

# Determination of Elemental Composition of Zr-Nb Alloys by Glow Discharge Quadrupole Mass Spectrometry

Raparathi Shekhar<sup>a</sup>, \*J. Arunachalam<sup>a</sup>, G. Radha Krishna<sup>b</sup>, H.R. Ravindra<sup>b</sup>, and B. Gopalan<sup>b</sup>

<sup>a</sup> National Centre for Compositional Characterization of Materials  
Bhabha Atomic Research Centre, ECIL Post, Hyderabad 500062, India

<sup>b</sup> Control Laboratory, Nuclear Fuel Complex, ECIL Post, Hyderabad 500062, India

## INTRODUCTION

Zr-Nb alloys with varying niobium compositions have been widely used 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 the preferred structural material for pressure tubes of CANDU type Pressurised Heavy Water Reactors, Zr-1%Nb is used as a fuel cladding material in Pressurised Water Reactors. In view of these important applications, assessment of chemical purity, especially in the determination of trace elements, is of importance. The content of the alloying element niobium, which enhances the mechanical strength and creep-resistance properties of the virgin metal, is present within a narrow concentration range and is also required to be accurately determined. The allowed specifications are  $2.5 \pm 0.3\%$  in Zr-2.5%Nb alloys and  $1.0 \pm 0.1\%$  in Zr-1%Nb alloys.

A wide range of analytical methods such as (chemical) Differential Spectrophotometry (2,3), X-ray Fluorescence Spectrometry (XRFS) (4), DC-Arc Emission Spectrography (DC Arc ES), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and the electro-analytical techniques are employed routinely for the determination of niobium content and the concentrations of other trace elements in Zr-Nb alloys. However, these methods involve tedious matrix separation procedures to determine impurities at trace levels.

\*Corresponding author.  
E-mail: arunccm@rediffmail.com

## ABSTRACT

The simultaneous determination of trace elements and niobium in Zr-Nb alloys with varying niobium concentrations has been carried out by Glow Discharge Quadrupole Mass Spectrometry (GD-QMS). The Relative Sensitivity Factors (RSF) for the analytes were generated using a certified reference material of a zirconium alloy (zircaloy, non-similar matrix composition). GD-QMS results have been found to be in good agreement with the certified concentrations for several elements of other zirconium-based certified reference materials (zirconium metal and alloys).

This technique is a viable alternative to validate conventional atomic emission and other spectrometric techniques used for the determination of impurities in zirconium-based alloys. With the optimized discharge conditions and pre-sputtering time, the precision of measurements achieved were typically 1% RSD for the majority of elements present at  $\text{mg kg}^{-1}$  levels, 10% RSD for  $\mu\text{g kg}^{-1}$  levels, 0.05% RSD for zirconium (matrix), and 0.05% RSD for niobium (alloying element).

The detection limits for the analytes were found to be at sub-ppm levels with an integration time of 20 ms, 140 points, and four repetitive scans. Molecular interferences observed due to oxygen, matrix, and argon are also listed.

The Differential Spectrophotometric method used for the estimation of niobium at higher concentrations involves the formation of a yellow niobium peroxide complex in concentrated sulphuric acid. This method yields somewhat lesser sensitivities. However, a

molar absorptivity of  $\epsilon = 1 \times 10^3$  is adequate for the determination of niobium at percentage levels. XRFS is the method of choice for the quick estimation of the major constituents, with suitable reference materials for calibration. However, for the determination of trace constituents in the presence of matrix, XRFS is not quite suitable due to poor sensitivity. The main problem in the emission spectrometric analysis of zirconium and its alloys is the undesirable line-rich emission spectrum of zirconium which leads to spectral interferences (5). In addition, in emission spectrometric methods, the practical detection limits achieved for some elements (like boron) are not adequate for quantification in sub-ppm levels (6). In ICP-MS there is a limitation on the total matrix content, which cannot exceed 0.1–0.2% for effective nebulization. Hence, multiple dilutions are required. Also, the use of HF in dissolution is restrictive with respect to routine use.

GD-QMS offers the advantage of multielement analysis (major, minor, trace, and ultratrace levels) in a single run and exhibits a low matrix dependence for trace elemental analysis of solids. With glow discharge, the sample acts as a cathode, and neutral atoms are sputtered from the surface of the sample and then ionized in the plasma by penning ionization and/or electron impact ionization (7). In GD-MS, the quantification requires the generation of RSF values using suitable solid reference materials. In addition, due to the stability of the plasma, GDMS is superior to the traditionally used spark source mass spectrometry (SSMS) for the analysis of solids and offers a better precision for quanti-

tative analysis. Again, the quantitative separation of zirconium from other trace and ultratrace elements requires multiple solvent extraction steps which are highly tedious and time-consuming, which is obviated in direct solid sample analysis.

