



MEASUREMENT OF HAFNIUM AND ZIRCONIUM IN ZIRCONIUM ORES: OUTCOME OF A NATIONAL INTERCOMPARISON EXERCISE, ZH-A

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A case study is presented in this paper in which a Zirconium pilot plant was set up for the production of zirconium for the cladding of fuel rods. Hafnium occurs in combination with zirconium and is a neutron absorber. Therefore, its concentration has to be kept within tolerance limits and monitored throughout the production process. Five Pakistan Atomic Energy Commission (PAEC) laboratories using different techniques measured the concentrations of Zr and Hf with a wide range of results, i.e. more than three times the standard deviation. Therefore, a national intercomparison exercise, ZH-A was conducted to remove discrepancies and improve analytical procedures in the measurement of hafnium and zirconium in zirconium ores. The ZH-A series of reference samples, prepared at the Pakistan Institute of Nuclear Science and Technology (PINSTECH), were used for this purpose. It was observed that the measurement errors decrease with an increase in Hf concentration (~298 ppm to 1.75%) for all techniques used in this exercise. This was especially significant for Atomic Absorption Spectrometry (AAS). Measurement errors for Hf using AAS are also the highest. Neutron activation analysis (NAA) was found to be the most reliable of all the tested techniques for the measurement of both Hf and Zr in zirconium ores due to its high sensitivity and accuracy.

Keywords: National Intercomparison Run ZH-A, Zirconium, Hafnium, Cladding, ZH-A reference samples

1. Introduction

The quality of analytical data is dependant upon many variables such as type of equipment, their calibration or standardisation, validation of methods, as well as training and experience of analysts and supervisors. In order to obtain reliable results, the performance and strict adherence to quality assurance practices are vital and both internal and external quality assurance measures need to be implemented [1,2]. These include the performance of quality assurance or proficiency test exercises. Quality assurance exercises can be carried out for many reasons, which include; (i) to compare the suitability of different techniques for analysis at different concentration levels, (ii) to compare procedures and the performances of different laboratories and (iii) to produce in-house certified reference materials. Quality assurance includes all those planned and systematic actions necessary to provide adequate confidence that a product or service will satisfy given requirements for quality. It involves the following steps:

1. *Sampling precautions:* This includes labelling of samples, record maintenance and all measures to avoid cross contamination.

2. *Calibration:* The regular calibration of instruments etc. to obtain reproducible results.
3. *Training:* Manpower training and assessment of the worker's eligibility to perform assigned tasks.
4. *Instrument maintenance:* Regular servicing, calibration and repair of instrument to maintain them in good working order.
5. *Audit and review:* Documentation of procedures, problems, results etc. for future use and for reference purposes.
6. *Participation in both national and international intercomparison exercises:* The use of Standard Reference Materials (SRMs) for the evaluation of Laboratory practices and capabilities.

Zirconium is used as a cladding material for nuclear fuel in nuclear reactors. Zr and Hf occur together in nature as oxides and silicates. The higher neutron absorption cross section (σ) of Hf requires that the amount of Hf in Zr ores has to be minimised which entails that its concentration be monitored throughout the processing procedure. In nuclear grade ZrO_2 the Hf concentration has to be

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kept < 100 ppb. Hence when a zirconium pilot plant was set up for the extraction of Zr from zirconium ores, five Pakistan Atomic Energy Commission (PAEC) laboratories, using different techniques, monitored the amounts of Hf and Zr during the production process. Large inconsistencies were observed in the results reported by all the participating laboratories, i.e. more than three times the standard deviations. In order to assess the performance of different laboratories, using different techniques and to help develop analytical procedures, a set of Zr/ Hf reference samples, termed ZH-A series, were prepared by the Neutron Activation Analysis (NAA), Miniature Neutron Source Reactor (MNSR) laboratory at the Nuclear Chemistry Division (NCD), PINSTECH. These were distributed to the same five PAEC laboratories and their results were statistically analysed to evaluate the performance of each laboratory and the suitability of the technique used. The findings of this national intercomparison run, ZH-A, are presented in this paper.

