Standard Test Method for Determining Hafnium in Zirconium and Zirconium Alloys By Direct Current Plasma—Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation E1552; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of hafnium in zirconium and zirconium alloys with composition greater than 0.003 % (30 mg/kg).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

B349/B349M Specification for Zirconium Sponge and Other Forms of Virgin Metal for Nuclear Application
B350/B350M Specification for Zirconium and Zirconium Alloy Ingots for Nuclear Application
B351/B351M Specification for Hot-Rolled and Cold-Finished Zirconium and Zirconium Alloy Bars, Rod, and Wire for Nuclear Application
B352/B352M Specification for Zirconium and Zirconium Alloy Sheet, Strip, and Plate for Nuclear Application
B353 Specification for Wrought Zirconium and Zirconium Alloy Seamless and Welded Tubes for Nuclear Service (Except Nuclear Fuel Cladding)
B493 Specification for Zirconium and Zirconium Alloy Forgings
B494/B494M Specification for Primary Zirconium
B495 Specification for Zirconium and Zirconium Alloy Ingots
B523/B523M Specification for Seamless and Welded Zirconium and Zirconium Alloy Tubes
B550/B550M Specification for Zirconium and Zirconium Alloy Bar and Wire
B551/B551M Specification for Zirconium and Zirconium Alloy Strip, Sheet, and Plate
B614 Practice for Descaling and Cleaning Zirconium and Zirconium Alloy Surfaces
B653/B653M Specification for Seamless and Welded Zirconium and Zirconium Alloy Welding Fittings
B658/B658M Specification for Seamless and Welded Zirconium and Zirconium Alloy Pipe
B752 Specification for Castings, Zirconium-Base, Corrosion Resistant, for General Application
B811 Specification for Wrought Zirconium Alloy Seamless Tubes for Nuclear Reactor Fuel Cladding
E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample, in the form of drillings, chips, milling, turnings, or powder, is dissolved in dilute hydrofluoric acid (HF). The hafnium content is measured using a direct current plasma (DCP) spectrometer, which is calibrated with reference solutions of hafnium in the presence of zirconium. The microprocessor is programmed to display the results in micrograms per millilitre (µg/mL).

5. Significance and Use

5.1 When zirconium materials are used in nuclear applications, it is necessary that hafnium, a neutron absorber, be present only at very low concentrations.

5.2 This test method is useful in testing materials for compliance with the compositional requirements as given in

[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Specifications B349/B349M, B350/B350M, B351/B351M, B352/B352M, B353, B493, B494/B494M, B495, B523/B523M, B550/B550M, B551/B551M, B653/B653M, B658/B658M, B752, and B811.

6. Apparatus

6.1 *Plastic Labware:*

6.1.1 *Beakers,* 100 mL, disposable, polypropylene, or 125 mL polytetrafluoroethylene (PTFE) are satisfactory.

6.1.2 *Volumetric Flasks*—Linear polyethylene (LPE) or polymethylpentene (PMP) are satisfactory.

NOTE 1—Plastic volumetric flasks change dimension as they age and therefore must be recalibrated periodically.

6.2 *Spectrometer— Modified Czerny-Turner*, using an Echelle grating with 30° prism for order separation providing a reciprocal linear dispersion of about 0.1 nm/mm in the 80 to 85th order. The instrument is operated in the sequential mode.

6.3 *Excitation Source:*[3]

6.3.1 *D-C Plasma,* formed by a tungsten cathode and two carbon anodes in an inverted "Y" configuration, having a current output of 7 A at 40 V.

6.3.2 Glass spray tube shall be replaced with one made from PTFE or pyrolytic graphite to prevent hydrofluoric acid attack on the glass.

6.4 *Argon*—Commercially available as prepurified gas or liquid is satisfactory.

7. Reagents and Materials

7.1 *Purity and Concentration of Reagents*—The purity and concentration of chemical reagents shall conform to the requirements prescribed in Practices E50.

7.2 *Pure Metals:*

7.2.1 *Hafnium Metal or Hafnium Dioxide,* of highest purity available and having a known impurity content.

NOTE 2—Many hafnium materials contain residual zirconium in quantity sufficient to affect the hafnium value.

7.2.2 *Zirconium Metal,* of the highest purity available and having a known hafnium content.

7.3 *Reference Materials:*

7.3.1 *Standard Reference Materials (SRM):*[4]One Zircaloy-4, SRM 360b, containing 78.5 mg/kg hafnium, is available.

7.3.2 Other reference solutions can be prepared by dissolving zirconium metal in HF. A solution of hafnium metal dissolved in HF is added to the zirconium solution to produce the required concentrations.

8. Hazards

8.1 This method involves the use of concentrated hydrofluoric acid. Read and follow label precautions carefully before using.

8.2 Refer to Practices E50, 7.5.11, for more information.

9. Preparation of Apparatus

9.1 Conduct start-up and wavelength adjustment in accordance with the manufacturer's instructions.

9.1.1 Optimize the hafnium wavelength at 264.14 nm or 282.02 nm while introducing the 1 mg/mL solution prepared in 10.2.

9.1.2 Enter the appropriate concentration values (microgram per millilitre) for the high and low reference materials into the microprocessor.

9.2 *Replication:*

9.2.1 Set the microprocessor to average three integrations at 10 s each.

9.3 *Direct Current Plasma—Instrument Parameters:*

Current, A	7
Voltage, V	40
Gas	Argon, 99.9 % min
Flow rate, L/min	8
Entrance slits, µm	50 wide by 300 high
Exit slits, µm	25 wide by 300 high

10. Preparation of Calibration Solutions and Specimens

10.1 *Preparation of Calibration Solutions:*

10.1.1 Weigh 1.0 g SRM to the nearest 1 mg into a plastic beaker. Add 20 mL water and, in small increments, add 10 mL HF (48 %) and cover with a plastic cover. When the reaction subsides, add 2 mL nitric acid (HNO_3) and place the beaker on a steam bath for 10 min to assure complete dissolution of the specimen.

