

Direct Analysis of Zirconium-93 in Nuclear Site Decommissioning Samples by ICP-QQQ

Using MS/MS mass-shift mode to resolve ^{93}Zr
from ^{93}Nb without chemical separation



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Introduction

Zirconium-93 is a long-lived radionuclide that is produced by nuclear fission of uranium and plutonium. It is also formed by neutron activation of stable zirconium in nuclear fuel cladding in pressurized water reactors. Therefore, ^{93}Zr is an important element to monitor during the decommissioning of nuclear sites. The long half-life of ^{93}Zr (1.61×10^6 years (1)) means it is a significant contributor to the total waste inventory over long timescales. Clearly, there is a need to accurately quantify ^{93}Zr in various complex decommissioning wastes as part of the initial site characterization process. Also, monitoring of waste repositories and the environment around nuclear sites following decommissioning is needed.

Zirconium-93 decays to stable ^{93}Nb by beta emission, but with a low decay energy that makes measurement by decay counting methods challenging. With its long-half-life, ^{93}Zr is well suited to measurement by ICP-MS (1 Bq/g is equivalent to 1.1×10^4 pg/g), which offers a high throughput alternative to decay counting

techniques. However, accurate measurement by ICP-MS is affected by the isobaric interference from ^{93}Nb (100% abundance), as well as potential radioactive ^{93}Mo , and polyatomic ion interference from $^{92}\text{Mo}^1\text{H}^+$ and $^{92}\text{Zr}^1\text{H}^+$. The removal of these interferences traditionally requires time-consuming, multistage extraction and/or chromatographic separation before measurement, using a significant number of reagents and materials (2, 3). Also, since ^{93}Nb is monoisotopic, it is challenging for the analyst to be confident that complete interference removal has been achieved before measurement.

In this study, triple quadrupole ICP-MS (ICP-QQQ) was used for the rapid and direct low-level measurement of ^{93}Zr in decommissioning samples below International Atomic Energy Agency (IAEA) regulatory limits (4). Reactive gases were used in the collision/reaction cell (CRC) of the ICP-QQQ to separate the isobaric overlap from ^{93}Nb on ^{93}Zr , eliminating the need for chromatographic separation. Isobaric ion interferences can be separated using ICP-QQQ when the cell gas reacts quickly with one of the elements to form a product ion, while the other element does not react (or reacts slowly). This “chemical” resolution method significantly reduces the procedural time and secondary waste associated with decay counting and alternative mass spectrometric procedures. With its fast analysis times, ICP-QQQ offers a cost-effective method for the analysis of nuclear decommissioning samples.

ICP-QQQ with MS/MS mode

ICP-QQQ is a well-established technique that is especially suitable for improved control of spectral, doubly charged ion, and isobaric interferences using reactive cell gas methods (5). Compared to conventional single quadrupole ICP-MS, ICP-QQQ has an additional mass filter before the CRC. This extra mass filter prevents all ions apart from the target mass from entering the CRC, so the reaction chemistry in the cell can be controlled. This double mass filter approach is only possible with a tandem MS (or MS/MS) configuration, which provides unprecedented control of the ion-molecule reaction chemistry used in CRC-ICP-MS methods.

Experimental

Standards and sample preparation

Calibration standards were prepared by diluting an NPL-standardized ^{93}Zr stock solution in 0.3 M HNO_3 over a concentration range of 53.8 to 1.1×10^5 pg/g (equivalent to 5.0×10^{-3} to 10.0 Bq/g). To provide matrix matched calibration standards, the same standards were also prepared in dissolved steel and aqueous decommissioning waste solutions. To determine the separation factor of ^{93}Zr and

^{93}Nb , increasing concentrations of ^{93}Nb were spiked into 0.3 M HNO_3 and steel solutions which contained the same concentration of ^{93}Zr .

Instrumentation

An Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was used for all work on active samples containing ^{93}Zr . The sample introduction system consisted of a quartz torch with 2.5 mm i.d. injector, a quartz spray chamber, glass concentric nebulizer, and nickel-tipped interface cones.

To separate ^{93}Zr and ^{93}Nb using ICP-QQQ, both O_2 and NH_3 cell gases were investigated. Helium was added as a buffer gas and H_2 was also added to the cell to see if it enhanced product ion formation.

