

Separation of Hafnium from Zirconium and Their Determination: Separation by Anion-Exchange

Lawrence A. Machlan and John L. Hague

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A procedure is described for the separation of hafnium from zirconium and their individual determination. The sample is dissolved in sulfuric and hydrofluoric acids and the hydrofluoric acid removed by fuming. After dilution with water, the solution is transferred to a column containing a strong quaternary amine anion-exchange resin (Dowex-1). The hafnium is eluted with diluted (3.5 percent by volume) sulfuric acid solution. Zirconium is removed by elution with 10 percent by volume sulfuric acid solution. The elements are precipitated with cupferron, ignited, and weighed as the oxides. For samples containing from twenty to eighty percent of zirconium, a second separation of the hafnium fraction using the column is necessary.

1. Introduction

The use of hafnium and zirconium in nuclear applications has made the separation and determination of the two an important problem. Because hafnium and zirconium are very difficult to distinguish chemically, they can, for many uses, be considered as one constituent. However, since hafnium and zirconium have very different nuclear properties, it is important to know the relative amounts of each present in materials used in the nuclear reactor field.

The difficulties encountered in separating hafnium from zirconium are well known [6, 7].¹ It has been shown [1] that a separation of hafnium and zirconium can be obtained by anion-exchange in sulfuric acid solution.

The method described here has been used to determine hafnium and zirconium in mixtures of the two elements containing 80 percent or less of zirconium. Work is in progress to apply the method to materials containing more than 80 percent of zirconium.

The samples are dissolved in a sulfuric-hydrofluoric acid solution and the hydrofluoric acid is fumed off. The solution is diluted with water to 3.5 percent by volume of sulfuric acid and transferred to an anion-exchange column. The hafnium is eluted with a 3.5 percent sulfuric acid solution and then the zirconium is eluted with a 10 percent sulfuric acid solution. For samples containing more than about 20 percent of zirconium the hafnium fraction may contain some zirconium and a second separation using the column is necessary to insure complete separation. The hafnium and zirconium are precipitated with cupferron, ignited, and weighed as HfO_2 and ZrO_2 .

The procedure for samples containing less than 20 percent of zirconium requires approximately 3 days to carry to completion, as about 12 hr are required for the ion-exchange separation, and the

remaining time is required for dissolving the sample and for making the cupferron precipitations.

2. Procedures

2.1. Ion-Exchange Columns

The columns used in these experiments were constructed of polystyrene tubes approximately 12 in. long and 1 in. i.d. A simple column can be prepared from such tubing as follows: Insert a piece of polystyrene tubing 6 in. long, $\frac{1}{8}$ in. o.d. (with a $\frac{1}{8}$ in. wall) through a No. 5 waxed, rubber stopper, so that one end of the tubing is flush with the small end of the stopper. Attach another 6 in. length of the same tubing with a 2-in. length of Tygon R tubing. Insert the rubber stopper into the bottom of the 1-in. i.d. tube. Attach a hose-cork clamp, used to control the flow rate, to the Tygon tubing. Columns suitable for continuous operation have previously been described for both glass [4] and plastic [5] assemblies, and these are convenient to use if a number of analyses are to be performed.

The anion-exchange resins used were Dowex-1, 200- to 400-mesh, having 8 percent of divinylbenzene crosslinkages. Experience during several years has shown that the mesh size of these resins may vary considerably from lot to lot. To select resin of suitable size, the material as received is air-dried, and sieved through a 270-mesh sieve. Most of the very fine material is removed from the fraction passing the 270-mesh sieve, as follows: Prepare a suspension of the resin in diluted² hydrochloric acid (1 + 19). The coarser fraction is allowed to settle for 10 to 15 min, and the fines removed by decantation. Repeat the process several times, until most of the very fine material is removed.

Load the column with resin as follows: Cover the bottom of the column with a $\frac{1}{4}$ - to $\frac{1}{2}$ -in. layer of acid-resistant, polyvinyl chloride plastic "wool." Add

¹ Figures in brackets indicate the literature references at the end of this paper.

