

Comprehensive Isotopic and Elemental Analysis of a Multi-Oxide Glass By Multicollector ICP-MS in Isotope Substitution Studies

Mitroshkov AV*, Ryan JV, Thomas ML and Neeway JJ

Environmental Systems Group, Pacific Northwest National Laboratory, USA

Abstract

Multicollector ICP-MS was used to comprehensively analyze different types of isotopically modified glass created to investigate the processes of glass corrosion in the water. Analytical methods were developed for the analyses of synthesized, isotopically modified solid glass and the release of glass constituents upon contact with deionized water. To validate the methods, results from an acid digestion sample of the Analytical Reference Glass showed good agreement when compared to data from multiple prior analyses on the same glass [1]. In this paper, we present the results of the comprehensive analysis of the acid digestion of six types of isotopically modified glass and the release of glass constituents into water corrosion after one year of aqueous corrosion.

Keywords: Isotopically modified glass; Multicollector; Isotopic ratios; Water corrosion

Abbreviations: ARG: Analytical Reference Glass; DSN: Desolvating Nebulizer; HR: High Resolution; ICP: Inductively Coupled Plasma; IS: Internal Standard; LA: Laser Ablation; MC: Multicollector; MS: Mass Spectroscopy; RR: Round Robin.

Introduction

Vitrification is used by many countries to immobilize radioactive wastes due to the technical reliability of the process and long-lasting stability of the material. Nevertheless, glass can corrode in aqueous environments over long time periods. To investigate the mechanisms of glass corrosion in water, experiments were conducted in which coupons of glasses with nominally equivalent chemical compositions but two different isotopic ratios were immersed in 90°C water for extended times. Periodically, small aliquots of solution were sampled and analyzed. After a certain period of time, the coupon solutions were swapped, effectively creating a system in which the chemical composition of the solution was unchanged but in which the isotopic differences enabled tracking of the provenance of ions into and out of the corroding glass systems. To be specific, the diffusion and exchange of ions between solid and liquid phases is measurable if there is a way to distinguish between ions in the solid phase, either from the pristine glass or from alteration layers formed as a result of aqueous corrosion, and those in solution.

Glass is one of the most difficult objects for elemental analysis because of its complexity and the presence of many elements in high concentrations that can produce interferences with the detection of other elements in lower concentrations. In recent years, Laser ablation inductively coupled plasma-mass spectroscopy (LA-ICP-MS) has been considered the method of choice for elemental analyses of solid glass samples [2,3]. The LA-ICP-MS method does not require time- and labor-consuming sample preparation; it can be conducted on relatively low-volume samples with satisfactory levels of accuracy and precision. Although, as we can see from Trejos et al. [2,3] the level of precision for the LA-ICP-MS method (~10%) is noticeably higher than the precision normally achieved in the liquid solution aspiration ICP-MS method (0.1-1.0%). In our isotope substitution study, we had very limited amounts of

each glass type and needed to analyze the full content of the small glass samples with a simple sample preparation. Simple sample preparation techniques were developed and the solid glass and solutions in acidic water were analyzed by three different methods: 1) isotopic ratio analysis for seven elements with modified isotopic ratios: Li, B, Si, Ca, Fe, Zn, and Mo; 2) compositional analysis of all elements of interest in the glass; and 3) group analysis of five selected elements of interest, where the combination of elemental and isotopic methods was used. During the method development, Analytical Reference Glass (ARG) was used as a model sample. The composition of ARG had previously been analyzed by seven different laboratories during six rounds of round-robin tests [1]. A wide range of analytical procedures have been used by the participating laboratories, including atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, direct current plasma-emission spectroscopy, and ICP-MS techniques. The consensus average relative error for round-robin tests 1 through 6 was 5.4%, with values ranging from 9.4 to 1.1%. The results of our ARG analyses are in good agreement with previously reported results of the round-robin research.

Experimental

Instrumentation

The instrument used in our study was a multicollector (MC) ICP-MS Nu Plasma HR (Nu Instruments, Wrexham, UK) fitted with a desolvating nebulizer (DSN) (Aridus II, CETAC, NB, USA). The MC is equipped with 14 Faraday cups and 3 ion counters. The use of the Aridus II was essential because it accounts for much lower molecular ion interferences relative to the use of wet plasma.

*Corresponding author: Alex V Mitroshkov, Research Scientist, Environmental Systems Group, Pacific Northwest National Laboratory, USA, Tel: 509-371-7113; Fax: 509-371-7174; E-mail: alex.mitroshkov@pnnl.gov

Received January 28, 2016; Accepted March 27, 2016; Published April 07, 2016

Citation: Mitroshkov AV, Ryan JV, Thomas ML, Neeway JJ (2016) Comprehensive Isotopic and Elemental Analysis of a Multi-Oxide Glass By Multicollector ICP-MS in Isotope Substitution Studies. J Chromatogr Sep Tech 7: 320. doi:10.4172/2157-7064.1000320

Copyright: © 2016 Mitroshkov AV, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

The sampler cone and the skimmer cone diameters for dry plasma were 0.9 mm and 0.6 mm, respectively. Aridus II was used in all analyses, except the analyses for boron. Typical instrument and acquisition settings have had relatively small variations from one element to another and are listed in Table 1.

Sample preparation

The amounts of glass material available for analysis were very small—a few hundreds of milligrams. Therefore, there was no possibility for replicate sample preparations with fractionations. The glass was ground before digestion. The 20–100 mg samples of glass were digested first with 1 mL of concentrated HF with 0.1 g of mannitol at 50°C for 48 hr. After digestion, the samples were evaporated to 25–75 µL of liquid and further digested with 1 mL of concentrated HNO₃ at 50°C for 9 hr. After the second digestion, 15 mL of deionized water was added to the digests and the solutions were sonicated. This was considered a stock solution, which were diluted 200–10,000 times for various analyses.

