deconvolution is processed. These improvements would render this analytical technique more convenient for solving specific problems requiring high resolving power (>10 000) from the mass spectrometer.

Registry No. TCDD, 1746-01-6.

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Determination of Hafnium in Zirconium Metal and Zircaloy 4 Metal Standard Reference Materials by Isotope Dilution Spark Source Mass Spectrometry

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A procedure has been developed for the determination of microgram per gram concentrations of hafnium in zirconium metal and zircaloy 4 metal Standard Reference Materials (SRM's) by stable isotope dilution spark source mass spectrometry. The concentration of hafnium in these SRM's ranges from 200 μg/g in SRM 1236 to 32 μg/g in SRM 1237. One-half-gram samples were spiked with ^{179}Hf and dissolved in a mixture of hydrofluoric and sulfuric acids and the isotopically altered Hf was separated from Zr by cation exchange chromatography using 0.32 M sulfuric acid as an eluant. The isotopically altered, purified hafnium was evaporated onto 200 mesh gold powder which was subsequently homogenized and pressed into electrodes. The altered isotopic ratios were determined by spark source mass spectrometry using electrical detection.

The ability to accurately measure microgram per gram concentrations of hafnium in zirconium and zircaloys is of paramount importance to the nuclear industry. Because of their chemical and physical properties, especially their low cross section for thermal neutrons, these materials are well suited to nuclear power applications (*1*). Unfortunately, hafnium, which is present in percent amounts in zirconium ores, has 640 times higher neutron absorption than zirconium and must therefore be reduced to low microgram per gram concentration levels. This is especially important in nuclear reactors, since the amount of hafnium present has a direct effect on the efficiency of the reactor core and thus, the cost of producing nuclear power. In addition, the total amount of hafnium in the reactor core affects the reactor shutdown margin, a major safety concern.

In response to requests from the nuclear industry, the NBS Office of Standard Reference Materials initiated a program for the production and certification of zirconium and zircaloy Standard Reference Materials (SRM's). The zircaloy SRM's are zircaloy 4 metal, a material used chiefly in the manufacture of fuel rods and structural parts for pressurized water reactors (*1*).

The separation of hafnium and zirconium from each other is difficult because of their similarity in chemical behavior (*2*, *3*). This problem is amplified when the separation of microgram per gram concentrations of hafnium from zirconium is attempted. The separation of hafnium from zirconium by ion exchange chromatography has been reported by a number of authors (*3–7*). A number of approaches were investigated radiochemically with ^{95}Zr and ^{181}Hf tracers. Ultimately, cation exchange chromatography using 0.32 M H_2SO_4 as an eluant proved to be the most effective separation medium for isolating trace elements of hafnium from the zirconium and zircaloy matrices. The final procedure, which was adapted from the work of Kolosova et al. (*7*) and Nelson et al. (*4*), utilizes three cation exchange columns. The first two columns were used to separate the hafnium from the zirconium matrix and the third column was used to eliminate additional impurities that prevent thorough mixing of the sample with gold powder, a process used in fabricating electrodes for sparking in the mass spectrometer.

EXPERIMENTAL SECTION

Instrumentation. The mass spectrometer used in this work is a JEOL Model JMS-O1BM-2 spark source mass spectrometer (SSMS). All work was performed by using electronic detection with ion multiplier amplification. The collector slit at the exit of the magnet gap was adjusted to give an approximate resolution of 1600 for mass scans, and opened to give an approximate resolution of 350 for isotopic ratio measurements. At this resolution, flat-topped peaks are obtained and therefore small peak displacements will not cause changes in ion currents through clipping of peak tails. Power to the rf amplifier is set at 4.2 kV, providing approximately 50–60 kV peak to peak rf voltage (open gap). Sparking conditions are set at 100 pulses/s, with a 40-μs pulse length. Sparking is maintained with an automatic gap controller which senses the rf breakdown voltage between the sample electrodes. The controller is adjusted to maintain the widest possible gap that provides constant uninterrupted sparking. These conditions normally provide maximum ion currents from a sample. Ion accelerator and electrostatic sector voltages are normally +28 kV and ±1400 V, respectively.