Instrument operating conditions were established using stable isotope standards. A 10 ng/g mixed stable element standard containing ^{90}Zr and ^{93}Nb was analyzed and product ion scans were obtained for each precursor ion mass. Q1 was first set to m/z 90 (for Zr) and then m/z 93 (for Nb), while Q2 was scanned to identify the most abundant product ions formed from reactions of ^{90}Zr and ^{93}Nb with each cell gas. The optimal cell gas for interference removal was found to be NH_3 with He and H_2 . The instrument conditions were then optimized for sensitivity, focusing on cell gas flow rate, octopole bias, and energy discrimination. The operating conditions (Table 1) were validated using active samples.

Table 1. 8800 ICP-QQQ operating conditions.

Parameter	Setting	
	Stainless Steel	Aqueous Waste Samples
Scan Mode	MS/MS (Q1=93, Q2=195)	
Plasma Conditions	HMI	General Purpose
Integration Time (s)	0.1	
Carrier Gas (L/min)	0.60	0.95
Dilution Gas (L/min)	0.35	0.00
Helium Flow Rate (mL/min)	2.0	
Hydrogen Flow Rate (mL/min)	3.0	
Ammonia Flow Rate (% of maximum flow rate)	15 (1.5 mL/min)	
Octopole Bias (V)	-2.8	
Energy Discrimination (V)	-9.0	
Octopole RF (V)	180	

Results and discussion

Calibration

The zirconium-93 calibration standards were analyzed using the 8800 ICP-QQQ using the General Purpose parameters in Table 1. The detection limit was calculated as 6.5 pg/g (0.6 mBq/g).

Instrument sensitivity and interference removal

During method optimization using a 10 ng/g mixed stable element standard, different product ions were monitored to assess interference removal efficiency. The product ion scans identified multiple product ions using both O₂ and NH₃ as reaction gases. A Zr/Nb separation factor of > 5 × 10³ was achieved using Zr-NH₃ product ions: Zr(NH₃)₂NH₂⁺ (mass-shift of 50) and Zr(NH₃)₅⁺ (mass-shift of 85), and Zr-O₂ product ions: ZrO₃⁺ (mass-shift of 48), and Zr(OH)₃⁺ (mass-shift of 51). However, the optimal Zr/Nb separation was achieved with a mass shift of 102, measuring the product ion Zr(NH₃)₆⁺. This finding agrees with a previous study that first demonstrated measurement of ⁹³Zr by ICP-QQQ (6).

Figure 1 shows that, if ⁹³Zr was measured on mass, Nb concentrations of 10 pg/g and above would contribute to the signal at *m/z* 93, leading to interference on ⁹³Zr (blue bars). By comparison, when mass 195 (⁹³Zr(NH₃)₆⁺) was monitored in MS/MS mass-shift mode, the background counts from Nb remained below 10 cps at concentrations up to 5 × 10⁴ pg/g Nb (white bars). The results show the successful removal of the ⁹³Nb isobaric interference on ⁹³Zr up to 5 × 10⁴ pg/g Nb, using the MS/MS mass-shift method.

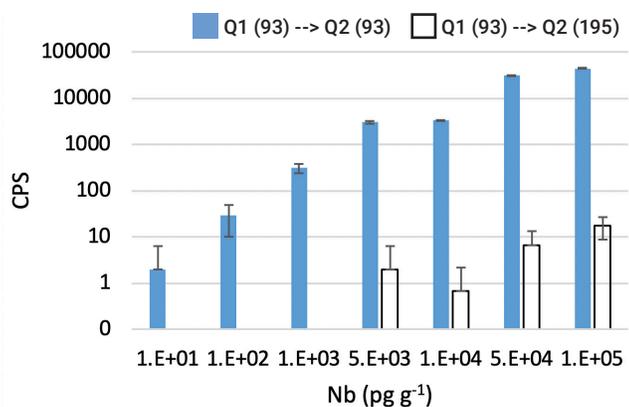


Figure 1. Background at *m/z* = 93 and 195 with increasing Nb concentration (Q1 set to *m/z* = 93 in both cases).