Mannitol plays a significant role by retaining the boron in solution, as was mentioned in Ref. [4]. In addition, the results of Ref. [5] indicated that the addition of mannitol and proper control in the evaporation process were effective in preventing the loss of several other elements, including Ti, Ge, Sn and Sb. In Ref. [6], the authors suggest that closed-vessel microwave digestion and H₃PO₄–HNO₃–HF reagents may limit boron volatilization during both digestion and subsequent acid-drying processes. We have also found that the presence of mannitol is essential for preventing the loss of Si. The losses of Si in the absence of mannitol were observed to be in the range of 20–50%.

ARG also was used to evaluate the fusion method as an alternative to the acid digestion method [7]. The analytical results for the fusion method in the experiments done with ARG turned out to be unsatisfactory: the sample dissolutions were significantly contaminated by the impurities in the fusion reagents and some of the elements exhibited poor recoveries.

Standards

For quantitative and isotopic analyses, separate standards with natural ratios for each element at 1000 ppm concentration were used (High Purity Standards, SC, USA). The natural isotopic ratios of the standards were confirmed when the samples with natural isotopic ratios were analyzed after calibration and determination of mass bias factors. The difference in the isotopic ratios of interest between the standards and the samples with presumably natural ratios did not exceed 0.2%, which was sufficient for the work conducted in this experiment.

HR MC-ICP-MS Settings	
Forward power	1050–1300 W
Coolant gas	13–14 L/min
Auxiliary gas	1.2–2.0 L/min
Nebulizer pressure	33–39 psi
Resolution	400
Aridus II Desolvating Nebulizer Settings	
Sweep gas flow	4–6 L/min
Spray chamber	110°C
Desolvator	160°C
Solution introduction rate	150–200 µL/min.

Table 1: Instrument and acquisition settings for the Nu Plasma HR MC-ICP-MS (the optimal setting values change from day to day).

As a control, two glasses with the same nominal composition but natural isotopic ratios were also tested under the same corrosion conditions as the isotopically modified samples. It was confirmed that, despite the growing concentration of all elements in the water solution during the experiments, the isotopic ratios of the elements of interest remained natural for two non-modified glasses. This fact confirms the validity of the method, indicating that the correct isotopic analyses are possible even in such complex mixtures without significant interferences from other elements.

Quantitation

During the method development, the Internal Standard (IS) method for quantitative analyses was attempted through the addition of an IS, containing eight elements: Bi, Ho, In, Lu, Rh, Sc, Tb, and Y (High Purity Standards, SC, USA). In order to cover the low side of the mass scale, Be was also added to this standard. The routine external standard method does not work accurately for ICP-MS analyses because of the instability of the flow rate of the solution and corresponding change of the MS response.

With the IS method, aliquots of IS solution were added to both the analyzed solution and the Calibration Standard so that the concentration of the IS was 20 ppb in both. The closest IS was used for the quantitation of the analytes. For example, Be was used for quantitation of Li, Sc was used for quantitation of Ca, etc. It was found that, although in many applications such an approach can work, in comprehensive glass analyses the implementation of this method is problematic. The reason is that IS contains some elements in relatively low concentrations, which we have to analyze in the glass, and glass samples contain some elements of IS.

Therefore, the use of an External Standard method was required, and for more accurate analyses every sample was bracketed with two Calibration Standard runs, before and after the sample. The bracketing compensates very significantly for the drift of flow rate of the DSN and, accordingly, for the drift of MS response. As a result of this approach, the accuracy of our quantitative elemental analyses was typically in the range of 2–5%.

The isotopic ratios of some of the elements in water changed by 2–3 orders of magnitude over the course of these experiments. Therefore, the requirement for isotopic analysis accuracy was not as strict and the mark was set at 1%. In most cases, our accuracy significantly exceeded the requirements. When the signals from the isotope ions were comparable in value and significantly exceeded the background level, like for Li and Mo, our accuracy was better than 0.1% and precision was in the range of 0.01%.

Zinc and iron were present in the solutions in much lower concentrations than other elements of interest. For Zn and Fe, when the intensities of measured ions were in 1×10^{-3} – 1×10^{-4} V range, the precision and accuracy for isotopic ratios were significantly lower and in the range of 2–3%.

Background

The MS reading for a certain m/z value, when only the blank solution of 2% HNO₃ is aspirated, is considered a background or zero-point baseline. It consists of elements present in the Milli-Q water and nitric acids used in the process of preparing 2% nitric acid as well as some single atom or polyatomic interferences (e.g., ArO for ⁵⁶Fe). Whatever it is, we use on-peak zeros when we measure the signal in the 2% nitric acid blank solution, save it in

the memory, and subtract it from the signal measured during the standard or sample runs. In cases when the background was more or less substantial (in other words, was significantly higher than the off-peak background, as for example, for Li and B), the sample dilution was adjusted such that the signal from the measured element was much higher than the ever-changing background. In this way, the effect of the instability of the background on the results is minimized. For Li, for example, the samples were diluted so that the measured value for ^7Li was in the region of 2-5 V. The background peak for ^7Li was in the region 2.5×10^{-3} V. It is obvious that the observed changes in the background-in the range of 5×10^{-5} to 2×10^{-4} V-could not have significant effect of the final results of the analyses.