Application of GDMS to determine the elemental composition has been reported (8) only for zircaloy NBS standards by generating the RSF values on other zircaloy NBS standards of similar composition. We had reported earlier on the use of GD-QMS for the determination of specific (single) elements such as tin (9), chlorine (10), and boron (6) in zirconium-based alloys.

In the present work, a detailed study has been made on the multi-element analysis of zirconium, Zr-Nb, and other zirconium alloys for matrix and trace elements by GD-QMS. The discharge conditions, stabilization time for GD signal and the possible isobaric interferences on isotopes of various analytes are reported. A comparison of the GD-QMS results with those obtained from DC Arc OES, as well as with certified values of elements in Zr-Nb alloys and zirconium metal standards, and other zircaloy standard samples, are presented.

## EXPERIMENTAL

### Instrumentation

A quadrupole GD-MS, Model GQ230 (VG Elemental, U.K.), was used for the present work. The instrumental parameters are listed in Table I. This instrument was located in our Ultra Trace Analysis Laboratory, inside a class 200 clean room. The discharge was operated in current mode where the discharge voltage was adjusted by changing the flow rate of argon gas using a gas inlet valve. The discharge gas was argon (99.9999% purity); which was additionally purified with an on-line active metal getter. The system interlock

gate was operated using compressed argon gas (65 psi) of 99.9995% purity.

The dual detector system (Model No.4870V, Galileo Electro-Optics Corp., USA) utilizes an electron multiplier for ion counting for trace elements (ion currents  $< 1 \times 10^6$  ions  $\text{sec}^{-1}$ ) and a Faraday cup for measurement of major and minor elements (ion currents  $> 1 \times 10^6$  ions  $\text{sec}^{-1}$ ). The detector system provides a dynamic range of more than eight orders of magnitude, i.e.,  $1 \times 10^1 - 1 \times 10^{10}$  ions  $\text{sec}^{-1}$ . Control of instrument and data acquisition was handled by Glo-Quad software. The peak jump mode was used for the data acquisition. A 10-mm anode opening diameter flat sample holder was used. The GD cell in the instrument was cryogenically cooled with liquid nitrogen in order to minimize residual gaseous contaminants.

### Mass Calibration

A high-speed stainless steel (HSS) disc containing major elements ranging from carbon ( $m/z=12$ ) to tungsten ( $m/z=184$ ) as constituents was chosen for the mass calibration. A small amount of solder (tin-lead alloy) material was also embedded into the HSS sample surface to add Sn (mid mass range  $\sim 120$  amu) and Pb (higher mass  $\sim 208$  amu) masses as well to obtain a more linear mass calibration over the entire mass range.

**TABLE I**  
**Instrumental**  
**Operating Parameters**

Discharge Voltage	1.2 kV
Discharge Current	3.0 mA
Argon flow rate	23.3 sccm
Temperature during discharge	-166°C
Vacuum (at the quadrupole region)	$1 \times 10^{-6}$ mbar
Resolution	300 $M/\Delta M$

### Collector Calibration

Collector calibration was done on a daily basis. The Faraday cup and Electron Multiplier detectors were cross-calibrated by measuring the signal intensity at mass 76 ( $^{40}\text{Ar}^{36}\text{Ar}^+$ ). Detector calibration factor was adjusted to be  $2560 \pm 200$  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.

### Procedure

#### Sample Preparation for GD-QMS

The surface of different Zr-Nb alloy samples, zircaloy standard samples, and zirconium metal samples were polished to 300 grit with a belt grinder, cleaned with methanol, and then dried under an infrared lamp. Individual samples were loaded into the GD system and degassed under vacuum (around  $1 \times 10^{-3}$  mbar) prior to analysis for the removal of atmospheric contaminants. The discharge parameters were optimized to obtain maximum intensity in the form of counts per second ( $6 \times 10^5$  ions  $\text{sec}^{-1}$ ) for  $^{90}\text{Zr}^+$ . The sample surface was etched with the plasma at a discharge voltage of 1.2 kV and a current of 3.0 mA for 40 minutes in order to eliminate the initial embedded surface contaminants and obtain a constant standing signal.

