
Analyte:	Hafnium	Method No.:	S194
Matrix:	Air	Range:	0.26 - 1.05 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision (\overline{CV}_T):	0.086
Procedure:	Filter collection, acid digestion, plasma emission spectroscopy	Validation Date:	8/4/78

1. Synopsis

Hafnium, collected on mixed cellulose ester membrane filter, is digested in steps using nitric, perchloric and hydrofluoric acids.

- 1.2 The solutions of samples and standards are analyzed by emission spectroscopy with a D.C. plasma excitation source. The intensity of the emission at 264.1 nm is proportional to the hafnium concentration.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was validated over the range of 0.262 - 1.045 mg/cu m at an atmospheric temperature and pressure of 27°C and 768 mm Hg, using a 90-liter sample.
- 2.2 The upper limit of the method is dependent on filter loading since this will affect flow measurement. Dilution may be used as appropriate to maintain samples within desired concentration range.

The method may be extended to higher values by further dilution of the sample solution. The detection limit of the method has not been established; however, standard solutions containing 50 ppb hafnium could be analyzed within $\pm 12\%$ when measured against a 1 ppm standard.

3. Interferences

When other compounds are known to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

There are no known spectral line interferences for the hafnium plasma emission spectroscopic analysis at 264.1 nm.

4 Precision and Accuracy

The Coefficient of Variation (\overline{CV}_T) for the combined analytical and sampling method in the range of 0.26 - 1.05 mg/cu m was 0.0861. This value corresponds to a 0.043 mg/cu m standard deviation at the OSHA standard concentration. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average of 95% of the time over the validation range. A collection efficiency of at least 99.8% was determined for the collection medium, and the dilution ratios of samples collected at 0.5, 1 and 2X the OSHA standard were within 4.6% of measured dilution ratios, thus no bias was introduced in the sample collection step. The analytical method recovery was determined to be 99.3% for a collector loading of 25.0 μg . In storage stability studies the mean of samples analyzed after seven days was within 1.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

The method is simple and specific for hafnium.

The digestion procedure is time-consuming due to the large number of steps involved.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Filter. The filter unit consists of a 37-mm diameter, 0.8 micrometer pore size, mixed cellulose ester filter (Millipore AA or equivalent).

6.1.2 Filter Holder. The filter is placed in a two-piece filter holder held together by tape or a shrinkable band.

6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate is needed. The pump must be calibrated with a representative filter unit in the line.

6.1.4 Thermometer.

6.1.5 Barometer.

6.1.6 Stopwatch.

Plasma emission spectrometer, direct current, Spectrametrics, Inc., Spectraspan III or equivalent.

6.2.1 Argon (for direct current plasma excitation source)

6.2.2 Pressure regulators, two-stage, for each compressed gas tank used.

Pipetes, delivery or graduated, 1, 5, 10-mL and other convenient sizes for making standards.

Nalgene or equivalent volumetric flasks, 10-mL, 100-mL, and other convenient sizes.

Beakers, 100-mL, Teflon.

Sand bath, maintained at 150°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better

Water, distilled or deionized.

Nitric Acid.

Perchloric Acid.

5% Hydrofluoric Acid. Prepare by adding 50 mL concentrated HF to 1 liter of distilled water.

Hafnium Standard Solutions in 5% HF. Prepare as necessary by volumetric dilution of 1000 ppm hafnium aqueous standard solution (Spex Industries, Inc.) with 5% HF.

8. Procedure

Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6M nitric acid, tap water and distilled or deionized water, in that order, and then dried.

8.2 Collection and Shipping of Samples

Assemble the filter in the two-piece filter holder and close firmly to insure that the edge of the filter is sealed. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage may occur around the filter. The filter holder is held together by plastic tape or a shrinkable band. A piece of flexible tubing is used to connect the holder to the pump.

Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

- 8.2.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

A sample size of at least 90 liters is recommended. Sample at a known flow rate between 1.5 and 2.0 liters per minute. The flow rate should be known with an accuracy of $\pm 5\%$.

- 8.2.5 Turn the pump on and begin sample collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

- 8.2.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If the pressure reading is not available, record the elevation.

- 8.2.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and the outlet.

- 8.2.8 Carefully record sample identity and all relevant sample data.

- 8.2.9 Obtain a blank sample by handling one filter in the same manner as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every batch or partial batch of ten samples.

- 8.2.10 The filter holders should be shipped in a suitable container designed to prevent damage in transit.

8.2.11 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon cap.