Analytical Methods

Li isotopic analyses

For Li analyses, two Faraday cup detectors on opposite sides of the detector array were used: L4 and H6 (Table 2). Other Faraday cups (H5-H1 and L1-L3) and ion counters (IC0-IC2 detectors) were not used in this work.

The tuning parameters of MS for Li isotopic analyses are rather extreme, because Li is on the lower limit of the mass range of MS. The electronic lenses of MS are involved, which are not normally involved in the tuning for other elements. Once tuning values are determined, it is important to keep once found tuning values saved in the tuning file.

The most important part of Li isotopic and quantitative analyses is the minimization of the background, which consists of Li impurities present in acid and water used in preparation of solutions, some scattered ions, and C^{2+} and N^{2+} [8]. The problem is that when minimizing the interferences the sensitivity of the system decreases. Therefore, a compromise between minimization of the background and optimization of sensitivity must be found.

The DSN, Aridus II, is also used for Li analyses. Normally, for other elements, we use a QuickWash attachment with a 5% HNO_3 /0.02% HF washing solution to wash the previous analytical run materials from the system, This washing solution cannot be used for Li analyses, because when we use it the background rises significantly and does not diminish for a few minutes. Instead of an acid solution, pure Milli-Q water was used for quick removal of Li from the spray chamber of the DSN.

One of the main sources of instability in Li and other element isotopic ratio measurements is the instability of the DSN flow rate. This instability causes changes in the mass bias correction factor. Although our method of bracketing the sample with two standards runs partially compensates for this instability, stabilizing the solvent flow rate can significantly increase the accuracy of analyses. Currently, the DSN uses the self-aspiration mode for delivering solvent into the MS.

Boron isotopic analysis

Boron cannot be analyzed with the DSN because of losses in the process of desolvation, so the direct self-aspiration method was used. The same detector layout was used for B as for Li (Table 3).

The main problem with boron analyses is the very slow washout from the spray chamber of the MS. According to Ref. [6] and Ref. [9], the use of 2% ammonia as the rinse solution may effectively eliminate memory effects and accelerate the washout of

boron during ICP-MS analysis. We have found that maintaining the spray chamber at room temperature, when Peltier is turned off, can reduce washout time by approximately 50%.

Silicon isotopic analyses

Isotopic analyses of silicon are complicated by the presence of polyatomic interferences such as $^{14}\text{N}_2^+$ and $^{12}\text{C}^{16}\text{O}^+$ for ^{28}Si , $^{14}\text{N}_2^+\text{H}^+$ and $^{12}\text{C}^{16}\text{O}^+\text{H}^+$ for ^{29}Si , and very strong $^{14}\text{N}^{16}\text{O}^+$ and some minor interferences like $^{60}\text{Ni}^{2+}$ for ^{30}Si [10,11]. It is possible, by using higher resolution and a 0.05 mm source slit, to partially resolve $^{30}\text{Si}^+$ from $^{14}\text{N}^{16}\text{O}^+$. The interferences for $^{28}\text{Si}^+$, $^{29}\text{Si}^+$, and $^{30}\text{Si}^+$ are minimized by adjusting the parameters of the DSN, mostly sweep gas flow rate. Interferences measured during the blank run are subtracted from the measurements obtained during the sample or standard run. As one can see, the proper conditions for the DSN allow for a nearly complete elimination of interferences for ^{29}Si and ^{30}Si . It is worthwhile to mention that we do not use nitrogen as makeup gas for DSN, which is recommended to be added at a small rate to the flow Ar to reduce the noise and increase the response of MS. The absence of nitrogen in this particular case is partially responsible for minimizing the interferences. Previously, the reduction of 90% of polyatomic interferences for Si by the Aridus II DSN compared to wet plasma was reported [10]. In our experiments, the reduction of interferences is estimated to be two orders of magnitude as compared to the wet plasma. As shown in Figure 1, the total coincidence of all peaks was not required, which is different than our typical procedure for most elements. Calcium is a good example of good coincidence of all peaks (Figure 2). In the case of Si, the peaks were adjusted in such a way that only part of the flat top of ^{30}Si coincided with ^{28}Si and ^{29}Si , leaving the part of peaks affected by the interference aside.

The bottom part of Figure 1 shows the analysis of 10 ppb with interferences. This is not the optimal tuning of MS for Si. These interferences can be reduced significantly by adjusting the parameters of MS and DSN. This condition was chosen for demonstration that even in the presence of relatively high interferences one can do isotopic analyses using the left part of the peaks free of interferences.

Ca isotopic analysis

Calcium is one of the elements most difficult to analyze using ICP-MS methods because of significant interferences for practically all Ca isotopes. $^{40}\text{Ca}^+$ has a very strong interference from $^{40}\text{Ar}^+$, $^{42}\text{Ca}^+$ is affected by $^{40}\text{Ar}^1\text{H}_2^+$ and $^{14}\text{N}_3^+$, ^{43}Ca is influenced by $^{27}\text{Al}^{16}\text{O}$ and $^{14}\text{N}_3^1\text{H}^+$, and ^{44}Ca is influenced by $^{12}\text{C}^{16}\text{O}_2$, $^{14}\text{N}_2^{16}\text{O}$ and $^{28}\text{Si}^{16}\text{O}$ [11,12]. Because of the abundance of Ar in the plasma, the influence of ^{40}Ar on ^{40}Ca is so strong that in normal conditions it is practically impossible to analyze ^{40}Ca . It is possible, though, when the RF Power is low and we work with cold plasma. In this case, the ^{40}Ca signal can be measured at the top of the ^{40}Ar peak. This method has been described in the literature [13] and the results are satisfactory for some applications. The shortcoming of this

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
^6Li													^6Li

Table 2: Detector layout for Li analysis.