The analytical measurements were carried out at a mass step of 0.01 amu with 140 points. A single scan of the Faraday detector for major and minor elements and 20 scans of the electron multiplier for trace and ultratrace elements were used. Four repetitive measurements were recorded.

## RESULTS AND DISCUSSION

### Discharge Parameters

The studies (11) of the influence of discharge current on the ion

yield indicated that the optimum discharge current is 3.0 mA (with a discharge voltage of 1.0 kV). The 3.0 mA current results in a maximum ion beam intensity, the lowest level of atmospheric and gas-matrix combinations, and a drastically reduced contribution of molecular species (e.g., matrix dimers, etc.). Thus, the discharge current was fixed at 3.0 mA using constant current mode. The discharge voltage at 1.2 kV compared to 1.0 kV resulted in a maximum ion intensity for  $^{90}\text{Zr}^+$  ion. In our earlier studies (10), the use of 1.2 kV and 3.0 mA gave good results for chlorine in Zr-2.5%Nb alloys. Therefore, discharge conditions of 1.2 kV and 3.0 mA were used for all samples.

## Studies on Stabilization Time

Pre-sputtering of the sample (surface) was carried out at the discharge parameters described above. A separate experiment was carried out to determine the actual stabilization time required for the GD signal with respect to elimination of surface contaminants in GD-QMS. The raw counts of some of the common contaminant elements (Na, Mg, Si, Ca) were recorded and converted into ion beam ratios (IBR). The ion beam ratio values were obtained by computing the ratio of raw counts of each isotope normalized to 100% to the abundance normalized raw counts of  $^{90}\text{Zr}^+$  ion. These IBRs were plotted against each pre-sputter time in Figure 1. The figure reveals that the contamination originating from the sample surface was removed by plasma etching within 35–40 minutes. The GD signal stability was achieved after 40 minutes. Therefore, each sample was pre-sputtered for 40 minutes and the quantitative measurements were made after 40 minutes.

## Quantification

Accurate quantitative results in GD-QMS would require the genera-

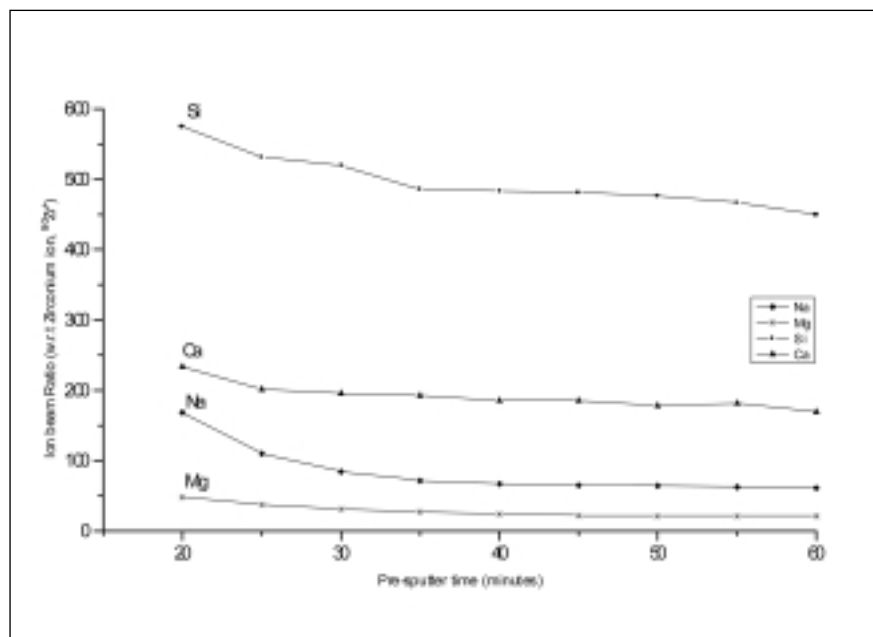


Fig. 1. Dependence of GD signal on pre-sputter time.

tion of matrix-matched RSF values calculated from certified reference samples with the same or similar composition of the sample to be analyzed. But certified reference materials with the same or similar composition for Zr-Nb alloys for trace and ultratrace levels are not available. Hence, a different composition zirconium alloy matrix (zircaloy, Teledyn standard ZrX868-16D; major elements: Zr, Sn, Fe, Cr) standard, in which several elements were certified, was used for the generation of RSF values for all of its certified elements. Table II lists the RSF values and IBRs for all certified elements. The usability of these RSF values for the determination of elemental concentrations in zirconium metals and Zr-Nb alloys containing different niobium concentrations was investigated.

