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Determination of boron in Zr–Nb alloys by glow discharge quadrupole mass spectrometry

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Abstract

Direct determination of boron in Zr–2.5%Nb, Zr–1%Nb alloys and zirconium metals which are extensively used as structural materials in nuclear reactors has been carried out by glow discharge quadrupole mass spectrometer (GD-QMS). Relative sensitive factor (RSF) values for boron were determined using different solid standard reference materials (Zircaloy and steel). A comparison of the GD-QMS results obtained using these RSF values, with DC–Arc-AES (direct current arc atomic emission spectrometry)/certified values showed reasonably good agreement in all the Zr-based materials analysed for boron in the range of 0.1–7 mg kg^{-1}. Quantitation of boron in Zr matrix is possible even with a steel standard when certified for Zr and B. Internal precision (intra-sample precision) was found to be typically ±4% RSD (relative standard deviation) and the inter-sample precision was ±10% RSD for boron at ~0.1 mg kg^{-1} levels. The overall accuracy of the procedure was found to be ±8% at ~0.5 mg kg^{-1} levels of boron using Zircaloy and steel standards. Under optimised experimental conditions the detection limit for boron was found to be ±13 μg kg^{-1}.

1. Introduction

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 and ternary zirconium alloys [1]. While the Zr–2.5% Nb alloy is used as a structural material for pressure tubes of CANDU-pressurised heavy water reactors, Zr–1%Nb is used as a fuel cladding material in pressurised water reactors. In view of its important applications, characterisation for chemical purity with respect to many critical trace impurities (B, Hf, Cd, etc.) assumes importance. Boron, 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 boron in these alloys is 0.5 mg kg^{-1}.

Determination of boron at trace and ultra trace levels is carried out by either wet chemical procedures using inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass

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spectrometry (ICP-MS), and spectrophotometer or by direct solid analytical techniques like direct current arc-atomic emission spectrometry (DC Arc-AES). Using ICP-AES technique, direct analysis of boron at 0.5 mg kg^{-1} levels and below in zirconium matrix is not possible without the interference correction or matrix separation due to spectral interference of matrix zirconium, which produces a line rich emission spectrum [2]. Panday et al. [3] reported the determination of trace elements in Zircaloy matrices based on a direct analysis as well as after matrix separation using ICP-MS technique. But a high matrix concentration (1000 mg ml^{-1}) was used for the direct analysis of trace elements. But consequently it can affect the ultra-trace analysis of other matrix samples using the same ICP-MS dedicated for different samples. The reported [3] matrix separation procedure involves multiple chemical processes and time-consuming steps.

Spectrophotometric (Colorimetric) procedures [4] involve the distillation of boron as volatile methyl borate and complexation with suitable reagent. This method is highly cumbersome and prone to contamination from laboratory environment, water and glasswares as it involves multiple chemical processes.

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). No report in the literature is available on the determination of boron in zirconium matrix using LA-ICP-MS. DC Arc-AES technique is routinely used for analysis of boron [5,6] and other trace elements in zirconium matrices. Apart from extensive sample preparation, the method involves carrier distillation of analyte with suitable carrier material to volatilise boron present in the sample to the arc region. Separate calibration standards are required to be prepared for Zircaloy and Zr–Nb alloys for matching the sample matrix composition. Linear calibration obtained using DC Arc-AES technique is limited to one or two orders of magnitude only. By this technique boron concentration levels at 0.5 mg kg^{-1} and above can be determined with the precision of ∼±20% and accuracy of ±30% [6].

GD-MS is a highly sensitive direct solid analysis technique and is capable of measuring major, minor, trace and ultra trace constituents of solid material simultaneously. The use of GD-MS to determine the elemental composition including boron in Zircaloy standards has been reported in the literature using same matrix composition standards (i.e. Zircaloy) only [7]. Our earlier work was reported on the multi-elemental determination of Zr–Nb alloys excluding boron by GD-QMS using only Zircaloy standards [8].

This paper details a method on the determination of boron in various Zr-based materials (Zr–2.5%Nb alloys, Zr–1%Nb alloys, Zircaloy, metals) using both matrix-matched standard (Zircaloy) and alternative matrix standard (steel) by low resolution GD-MS (GD-QMS). The values obtained for several samples and standards are compared with those obtained by DC Arc-AES technique and with certified values of boron. The optimised parameters, stabilisation time for boron in zirconium and iron matrices, and possible isobaric interferences on boron isotopes and figures of merit for the method are also reported.