Measurement of decommissioning samples

Spiked stainless steel

Inactive stainless steel dissolved in concentrated nitric acid was provided as part of a European Metrology Research Program (EMRP) project. Samples were evaporated to near-dryness and made up in an equal volume of 0.3 M HNO₃. A further 1 in 10 dilution was made, giving approximately 20x total dilution (5% total dissolved solids, TDS). A semiquantitative scan of the sample was performed using the 8800 ICP-QQQ to determine the sample composition. The most abundant elements detected in the diluted solution were Fe (out of range), Cr (2 µg/g), Mg (20 µg/g), Ni (2.5 µg/g), Cu (10 µg/g), Mo and Sn (both 1 µg/g). The Nb concentration in the diluted steel samples ranged from 0.5 to 1.4 × 10⁴ pg/g. The steel samples were run using the optimized operating conditions for the measurement of ⁹³Zr (Table 1). No background was measured at *m/z*=195, which also demonstrates removal of any potential polyatomic ion interferences on ⁹³Zr from ⁹²Mo¹H⁺ and ⁹²Zr¹H⁺.

The spiked steel samples (spiked with ⁹³Zr and ⁹³Nb) were initially run on the 8800 without dilution, using ¹⁰¹Ru as an internal standard. However, even using the High Matrix Introduction (HMI) system with aerosol dilution on the 8800, the 5% steel matrix caused significant matrix deposition on the cones after running four to five samples. The nominal TDS limit for HMI is 3%. The matrix tolerance could potentially be improved with the UHMI available on the 8900 ICP-QQQ, which allows matrix levels up to 25% TDS to be analyzed.

Following a 1 in 10 dilution, the instrument sensitivity for the spiked steel was similar to the ⁹³Zr calibration standards. Figure 2 shows the calibration curve of ⁹³Zr in the dissolved stainless steel matrix, measured as Zr(NH₃)₆⁺. The method detection limit (MDL) was 8.6 pg/g (0.8 mBq/g), which is significantly lower than the exemption limit of 10 Bq/g defined by IAEA/RS-G 1.7 (4).

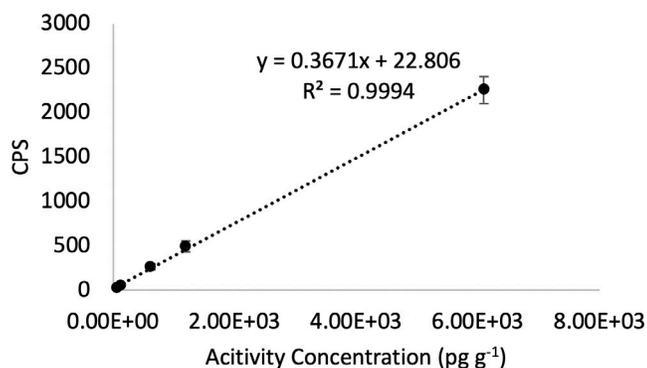


Figure 2. Dissolved stainless steel spiked with ^{93}Zr , measured as $\text{Zr}(\text{NH}_3)_6^+$ using ICP-QQQ.

Aqueous waste samples

Aqueous wastes containing a range of decommissioning radionuclides were measured without any sample treatment using the 8800 ICP-QQQ. General Purpose plasma conditions were used rather than HMI mode. The maximum Nb concentration was 1×10^4 pg/g, with a background of <20 cps at $m/z=195$, compared to $\sim 40,000$ cps when measured on mass at $m/z=93$ in He mode. The average ICP-MS/MS reaction cell interference removal factor (equivalent to the decontamination factor quoted for radiochemical separation experiments) was 3.5×10^3 , with an MDL of 1.1 pg/g (0.1 mBq/g). This DL is significantly below the IAEA out-of-scope limit, and the World Health Organisation (WHO) drinking water regulation limit of 0.1 Bq/mL (4, 7). The results show that this ICP-QQQ method is suitable for the direct measurement of ^{93}Zr in drinking water samples.

Comparing the 8900 and 8800 ICP-QQQ

At NPL we also have access to a newer Agilent 8900 ICP-QQQ, but this instrument is in a laboratory that does not handle radioactive samples. To evaluate the relative performance of the 8800 and 8900, we used a stable, natural Zr standard to run a comparative test between the two instruments. For this comparison, the $^{90}\text{Zr}(\text{NH}_3)_6^+$ product ion was used as an analog of the target $^{93}\text{Zr}(\text{NH}_3)_6^+$ product ion. The 8900 was operated using the same General Purpose instrument operating conditions shown in Table 1.