## Usability of RSF Values

The RSF values for certified elements were generated using their corresponding IBR measured in the zircaloy standard by GD-QMS. These RSF values were applied to

IBR values of each Zr-Nb ingot sample and other zirconium standards. The quantitative results so obtained for several elements are listed in Tables III–VI, which provide a comparison of the results for Zr-Nb alloys obtained by GD-QMS against DC Arc-OES and the certified concentrations.

Table III shows that GD-QMS values are in very good agreement with the certified values for the elements Si, P, Ti, V, Cr, Cu, Zr, Nb, Mo, Sn, Hf, Pb, Ca, and Cd in the ZrX869-25B standard and for the elements P, Ti, V, Cr, Mn, Fe, Ni, Cu, Zr, Nb, Mo, Hf, Ca, Cd in the ZrX867-16D standard. Somewhat higher values compared to the corresponding certified values for the elements Co, Ta, W, Na, and Mg (in the ZrX869-25B standard) and for Si, Co, Sn, Ta, W, Na, and Mg (in the ZrX867-16D standard) were obtained by GD-QMS. The GD values were lower compared to the corresponding certified values for the elements Mn, Fe, Ni in ZrX869-25B standard and Pb in ZrX867-16D standard. These (minor) disagree-

**TABLE II**  
**Relative Sensitivity Factors Generated Using ZircaloyTeledyn Std.**  
**(Zrx868-16D) Certified Values by GD-QMS**

Elements	Zircaloy Teledyn Std. Zrx868-16D Certified Values (mg kg <sup>-1</sup> )	GD-QMS Ion Beam Ratios (mg kg <sup>-1</sup> )	RSF Value Generated
<sup>30</sup> Si	179±4	471±15	0.380
<sup>31</sup> P	35±3	49±2	0.712
<sup>49</sup> Ti	122±16	400±7	0.305
<sup>51</sup> V	93±5	303±7	0.307
<sup>52</sup> Cr	580±26	521±5	1.114
<sup>55</sup> Mn	56±2	52±1	1.087
<sup>56</sup> Fe	2787±66	4198±51	0.665
<sup>60</sup> Ni	134±6	165±2	0.209
<sup>59</sup> Co	42±1	61±1	0.686
<sup>63</sup> Cu	83±2	17±0.4	4.755
<sup>90</sup> Zr	98.709%	98.847±0.017%	1.000
<sup>93</sup> Nb	570±12	550±14	1.037
<sup>98</sup> Mo	128±2	66±2	1.948
<sup>119</sup> Sn	1.23±0.03%	0.228±0.006%	5.413
<sup>178</sup> Hf	178±6	66±1	2.716
<sup>181</sup> Ta	716±4	181±2	3.959
<sup>182</sup> W	112±13	24±0.2	4.596
<sup>208</sup> Pb	101±11	8.4±0.3	12.035
<sup>23</sup> Na	<10	64±3	<0.156
<sup>24</sup> Mg	<5	22±1	<0.224
<sup>44</sup> Ca	<10	283± 3	<0.009
<sup>114</sup> Cd	<0.2	56±2	<0.004

ments noted may be due to the compromised optimised conditions used for the determination of many elements. Hence, certain deviations were seen with respect to the certified concentrations. The results shown in Tables IV and V indicate that there is good agreement for GD values with the certified values of hafnium in zirconium metals and zircalloys, and also for indicated values of the elements in the zirconium metals and zircalloy standards. Tables VI and VII indicate that the RSFs generated provide fairly accurate values for the elements (Cr, Fe, Ni, Cu, Nb, Sn) in Zr-2.5%Nb samples and (P, Ti, Cr, Mn, Fe, Ni, Cu, Nb, Mo, Cd, Sn, Hf, Pb, Ca) in Zr-1%Nb alloys in com-

parison to DC Arc AES values. The agreement seen reveals that the computed RSF values from zircaloy standard (non similar matrix composition) are quite applicable to zirconium based samples such as pure metal as well as Zr-Nb alloys with varying niobium concentrations.

In our earlier study of tin (9) analysis by GD-QMS, we found that the RSF value of tin in zirconium matrix (zircaloy) was 1.39 and 4.93 at liquid nitrogen temperatures (i.e., with cooling the sample) and ambient temperature (i.e., without cooling the sample), respectively, at a discharge voltage of 1.1 kV and 1.0 mA. In the present study, the

RSF value of tin in zirconium matrix was 5.413 at discharge voltage of 1.2 kV and 3.0 mA at liquid nitrogen temperatures. The change in RSF values with respect to the discharge parameters is being investigated.