2. Experimental

2.1. Preparation of reference samples

In order to prepare the ZH-A series of reference samples, 5 bulk aliquots samples (~10 kg) were taken from various stages of the Zr processing plant. These were homogenized and processed [3]. The NAA, MNSR laboratory, certified the ZH-I reference sample and also provided the reference or expected values of Zr and Hf for the remaining four ZH-A samples using analytical grade ZrO₂ and HfO₂ (Johnson and Matthey Materials Technology, UK, 99.99%). The data are presented in Table 1. The methodology involved in NAA is discussed in the paper by Waheed et. al. [4] and given in Table 2 [5]. The ZH-A reference samples were distributed to the participating laboratories for analysis using available analytical techniques alongwith ZH-I which was provided as a secondary standard. As the ZH-A reference samples were obtained from the Zr processing pilot plant, the amount of Zr was in the range 65-75% while the amount of Hf varied from ~2% to ppm levels. Therefore, these samples were considered useful in evaluating the performance of different techniques with variation in Hf and Zr concentrations.

The ZH reference samples were analysed by the participating laboratories, using available techniques. These included NAA, atomic absorption spectrometry (AAS), x-ray fluorescence spectrometry (XRFS) and atomic emission

spectrometry (AES). Two laboratories performed analysis using XRFS but one laboratory, Code No 105, used the method of standard addition (XRFS1). The NAA MNSR laboratory certified ZH-I and provided the reference/ expected concentrations for Zr and Hf while the NAA laboratory (Code No. 104) participated in the intercomparison exercise. Details of the participating laboratories and techniques used are presented in Table 3.

3. Laboratory Performance Evaluation

In order to evaluate the performance of individual laboratories, the results from at least two laboratories, obtained using two or more techniques were subjected to the following tests:

3.1. *Student's 't' test: In calculating the overall mean (consensus value) the outliers were subjected to this test [6-10].*

$$\pm t = \frac{(X_{ave} - \mu)(\sqrt{N})}{s} \quad (1)$$

where X_{ave} = observed/ calculated mean value, μ = certified value (from expected values provided by NAA, MNSR laboratory), N = number of readings and s = standard deviation of the observed mean value. If the calculated value of t exceeds that tabulated at the required 95% confidence level then the mean is unacceptable and another mean is calculated excluding the outlier.

3.2. *z-score: z-scores were calculated according to the equation:*

$$z = \frac{(X_i - X_{ave})}{s_b} \quad (2)$$

where X_i = arithmetic mean of the reported value of the analyte concentration in the sample (laboratory value), X_{ave} = consensus value, s_b = standard deviation, based on the fact that the laboratories have a relative bias equal to or better than $2s_b$, where $2s_b = 25\%$ for Hf and $2s_b = 10\%$ for Zr. Therefore, the values of s_b have been taken as 12.5% and 5% for Hf and Zr respectively. These values are on the higher side as the amounts of both elements in these samples is generally in % levels.

For z-scores

$$|z| \leq 2 = \text{satisfactory results}$$

Table 1. Information values for ZH-A series of reference samples obtained using INAA by NAA, MNSR Laboratory, NCD, PINSTECH (No. of determination = 10).

Reference sample	Hf (ppm)	Zr (%)
ZH-I	17500 ± 400	67.8 ± 1.4
ZH-III(a)	1592 ± 80	70.4 ± 1.4
ZH-III(b)	1408 ± 46	69.1 ± 1.3
ZH-IV	300 ± 20	Not known
ZH-V	18200 ± 900	Not known

Table 2. Nuclear data for the estimation of Hf and Zr in ZH-A reference samples using INAA [5].

Target Nuclide	σ (barns)	Isotope Formed	t _{1/2}	E _γ (keV)	Intensity (%)
¹⁸⁰ Hf	13.5	¹⁸¹ Hf	42.39d	133.0	41.7
				482.2	82.8
⁹⁴ Zr	0.053	⁹⁵ Zr	64.03d	724.2	44.1
				756.7	54.5

Irradiation time 1 hr
 Cooling time 1 d
 Counting time 1800 s

Table 3. Techniques used in intercomparison run ZH-A for Hf and Zr in ZH-A reference samples.

Laboratory code	Technique used
101	Atomic Emission Spectrometry (AES)
102	Atomic Absorption Spectrometry (AAS)
103	X-ray Fluorescence Spectroscopy XRF-WD (XRFS)
104	Neutron Activation Analysis (NAA)
105	X-ray Fluorescence Spectroscopy XRF-WD - Standard Addition Method (XRFS1)

2 < |z| < 3 = results are questionable

|En| or |u| > 1 = unsatisfactory results

|z| ≥ 3 = unsatisfactory results

If a particular result fails to satisfy either or all of the above tests, it is rejected. It should be noted that consensus values have been used to calculate the z and u-scores as the expected amounts of Zr in ZH-IV and ZH-V are unknown.