Analysis of Samples

- 8.3.1 Open the filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 100-mL Teflon beaker.
- 8.3.2 Add 3 mL HNO_3 , cover and evaporate on sand bath to complete dryness. This step is then repeated once.
- 8.3.3 Add 3 mL HNO_3 and five drops HClO_4 ; again evaporate to dryness.
- 8.3.4 Add 1 mL HNO_3 and 5 mL HF; evaporate to dryness.
- 8.3.5 Add 1 mL HNO_3 and 5 mL HF; evaporate until no more than a droplet of solution remains. Under no circumstances, however, should the sample be allowed to go to dryness as residual carbon may render hafnium insoluble. If this happens, this step must be repeated.
- 8.3.6 Add 3-5 mL 5% HF, swirl, cover and cool.
- 8.3.7 Transfer solution into a 10-mL volumetric flask and fill to mark with 5% HF.
- 8.3.8 Mix thoroughly and transfer into clean dry plastic container until emission analysis can be made.
- 8.3.9 Rinse all glassware used immediately free of HF.
- 8.3.10 Plasma emission analysis; see Section 9.

Determination of Sample Recovery

- 8.4.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest.
- 8.4.2 Procedure. A known amount of hafnium, equivalent to that present in a 90-liter sample at the selected level, is added to a mixed cellulose ester filter and air-dried. Twenty-five, 50 and 100-microliter aliquots of the 1000 ppm Hf standard solution are added to the filters and air dried to produce samples equivalent to 90-liter

collections at 0.5, 1 and 2X the OSHA standard. Six filters at each of the three levels are prepared and allowed to stand overnight. A parallel blank filter is also prepared except that no sample is added to it. All filters are then analyzed as described in Section 8.3.

The sample recovery equals the average weight in μg recovered from the filter divided by the weight in μg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Filter Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

9. Calibration and Standardization

Note: Operation of the Spectrometrics, Inc., Spectraspan III Plasma Emission Spectrometer used to obtain the data presented in the Hafnium Backup Data Report No. S194 is largely microprocessor-controlled and thus involves a minimum of operator intervention. For this reason, the analysis procedure given below is intended to be a general outline of the steps involved in an analysis rather than a detailed procedure for operation of the instrument. If equivalent emission spectroscopic instrumentation is used, refer to the appropriate manufacturer's instructions for operation.

The 2641 Å Hf emission line is used for all analyses.

Calibrate the instrument according to the manufacturer's instructions using a calibration solution of hafnium in 5% HF (Section 7.5) and a blank solution containing only 5% HF. The concentration of hafnium in the calibration solution should be approximately equal to or greater than the concentration of hafnium anticipated in the samples. In no case should the concentration of hafnium in the calibration solution be greater than ten times the concentration of hafnium found in the samples.

To assure that the instrument response is linear over the concentration range chosen, prepare a standard solution of hafnium in 5% HF having a concentration of hafnium equal to one-tenth that of the calibration standard. Analyze the dilute hafnium standard as if it were an unknown sample. The resulting concentration of hafnium found in the diluted standard should be $\pm 5\%$ of the nominal concentration; if the concentration of hafnium found in the diluted standard is not within these limits, recalibrate the instrument using a standard solution of hafnium in 5% HF having a concentration of hafnium less than that of the original calibration standard. Recheck for linear instrument response as described above.

Analyze the Samples. To obtain the best precision, the standard solution of hafnium in 5% HF should be rerun periodically to assure the absence of instrument drift. Recalibrate the instrument as necessary.

- 9.5 For any samples in which the concentration of hafnium is found to be greater than the concentration of hafnium in the calibrated standard or less than one-tenth the concentration of hafnium in the calibrated standard, the instrument should be recalibrated using a standard solution of hafnium in 5% HF having an appropriate concentration based on the apparent concentration of hafnium in the samples found in Step 9.4. Alternatively, samples having a high concentration of hafnium may be diluted with 5% HF to bring the concentration of hafnium into an appropriate range.

Record the concentrations of hafnium found in the samples.

10. Calculations

- 10.1 Record the sample concentration, in ppm, from either the instrument print-out or manually constructed calibration curve as appropriate. Multiply the concentration by the total volume of the sample solution, usually 10 mL.

$$\mu\text{g/sample} = \text{ppm (or } \mu\text{g)} \times \frac{10 \text{ mL}}{\text{mL Sample}}$$

- 10.2 Corrections for the sample blank (Section 8.2.9) must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in sample blank filter}$$

- 10.3 Divide the weight of analyte found on each filter by the recovery (Section 8.4) to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight found}}{\text{Recovery}}$$

- 10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P₁ = pressure during calibration of sampling pump
(mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.

11.2 Backup Data Report for Hafnium, S194, prepared under NIOSH Contract No. 210-76-0123, 8/4/78.