A simple method for determining Hf in Zr and Zr alloys by ICP-AES

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Abstract This paper describes a rapid, accurate and precise method for determination of trace hafnium (Hf) in zirconium and zirconium alloys by inductively coupled plasma atomic emission spectrometry (ICP-AES). It was found that using a mixture of sulfuric acid (H₂SO₄) and ammonium sulfate (NH₄)₂SO₄, the total sample dissolution time was 15 min. Experimental works revealed that a high Zr concentration would result in a significant decrease in the peak height of the analyte lines, which was corrected by standard addition method. The performance of the developed method was evaluated by calculating the recovery percent and using standard reference material analysis. The recoveries were in the range of 97.6%–99.5% and the relative standard deviations were within 0.8%–3.0%. The detection limit (3 σ) of Hf was found to be 0.01 µg·g⁻¹, respectively. The proposed technique, with high precision and accuracy, was applied to the analysis of trace Hf in zirconium-niobium ingots and tubes for the first time in Iran. **Key words** Zirconium alloys, Hafnium, ICP-AES, Fuel assembly

1 Introduction

Zirconium has a unique combination of properties that historically leads to its use as a structural material in nuclear fission reactors. Zirconium was chosen for this role since it provides desirable mechanical strength and processing characteristics common to other metals, but with a much lower thermal neutron absorption cross section. Equally as important, it is corrosion resistant in service, which is intimately related to its surface chemistry. Refs.[1–4] provide excellent overviews of nuclear technology and the role played by zirconium-based materials in boiling water reactor (BWR) and pressurized water reactor (PWR) applications. Zirconium metal is used in nuclear fuel cladding, chemical piping in corrosive environments, heat exchangers, and various specialty alloys.

Zr-Nb alloys with varying niobium compositions find extensive applications in nuclear technology due to their excellent corrosion resistant properties and higher mechanical strength than conventional ternary zirconium alloys^[5]. While the Zr-2.5% Nb alloy is used as a structural material for pressure tubes of CANDU-pressurized heavy water reactors, Zr-1%Nb is used as a fuel cladding material in pressurized water reactors. In view of its important applications, characterization for chemical purity with respect to many critical trace impurities (B, Hf, Cd, etc.) assumes importance. Hafnium, being a strong neutron absorber, has to be accurately determined at trace levels in various process intermediates like arc melted ingots and final products. The maximum permissible limit for hafnium in these alloys is 100 μ g·g⁻¹.

Determination of impurities at trace and ultra trace levels in zirconium and zirconium alloys is carried out by either wet chemical procedures using spectrophotometer^[6,7], direct current plasma-atomic emission spectrometry (DCP-AES)^[8], inductively coupled plasma-atomic emission spectrometry (ICP-AES)^[9,10], inductively coupled plasma-mass spectrometry (ICP-MS)^[11] or by direct solid analytical techniques like direct current arc-atomic emission spectrometry (DC Arc-AES)^[12,13], energy dispersive X-ray fluorescence^[14] and neutron activation analysis (NAA)^[15]. Using ICP-AES technique, direct analysis of hafnium at 100 $\mu g \cdot g^{-1}$ level and below in zirconium matrix is not possible without the interference

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correction or matrix separation due to spectral interference of matrix zirconium, which produces a line rich emission spectrum^[16,17].

Panday *et al*^[18] reported the determination of trace elements in Zircaloy matrices based on a direct analysis, or after matrix separation using ICP-MS technique. A high matrix concentration ($1000 \ \mu g \cdot mL^{-1}$) was used for the direct analysis of trace elements. Consequently it could affect the ultra-trace analysis of other matrix samples using the same ICP-MS dedicated for different samples. The matrix separation procedure involved multiple chemical processes and time-consuming steps.

For direct solid sample analysis, only a limited number of spectrometric techniques are available like laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), DC Arc-AES and glow discharge mass spectrometry (GD-MS)^[19]. DC Arc-AES technique is routinely used for analysis of hafnium^[20,21] and other trace elements in zirconium matrices.

No report in the literature is available on the direct determination of hafnium in zirconium matrix using ICP-AES in a simple and accurate way. This paper details a method on Hf determination in various Zr-based materials (Zr-2.5%Nb alloys, Zr-1%Nb alloys, Zircaloy, metals) using both matrix matched standard by ICP-AES.

In this work, a new method using dissolution in H_2SO_4 -(NH_4)₂SO₄ was developed. Standard addition method was used to compensate the depress effect of the high concentration Zr on the analyte peaks. Accurate and precise results were obtained, and the detection limit for the element investigated was low. Three kinds of zirconium alloy were determined using the proposed method.

2 Experimental

2.1 Apparatus

The measurements were performed with an ICP spectrometer (Ultima@C, France). For each analyte line, six replicate measurements were made. The operation parameters of the spectrometer are summarized in Table 1.

 Table 1
 Operation conditions of the ICP spectrometer

Parameters	Values
Frequency / MHz	40.68
Incident power / W	1000
Plasma gas flow rate / $L \cdot min^{-1}$	12
Auxiliary gas flow rate / $L \cdot min^{-1}$	2
Nebulizer gas flow rate / $L \cdot min^{-1}$	0.7
Observation height / mm	9
Wavelength used, Hf / nm	282.022

2.2 Reagents

All reagents used were of spectral reagent grade or of analytical reagent grade. Doubly distilled water was used throughout. Stock standard solutions $(1 \text{ g} \cdot \text{L}^{-1})$ of hafnium were bought from Merck Company prepared in 7% hydrochloric acid.