3.3. *u-score*: En number or u-score is given by:

$$E_n \text{ or } u = \frac{(X_i - X_{ave})}{\left(\sqrt{U_{lab}^2 + U_{ref}^2}\right)} \quad (3)$$

where X_i is the laboratory value, X_{ave} is the consensus value, U_{lab} is the uncertainty of a participant's result and U_{ref} is the uncertainty of the consensus value.

4. Results and Discussion

4.1. Comparison of the techniques used in national intercomparison exercise, ZH-A

The ZH-A national intercomparison was undertaken to remove discrepancies and improve analytical procedures in the measurement of hafnium and zirconium in zirconium ores. Thus it was required that the analytical results provided by any testing laboratory be traceable and accurate. Apart from these requirements the cost of analysis,

For En numbers or u-score
 |En| or |u| ≤ 1 = satisfactory results

time required for analyses, number of personnel involved, and availability of the technique are also factors that have to be taken into account. Two elements, Zr and Hf were quantified in this intercomparison exercise. The analytical techniques mentioned in Table 2 are those which were available in PAEC laboratories and can be used to determine both these elements without encountering any interferences. All of the used techniques, apart from NAA, can be performed by a single analyst using common reagents and sample preparation methods such as, dissolution and pellet formation etc, to obtain results for Hf and Zr in a short period of time. These techniques are relatively inexpensive and can be used routinely in a plant for performing such analyses. However, NAA not only requires an analyst for the preparation and analysis of a sample but also requires a group of people to operate a reactor in accordance with set safety measures. The cost of a single reactor run is also substantial. For these reasons, this technique may not be available to many and due to its high cost should only be used where high accuracy and sensitivity is required as

in providing expectant values for proficiency test (PT) exercises. Any technique, which involves sample manipulation prior to analysis, will of course suffer from contamination problems making them less sensitive than NAA where minimal sample preparation is required. In the present study a set of samples can be analysed within 2 days using NAA as a cooling period of this duration is required for obtaining optimum results and for the safety of the analyst. However, if elements such as Fe or Cr had to be quantified the analysis time would increase considerably due to the much longer cooling period that will be required for isotopes of these elements.

4.2. Findings of intercomparison run ZH-A

The results (on dry weight basis) are presented in Tables 4 to 8 along with the z and u scores for all the participating laboratories. During the national intercomparison run ZH-A, ZH-I reference sample was analysed by all laboratories and was also used as a secondary standard in most cases to analyse the remaining ZH-A series of samples. The composition of ZH-I, as given in Table 4, was

Table 4. Results of national intercomparison run ZH-A for Hf and Zr in ZH-I reference sample.

Lab. code No.	Standard used	Lab. mean	Deviation from expected value	Lab. std. deviation (SD)		Overall average of accepted means	z-score	u-score	Result status
				Abs. SD	RSD (%)				
Hafnium (%)									
104 (NAA)	¹⁸⁰ HfO ₂	1.75	+0.00	±0.04	2.29		+0.00	0.00	Acceptable
102 (AAS)	B.C.S. 388 (Zircon)	1.74	-0.01	±0.06	3.43		-0.05	0.11	Acceptable
105 (XRFS1)	Lab. 105 Std.	1.77	+0.02	±0.06	3.43	1.75±0.09	+0.09	0.22	Acceptable
103 (XRFS)	Lab. 103 Std.	*2.02	+0.27	±0.03	1.71		+1.23	0.95	Rejected
101 (AES)	-	-	-	-	-		-	-	-
Zirconium (%)									
104 (NAA)	⁹⁰ ZrO ₂	67.80	-0.61	±1.40	2.05		-0.18	0.30	Acceptable
102 (AAS)	B.C.S. 388 (Zircon)	69.78	+1.37	±0.80	1.17		+0.40	0.81	Acceptable
105 (XRFS1)	Lab. 105 Std.	67.79	-0.62	±0.51	0.75	68.41±1.49	-0.18	0.39	Acceptable
103 (XRFS)	Lab. 103 Std.	68.26	-0.15	±0.11	0.16		-0.04	0.10	Acceptable
101 (AES)	-	-	-	-	-		-	-	-

¹⁸⁰ Johnson and Matthey Materials Technology, UK, 99.99%

* Rejected by t-test. Not included in the overall average

Table 5. Results of national intercomparison run ZH-A for Hf and Zr in ZH-III(a) reference sample.