² Diluted hydrochloric acid (1 + 19) denotes 1 volume of concentrated hydrochloric acid, sp. gr. 1.18, diluted with 19 volumes of water. If no dilution is specified, the concentrated analytical reagent is meant.

portions of the resin suspension so as to obtain a settled column of the resin that is 22 cm high. Wash the loaded column with approximately 100 ml of diluted nitric acid (1+9), and then perform several washing cycles by alternate additions of diluted hydrochloric acid (1+9) and diluted hydrochloric acid (3+1) to remove the remaining fines. Finally, wash the column with diluted sulfuric acid (7+193), to convert the resin to the sulfate form. Approximately 350 to 400 ml of sulfuric acid solution will be required, and the removal of the chloride can be followed by testing portions of the eluate with silver nitrate solution. The resin charge should not be allowed to become dry.

2.2. Reagents

Sulfuric acid solution (3.5 percent).—Add 70 ml of sulfuric acid to 1,930 ml of water, mix well, and cool to room temperature. This solution is referred to as 3.5 percent sulfuric acid solution in the procedure.

Cupferron solution (60 g/liter).—Dissolve 30 g of cupferron in 450 ml of water, dilute to 500 ml, and filter through a dry filter. This solution should be cooled to about 5 °C and prepared as needed, as the solution is not stable.

Cupferron wash solution.—Add 25 ml of cupferron solution to 975 ml of cold (5 °C) diluted hydrochloric acid (1+9). Prepare as needed.

2.3. Procedure

Transfer 0.5 g of the metal sample (accurately weighed) to a covered 25-ml platinum crucible and add a suitable quantity (14 ml for samples containing less than 20 percent of zirconium, 21 ml for samples containing from 20 to 60 percent of zirconium, and 28 ml, with some evaporation, for samples containing from 60 to 80 percent of zirconium) of diluted sulfuric acid (1+3) and 5 to 6 drops of hydrofluoric acid. The sample will dissolve at room temperature. (If the sample is in the oxide form transfer an amount of sample equal to 0.5 g of hafnium and zirconium to the crucible, and add a suitable quantity (see above) of diluted sulfuric acid (1+3) and 2 to 3 ml of hydrofluoric acid. Heat gently on an air bath to dissolve.) After the sample dissolves, wash the cover with water and place the uncovered crucible on a sand or air bath. Evaporate the solution to fumes of sulfuric acid, cool, and wash down the walls of the crucible with water. Evaporate the solution to fumes again, cool, quantitatively transfer the solution to a 400-ml beaker, and add sufficient water to give a 3.5 percent sulfuric acid solution.

Transfer the solution of the sample in small increments (10 to 15 ml) to the equilibrated ion-exchange column. Wash the beaker four or five times with 5-ml portions of the 3.5 percent sulfuric acid solution, transferring the washings to the column and allowing the solution to drain to the top of the resin each time. Finally wash down the sides of the column several times with a total of approximately 50 ml of the same solution.

a. For Samples Containing Less Than 20 Percent of Zirconium

Discard the first 125 ml² of solution from the column. Continue adding the 3.5 percent sulfuric acid solution. Collect the second fraction of 550 ml (see footnote 3), containing the hafnium, in an 800-ml beaker. Replace the beaker with a 600-ml beaker to catch the zirconium fraction. Allow the solution to drain to the top of the resin and wash the sides of the column with 3 or 4 portions (a total of about 20 ml) of diluted sulfuric acid (1+9), allowing the solution to drain to the top of the resin each time. Add a total of 250 ml of diluted sulfuric acid (1+9) and remove the beaker containing the zirconium fraction. Equilibrate the ion-exchange column for the next elution cycle by passing 400 ml of 3.5 percent sulfuric acid solution through the resin and allowing the solution to drain to the top of the resin.