Reagents and Ion Exchange Columns. The acids and water were purified by subboiling distillation prior to use as described by Kuehner et al. (*8*). The ^{179}Hf was in the form of hafnium oxide

enriched to 87% and was obtained from Oak Ridge National Laboratories. It was dissolved in a solution of HNO_3 and H_2SO_4 and diluted to obtain a concentration of 103.9 $\mu g/g$. The cation exchange resin was Bio-Rad AG 50X8, 100–200 mesh. Column 1 contained 18 cm × 1.5 cm of resin and column 2 contained 13 cm × 1.5 cm of resin. Both columns were cleaned prior to loading the sample by eluting with 40 g of 8 N HCl followed by 80 g of H_2O. The third column contained 3.3 cm × 1.1 cm of resin and was cleaned by eluting with 25 g of 8 N HCl followed by water until the washings had a pH of 7. High-purity gold powder reported to be 99.9999% was used throughout the analysis.

Sample Preparation. One-half-gram samples of the zirconium and zircaloy SRM's in chip form were weighed into Teflon–FEP beakers and spiked with sufficient ^{179}Hf solution to yield a ratio of weight of spike to weight of natural hafnium of about 1.15 to 1. The spiked samples were dissolved and equilibrated by digesting with 15 g of a mixture of 18 M H_2SO_4, 28 M HF, and H_2O in a 4:1:10 ratio at approximately 90 °C for a minimum of 8 h. The samples were evaporated to dryness and the residues were redissolved in 0.32 M H_2SO_4 and transferred to 150-mL tall-form quartz beakers. The solution was evaporated to dryness; the residue was dissolved in 10 g of H_2O; and the solution was loaded onto column 1. The zirconium fraction was eluted with 80 g of 0.32 M H_2SO_4 and the hafnium was eluted with 120 g of 0.32 M H_2SO_4. The hafnium fraction was evaporated to dryness, redissolved in 5 g of H_2O, and loaded onto column 2. The beaker was rinsed with 5 g of H_2O and the washings were also loaded onto the column. The zirconium fraction was eluted with 50 g of 0.32 M H_2SO_4 and the hafnium was eluted with 120 g of 0.32 M H_2SO_4. The hafnium fraction was evaporated to dryness, redissolved in 5 g of 0.15 M HCl, and loaded onto column 3. The loaded column was washed with 2 M HCl (approximately 50 g) until a flame test indicated that sodium was absent. The hafnium was eluted with 20 g of a 9:1 mixture of HCl and HF into a Teflon–FEP beaker. The hafnium fraction was evaporated to about 0.1 mL, 0.2 mL of HNO_3 was added, and the solution was evaporated to one drop. Fifty milligrams of gold powder was added and the solution was evaporated to dryness. An additional 0.5 mL of HNO_3 was added and evaporated to dryness.

Calibration of the ^{179}Hf Spike. The calibration of the hafnium spike was accomplished by using two different sources of natural hafnium, the pure metal and hafnium oxide. Hafnium metal is the preferred standard because its stoichiometry is known; however, it is typically contaminated with approximately 3% zirconium. All other impurities, as measured by direct sparking on the SSMS, total less than 0.1%. To determine the zirconium content, a sample of the metal was dissolved, aliquots were spiked with ^{91}Zr, and altered ^{91}Zr/^{90}Zr ratios were measured by isotope dilution spark source mass spectrometry (IDSSMS). The zirconium content was found to be 3.02%. The high-purity hafnium oxide was analyzed by direct sparking on the SSMS and was found to contain less than 0.05% zirconium, or any other impurity.

The spike and natural hafnium solutions were weighed into Teflon–FEP beakers to produce a microgram total spike to microgram total natural ratio of 1.1. The solutions were blended and then, like the samples, were maintained at approximately 90 °C for at least 8 h to assure equilibration. The samples were then evaporated onto 50 mg of gold powder for determination of the isotope ratios by IDSSMS.