### Spectral Interferences

Some of the dominant molecular ionic species noted in the GD-QMS spectrum of the zirconium matrix are given in Figure 2. The interference from the Zr<sup>+2</sup> (Figure 2a) ion species significantly affects the determination of Sc and Ti (<sup>45</sup>Sc, <sup>46</sup>Ti, <sup>47</sup>Ti, and <sup>48</sup>Ti). Hence, <sup>49</sup>Ti was used for quantification of titanium. Molecular ionic species formed by oxides and argides with the matrix are interfering with the elements Pd, Ag, Cd, Sn (mass numbers: 106, 107, 108, 110, 112; Figure 2b) and Xe, Ba (mass numbers: 130, 131, 132, 134, 136; Figure 2c), respectively. Other isobaric interferences due to argon gas are observed: <sup>40</sup>Ar<sup>+4</sup>, <sup>40</sup>Ar<sup>+3</sup>, <sup>40</sup>Ar<sup>+2</sup>, <sup>40</sup>Ar<sup>36</sup>Ar<sup>+</sup>, <sup>40</sup>Ar<sub>2</sub><sup>+</sup>, and <sup>40</sup>Ar<sub>3</sub><sup>+</sup>.

### Analytical Precision

Tables III-VII also show internal reproducibility of the determinations in the Zr-Nb alloy samples at trace and ultratrace levels. The uncertainties in these estimates are expressed as overall standard deviations, and the computed % RSDs are based on multiple measurements under the given discharge conditions (n=4). The overall precision for the determination of analytes was typically 1% RSD for the majority of the elements present at mg kg<sup>-1</sup> levels, 10% RSD for µg kg<sup>-1</sup> levels, 0.05% RSD for zirconium (matrix), and 0.05% RSD for niobium (alloying element). These data are indicative of the stability of the GD plasma during the measurements and the degree of homogeneity of the sample at trace and ultratrace levels in the alloy.