To the second fraction, containing the hafnium, add 65 ml of hydrochloric acid. Cool to 5 °C, and add slowly while stirring, 100 ml of cupferron solution. Add a ball of paper pulp equivalent to about one 11-cm. filter paper, stir until the pulp is well dispersed, and allow the precipitate to settle. Filter through a double 7-cm close-textured filter paper fitted to a Büchner funnel and precoated with some paper pulp. Transfer the precipitate to the funnel and wash, using 300 ml of cupferron wash solution. Transfer the precipitate and paper to a weighed 25-ml platinum crucible, and ignite at a low temperature until the carbon is gone. Finally ignite to constant weight at 1,100 °C, and weigh as hafnium dioxide.

To the third fraction, containing the zirconium, add 15 ml of hydrochloric acid. Cool to 5 °C and add slowly with stirring 50 ml of cupferron solution. Add a ball of paper pulp equivalent to about one 11-cm filter paper, stir, and allow the precipitate to settle. Filter, wash, and ignite the zirconium precipitate as described for hafnium. Weigh the zirconium as the dioxide.

b. For Samples Containing From 20 to 80 Percent of Zirconium

Discard the first 125 ml (see footnote 3) of solution from the column. Add a sufficient⁴ quantity of 3.5 percent sulfuric acid solution to elute all of the hafnium and some (10 to 50 mg) of the zirconium. Collect this second fraction in an 800-ml beaker. Replace the beaker with a 600-ml beaker and continue the elution of zirconium as described in section 2.3a.

To the second fraction, containing the hafnium, and some zirconium, add 65 ml of hydrochloric acid, and continue the procedure as described for hafnium in section 2.3a, until the precipitate is ignited at low temperature. Reserve the oxides for a second separation using the column.

To the third fraction, containing zirconium, precipitate using 50 to 100 ml of cupferron solution,

² Each column must be calibrated to determine the volume of solution needed to elute the hafnium and zirconium. This is necessary because the resins and column loadings vary somewhat with different lots of resin.

⁴ The quantity, approximately 600 to 600 ml, will depend on resin, column loading, and relative amounts of hafnium and zirconium.

filter, and ignite as described for zirconium in section 2.3a. This is zirconium fraction one.

To the reserved oxides from the second fraction, add 14 ml of diluted sulfuric acid (1+3) and 1 to 2 ml of hydrofluoric acid. Heat gently on an air bath to dissolve. After the oxides dissolve, wash the cover with water and place the uncovered crucible on a sand or air bath. Evaporate the solution to fumes of sulfuric acid, cool, and wash down the walls of the crucible with water. Evaporate the solution to fumes again, cool, quantitatively transfer the solution to a 250-ml beaker, and dilute to 100 ml with water.

Transfer the solution in small increments (10 to 15 ml) to the equilibrated ion-exchange column. Wash the beaker four or five times with 5-ml portions of the 3.5 percent sulfuric acid solution, transferring the washings to the column. Finally wash down the sides of the column several times with approximately 50 ml of the same solution. Continue as described in section 2.3a to obtain the

hafnium fraction and zirconium fraction two. Calculate the zirconium percentage from the sum of the two zirconium fractions and the hafnium percentage from the final hafnium fraction.

3. Elution of Elements With Sulfuric Acid Solutions

It has been shown previously [1] that hafnium can be separated from zirconium using 3.5 percent sulfuric acid solution to elute from resin having 8 percent of divinylbenzene crosslinkages having a maximum particle-sizing of about 50μ (passing through a 270-mesh sieve). To obtain more separation the height of the resin column was increased to 22 cm. This separation, while not as great as other separations using ion-exchange [2, 3, 8, 9], is adequate if care is taken in setting up the columns, calibrating each column, and in preparing the solution used for the ion-exchange separation. The first three curves in figure 1 give the separation of hafnium from zirconium