2. Experimental

2.1. Instrumentation

2.1.1. GD-QMS

A quadrupole GD-MS, Model GQ230 (VG Elemental, UK), was used for the analysis. The parameters such as operating mode, use of detectors and mass calibration of GD-QMS are same as those described in detail in our earlier paper [9]. The dual detector system (Model No. 4870V, Galileo Electro-Optics Corp., Sturbridge, MA, USA) utilizes an electron multiplier for ion counting for trace elements (ion currents $< 3 \times 10^{-13}$ amp) and a Faraday cup for the measurement of major and minor elements (ion currents $> 3 \times 10^{-13}$ amp).

2.1.1.1. Collector calibration. The Faraday cup and Electron Multiplier detectors were cross-calibrated by measuring the signal intensity at mass 76 ($^{40}Ar^{36}Ar^+$). Detector calibration factor was adjusted to be 2760 ± 200 by adjusting the HT voltage to the electron multiplier before the scanning. The collector calibration was done using a mass step of 0.01 amu and 120 points in peak scan.

2.1.1.2. Operating parameters

Discharge voltage	1.2 kV
Discharge current	3.0 mA
Argon flow rate	20.5 sccm
Temperature during discharge	−164 °C
Vacuum (at the quadrupole region)	8×10^{-5} Pascal
Resolution ($M/\Delta M$)	300

3. Procedure

3.1. Sample preparation for GD-QMS

Being a surface technique, surfaces of all the samples and standards were milled. Sample typically of size 20 mm × 20 mm were cleaned with methanol, dried under infrared lamp and mounted on the flat sample holder

Table 1
Elemental composition of major elements in the standards

Element	Zircaloy Teledyne Std (X868-13D) wt%	Zircaloy Teledyne Std (X867-16D) wt%	Zircaloy Teledyne Std (X869-25B) wt%	Zr metal Std NBS 1234 wt%	Zr metal Std NBS 1236 wt%	Zircaloy NBS Std 1237 wt%	Zircaloy NBS Std 1238 wt%	Zircaloy NBS Std 1239 wt%
Zr	98.16	97.60	97.87	99.84	99.29	97.62	97.96	97.78
Cr	0.058	0.163	0.105	0.005	0.025	0.151	0.058	0.105
Fe	0.278	0.163	0.224	0.024	0.170	0.165	0.250	0.230
Sn	1.23	2.00	1.65	0.0015	0.006	1.90	1.26	1.61

with an anode opening diameter of 10 mm. The GD cell of the Mass spectrometer was cryogenically cooled with liquid nitrogen in order to minimise residual gaseous contaminants. Each sample was loaded into the GD system and evacuated to a vacuum of around 1×10^{-1} Pascal prior to the analysis for the removal of surface atmospheric contaminants.

The analytical measurements were carried out at a mass step of 0.01 amu with 140 points. However, 120 points used for detectors calibration has no affect on the analytical measurements. Because the signal intensities measured, for same ion by both the detectors (Faraday and Electron Multiplier) under the same number of points, are ratioed to compute the detector calibration factor. The 140 points used for the analytical measurement was to obtain better signal to noise ratio for each isotope. A single scan for Faraday cup (for zirconium isotope) and 20 scans for electron multiplier (for boron isotopes, 10 & 11) were used for each measurement. Four repetitive measurements were recorded for each sample.