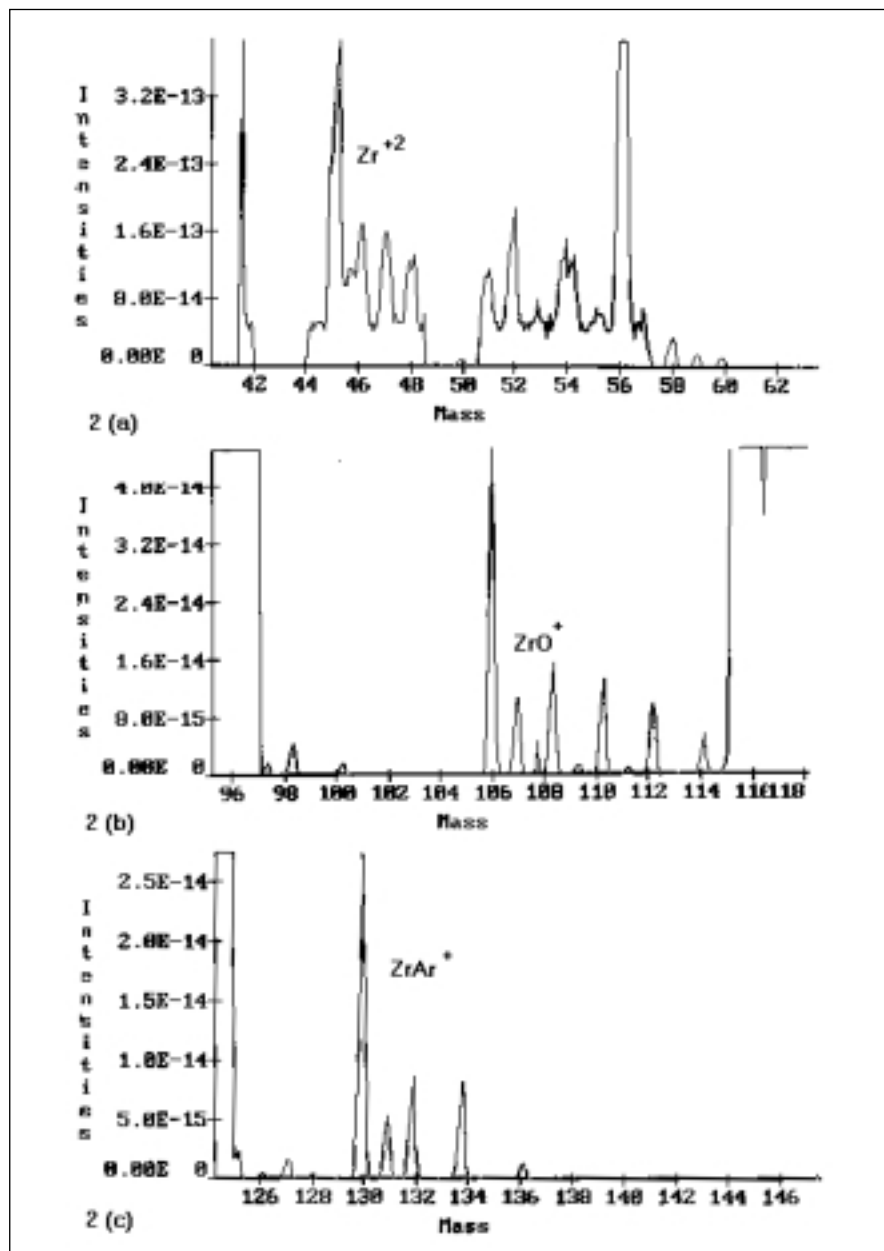


Fig. 2 (a,b,c). Molecular ionic species observed in the GD-QM Spectrum of Zr.

## Detection Limits

Unlike other spectrometric techniques, in GD-QMS the blank (baseline) signal cannot be measured independently without the sample. In our measurements, each isotope region is measured using 140 points across with a mass step of 0.01 amu. The total width of the scanning window is about 1.4 amu of which 0.8 amu in the center 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 is converted into the corresponding concentration value using the computed concentration of the element (isotope). For most of the analytes, the detection limits were found to be in the sub-ppm levels.

## CONCLUSION

The sensitivity offered by GD-QMS enables the accurate determination of trace constituents in Zr and Zr-Nb based alloys at concentration levels much lower than their specified levels. This, in turn, enables assessment of the efficiency of the manufacturing processes.

This study provides such an assessment of the Zr-Nb alloy samples manufactured indigenously. Even though GD-MS is not available as a routine analytical technique in many laboratories, an assessment of the measurement accuracy by other analytical techniques with different physico-chemical principles with a technique capable of direct analysis would better enable quality improvement steps implemented in bulk production of critical components such as nuclear-grade zirconium metal and alloys.

**TABLE III**  
**Comparison of GD-QMS Concentrations With Certified Values of Zircaloy Teledyne Standards**

Elements	Zircaloy Teledyn Std Zrx869-25B		Zircaloy Teledyn Std. Zrx867-16D	
	Certified Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )	Certified Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )
Si	94±10	93±1	31±3	59±1.5
P	49±8	38±0.6	102±7	112±2.1
Ti	55±1	55±0.01	19±4	17±0.4
V	47±4	42±0.2	20±1	17±3
Cr	1057±32	991±22	1630±26	1630±10
Mn	54±1	44±0.4	6±1	5±0.1
Fe	2247±35	2090±10	1630±40	1640±20
Ni	68±5	30±3	33±3	34±1
Co	17±1	23±0.09	10±1	18±0.6
Cu	36±1	37±0.3	8±1	7±0.2
Zr	97.872%	97.799±0.016%	97.604%	97.186±0.029%
Nb	276±16	263±2.4	102±10	96±1.5
Mo	59±1	53±0.4	10±1	11±0.3
Sn	1.65±0.03%	1.681±0.018%	2.00±0.02%	2.344±0.026%
Hf	77±4	85±1.3	31±3	36±0.5
Ta	396±5	442±5	207±7	241±4
W	46±9	60±0.9	23±2	39±0.7
Pb	44±1	47±0.7	16±1	8.0±0.2
Na	<10	<24	<10	<59
Mg	<5	<16	<5	<32
Ca	<10	<5	<10	<9
Cd	<0.2	<0.25	<0.2	<0.35

**TABLE IV**  
**Comparison of GD-QMS Concentrations With Indicated Values of NBS Zirconium Metal Standards**

Elements	Zr Metal NBS Std 1234		Zr Metal NBS Std 1236	
	Indicated (by NBS) Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )	Indicated (by NBS) Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )
Si	40	69±1	205	192±9
P	7	10±0.2	19	30±0.4
Ti	20	19±0.6	185	206±1.3
V	5	6±0.2	20	70±0.7
Cr	55	110±2.3	250	355±12
Mn	10	23±0.6	45	46±0.1
Fe	240	385±15	1700	1630±20
Ni	20	16±0.8	140	127±2.6
Co	5	23±0.09	50	39±0.2
Cu	<10	35±0.5	250	243±0.9
Zr	99.837%	99.858±0.016%	99.288%	99.461±0.006%
Nb	55	42±1.3	600	606±4.5
Mo	2	15±0.6	100	120±1.0
Sn	15	16±0.9	60	104±4
Hf	46±3*	45±2	198±6*	181±7
Ta	85	95±5	700	668±16
W	25	27±1.4	140	188±5
Pb	5	10±0.8	25	46±1

\* Certified value.