10.1.2 Cool the solution, transfer to a 100 mL plastic volumetric flask, dilute to volume and mix.

10.2 *Preparation of Hafnium Solution (1 mg/mL):*

10.2.1 *Hafnium Metal*—Weigh 0.1 g of the pure hafnium to the nearest 0.1 mg, into a plastic beaker. Add 20 mL water and, in small increments, add 10 mL HF. Cover with a plastic cover and place beaker on a steam bath until dissolution is complete. Cool the beaker, transfer to a 100 mL plastic volumetric flask, dilute to volume, and mix.

10.2.2 *Hafnium Dioxide*—Weigh 0.1179 g of the pure HfO_2 to the nearest 1 mg into a plastic beaker. Add 30 mL HF, cover with a plastic cover and place the beaker on a steam bath until dissolution is complete. Cool the beaker, transfer to a 100 mL plastic volumetric flask, dilute to volume, and mix.

NOTE 3—Hafnium metal and HfO_2 weights must be correspondingly increased as total hafnium content decreases because of impurity content.

10.3 *Preparation of Hafnium Spiking Solutions:*

10.3.1 *Solution* (100 µg/mL)—Transfer 10.0 mL of the 1 mg/mL solution, prepared in accordance with 10.2, into a 100 mL plastic volumetric flask, dilute to volume, and mix.

10.3.2 *Solution* (10 µg/mL)—Transfer 10.0 mL of the 100 µg/mL solution, prepared in accordance with 10.3.1, into a 100 mL plastic volumetric flask, dilute to volume and mix.

[3] This instrument is no longer manufactured; however there are many instruments of this type which are still in current use. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.

TABLE 1 Statistical Information

Test Sample	Certified mg/kg Hf	Assigned Value	Amount Found	Repeatability (R1 E173)	Reproducibility (R2 E173)
NIST SRM 1234	46	...	46.1	6.4	9.3
NIST SRM 1235	95	...	91.7	7.7	15.5
NIST SRM 1236	198	...	195.3	14.3	32.1
Production Specimen	...	614	612.3	41.0	87.8

TABLE 2 Preparation of Synthetic Reference Solutions

Concentration[A]		Concentration of Spiking Solution, µg/mL	Volume of Spiking Solution, mL
mg/kg (ppm)	µg/mL		
30 + *b*[B]	0.3	10	1.5
50 + *b*	0.5	10	2.5
100 + *b*	1.0	10	5.0
200 + *b*	2.0	10	10.0
500 + *b*	5.0	100	2.5

[A]Values given in mg/kg (ppm) and micrograms per millilitre (µg/mL) are only true if the zirconium matrix material is hafnium-free. If hafnium is present in the matrix material, its value must be added to the spiked value.
[B] The letter *b* indicates blank.

10.4 *Preparation of Synthetic Reference Materials:*

10.4.1 For each calibration point required, weigh 0.5 g of the pure zirconium metal to the nearest 1 mg into a plastic beaker. Add 10 mL water and, in small increments, add 5 mL HF (48 %) and cover with a plastic cover. Continue as described in 10.1.1.

10.4.2 Cool the solution and transfer to a 50 mL plastic volumetric flask. Reserve sufficient volume for the hafnium spike.

10.4.3 Transfer known quantities of the appropriate hafnium spiking solution prepared in 10.3 to each flask as given in Table 2.

10.5 *Preparation of Specimens:*

10.5.1 Samples shall be clean and oil free. Refer to Practice B614 for cleaning procedures.

10.5.2 Weigh duplicate 1.0 g portions, to the nearest 1 mg, into a plastic beaker. Dissolve the samples as described in 10.1.1 and 10.1.2.

11. Calibration and Standardization

11.1 *Calibration*—The system sets a two-point calibration curve in the microprocessor.

11.1.1 "Auto/Range" will set the intensity of the high reference material into memory while being introduced into the plasma.

11.1.2 "Low Standard" will set the intensity of the low reference material into memory while being introduced into the plasma.

11.2 *Standardization*—The frequency of standardization will depend upon the long term stability of the instrument.

11.2.1 To ensure that the instrument is in calibration, introduce the high, low, or an intermediate reference material as a test solution. If the reading deviates by more than 5 % from the established value, recalibrate as described in 11.1.

12. Procedure

12.1 Introduce up to four test solutions in a series into the plasma with the instrument set to average three readings for 10 s each.

12.2 Check the calibration after every four test solutions by measuring a reference material as a test solution. If the reading deviates by less than 5 % from the established value, continue with the next series of tests. If the standard deviates by more than 5 %, recalibrate as described in 11.1 and remeasure the test solutions.

12.3 Procedures for "drift correction" are described in Guide E1097.

13. Calculation

13.1 Calculate the average of the three readings (microgram per millilitre) as follows:

$$\text{Hafnium, mg/kg (ppm)} = A \times B/C \quad (1)$$

where:

A = concentration of hafnium in test solution, µg/mL,
B = volume of final test solution, mL, and
C = weight of sample, g.

14. Precision and Bias

14.1 *Precision*—Five laboratories cooperated in testing four specimens. Precision data are given in Table 1.

14.2 *Bias*—No bias was detected in the interlaboratory test results of the NIST SRMs that were included, nor in the higher concentration production sample that had been assigned a composition value for hafnium.

15. Keywords

15.1 d-c plasma; hafnium; zirconium