3.2. Samples analysed

Zircaloy certified reference material (CRM), procured in late 1960's, Zircaloy-X868-13D (certified concentration for boron is 3.2 ± 0.3 mg kg^{-1}, from M/s. Teledyne Wahchang, Albany, USA) and low alloy steel standard reference material (SRM) NIST-1762 (boron is certified to be 40 ± 2 mg kg^{-1} and zirconium is 300 ± 20 mg kg^{-1}) were used, in the form of disk, as standards for boron to compute relative sensitivity factors (RSFs). The Zr–Nb alloys (Zr–1%Nb, Zr–2.5%Nb), Zircaloy standards, also procured in late 1960's (Teledyne standards: ZrX867-16D, B:0.45 ± 0.01 mg kg^{-1}; ZrX869-25B, B:0.29 ± 0.06 mg kg^{-1} & NIST SRMs: 1237, B:0.4 mg kg^{-1}; 1238, B:2 mg kg^{-1}; 1239, B;0.25 mg kg^{-1}) and zirconium NIST SRMs, metal standards (1234, B: < 0.2 mg kg^{-1}, 1236, B:7.0 mg kg^{-1}) were all analysed as samples for the purpose of comparison of the GD-QMS values. Though boron has to be analysed at the ingot stage itself, the present analysis was done on the final component, as there will not be any contamination or introduction of boron from any other source into the final product. And before making the ingot, all the raw materials of the ingot were analysed for boron and found that the boron was present within the limits. The NIST Zircaloy and Metal SRMs (1237, 1238, 1239, 1234, 1236) were analysed to identify the level of agreement against even with the indicated values (approximate values). The major composition of all these standards was listed in Table 1.

4. Results and discussion

4.1. Discharge parameters

A study of discharge current on the ion yield revealed [10] that the optimum discharge current is the 3.0 mA for efficient sample cooling with low molecular ion interferences and maximum ion beam intensity. Thus the discharge current was optimised at 3.0 mA using constant current mode option of the system. The discharge voltage at 1.2 kV resulted in a maximum ion intensity at constant discharge current of 3.0 mA for both matrices (6×10^5 ions s^{-1} for $^{90}Zr^+$ ion for Zr matrix and 3×10^5 ions s^{-1} for $^{56}Fe^+$ ion for Fe matrix samples). Earlier it was also observed that the same discharge parameters resulted in sufficient signal intensity for chlorine present at ultra-trace levels along with high signal intensity for zirconium in Zr–2.5%Nb alloys [9]. Our experiments on other Zr-based samples (metals, Zircaloys) also showed that the same discharge parameters resulted in maximum matrix intensity along with sufficient signal for boron. Thus in general, these parameters appear to be suitable for different types of zirconium-based materials for determination of trace/ultra-trace level constituents. Hence same discharge parameters were used for boron determination in all these samples.

4.2. Studies on stabilisation time for boron determination

Pre-sputtering of the sample was carried out using the optimised discharge parameter settings. This is critical since the intensities of the spectral lines as a function of the time are not the same for all the elements even in same matrix. In order to reduce these effects the specimen was pre-sputtered until the intensities had become more or less constant. Extensive studies were carried out to arrive at actual stabilisation time required for the pre-sputtering and subsequent determination of boron by GD-QMS. The boron signal was monitored at different pre-sputter intervals ranging from 20 to 60 min. The raw counts were converted into ion beam ratios (IBR) for boron (i.e. $^{11}B^{+}/^{90}Zr^{+}$ and $^{11}B^{+}/^{56}Fe^{+}$). Two graphs (Fig. 1(a) for Zr matrix and (b) for Fe matrix) with these IBR values of boron were plotted against pre-sputter time. Since the IBR value of boron in steel standard is far away from that of boron in Zircaloy standard, the two graphs are presented with the different scales.

The graph (Fig. 1(a)) shows that the boron signal was continuously decreasing upto 40 min of pre-sputter time and there onwards the signal was varying due to the material in homogeneity. And the variation in boron signal in Fig. 1(b) also was very less after 40 min of pre-sputter time. From the data points of Fig. 1(a), 18.896 (40 min), 18.932 (45), 19.334 (50), 18.890 (55) and 18.867 (60), it can be seen that the signal was within ±4% after 40 min of pre-sputter. Similarly from the data points of Fig. 1(b), 124.454 (40 min), 124.904 (45), 122.560 (50), 123.197 (55) and 122.723 (60), the signal variation was found to be within ±3% after 40 min of pre-sputter. Hence the minimum 40 min of pre-sputter time was required to obtain a stable signal for boron determination using GD-QMS technique. In our earlier work [9] for chlorine in zirconium matrix, minimum 50 min of pre-sputter time was found to be essential. In general, elements of higher concentration require less pre-sputter time (20–30 min) only. But our experiments on Zr based samples have revealed that trace or ultra-trace level elements require more sputter time 30–40 min (e.g. boron). The trace (gaseous) element like chlorine required little more sputter time (~50 min). Thus it appears pre-sputtering of the samples to about 40–50 min would be required to remove any surface contaminations, prior to actual determination of the trace elements by GD-QMS.