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
^{11}B													^{10}B

Table 3: Detector layout for B analysis.

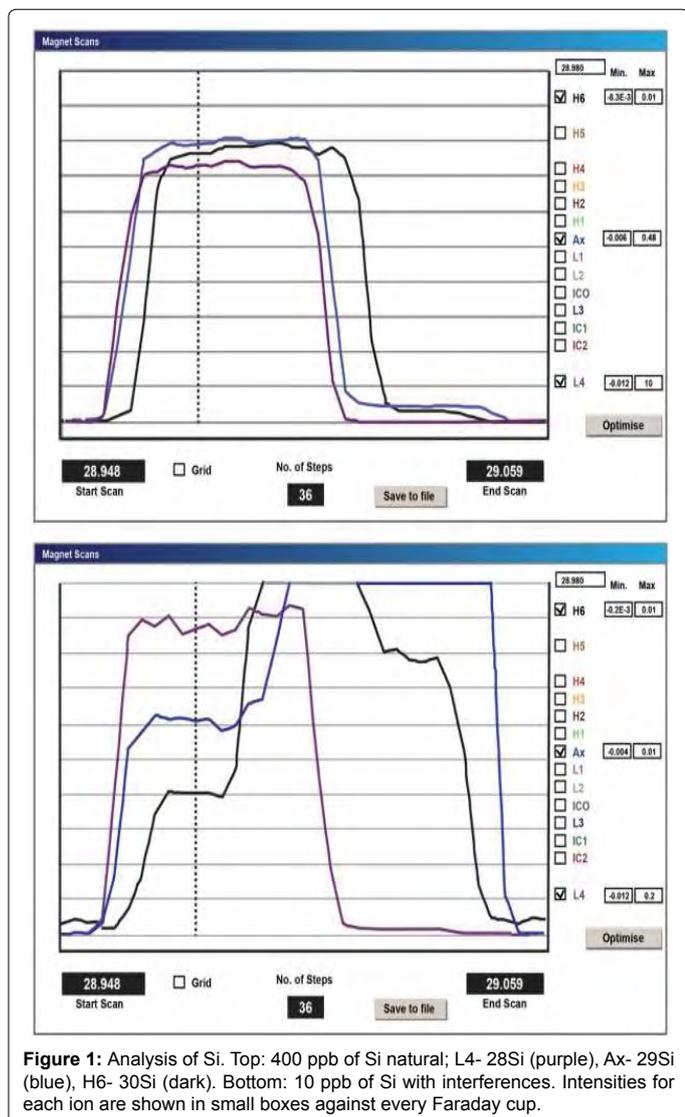


Figure 1: Analysis of Si. Top: 400 ppb of Si natural; L4- 28Si (purple), Ax- 29Si (blue), H6- 30Si (dark). Bottom: 10 ppb of Si with interferences. Intensities for each ion are shown in small boxes against every Faraday cup.

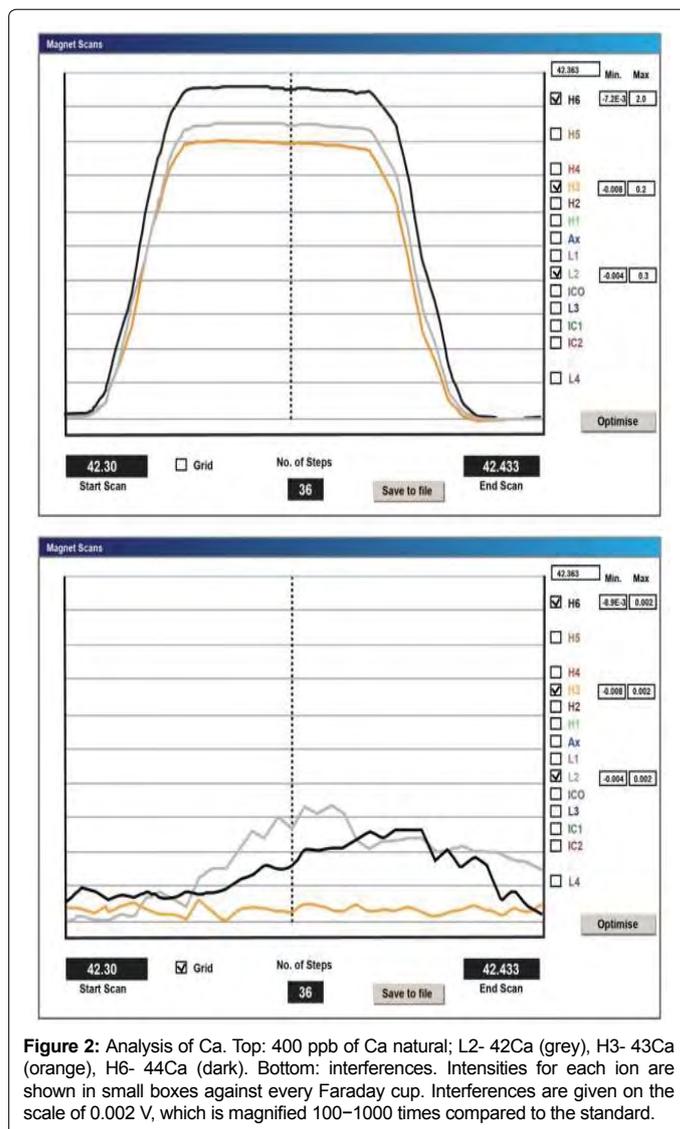


Figure 2: Analysis of Ca. Top: 400 ppb of Ca natural; L2- 42Ca (grey), H3- 43Ca (orange), H6- 44Ca (dark). Bottom: interferences. Intensities for each ion are shown in small boxes against every Faraday cup. Interferences are given on the scale of 0.002 V, which is magnified 100-1000 times compared to the standard.