Lab. code No.	Standard used	Lab. mean	Deviation from expected value	Lab. std. Deviation (SD)		Overall average of accepted means	z-score	u-score	Result status
				Abs. SD	RSD (%)				
Hafnium (ppm)									
104 (NAA)	ZH-I	1800	+208	±54	3.26	1658±226	+0.69	0.61	Acceptable
102 (AAS)	ZH-I	1922	+330	±165	9.95		+1.27	0.94	Acceptable
105 (XRFS1)	Lab. 105 Std.	1575	-17	±169	10.19		-0.40	0.29	Acceptable
103 (XRFS)	Lab. 103 Std.	1700	+108	±23	1.39		+0.20	0.19	Acceptable
103 (XRFS)	ZH-I	1428	-164	±20	1.21		-1.11	1.01	Rejected
101 (AES)	ZH-I	1522	-70	±138	8.32		-0.66	0.51	Acceptable
Zirconium (%)									
104 (NAA)	ZH-I	70.70	+0.30	±2.10	2.95	71.24±2.82	-0.15	0.15	Acceptable
102 (AAS)	ZH-I	73.14	+2.74	±0.50	0.70		+0.53	0.66	Acceptable
105 (XRFS1)	Lab. 105 Std.	68.63	-1.77	±1.66	2.33		-0.73	0.80	Acceptable
103 (XRFS)	Lab. 103 Std.	73.17	+2.77	±0.13	0.18		+0.54	0.68	Acceptable
103 (XRFS)	ZH-I	72.69	+2.29	±0.14	0.20		+0.41	0.51	Acceptable
101 (AES)	ZH-I	69.09	-1.31	±0.70	0.98		-0.60	0.74	Acceptable

Table 6. Results of national intercomparison run ZH-A for Hf and Zr in ZH-III(b) reference sample.

Lab. code No.	Standard used	Lab. mean	Deviation from expected value	Lab. std. Deviation (SD)		Overall average of accepted means	z-score	u-score	Result status
				Abs. SD	RSD (%)				
Hafnium (ppm)									
104 (NAA)	ZH-I	1442	+34	±44	3.24	1360.0±179.6	+0.48	0.44	Acceptable
102 (AAS)	ZH-I	*1829	+421	±188	13.82		+2.76	1.80	Rejected
105 (XRFS1)	Lab. 105 Std.	1289	-119	±109	8.01		-0.42	0.34	Acceptable
103 (XRFS)	Lab. 103 Std.	1438	+30	±32	2.35		+0.46	0.43	Acceptable
103 (XRFS)	ZH-I	1236	-172	±14	1.03		-0.73	0.69	Acceptable
101 (AES)	ZH-I	1395	-13	±132	9.71		+0.21	0.16	Acceptable
Zirconium (%)									
104 (NAA)	ZH-I	70.10	+1.00	±1.75	2.50	69.93±1.88	+0.05	0.07	Acceptable
102 (AAS)	ZH-I	69.68	+0.58	±0.66	0.94		-0.07	0.13	Acceptable
105 (XRFS1)	Lab. 105 Std.	*64.66	-4.44	±1.85	2.65		-1.51	2.00	Rejected
103 (XRFS)	Lab. 103 Std.	70.20	+1.10	±0.10	0.14		+0.08	0.14	Acceptable
103 (XRFS)	ZH-I	69.75	+0.65	±0.10	0.14		-0.05	0.10	Acceptable
101 (AES)	ZH-I	*68.10	-1.00	+0.51	0.73		-0.52	0.94	Rejected

Rejected by t test. Not included in the overall average

Table 7. Results of national intercomparison run ZH-A for Hf and Zr in ZH-IV reference sample.