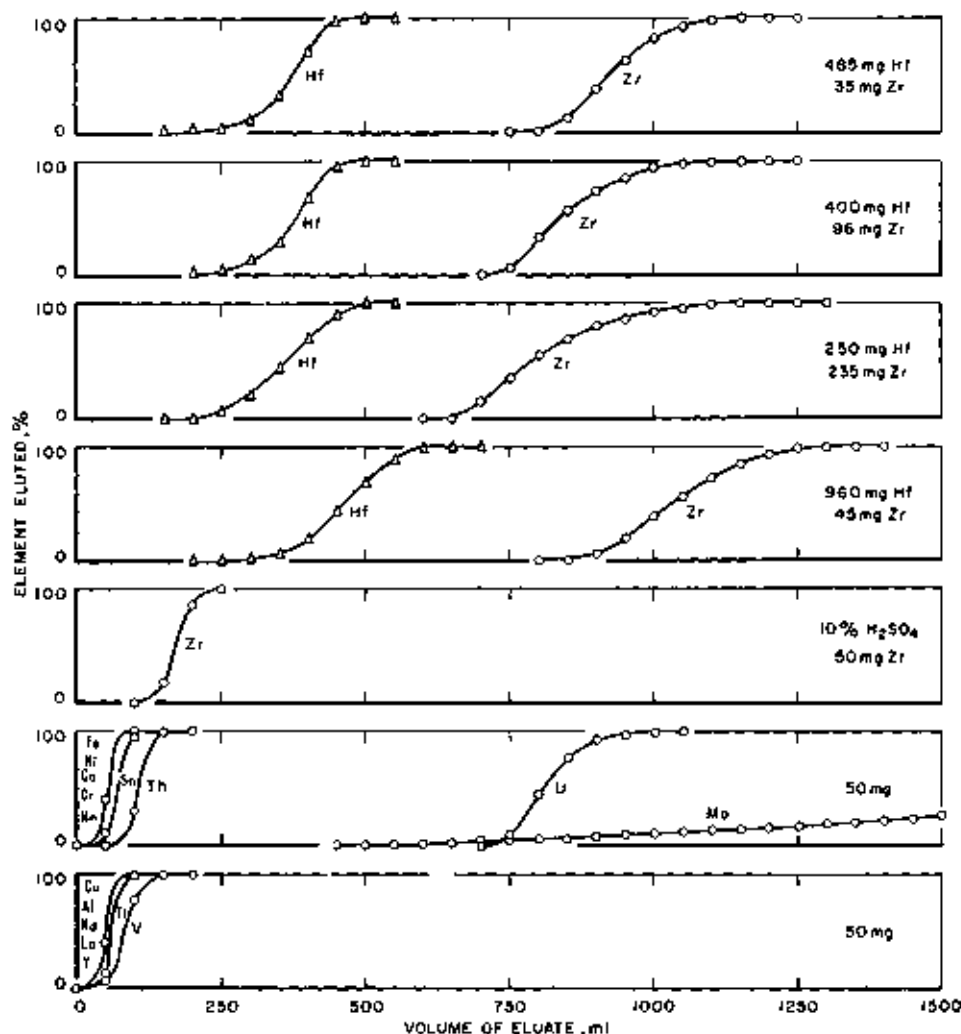


FIGURE 1. Elution behavior of elements.

um in 0.5 g samples of increasing zirconium-hafnium ratio by elution with 3.5 percent sulfuric acid solution. The fourth curve shows the separation obtained on a 1 g sample of hafnium metal by elution with 3.5 percent sulfuric acid solution. To obtain a reasonable volume of separation between the hafnium and the zirconium fractions, it is recommended that 0.5 g samples be used and that samples containing more than 20 percent of zirconium be determined by a double ion-exchange separation. To reduce the volume of solution needed to elute the zirconium, it was eluted with a 10 percent sulfuric acid solution. The fifth curve gives the zirconium elution curve in 10 percent sulfuric acid solution.