approach is its relatively low sensitivity and we could not afford it in our experiments. We have used hot plasma and concentrated our efforts on measuring $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$ ratios. In these experiments, the analyzed mixtures contained natural Ca and isotopically modified Ca, the ratios of which were known. In these circumstances, knowledge of $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$ allows for simple calculations of $^{42}\text{Ca}/^{40}\text{Ca}$, $^{43}\text{Ca}/^{40}\text{Ca}$, and $^{44}\text{Ca}/^{40}\text{Ca}$ ratios, which were essential for the experiments. Figure 3 demonstrates the analysis of the 400 ppb Ca standard and shows interferences on different scales, because the interferences are 100-1000 times lower in intensity than in the Ca isotope readings. The interferences are minimized by optimizing the parameters of the plasma and AridusII DSN.

Iron isotopic analyses

The problems associated with isotopic analyses of iron are related to strong interferences from $\text{Ar}^{40}\text{O}^{16+}$ for $^{56}\text{Fe}^+$ and $\text{Ar}^{40}\text{N}^{14+}$ for $^{54}\text{Fe}^+$ [14,15]. The molecular mass of $\text{Ar}^{40}\text{O}^{16}$ is so close to ^{56}Fe that the maximum resolving power available is required. For these purposes, the source slit is set up in middle position (0.05 mm slit) and alpha slits are set up in the positions: $\alpha_1=65$ and $\alpha_2=75$. The ratio of interest was $^{57}\text{Fe}/^{56}\text{Fe}$, but the ratio $^{54}\text{Fe}/^{56}\text{Fe}$ was also

measured. This ratio is strongly affected by the presence of ^{54}Cr in the solution [15] so the data obtained for this ratio were not used in the final analysis.

Zn and Mo isotopic analysis

Compared to Ca, Si, and Fe isotopic analyses, the Zn and Mo isotopic analyses are much more straightforward. The detector layouts for Zn and Mo are shown in Tables 4a and 4b.

The significant ratios for the experiments were $^{68}\text{Zn}/^{64}\text{Zn}$ for Zn and $^{95}\text{Mo}/^{98}\text{Mo}$ for Mo, although other ratios, such as

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
		^{68}Zn			^{67}Zn			^{66}Zn					^{64}Zn
								^{70}Zn					

Table 4a: Detector layout for Zn analyses. Mass separation: 0.333. Two cycles are implemented with ^{70}Zn measured in the second cycle.

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
^{100}Mo		^{98}Mo		^{97}Mo		^{96}Mo		^{95}Mo		^{94}Mo			^{92}Mo

Table 4b: Detector layout for Mo analyses. Mass separation: 0.5. All isotopes are analyzed in one cycle.

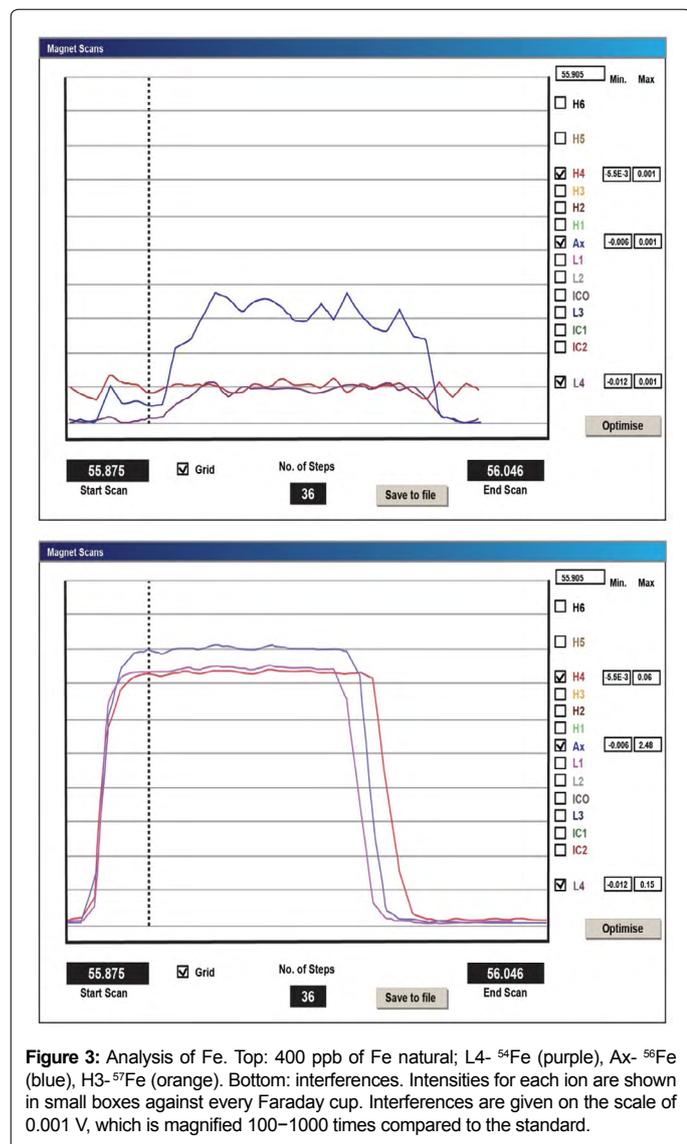


Figure 3: Analysis of Fe. Top: 400 ppb of Fe natural; L4- ⁵⁴Fe (purple), Ax- ⁵⁶Fe (blue), H3- ⁵⁷Fe (orange). Bottom: interferences. Intensities for each ion are shown in small boxes against every Faraday cup. Interferences are given on the scale of 0.001 V, which is magnified 100–1000 times compared to the standard.