Lab. code No.	Standard used	Lab. mean	Deviation from expected value	Lab. std. Deviation (SD)		Overall average of accepted means	z-score	u-score	Result status
				Abs.SD	RSD (%)				
Hafnium (ppm)									
104 (NAA)	ZH-I	305	+5	±10	3.36	297.67±15.62	+0.20	0.40	Acceptable
102 (AAS)	ZH-I	*561	+261	±113	37.96		+7.08	2.31	Rejected
105 (XRFS1)	Lab. 105 Std.	-	-	-	-		-	-	-
103 (XRFS)	Lab. 103 Std.	316	+16	±12	4.03		+0.49	0.93	Acceptable
103 (XRFS)	ZH-I	272	-28	±10	3.36		-0.69	1.38	Rejected
101 (AES)	-	-	-	-	-		-	-	-
Zirconium (%)									
104 (NAA)	ZH-I	72.30	-	±1.70	2.36	72.13±1.71	+0.05	0.07	Acceptable
102 (AAS)	ZH-I	71.40	-	±0.43	0.60		-0.20	0.41	Acceptable
105 (XRFS1)	Lab. 105 Std.	*24.45	-	±0.40	0.55		-13.22	27.15	Rejected
103 (XRFS)	Lab. 103 Std.	72.60	-	±0.10	0.14		+0.13	0.27	Acceptable
103 (XRFS)	ZH-I	72.20	-	±0.10	0.14		+0.02	0.04	Acceptable
101 (AES)	-	-	-	-	-		-	-	-

* Rejected by t test. Not included in the overall average.

Table 8. Results of national intercomparison run ZH-A for Hf and Zr in ZH-V reference sample.

Lab. code No.	Standard used	Lab. mean	Deviation from expected value	Lab. std. deviation (SD)		Overall average of accepted means	z-score	u-score	Result status
				Abs. SD	RSD (%)				
Hafnium (%)									
104 (NAA)	ZH-I	1.51	-0.31	±0.03	1.80	1.67±0.16	-0.77	0.98	Acceptable
102 (AAS)	ZH-I	1.54	-0.28	±0.04	2.40		-0.62	0.79	Acceptable
105 (XRFS1)	Lab. 105 Std.	1.90	+0.08	±0.10	5.99		+1.10	1.22	Rejected
103 (XRFS)	Lab. 103 Std.	1.86	+0.04	±0.03	1.80		+0.91	1.17	Rejected
103 (XRFS)	ZH-I	1.60	-0.22	±0.02	1.20		-0.34	0.43	Acceptable
101 (AES)	ZH-I	1.62	-0.20	±0.12	7.19		-0.24	0.25	Acceptable
Zirconium (%)									
104 (NAA)	ZH-I	68.60	-	±2.20	3.17	69.37±2.46	-0.22	0.23	Acceptable
102 (AAS)	ZH-I	68.86	-	±0.10	0.14		-0.18	0.25	Acceptable
105 (XRFS1)	Lab. 105 Std.	*80.05	-	±2.44	3.52		+3.08	3.08	Rejected
103 (XRFS)	Lab. 103 Std.	70.52	-	±0.14	0.20		+0.33	0.47	Acceptable
103 (XRFS)	ZH-I	70.11	-	±0.20	0.29		+0.21	0.30	Acceptable
101 (AES)	ZH-I	68.84	-	±1.07	1.54		-0.15	0.20	Acceptable

* Rejected by t test. Not included in the overall average.

determined using standards prepared by the individual laboratories from high purity materials. The results obtained by individual laboratories using different techniques for the ZH-A series of samples are discussed in the following paragraphs.

4.2.1. Measurement of Hf in ZH-A reference samples

Laboratory 101 reported results for only the ZHIII(a), ZHIII(b) and ZH-V reference samples. All three results were found to be acceptable by the t test and their z and u scores. ZH-IV has the lowest amount of Hf but ZH-I has around 1.75% Hf. Therefore, some other factor apart from the concentration of Hf in the sample is responsible for results not being obtained and reported for ZH-I. Laboratory 102 reported results for the entire ZH-A series of reference samples. However, the results for ZH-IV and ZHIII(b), which contained the lowest concentrations of Hf were rejected while the results for the remaining three ZH-A reference samples fulfilled the evaluation criteria. Hf has a tendency for solution instability making it more difficult to measure by techniques requiring dissolution [11].

From Table 4, it can be seen that the results for Hf in ZH-I have not been accepted for Laboratory 103. Tables 5 to 8 show that Laboratory 103 has used both an in-house standard (Laboratory 103 standard) and ZH-I to analyse the remaining ZH-A reference samples. The results of Hf in ZH-III(a) and ZH-IV have failed to meet the criteria wherever ZH-I has been used as the standard, whereas only the results of ZH-V in Table 8 have been rejected when the in-house standard has been used. This shows that there may be some problem, such as in the preparation of ZH-I pellet and the sample prepared may not be homogeneous. Hence the analysis of any subsequent samples using the ZH-I sample may not provide reliable results.