**TABLE V**  
**Comparison of GD-QMS Concentrations With Indicated Values of NBS Zircaloy Standards**

Elements	Zr Metal NBS Std 1237		Zr Metal NBS Std 1238		Zr Metal NBS Std 1239	
	Indicated (by NBS) Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )	Indicated (by NBS) Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )	Indicated (by NBS) Values (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )
Si	35	66±3	170	90±0.1	95	130±2
P	62	125±4	20	31±2.3	26	50±0.8
Ti	30	21±0.7	100	101±3.3	40	75±1.3
V	10	23±0.7	25	72±1.8	15	56±0.8
Cr	1510	1770±40	580	636±7.6	1055	1120±10
Mn	10	9±0.4	60	50±1.3	50	54±0.8
Fe	1650	1640±30	2500	2630±80	2300	2160±30
Ni	40	24±0.7	100	94±2.3	45	30±0.5
Co	10	15±0.5	40	32±0.6	15	24±0.5
Cu	<10	8.5±0.2	60	37±0.3	30	45±1
Zr	97.616%	97.059±0.114%	97.957%	98.304±0.056%	97.776%	96.647±0.042%
Nb	85	105±2.5	550	483±11	220	261±5
Mo	<10	12±0.6	120	99±1.4	45	57±2
Sn	1.9%	2.476±0.109%	1.26%	1.040±0.045%	1.61%	2.785±0.043%
Hf	31±3*	37±1.6	178 ± 6*	140±4.0	77±4*	84±2.5
Ta	200	226±8	700	547±15	400	413±12
W	25	33±1.5	95	88±0.6	45	57±0.3
Pb	15	14±0.7	80	78±1.5	30	46±2

\* Certified value.

**TABLE VI**  
**Comparison of GD-QMS Concentrations With Chemical Values in Zr-2.5% Nb Alloy Coolant Tube Samples**

Elements	Zr-2.5% Nb Sample No. 1		Zr-2.5% Nb Sample No. 2	
	DC Arc OES (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )	DC Arc OES (mg kg <sup>-1</sup> )	GD-QMS (mg kg <sup>-1</sup> )
Cr	150	128±5	160	149±4
Fe	700	648±99	810	757±3
Ni	<70	19±2	< 70	20±1
Cu	<30	10±0.2	< 30	4.7±0.1
Nb*	2.6%	2.856±0.007%	2.6%	2.637±0.025%
Sn	29	21±1	42	26±1

DC Arc OES: DC Arc Optical Emission Spectrographic method.

\* : Analyzed by X-Ray Fluorescence Spectrometric method.

## ACKNOWLEDGMENTS

The authors thank Dr. J.P. Mittal, Director, Chemistry and Isotope Group, BARC, and Shri P.S.A. Narayanan, DCE (QA, MS & C), NFC, for their encouragement and constant support in carrying out the present work.