⁶⁶Zn/⁶⁴Zn, ⁶⁷Zn/⁶⁴Zn, and ⁷⁰Zn/⁶⁴Zn for Zn and ⁹²Mo/⁹⁸Mo, ⁹⁴Mo/⁹⁸Mo, ⁹⁶Mo/⁹⁸Mo, ⁹⁷Mo/⁹⁸Mo and ¹⁰⁰Mo/⁹⁸Mo for Mo have been measured.

Group analysis

During the experiment, a group of five elements (La, Ba, Ce, Pr, Nd) had to be analyzed quantitatively with accuracy better than the accuracy of elemental analyses, but they did not require isotopic analyses. For this purpose, we developed a method we term “group analysis.” Normally, MC-ICP-MS has two different modes of analyses: isotopic and elemental. As mentioned before, when using the elemental method the peaks are quickly scanned from the bottom to the top, but there is no centering on the middle of the peak. For the above-mentioned elements, we used the isotopic mode with centering on one of the peaks of one isotope of every element with five different cycles and the detector layout shown in Table 5. This allowed for quick elemental-mode-like jumps from one element to another with the advantage of using the centering made possible by using the isotopic method.

It is possible to run these kinds of analyses in two or three

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
						¹⁴⁶ Nd							
						¹⁴¹ Pr							
						¹⁴⁰ Ce							
						¹³⁹ La							
						¹³⁷ Ba							

Table 5: The detector layout for group analysis.

cycles [16] by involving detectors other than Ax Faraday cups. However, it was decided to use this slower method to allow for precise centering on every chosen isotope.

Elemental analysis

In the elemental analysis mode, only the central Faraday cup (Ax) is used and the system quickly jumps from one isotope peak of a certain element to the isotope peak of another element. The scan rate is 1000 ms/amu and the dwell time is 2 s. Unlike in isotopic analyses, where the MS has the ability to find precisely the center of the peak, the accurate centering of every peak is unavailable in the elemental analysis. Therefore, it is important to calibrate the mass scale very accurately.

To do so, two different standards are used: 1) the IS, containing eight elements: Bi, Ho, In, Lu, Rh, Sc, Tb, Y (High Purity Standards, SC, USA) and 2) the ICP-MS standard, containing 68 elements (High Purity Standards, SC, USA). Beryllium is also added to the IS to cover the low side of mass scale. The IS provides a 9-point mass range calibration, followed by the ICP-MS standard, which provides a 66-point calibration. The concentration of the ICP-MS standard is 10 ppb, and it is used also as a quantification standard.

After the mass scale is calibrated, and the AridusII and MS are thoroughly washed, the blank sample (2% HNO₃) is run. After the blank sample is run, the background values, obtained during the zero run, are subtracted from the standard and from the sample values. The blank cannot be run before the standard, because the precise mass range calibration is not available before the standard is run.

Results and Discussion

The actual results of the isotope substitution studies will be reported separately in a paper dealing specifically with what those findings reveal about the mechanisms behind long-term glass corrosion. As an example, however, the results for boron are presented here. The measured value of ¹⁰B/¹¹B as a function of time is presented in Figure 4 for the two non-exchanged solutions (SN1-7 and SE1-7) and their exchanged counterparts (SN8-14 and SE8-14). The initial ¹⁰B/¹¹B ratios for both the enriched samples (SE1-7 and SE8-14) and the non-enriched samples (SN1-7 and SN8-14) are also presented as solid lines to lead to the eye. As expected, the ¹⁰B/¹¹B ratio for the non-exchanged samples remains relatively constant throughout the duration of experiment. On the other hand, the ¹⁰B/¹¹B ratio for the exchanged samples changes dramatically, by roughly two orders of magnitude, following the exchange of the two solutions containing the different boron isotopic signatures. After the solution exchange, the glass coupons continue to corrode and the ¹⁰B/¹¹B ratio slowly evolves as a greater amount of either enriched or non-enriched boron is leached into

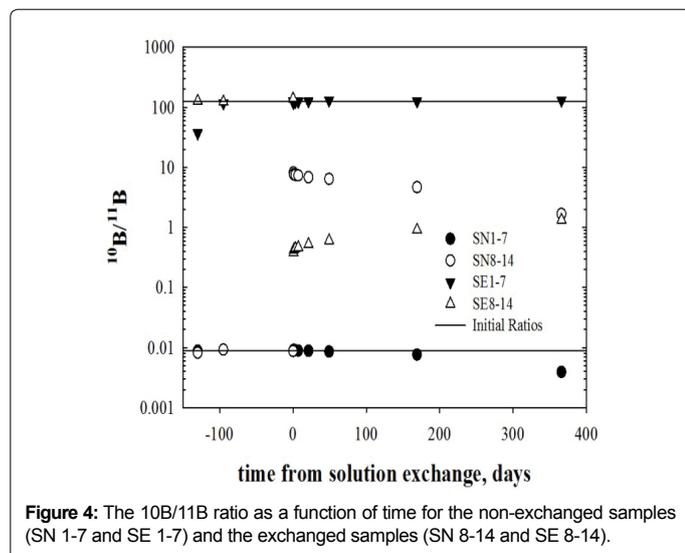


Figure 4: The $^{10}\text{B}/^{11}\text{B}$ ratio as a function of time for the non-exchanged samples (SN 1-7 and SE 1-7) and the exchanged samples (SN 8-14 and SE 8-14).

the contacting solution.