Laboratory 104, using NAA reported results for all of the ZH-A reference samples. The complete data set fulfilled the evaluation criteria and were declared acceptable. This is not unexpected as NAA, being one of the most sensitive available techniques, is most commonly used in Proficiency Test Exercises to determine expected values for test samples and for certification of SRMs. Laboratory 105 reported the results for all ZH-A reference samples except ZH-IV, which has the lowest Hf content. Of the four reported results the results for ZH-V have been rejected while the remaining data have been deemed acceptable. This may be due to the fact that the amount of Hf

in this particular reference sample is the highest and addition of a small amount of Hf may not change the overall composition of the sample significantly.

4.2.2. Measurement of Zr in ZH-A reference samples

Analysis of Zr results in the ZH-A samples in Tables 4 to 8 shows that fewer results have been rejected by our evaluation method as compared to the Hf results. This is not surprising since the amount of Zr being investigated is in the range 68-71% and the amount of Hf is less than 2%. Generally all the techniques such as NAA, AAS and XRFS provided acceptable results for the estimation of Zr in the ZH-A samples whereas 60% of the XRFS1 (standard addition method) results have been rejected. The amounts of Zr in ZH-A series of samples have been underestimated in most samples, grossly in the case of the ZH-IV reference sample. Only in reference sample ZH-V, it has been overestimated significantly. This may be due to the fact that the ZH-A reference samples already contain zirconium in 65-70% levels. Therefore spiking with additional small amounts of Zr may not change their composition significantly, leading to erroneous results.

4.3. Overview of results

In order to see the effect of Hf and Zr concentrations on the precision of each technique, the relative measurement error for each technique has been plotted against Hf and Zr concentrations in Figs. 1 and 2, respectively. Figure 1 shows that the measurement error is dependant on the Hf concentration for AAS and XRFS1. Generally, the measurement errors are below 10% apart from the results for AAS, especially at low Hf concentrations. From Figure 2 it is clear that the measurement errors are all independent of Zr concentration and are below 4% for all tested techniques as the amount of Zr present in the samples is in percentage levels. From these Figures it can also be seen that for the measurement of Hf, AAS has the broadest relative measurement error range (2.4 to 37.96 %). NAA and XRFS appear to be the most precise techniques with the narrowest error range (1.8 to 3.36 and 1.39 to 4.03 % respectively). For Atomic Emission Spectroscopy (AES) and XRFS1 the relative measurement errors are generally around 10% (6.32 to 9.71 and 3.45 to 10.19 % respectively). From Figure 2, it can be seen that AAS, AES and NAA have similar precision but AAS

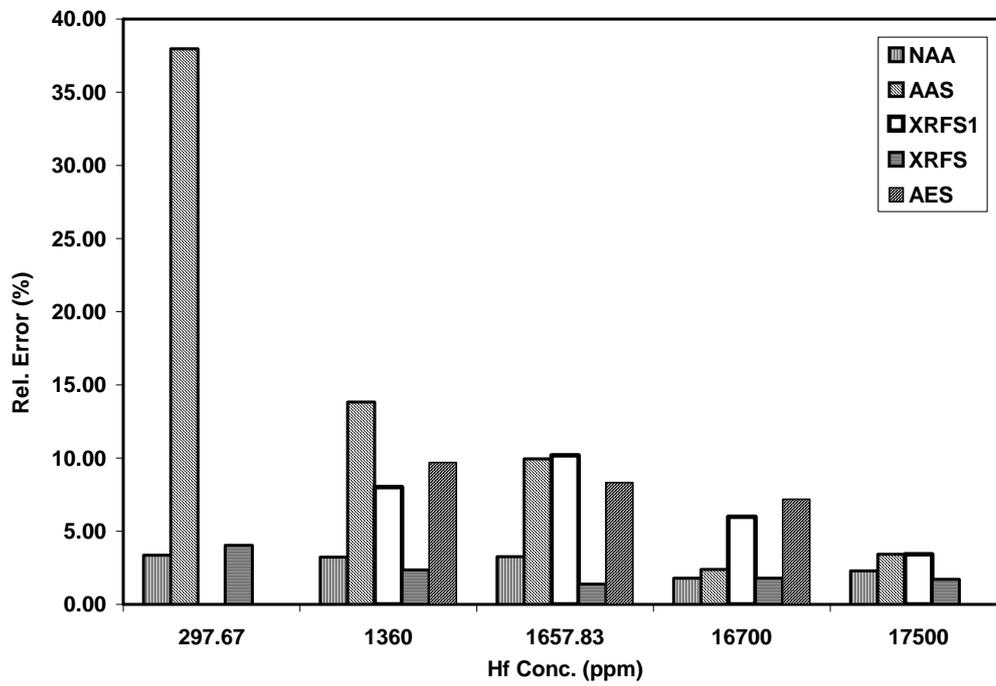


Figure 1. Variation in relative percentage error with Hf concentration.