*Received July 31, 2003.*

**TABLE VII**  
**Comparison of GD-QMS Concentrations With Chemical Values of Zr-1% Nb Alloy Samples**

Ele- ments	Zr-1%Nb Sample No. 1		Zr-1%Nb Sample No. 2		Zr-1%Nb Sample No. 3		Zr-1%Nb Sample No. 4		Zr-1%Nb Sample No. 5	
	DC Arc AES (mg kg <sup>-1</sup> )	GD- QMS (mg kg <sup>-1</sup> )	DC Arc AES (mg kg <sup>-1</sup> )	GD- QMS (mg kg <sup>-1</sup> )	DC Arc AES (mg kg <sup>-1</sup> )	GD- QMS (mg kg <sup>-1</sup> )	DC Arc AES (mg kg <sup>-1</sup> )	GD- QMS (mg kg <sup>-1</sup> )	DC Arc AES (mg kg <sup>-1</sup> )	GD- QMS (mg kg <sup>-1</sup> )
P	< 10	3.9±0.1	< 10	7.7±0.2	< 10	4.7±0.1	< 10	8.7±1.4	< 10	4.3±0.2
Ti	< 25	5.0±0.1	< 25	9.9±0.3	< 25	14±0.3	< 25	5.7±0.1	< 25	6.0±0.3
Cr	<100	86±8	<100	111±2	<100	108±2	<100	88±1	<100	93±7
Mn	24	20±0.3	27	24±0.2	27	26±0.6	26	24±0.4	29	26±2
Fe	280	306±10	305	328±8	275	338±7	325	329±12	315	301±7
Ni	< 70	20±0.2	< 70	24±1	< 70	24±1	< 70	13±4	< 70	15±1
Cu	< 30	6.9±0.3	< 30	9.6±0.2	< 30	8.4±0.3	< 30	12±0.2	< 30	29±1
Nb*	1.08	1.135± 0.009%	1.1%	1.158± 0.005%	1.1%	1.116± 0.004%	1.1%	1.102± 0.005%	1.1%	1.137± 0.037%
Mo	< 25	0.90±0.05	< 25	1.0±0.05	< 25	1.2±0.1	< 25	0.91±0.01	< 25	0.88±0.05
Cd	< 0.3	<0.01	< 0.3	<0.76	< 0.3	<0.01	< 0.3	<0.8	< 0.3	<0.01
Sn	< 25	6.6±0.3	< 25	7.2±0.7	< 25	7.6±0.8	< 25	7.9±0.7	< 25	6.9±0.3
Hf	< 50	16±0.4	< 50	14±0.2	< 50	15±0.8	< 50	15±0.3	< 50	15±0.7
Pb	< 25	8.5±0.2	< 25	7.3±0.3	< 25	7.7±0.8	< 25	8.4±1.2	< 25	9.5±0.1
Ca	<25	6.3±0.2	<25	4.7±0.9	<25	4.5±0.1	<25	4.0±0.1	<25	3.2±0.1

DC Arc OES: DC Arc Optical Emission Spectrographic method .

\* : Analyzed by X-Ray Fluorescence Spectrometric method.

## REFERENCES

1. K.N. Choo, Y.H. Kang, S.I. Pyun, and V.F. Urbanic, Journal of Nuclear Materials 209, 226 (1994).
2. M. Schafei and F. Schutle, Z. Anal. Chem. 149, 73 (1956).
3. G. Scharlot and J. Saulnier, Chim. Anal. (Paris), 35, 51 (1953).
4. H.R. Ravindra, G. Radhakrishna, R. Narayan Swamy, and B. Gopalan, Estimation of Niobium in Zr-Nb alloys by X-ray Spectrometry, Proceedings of the National Workshop on "Testing and Characterisation of Materials," TACOM-90, held at Mumbai, India, 15-16th March, 1990, edited by E. Ramadasan, p.198-208 (1990).
5. I. Steffan and G. Vujicic, JAAS 9, 785 (1994).
6. Raparathi Shekhar, J. Arunachalam, G. Radha Krishna, H.R. Ravindra, and B. Gopalan, Determination of Boron at parts per billion levels in Zr-Nb alloys by Glow Discharge Quadrupole Mass Spectrometry. Communicated to 14th International Symposium on Zirconium in the Nuclear Industry, sponsored by the ASTM Committee B10 on Reactive and Refractory Metals and Alloys. Date of symposium: June 13-17, 2004, Stockholm, Sweden.
7. W.W. Harrison, K.R. Hess, R.K. Marcus, and J.L. King, Anal. Chem. 58(2), 341 (1986).
8. Keith Robinson and Edward F.H. Hall, Glow Discharge Mass Spectrometry for Nuclear Materials, Journal of Metals, April, 1987, p.14-16, Testing and Analysis.
9. R. Shekhar and J. Arunachalam, GD-QMS Analysis of Tin in Zirconium Alloy Matrix, p.686, 8th ISMAS Symposium on Mass Spectrometry, held December 7-9, 1999, at Hyderabad, India.
10. R. Shekhar, J. Arunachalam, H.R. Ravindra, and B. Gopalan, J. Anal. At. Spectrom. 18, 381 (2003).
11. GloQuad system Manual for Fisons Instruments (VG Elemental), Issue 2.0 (1993).
12. Laura Aldave de las Heras, Erich Hrnccek, Olivier Bildstein, and Maria Betti, J. Anal. At. Spectrom. 1011-1014, 17 (2002).