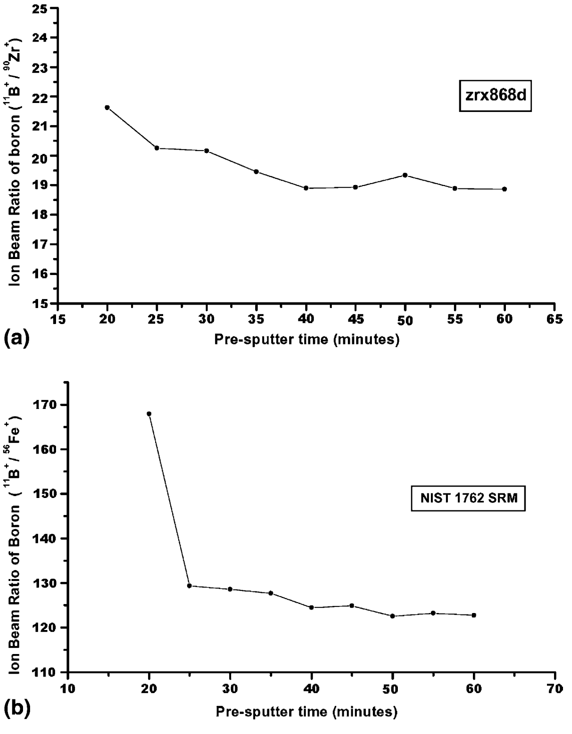

Fig. 1. Stabilisation time for boron in (a) Zirconium Matrix sample, (b) Iron Matrix sample.

4.3. Spectral interferences

Boron has two natural isotopes: ^{10}B (abundance, 19.9) and ^{11}B (80.1). A GD quadrupole mass spectrum of a zirconium sample containing boron 3.2 mg kg^{-1}, was given in Fig. 2 to show the molecular interferences produced due to the discharge gas (argon). The spectrum was recorded with the Faraday and electron multiplier detectors from mass 6 to 24 by skipping the masses from 18 to 22 to avoid the large argon peak at mass 20. It is evident from Fig. 2 that the argon produces molecular ions, $^{40}Ar^{3+}$ and $^{40}Ar^{4+}$, which interfere at masses 13.3 and 10, respectively. Due to low concentration of boron (3.2 mg kg^{-1}) the signal for boron was not observed by Faraday at mass 11, however the signal observed at mass 10 by Faraday was due to $^{40}Ar^{4+}$ ion only. The probability of formation of $^{40}Ar^{4+}$ ion at mass 10 was observed to be non-uniform in each sample, hence by using this isotope the quantification of boron at trace and ultra trace levels is not possible by quadrupole based (low resolution) GD-MS (GD-QMS). On the other hand, since the ^{11}B is free from spectral interferences due to discharge gas (argon) as well as matrix elements (zirconium & iron) and also having higher

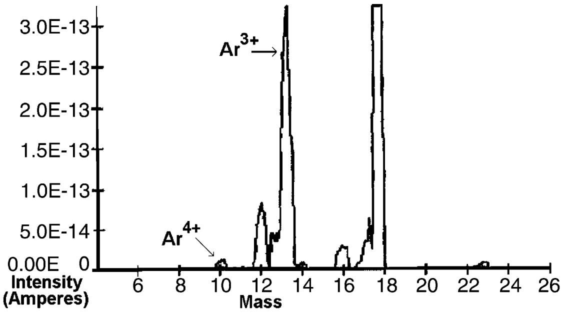

Fig. 2. GD Quardrupole Mass Spectrum Ar^{4+} ion on ^{10}B in zirconium matrix sample with a resolution of 300 and an integration time of 40 ms.

abundance value to give intense signal in the mass spectrum, ^{11}B was alone used for quantifying boron in all the samples. To determine boron by both the isotopes the other inert gas, neon, also cannot be used as an alternative discharge gas as it can also produce isobars ($^{20}Ne^{2+}$, $^{22}Ne^{2+}$) on both the isotopes of boron (10, 11). Only xenon gas, which does not have above effects, can be used as a discharge gas to determine boron with both of its isotopes by low resolution GD-MS (GD-QMS).