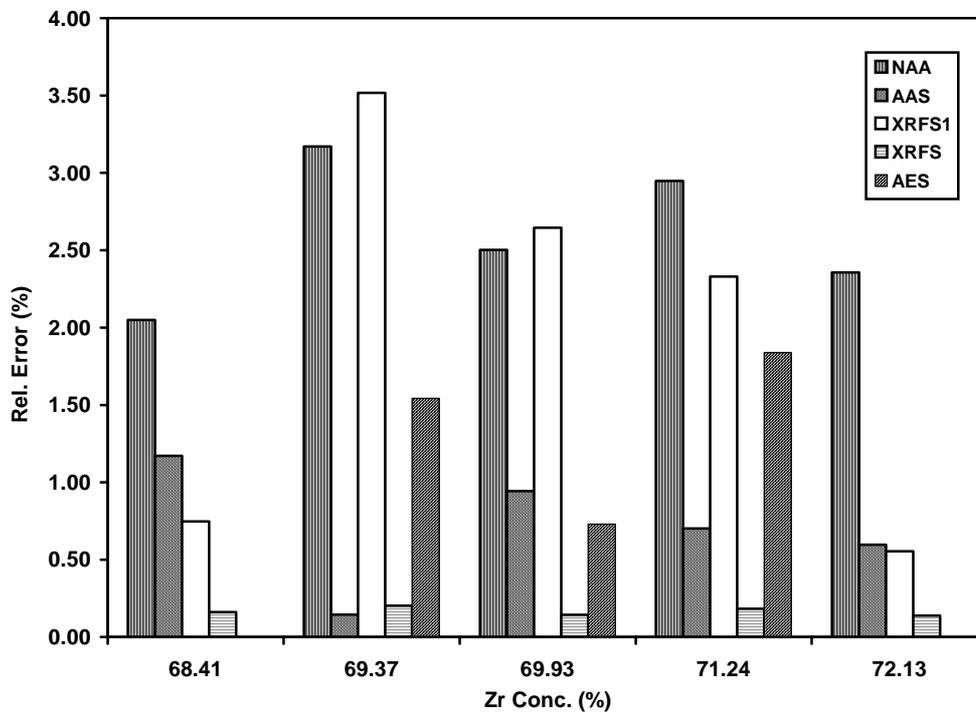


Figure 2. Variation in relative percentage error with Zr concentration.

appears to be the more accurate technique. From this plot it can also be seen that XRFS1 has the largest relative error range whereas the range for XRFS is the narrowest (0.55 and 3.52 % and 0.14 to 0.20 %, respectively).

Overall, AAS appears to be the least suitable technique for the measurement of low concentrations of Hf. For Zr measurement all of the results obtained by NAA, XRFS and AAS fulfilled the set criteria, whereas the results obtained by XRFS1 were most frequently rejected. This observation highlights the disadvantage of using an analytical technique which requires preparation of the sample prior to analysis. From this treatment NAA appears to be the best analytical technique for the determination of Zr and Hf in zirconium ore samples.

5. Conclusion

The national intercomparison ZH-A revealed that the relative measurement errors decrease with an increase in the amount of hafnium for AAS and XRFS1. This is most marked for AAS, especially for samples with the lowest Hf content such as ZH-IV (~298 ppm). NAA and XRFS are independent of variations in hafnium concentration. Relative measurement errors for the measurement of zirconium are below 4% for all the techniques used and for the concentration range investigated, i.e., ~68-71%. Zirconium results using XRFS1 (Standard Addition Method) were most frequently rejected. Large errors for hafnium measurements using AAS and the high frequency of the XRFS1 zirconium results being rejected was probably due to the preparation steps required prior to sample analysis for these techniques. NAA was found to be the best analytical technique for the determination of both elements in such matrices. Furthermore this exercise has clearly shown the need for routine intercomparison exercises to evaluate the quality of analytical data and validation of procedures.

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