Verification of analytical meth

Table 6 shows a comparison of the results of our analysis of ARG glass and the results of the round-robin test. The average difference for the concentrations of the element oxides between the round-robin (RR) results and ours is 0.80%. The results for each element were calculated as a percentage of the mass of each element oxide relative to the total sample mass. In theory, if the results are correct, the sum of all results for all of the elements should be close to 100%, depending on the accuracy of the analytical method. As can be seen from in Table 7, the total sum for the RR tests was 99.48% while the results from this study total 100.92%. It appears that sensitivity of our method was somewhat higher than the RR test and we were able to quantify more elements.

Conclusion

Methods for comprehensive analyses of glass-sourced solutions by MC-ICP-MS have been developed and the validity of the methods was confirmed on different glass samples, including digestions, fusions, and solutions resulting from aqueous glass corrosion. Although some errors in isotopic analyses of are still possible with such complex samples due to mutual interferences of different elements, it was proven for seven selected elements that accurate isotopic analyses for the ratios of interest are

	Concentration Mass% Oxide			Difference, %
	Round Robin	This Research		
		Isotopic Method	Elemental Method	
Ag ₂ O			nd	
Al ₂ O ₃	4.66	4.20		-9.87%
As ₂ O ₃			0.0006	
B ₂ O ₃	8.54	8.34		-2.34%
BaO	0.09		0.078	
BeO			0.005	
Bi ₂ O ₃			0.0001	
CaO	1.42	1.524		7.32%
CdO				
CeO ₂			0.0013	
CoO			0.0068	
Cr ₂ O ₃	0.1		0.1038	3.84%
Cs ₂ O			0.0008	
CuO	0.01		0.0059	
Er ₂ O ₃				
Eu ₂ O ₃				
Fe ₂ O ₃	14.02	15.05		7.35%
Ga ₂ O ₃			0.011	
Gd ₂ O ₃				
HfO ₂			0.0026	
K ₂ O	2.68		2.48	-7.46%
La ₂ O ₃			0.0006	
Li ₂ O	3.18	3.58		12.58%
MgO	0.87		0.74	
MnO ₂	2.32		2.24	-3.50%
MoO ₃			0.0007	
Na ₂ O	11.2	12.14		8.39%
Nb ₂ O ₅			0.0079	
Nd ₂ O ₃			0.0004	
NiO	1.04		1.0578	1.72%
P ₂ O ₅	0.27		0.4359	
PbO			0.0005	

PdO				
Pr2O3			0.00015	
Rb2O			0.0068	
Re2O7				
Rh2O3				
RuO2				
SO3				
Sb2O3			0.00027	
Sc2O3			0.00070	
SeO2				
SiO2	47.75	47.50		-0.52%
Sm2O3				
SnO2			0.0090	
SrO	0.0037		0.0030	
Ta2O5			0.0017	
TeO2			0.0067	
TiO2	1.17		1.2077	3.22%
Tl2O3			0.00007	
U3O8			0.00067	
V2O5			0.0242	
WO3			0.0006	
Y2O3			0.0007	
ZnO	0.02		0.0246	
ZrO2	0.14		0.1256	-10.31%
Sum	99.4837	92.33	8.59	0.80%
			100.92	Sum for both methods

Table 6: Comparison of the results of our analysis of ARG and the results of round-robin test.

Concentration reported as Wt% Oxide	AFC1 natural	AFC1 full	AFC1 enriched	SON68 natural	SON68 full	SON68 enriched
	Ag2O	0.037	0.053	0.074	0.035	0.050
Al2O3	8.16	10.33	11.32	6.36	6.46	5.92
As2O3	0.0014	0.0014	0.0015	0.0005	0.0039	0.0214
B2O3	9.89	11.67	8.43	14.69	17.30	12.46
BaO	0.662	0.716	1.012	0.506	0.551	0.678
BeO						
Bi2O3	0.00002	0.00019				0.00015
CaO	3.200	5.463	6.645	4.581	2.907	5.774
CdO	0.0389	0.0447	0.0504	0.0353	0.0349	0.0339
CeO2	0.124	0.124	1.301	0.049	0.348	1.000
CoO	0.00054	0.00096	0.00060	0.00069	0.00073	0.00111
Cr2O3	0.0012	0.0007	0.0015	0.581	0.611	0.596
Cs2O	1.224	1.248	1.266	1.306	1.241	1.298
CuO				0.0026	0.0041	0.0050
Dy2O3	0.0007	0.0012	0.0039	0.0014	0.0037	0.0002
Er2O3						
Eu2O3	0.016	0.028	0.129			
Fe2O3	0.052	0.059	0.027	3.40	3.36	3.31
Ga2O3	0.0825	0.0759	0.0949	0.0485	0.0914	0.0961
Gd2O3	0.0285	0.0319	0.1370			
HfO2	0.0153	0.0159	0.0191	0.0436	0.0473	0.0463
K2O						
La2O3	0.0460	0.0410	0.4940	0.0190	0.2160	0.7110
Li2O	3.993	4.424	4.382	1.913	2.039	4.006
MgO	0.0208	0.0401	0.0168	0.0211	0.0381	0.0088
MnO2	0.0007	0.0009	0.0007	0.4389	0.4692	0.4206
MoO3	1.891	1.770	1.794	1.964	2.109	2.254
Na2O	7.911	7.862	8.918	12.003	11.276	12.074