4.4. Relative sensitivity factor and quantitation

The raw counts of each element's isotope of each sample were normalized to 100% from their relative abundances. The ion beam ratio (IBR) values were generated by taking the ratio of abundances corrected raw counts of each element to the total sum of corrected raw counts of all the elements, including the matrix zirconium isotope. The relative sensitivity factor (RSF) value is generated by taking the ratio of true concentration (certified value in standard) of each element to its ion beam ratio (IBR). As the glow discharge is highly stable plasma, a single standard is sufficient for the calibration (i.e. for the generation of RSF value).

In GD-MS it is preferable to use matrix matched reference materials to obtain accurate results. Generally, GD-MS shows minimal matrix effects due to the decoupling of atomisation and ionisation process in the plasma and thereby minimising the stringent need of matrix matched solid standards for the analysis. It is however required to verify that the relative sensitive factors generated on various solid standards for a particular element are indeed independent of matrix or matrix composition. To understand this aspect, we have carried out a study on the applicability of RSF values of boron generated on two different matrices such as Zircaloy CRM (Teledyne standard, X868-13D) and low alloy steel SRM (NIST-1762) for the quantitative determination of boron in Zr–2.5%Nb, Zr–1%Nb alloys and zirconium metal samples. In addition two Zircaloy standards (Zircaloy Teledyne Standards: X867-16D & X869-25B) were also analysed to check the validity of GD-QMS results on same matrix composition samples.

The computed RSF values for boron were found to be 0.169 ± 0.002 (B/Zr, i.e. RSF of Zr = 1) for the Zircaloy standard and 0.321 ± 0.008 (B/Fe, i.e. RSF of Fe = 1) for the iron standard. And the RSF value for zirconium in the iron standard was found to be 2.276 ± 0.091 (Zr/Fe, RSF of Fe = 1). The ratio of the RSF values 0.321 (B/Fe, i.e. RSF of Fe = 1) and 2.276 (Zr/Fe, RSF of Fe = 1) produces a RSF value (0.141) of boron with respect to zirconium in iron standard. That is, 0.141 (B/Zr: boron with respect to Zr) in Fe matrix. Thus the normalised RSF values of boron were found to be 0.169 (B/Zr: boron with respect to Zr) in Zr matrix & 0.141 (B/Zr: boron with respect to Zr) in Fe matrix. On comparison, these two RSF values were found to be more or less close to each other (within 20% difference only). This reveals that the ionisation of boron with respect to zirconium is nearly same in both zirconium matrix and in iron matrix. The 20% difference between the two RSF values (0.169 of B/Zr in Zr matrix and 0.141 of B/Zr in Fe matrix) was due the low concentration of the zirconium (300 mg kg^{-1}) in iron standard. That is, the RSF value of Zr generated with the low concentration of Zr in iron standard was applied to the IBR of Zr of high concentration (~ 97–99% Zr in the Zr–Nb alloy samples and other zirconium samples) in all Zr based samples and then was normalised to 100%. Hence the accuracy was observed slightly poorer for the results obtained using steel standard.

The concentrations of boron in all Zr based samples and standards were determined using the both RSF values of boron obtained from Zircaloy standard and steel standard and then listed in Table 2. The DC-Arc-AES values and certified values for boron in these samples and standards were also listed in Table 2 for the comparison purpose. The percentage deviation of GD-QMS values from the certified values for boron in the two standards (X867 & X869) were computed and given in parenthesis in Table 2. The GD values of boron in these two standards obtained from Zircaloy and steel standards are found to be in good agreement with the certified values.

Table 2 indicates that the accuracy of the GD-QMS value is 8% when the boron levels are around 0.5 mg kg^{-1} using both the standards (Zircaloy and steel) and 14% (using Zircaloy) and 28% (using steel) when the boron levels are around 0.3 mg kg^{-1}. This reveals that there is a decrease in accuracy at lower boron levels. However even with the poor accuracy at lower levels of boron (~0.3 mg kg^{-1}), the GD value with upper error limit (e.g. 0.3 ± 0.09 mg kg^{-1} for ±30% variation) is still lesser than the acceptable limit of boron (0.5 mg kg^{-1}).

Thus the final concentration computed using the average value of the each standard (3.2 ± 0.3 mg kg^{-1} for X868 & 40 ± 2 mg kg^{-1} of steel standard) was found to be within the error limits of each standard (X867 & X869).