The last two curves give the elution characteristics of some other elements in 3.5 percent sulfuric acid solution. Iron (3), nickel (2), cobalt (2), chromium (3), manganese (2), copper (2), aluminum (3), neodymium (3), lanthanum (3), and yttrium (3) are eluted from the column without delay. Tin (4), thorium (4), titanium (4), and vanadium (5) are only slightly absorbed, all being eluted in 3 or 4 column volumes. Uranium (6) and molybdenum (6) are strongly absorbed. Elements that do not precipitate with cupferron, such as chromium, nickel, and cobalt, will not interfere with the determination of hafnium and zirconium by the recommended procedure. Elements that do precipitate with cupferron, such as iron, titanium, and molybdenum, would interfere in the recommended procedure. These elements are partially eluted into the discard fraction but to eliminate these interferences, the oxides can be redissolved and a mandelic acid or phosphate precipitation made.

4. Results

The results obtained by the recommended procedure on a series of synthetic oxide mixtures are given in table 1. The first six experiments were done by the procedure recommended for samples containing less than 20 percent of zirconium. These values require little comment, being within the usual limits of gravimetric methods. Experiments 7 to 10 were done by the procedure recommended for samples containing from 20 to 80 percent zirconium. These results show that for these compositions recoveries are within 2 to 5 parts per thousand. The oxides used in these experiments were obtained from previous ion-exchange separations. Spectrographic examination of these oxides indicated less than 100 ppm cross contamination.

The results obtained on synthetic metal samples are given in table 2. The metals used were "reactor grade" metals. The zirconium was nearly hafnium-free and the hafnium (sample 1 in table 3) contained approximately 2.14 percent zirconium. The zirconium added was calculated from the zirconium in the hafnium metal and the zirconium metal added. Spectrographic examination of the recovered oxides indicated less than 100 ppm zirconium in the hafnium fraction and less than 1 percent hafnium in the zirconium fraction.

The results obtained on two "reactor grade" hafnium metals is given in table 3.

TABLE 1. Results of determinations of zirconium and hafnium by the recommended procedure in various synthetic oxide mixtures

Experiment	Hafnium oxide			Zirconium oxide		
	Added	Found	Difference	Added	Found	Difference
1 ^a	mg 575.3	mg 574.9	mg -0.4	mg 33.6	mg 33.7	mg +0.1
2 ^a	574.9	574.7	-0.2	33.9	33.6	-0.3
3 ^a	574.7	575.6	+0.9	33.5	33.4	-0.1
4 ^a	478.8	478.6	-0.2	133.2	133.2	0.0
5 ^a	478.8	478.9	+0.1	132.2	132.0	-0.2
6 ^a	476.2	475.6	-0.6	127.2	127.2	0.0
7 ^b	294.0	296.6	+2.6	334.1	335.3	+1.2
8 ^b	294.0	293.8	-0.2	331.6	331.6	0.0
9 ^b	146.0	146.2	+0.2	602.1	602.8	+0.7
10 ^b	146.2	146.4	+0.2	499.4	499.6	+0.2

^a Experiments using the procedure: "For samples containing less than 20 percent of zirconium."

^b Experiments using the procedure: "For samples containing from 20 to 80 percent of zirconium."

TABLE 2. Results of determinations of zirconium and hafnium by the recommended procedure in synthetic metal samples

Experiment	Hafnium			Zirconium		
	Added	Found	Difference	Added	Found	Difference
1.....	mg 373.8	mg 374.7	mg +0.9	mg 36.2	mg 35.6	mg -0.6
2.....	464.2	465.2	+1.0	36.1	35.6	-0.5
3.....	479.9	479.8	-0.1	28.6	28.6	0.0

TABLE 3. Results of determinations of zirconium and hafnium by the recommended procedure in "reactor grade" hafnium metals

Sample number	Sample weight	Hafnium	Zirconium
1.....	g 0.5	% 97.97	% 2.15
1.....	0.5	97.96	2.06
1.....	0.5	97.81	2.21
1.....	0.5	97.85	2.16
2.....	0.5	95.55	4.42
2.....	0.5	95.29	4.70
2.....	0.5	95.35	4.77

5. References

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