order to expel most of the HCl (Note 5). Twenty milliliters of 10 $\underline{M}$ HNO_3, 10 mg of Mn^{++} carrier, and 1.5 g of $KClO_3$ are added either by slurrying with the HNO_3 or by the addition of small portions of the solid. After the initial evolution of Cl_2 has subsided, the mixture is heated

cautiously to boiling. The boiling is continued for 2 to 3 min to coagulate MnO_2, and the supernatant liquid is filtered off through a sintered-glass filter stick. The precipitate is dissolved in 10 ml of 10 $\underline{M}$ HNO_3 containing 2 to 3 drops of 30 per cent H_2O_2 and boiled for a few minutes to decompose the excess H_2O_2. Ten milliliters of 10 $\underline{M}$ HNO_3 and 1 g of $KClO_3$ are then added, and the mixture is boiled for 2 to 3 min to reprecipitate MnO_2. The supernatant solution is filtered off, and the MnO_2 is dissolved and reprecipitated a third time by the above procedure.

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

desired volume.

Notes

1. The fission-product concentrate is the aqueous phase obtained by the exhaustive ether extraction of uranyl nitrate and filtered to remove silica. Less than 1 g of uranyl nitrate per 50 ml of solution should be present. The starting material must be free of SiO_2 to prevent the loss of niobium by absorption.

2. If the zirconium-niobium mixture is isolated by the cupferron-chloroform method, it will be free of tellurium, and step 1 may be omitted.

3. Niobium is lost on the walls of the container if the solution is evaporated to dryness. The activity may be removed by boiling with 1 $\underline{M}$ KOH or 0.01 $\underline{M}$ oxalic acid, giving stable solutions of tracer as the niobate or as the oxalate complex, respectively. The oxalate may be removed before use by treating with aqua regia and fuming with HNO_3 to give a solution in HNO_3. Niobium tracer in HNO_3 or HCl loses activity rather quickly owing to adsorption on the walls of the glass container.

4. Any hexavalent tellurium activity initially present will be reduced to the tetravalent state by the HCl treatment, and from this state the reduction to the metal occurs readily with SO_2.

5. The presence of large amounts of HCl requires the addition of excessive quantities of $KClO_3$. This tends to interfere with the carrying of niobium on MnO_2.

6. It is usually necessary to add 1 drop in excess and then to dissolve the $Fe(OH)_3$ with a drop of 6 $\underline{M}$ HNO_3.

TESTS AND ANALYSES

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

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

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

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