NBS (NIST) Zircaloy and Metal SRMs (1237, 1238, 1239, 1234, 1236), though not certified for boron, were all analysed to identify the level of agreement of GD-QMS values against their indicated values (approximate values) given in Table 2. On comparison, the GD values were found to be in reasonable agreement with these values also using both the standards (Zircaloy and steel). The high difference (+49% relative to the reference value) in the accuracy for NBS 1236 is mainly due to the in homogeneity.

Similarly the GD values of all Zr–Nb alloys show a reasonable agreement with the limit values obtained by

Table 2
Comparison of boron concentration obtained by GD-QMS with the values obtained by other alternative technique

Sample code	DC arc-atomic emission spectrographic method/certified value (mg kg^{-1})	GD-QMS using Zircaloy standard (Teledyne X868-13D) (N = 4) (mg kg^{-1})	GD-QMS using Iron matrix standard (NIST 1762) (N = 4) (mg kg^{-1})	Internal precision (percentage RSD) (N = 4)
Zircaloy Teledyne Std (X867-16D)	0.45 ± 0.01[a]	0.49 ± 0.03 (8%)[b]	0.41 ± 0.02 (8%)[b]	5.1
Zircaloy Teledyne Std (X869-25B)	0.29 ± 0.06[a]	0.25 ± 0.01 (14%)[b]	0.21 ± 0.01 (28%)[b]	3.6
Zr metal (Sponge) Std NBS 1234	<0.2[c]	0.17 ± 0.01	0.14 ± 0.01	3.9
Zr metal (Sponge) Std NBS 1236	7.0[c]	10.45 ± 0.13	8.72 ± 0.11	1.3
Zircaloy NBS Std 1237	0.4[c]	0.49 ± 0.02	0.42 ± 0.02	3.9
Zircaloy NBS Std 1238	2.0[c]	2.75 ± 0.06	2.31 ± 0.05	2.2
Zircaloy NBS Std 1239	0.25[c]	0.29 ± 0.01	0.24 ± 0.01	2.0
Zr–2.5% Nb alloy 1	<0.5 ± 0.1[d]	0.40 ± 0.04	0.33 ± 0.01	9.8
Zr–2.5% Nb alloy 2	<0.5 ± 0.1[d]	0.45 ± 0.03	0.37 ± 0.02	6.1
Zr–1% Nb alloy 1	<0.5 ± 0.1[d]	0.11 ± 0.01	0.10 ± 0.01	3.9
Zr–1% Nb alloy 2	<0.5 ± 0.1[d]	0.24 ± 0.01	0.20 ± 0.01	2.9
Zr–1% Nb alloy 3	<0.5 ± 0.1[d]	0.23 ± 0.01	0.19 ± 0.01	2.4
Zr–1% Nb alloy 4	<0.5 ± 0.1[d]	0.19 ± 0.02	0.16 ± 0.01	8.9
Zr–1% Nb alloy 5	<0.5 ± 0.1[d]	0.16 ± 0.02	0.14 ± 0.01	9.6

[a] Certified value.
[b] Percentage deviation from the reference value.
[c] Approximate values indicated in NBS (Now NIST) certificates.
[d] DC-Arc-AES.

DC-Arc-AES technique. Thus even after considering the 8% accuracy at 0.5 mg kg^{-1} as well as 14% or 28% accuracy at $\leqslant$ 0.3 mg kg^{-1} also, the GD values for all Zr–Nb alloys were found to be within the permissible limits of boron using both the standards.

As the data obtained from matrix-matched standard is more accurate compared to that obtained from other non-matrix standards, the GD data (column 3 of Table 2) obtained from Zircaloy standard can be reported to the customer with 8% accuracy at 0.5 mg kg^{-1} levels and with 14% accuracy at $\leqslant$0.3 mg kg^{-1} levels. In absence of Zircaloy standard, the boron value obtained by steel standard, can also be reported with an accuracy of ±8% at 0.5 mg kg^{-1} levels and 28% accuracy at $\leqslant$ 0.3 mg kg^{-1} levels.

Thus a material containing boron above 0.5 mg kg^{-1} levels can be prevented from entering the reactor if its GD value for boron along with 8% error (accuracy) exceeds the specification limit of boron, 0.5 mg kg^{-1}.