Fabrication of Electrodes. The hafnium–gold powder mixture was transferred to a stainless steel mixing vial and mixed for 2 min using a 1 g stainless steel ball. The resulting gold pellets were pressed flat and repeatedly cut in half, stacked, and pressed. The gold disk from the last pressing was cut in half to form a pair of electrodes approximately 2 × 5 × 0.2 mm.

Instrumental Analysis Procedure. The electrodes were loaded into the source of the spark source mass spectrometer which was pumped to a pressure below 2×10^{-7} torr (2×10^{-5} Pa). The samples were presparked and a mass scan was made from 240 to 10 atomic mass units, using electrical detection. The ion multiplier gain was set to give detection limits of 0.1 ppm atomic for all elements present in the sample. The altered ^{178}Hf/^{179}Hf isotopic ratio was then measured using +1 ions in the peak switching mode. The peaks were switched magnetically under the control of a Hall probe gaussmeter. Three sets of measurements, each containing 25 ratios, were collected for each sample.

Each set required approximately 30 min of instrument time.

RESULTS AND DISCUSSION

IDSSMS using electrical detection has both the advantage of a wider dynamic range of ratio measurements and the potential for improved precision when compared to the photographic mode of ion detection. Photographic detection enables all ions to be collected simultaneously, and as a result, sample homogeneity does not affect the precision of the isotope ratio measurements if they are made within each individual exposure. Electronic detection, however, measures the intensity of each isotope sequentially, and the precision of the ratio measurements depends on both sample homogeneity and close control of instrumental sparking conditions.

For an analysis, in which electrical detection is used such as the determination of hafnium in zirconium, it is normally necessary to homogenize the sample with a high-purity conducting material. High-purity (99.9999%) graphite, silver, or gold powders are the most common mixing mediums used to produce conducting electrodes for SSMS analysis. A potential interference in sparking the homogenized samples is the formation of molecular ions consisting of major components of the sample (M) and the homogenizing medium (50–90% of the electrodes). With graphite, compounds containing MC^+, MC_2^+, MC_3^+, ..., are common. In fact, $^{12}C_{15}^+$ would interfere with ^{180}Hf if graphite were used as a mixing medium. The use of silver as a mixing medium can produce similar interfering compounds. Since gold has only one stable isotope at mass 197, a similar compound formation would not interfere with isotopic measurements in the 174 to 180 mass range of hafnium.

The most probable source of molecular line interferences in the determination of hafnium in a zirconium matrix using a gold mixing medium would be from the major components in the sample, such as Zr_2^+. The lowest Zr_2^+ mass that could interfere with the hafnium masses would be $^{90}Zr_2^+$, which would interfere with the ^{180}Hf$^+$. Although there was no visible evidence of these species, the isotope dilution analyses were performed by ratioing the ^{179}Hf spike isotope against the natural ^{178}Hf. The use of the 27.14% naturally abundant ^{178}Hf isotope instead of the 35.24% abundant ^{180}Hf isotope resulted in only a modest decrease in sensitivity while avoiding any chance of $^{90}Zr_2^+$ interference. In developing a procedure for isolating hafnium from the zirconium matrix, a single pass through the cation exchange column provided enough preconcentration of hafnium to give good SSMS sensitivity for isotope dilution analysis. Unfortunately, the relatively large amount of zirconium still present prevented the sample from mixing with the gold powder to give a well-homogenized gold sample electrode. A second cation exchange separation removed most of the remaining zirconium but, it was still necessary to rid the sample of other metallic impurities that were present at high enough levels to preclude homogenization of the sample and the gold powder. A final short column was used to remove these impurities from the isotopically altered hafnium solution.