The product ion scans obtained by the 8900 ICP-QQQ using the 10 ng/g mixed stable element standard agreed with the 8800 ICP-QQQ scan results. Both instruments identified $\text{Zr}(\text{NH}_3)_6^+$ at m/z 192 as the most intense ^{90}Zr product ion,

using a mass shift of 102. As shown in Table 2, measuring Zr as $\text{Zr}(\text{NH}_3)_6^+$ offered the most efficient Nb interference removal method. The results also show that a maximum separation factor of >10,000 was achieved with the 8900 compared to 6,200 on the 8800. The 8900 also detected intense ^{90}Zr product ions not detected on the 8800, most notably at m/z 206 ($^{90}\text{ZrN}(\text{NH}_3)_6$) and 207 ($^{90}\text{ZrNH}(\text{NH}_3)_6$) (Table 2).

Table 2. Zr/Nb separation factors for 8800 and 8900 ICP-QQQ. Based on product ion scans of ^{90}Zr and ^{93}Nb in a 10 ng/g mixed stable element standard. Zr-90 counts were scaled to 100% abundance for this calculation.

Q1/Q2 (m/z)	90/155	90/159	90/175	90/176	90/177	90/192	90/206	90/207
Mass-shift	65	69	85	86	87	102	116	117
Zr/Nb Separation Factor (8800)	<1	<1	<1	1	4	6,200	<1	<1
Zr/Nb Separation Factor (8900)	2,300	470	715	155	400	10,200	2,800	4,300

The 8900 offers higher sensitivity and lower backgrounds compared to the 8800, as verified by the data presented in Table 3. The stable element calibration standards were measured by both instruments. The counts per second (cps) for the $^{90}\text{Zr}(\text{NH}_3)_6^+$ product ion at m/z 192 obtained by the 8900 were significantly higher than the 8800 (Table 3). The sensitivity improvement of the 8900 is due to more efficient ion transmission in the interface vacuum stage. Also, axial acceleration (0.5 V in this study) improves reaction product ion energy, overcoming collisional attenuation and space-charge effects.

Table 3. Difference in instrument sensitivity and instrument detection limit (IDL) for stable Zr standards.

Parameter	8800 ICP-QQQ		8900 ICP-QQQ	
	90/90	90/192	90/90	90/192
^{90}Zr sensitivity (cps, 10 ng/g)	1,800	2,000	53,000	166,000
*IDL (pg/g)	6.5		0.1	
*IDL (mBq/g)	0.6		8.8×10^{-3}	

*IDLs were calculated from the 90/192 data.

Conclusion

ICP-QQQ has been successfully used for the direct and accurate measurement of the long-lived radionuclide ^{93}Zr in decommissioning samples below IAEA out-of-scope limits. Since ICP-QQQ with MS/MS uses reaction chemistry in the CRC to separate analytes and interferences, there was no need for a separation-step before measurement, simplifying and speeding up the analysis.

Both active and stable element standards containing Nb and Zr were used during method development. The study shows the Agilent 8800 ICP-QQQ with MS/MS can eliminate isobaric overlaps from ^{93}Nb on ^{93}Zr using NH_3/H_2 as the reaction gas. Nb doesn't react with NH_3/H_2 in the CRC, so Nb remains at m/z 93, allowing ^{93}Zr to be measured as $^{93}\text{Zr}(\text{NH}_3)_6^+$ at $m/z = 195$, free from interference.

The integrated HMI aerosol dilution technology extends the matrix tolerance of Agilent ICP-QQQ for the analysis of high matrix samples. The 8800 was used to analyze ^{93}Zr in dissolved steel (using HMI) and aqueous waste samples. An MDL of less than 1 mBq/g was achieved in both matrices, which is several orders of magnitude lower than regulatory limits for decommissioning wastes and drinking water. The study showed that the newer Agilent 8900 ICP-QQQ offers higher sensitivity and lower backgrounds compared to the 8800.

Compared to decay counting techniques, ICP-QQQ reduces the preparation time of samples dramatically, with sample-throughput further improved by the short measurement times of the technique. The ICP-QQQ method will be beneficial to analysts working in nuclear decommissioning and environmental monitoring labs.

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