Nb2O5						
Nd2O3	0.2077	0.3036	1.9011	0.1888	0.9879	1.8935
NiO				0.4893	0.4731	0.5059
P2O5	0.0703	0.1225	0.1653	0.3425	0.4508	0.3835
PbO	0.0002	0.0003	0.0004	0.0002	0.0005	0.0005
PdO						
Pr2O3	0.0545	0.0677	0.5344	0.0305	0.1863	0.4280
Rb2O	0.1840	0.1726	0.1816	0.0007	0.0010	0.0005
Re2O7						
RhO2	0.0192	0.0211	0.0194			
RuO2	0.0461	0.0444	0.0419			
SO3						
Sb2O3						
Sc2O3	0.0015	0.0014	0.0018	0.0034	0.0044	0.0045
SeO2	0.0075	0.0073	0.0302			
SiO2	57.00	55.46	51.56	43.20	41.77	40.30
Sm2O3	0.0408	0.0698	0.3309			
SnO2	0.0306	0.0289	0.0318	0.0245	0.0244	
SrO	0.2520	0.3230	0.4037	0.2249	0.3266	0.4171
Ta2O5						
TeO2	0.0847	0.0762	0.0867	0.0755	0.0759	0.0571
TiO2	0.0119	0.0119	0.0032	0.0094	0.0129	0.0047
Tb2O3	0.0005	0.0009	0.0034			0.0002
U3O8		0.0003				
V2O5	0.0015	0.0014	0.0011	0.0009	0.0012	0.0007
WO3	0.0051	0.0036	0.0488	0.0059	0.0090	0.0448
Y2O3	0.0217	0.0272	0.2060	0.0160	0.1081	0.1895
ZnO	0.0014	0.0013	0.0065	2.832	3.061	2.628
ZrO2	0.73	0.74	0.99	1.99	2.50	2.58
Sum, %	96.17	101.48	102.66	97.43	99.17	100.21

Table 7: The elemental analyses results obtained for six different isotopically modified glass samples.

achievable. All major and relatively minor components of the glass were identified and their concentrations were measured, and the total summarized content of six different isotopically modified glasses was close to 100%. The capabilities of MC-ICP-MS for comprehensive analyses of glass dissolution and glass corrosion samples with simple sample preparation have been demonstrated.

Acknowledgements

These studies were supported by the U.S. Department of Energy (DOE) through the Office of Nuclear Energy. We would like to thank Carmen Rodriguez of PNNL for help in glass preparation

References

- Smith GL, Marschman SC (1993) Nuclear Waste Analytical Round Robins 1-6 Summary Report, MRS Proceedings, pp: 333-461.
- Trejos T, Koons R, Becker S (2013) Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ -XRF, ICP-MS, and LA-ICP-MS. *Anal Bioanal Chem* 405: 5393-5409.
- Trejos T, Montero S, Almirall JR (2003) Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-MS. *Anal Bioanal Chem* 376: 1255-1264.
- Ishikawa T, Nakamura E (1990) Suppression of boron volatilization from a hydrofluoric acid solution using a boron-mannitol complex. *Anal Chem* 62: 2612-2616.
- Takeda K, Watanabe S, Naka H, Okuzaki J, Fujimoto T (1998) Determination of ultra-trace impurities in semiconductor-grade water and chemicals by inductively coupled plasma mass spectrometry following a concentration step by boiling with mannitol, *Analytica Chimica Acta* 377: 47-52.
- Dai SF, Song WJ, Zhao L, Li X, Hower CR, et al. (2014) Determination of Boron in Coal Using Closed-Vessel Microwave Digestion and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). *Energy & Fuels* 28: 4517-4522.
- ASTM Book of Standards (1967) Part 13, C169-13, American Society for Testing of Materials, Philadelphia.
- Choi MS, Shin HS, Kil YW (2010) Precise determination of lithium isotopes in seawater using MC-ICP-MS. *Microchemical Journal* 95: 274-278.
- Al-Ammar A, Gupta RK, Barnes RM (1999) Elimination of boron memory effect in inductively coupled plasma-mass spectrometry by addition of ammonia. *Spectrochim Acta Part B* 54: 1077-1084.
- van den Boorn SHJM, Vroon PZ, van Belle CC, van der Wagt B, Schwieters J, et al. (2006) Determination of silicone isotope ratios in silicate materials by high-resolution MC-ICP-MS using a sodium hydroxide digestion method. *J Anal At Spectrom* 21: 734-742.
- May TW, Wiedmeyer RH (1998) A Table of Polyatomic Interferences, in ICP-MS. *Atomic Spectroscopy* 19: 150-155.
- Wieser ME, Buhl D, Bouman C, Schwieters J (2004) High precision calcium isotope ratio measurements using a magnetic sector multiple collector inductively coupled plasma mass spectrometer. *J Anal At Spectrom* 19: 844-851.
- Wollenweber D, Strassburg S, Wunsch G (1999) Determination of Li, Na, Mg, K, Ca and Fe with ICP-MS using cold plasma condition. *Fresenius J Anal Chem* 364: 433-437.
- Weyer S, Schwieters J (2003) High precision Fe isotope measurements with high mass resolution MC-ICPMS. *International Journal of Mass Spectrometry* 226: 355-369.
- John SG, Adkins JF (2010) Analysis of dissolved iron isotopes in seawater. *Marine Chemistry* 119: 65-76.
- Baker J, Waight T, Ulebeck D (2002) Rapid and highly reproducible analysis of rare earth elements by multiple collector inductively coupled plasma mass spectrometry. *Geochimica et Cosmochimica Acta* 66: 3635-3646.