The concentration of hafnium was calculated by using the equation

$$[Hf](\mu g/g) = \frac{WK(A_{sp} - B_{sp}R)}{m(BR - A)} \qquad (1)$$

where R is the measured ^{178}Hf/^{179}Hf ratio, A_{sp} and B_{sp} are the abundances of ^{178}Hf and ^{179}Hf in the ^{179}Hf spike material, A and B are the abundances of ^{178}Hf and ^{179}Hf in natural hafnium, W is the mass (μg) of hafnium spike added, K is the ratio of the relative atomic weight of the natural element to the relative atomic weight of the spike material, and m is the mass (g) of sample. The spike calibration data, shown in Table I, indicate good agreement between the calibrations performed

Table I. ^{179}Hf Spike Calibration

sample	source of natural Hf	concn of hafnium spike, μg/g
1	metal[a]	100.45
2	metal[a]	99.22
3	metal[a]	99.13
4	metal[a]	98.76
5	oxide	100.27
6	oxide	99.96
	av	99.63

[a] Analysis of the hafnium metal by IDSSMS showed a zirconium content of 3.02%.

Table II. Hafnium in Zirconium SRM's

	amt of Hf, μg/g		
sample	SRM 1234	SRM 1235	SRM 1236
1	47.8	96.0	202.2
2	48.1	96.4	200.4
3	47.6	99.1	201.1
4	47.6	85.5[a]	201.3
av	48	97	201

[a] Unresolvable discrepancy believed to be due to weighing error during sample preparation. Not included in the average.

Table III. Hafnium in Zircaloy 4 SRM's

	amt of Hf, μg/g		
sample	SRM 1237	SRM 1238	SRM 1239
1	33.1	181.8	78.8
2	32.4	181.2	79.4
3	31.0	183.0	79.6
4	32.3	178.6	77.1
av	32	181	79

with hafnium metal and those performed with hafnium oxide. The standard deviation of all of the data is 0.7%. For the metal, this includes a correction factor for the zirconium content as determined by isotope dilution.

The data obtained for hafnium in the zirconium metal and zircaloy SRM's are shown in Tables II and III. Each sample number denotes a separate sampling of the SRM material. The concentrations ranged from a low of 32 μg/g for SRM 1237 to a high of 201 μg/g for SRM 1236. Since 0.5-g samples were analyzed, the actual amounts of hafnium measured ranged from 16 to 100 μg. The analytical blank correction was 0.14 μg/g for 0.5-g samples. For SRM 1237, which had the lowest hafnium concentration, this amounts to a correction of 0.4%. With the exception of SRM 1235, the internal precision for each SRM is very good. The data point denoted

Table IV. NBS Certified Concentrations of Hafnium in Zirconium and Zircaloy 4 SRM's[a]

SRM no.	designation	certified value,[b] μg of Hf/g
1234	zirconium A	46 ± 3
1235	zirconium B	95 ± 5
1236	zirconium C	198 ± 6
1237	zircaloy D	31 ± 3
1238	zircaloy E	178 ± 6
1239	zircaloy F	77 ± 4

[a] Reprinted by permission of NBS Office of Standard Reference Materials. [b] Certified value is based on measurements obtained by IDSSMS and neutron activation analysis. The estimated uncertainty is based on judgement and represents an evaluation of the combined effects of method imprecision, possible systematic error among methods, and material variability.

by "a" for SRM 1235, represents an anomaly that cannot be easily reconciled. This data point is 12% lower than the average of samples 1, 2, and 3. Because of the chemical and physical similarities of hafnium and zirconium metals, it is doubtful that this discrepancy is due to sample inhomogeneity. Since reevaluation of the sample by IDSSMS yielded the same ^{178}Hf/^{179}Hf ratio, it is thought that an error occurred during the weighing of the spike or the sample and the result has been excluded from the average.

Table IV lists the NBS Certified values for the concentration of hafnium in the zirconium metal and zircaloy SRM's which are available from NBS. The certified values are based on the IDSSMS results shown in Tables II and III and independent results obtained by neutron activation analysis.

Registry No. Hafnium, 7440-58-6; zirconium, 7440-67-7; Zircaloy 4, 11068-95-4.

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