Working standard solutions were prepared by appropriate dilution of the stock solutions with doubly distilled water. For obtaining these solutions, 0.50 mL from the stock solution was transferred to a 50.00 mL volumetric flask quantitatively. The concentration of this solution was 10 μ g·mL⁻¹. For preparing solutions containing 0.20, 0.40 and 0.80 μ g·mL⁻¹ Hf, 0.50, 1.00 and 2.00 mL from this solution was quantitatively added to a 25.00 mL volumetric flask, respectively.

2.3 Procedure

2.3.1 Sample preparation

About 0.5 g Zr-Nb alloy was weighted and placed into a 100 mL beaker, followed by adding 5 g $(NH_4)_2SO_4$ and 10 mL concentrated H₂SO₄. The total sample dissolution time was 15 min at 70–80 °C. After cooling to room temperature, the solution was transferred into a 100 mL volumetric flask and diluted to the mark with doubly distilled water. For each analysis, 4.00 mL from this solution was transferred to a 25.00 mL volumetric flask. Thus Zr concentration in final solution was about 800 µg·mL⁻¹.

2.3.2 Spectrum measurement

Six separate scans of a sample were averaged to reduce the noise in the measured data to get one smoother spectrum. Spectral intensities at various wavelengths over the spectral window, which is set to 50 pm (picometers), around the analyte line were collected.

3 Results and discussion

3.1 Selection of analysis line

The Zr concentration in a sample solution, in terms of Zr-Nb, is up to ~800 μ g·mL⁻¹, whereas that of the analyte is at μg^{-1} level. Furthermore, Zr has a complex atomic emission spectrum with numerous lines, which may lead to line overlapping with the analysis line. Thus it is necessary to carefully choose the analysis lines of the elements determined, in order to avoid a direct line overlapping. A Zr standard solution of 800 μ g·mL⁻¹ was then employed to scan around the prominent lines of the analyte so as to investigate the spectral interference of zirconium. Hf 282.022 nm line was selected as the analysis line for Hf, based on the consideration of both the sensitivity and intensity of the line and the spectral interference found. This line is the most sensitive line of the analyte. The other lines have interference (Fig.1).



Fig.1 Intensity versus wavelength curves for different hafnium lines.

3.2 Compensation of matrix effect

Standard addition method was used in this work to correct the matrix effect, as it is a reliable technique to compensate matrix effect, especially for elemental analysis when matrix-matched standards are not available. The final concentrations after adding Hf standard solution for calibration by standard additions were 0.20, 0.40 and 0.80 μ g·mL⁻¹ for Hf. The experimental results indicated that using standard additions, the matrix effect of Zr on the analytes could be satisfactorily compensated (Table 2).

Concentration		Zr-Nb ingot or tube		C2M	
of Hf solution	Added Hf / μg	Detected Hf	Recovery	Detected Hf	Recovery
(spiked) / $\mu g \cdot g^{-1}$		(Averaged) / µg	$(\text{mean} \pm \text{S.D.}) / \%$	(Averaged) / µg	(mean±S.D.) / %
0.20	5.00	4.925	98.5±1.2	4.975	99.5±1.0
0.40	10.00	9.760	97.6±3.0	9.80	98.0±2.2
0.80	20.00	19.90	99.5±1.2	19.80	99.0±0.8

 Table 2
 Analytical results of sample analysis and their recovery percents

3.3 Validity of the proposed approach

A standard reference material (SRM) with the matrix similar to the Zr-Nb alloys was prepared and analyzed to evaluate the efficiency of the developed analytical approach. The accuracy of the method was validated by obtaining amount found and by analogizing with standard reference material. Our analysis result is (46.3 ± 3.2) ppm for the NIST SRM 1234 standard reference material, in (46 ± 3) ppm of Hf.

The solutions were analyzed by ICP-AES using standard addition method. The recovery experiment was repeated for four times. The accuracy, precision and calculated recoveries for the analyte at different spiked amounts using the proposed technique are tabulated in Table 2. The results demonstrated that the developed method has high accuracy and precision.

3.4 Limit of detection

Detection limit is an important criterion for evaluating an analytical technique. The limit of detection (n=5) of the hafnium element in the metal, calculated from three times the blank standard deviation (113.13) divided by the slope of calibration curve (33938.77), equals to 0.01 µg·g⁻¹.

3.5 Sample analysis

Three types of zirconium alloy sample were analyzed by the proposed approach. All of them could be completely dissolved within 15 min. All sample solutions obtained were diluted to a volume of 100 mL with distilled water and followed by the analysis with ICP-AES. For all ICP-AES determinations, calibration performed by standard additions; was the concentrations added were 0.2, 0.4 and 0.8 μ g·mL⁻¹. For each sample, three replicate measurements were carried out. Hf contents in the Zr-Nb ingot, Zr-Nb tube and C2M alloy are 54±4.8%, 298±1.4% and $98\pm3.2\% \ \mu g \cdot g^{-1}$, respectively.

4 Conclusion

This method was shown fast, accurate and satisfactory determination of trace Hf in zirconium alloys by ICP-AES. The time required for sample preparation could be greatly reduced, the accuracy and precision of the analytical results of the target analyte is high and the detection limits is low. Hafnium determination using this method is simple, fast and accurate compared to methods used in Refs.[6–15].

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