Only limit values, i.e. <0.5 mg kg^{-1}, could be provided using DC Arc technique for Zr–Nb alloys for lower levels of boron, whereas definitive values for the boron could be obtained using GD-QMS. Based on the actual GD-QMS values (Table 2), it is evident that all the Zr–1%Nb alloys have significantly lower boron values compared to all Zr–2.5%Nb samples. This indicates that determination of boron at ultra trace levels using GD-QMS helped to evaluate the efficiency of chemical/metallurgical processes better when compared to DC Arc technique.

4.5. Analytical precision

Prior to the analysis by GD-QMS, the Zr–Nb samples were tested for homogeneity by Spark Source Optical Emission Direct Reading Spectrometry (unidirectional ARL 3560 point to plane) by analysing at various locations covering total 20 mm diameter area on the surface by sputtering an area of 5 mm diameter and 2–3 micron depth at each location. It was found that a steady signal (representing the homogeneity) was seen from one location to another location in all the samples [11].

Since the GD-QMS analysis covers a surface area of 10 mm diameter and $\sim$20 micron depth with single sample loading with multiple measurements, the analyses by GD-QMS for all these samples were performed with a single sample loading with multiple measurements on the same spot. The results are given in Table 2.

Table 2 (column 5) indicates that the internal precision (intra-sample precision: multiple measurements with a single sample loading) is typically ±1% RSD (relative standard deviation) for boron at few mg kg^{-1} levels and ±2% RSD for boron at $\sim$0.3 mg kg^{-1} levels and ±4% RSD for boron at $\sim$0.1 mg kg^{-1} levels. This indicates that the precision becomes poorer as the concentration levels comes down. For direct solid analysis techniques like GD-QMS, the internal precision is inclusive of both instrument precision as well as sample variability (in homogeneity).

A study on the inter-sample variability by GD-QMS was performed on a sample containing boron of

0.1 mg kg^{-1} levels. The inter-sample precision (consecutive measurements on the same sample with multiple loading) for boron was found to be (with one sigma): ±10%RSD for boron at ~0.1 mg kg^{-1} levels.

The internal precision (intra-sample variability) for zirconium (~97–99% Zr in the Zr–Nb alloy samples and other zirconium samples) was found to be 0.04% RSD. These data (internal precision values) are indicative of the stability of the GD plasma during the measurements and the degree of in homogeneity of the boron in the alloy. The good precision for Zr, 0.04%, indicates that the sample was of highly homogenous material within the amount of material sputtered (~20 microns depth and 10 mm diameter surface). In GD-QMS with repetitive determinations the above precision is normally observed for matrix element, if the material is highly homogeneous. The inter-sample precision for Zr was found to be 0.09%.

4.6. Detection limits

Unlike in other spectrometric techniques, in GD-QMS, the blank (baseline) signal cannot be measured independently without the sample. In our measurements each isotope region was measured using 140 points across with a mass step of 0.01 amu. The total width of the scanning window was about 1.4 amu of which 0.8 amu in the centre is integrated as the signal for the isotope. The signal for the baseline is measured at the wings of each peak. The detection limit in our case was defined as three times the standard deviation of this background signal [12], based on multiple scans ($n = 4$), which was converted into the corresponding concentration value using the computed concentration of the element (isotope). The detection limit for boron was computed to be 13 μg kg^{-1} with the integration time of 20 ms (total integration time, i.e. 20 scans with each integration time of 1 ms) and 140 points and the number of repetitive scans was 4 by GD-QMS.

5. Conclusion

The quantitative determination of boron in Zr–2.5%Nb, Zr–1%Nb alloys and zirconium metals is possible without the need of same matrix composition solid standards by GD-QMS. The boron content in Zr–Nb alloy solid samples and other zirconium based materials could be directly determined using GD-QMS without blank contamination problems and avoiding extensive sample preparation steps. A stabilisation time of 40 min is required for both the matrices, zirconium and iron, prior to the analysis. With the optimised conditions, the intra-sample precision was found to be ±4% RSD and the inter-sample precision was ±10% RSD for boron at ~0.1 mg kg^{-1} levels. The overall accuracy of the procedure was found to be within ±8% at ~0.5 mg kg^{-1} levels of boron using both standards, Zircaloy and steel. The achieved detection limit was 13 μg kg^{-1}. The determination of boron in Zr–Nb alloys and other zirconium based metals/materials by GD-QMS is quite possible even with steel standard solid reference materials.

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