

ICP - Mass Spectrometry

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Measurement of ^{90}Sr by Preconcentration/Matrix Separation and Reaction Cell ICP-MS

Introduction

The tsunami after the 2011 Tohoku earthquake devastated a vast coastal area of eastern Japan. The Fukushima Daiichi nuclear reactor suffered meltdowns of its uranium fuel rods, resulting in the release of radioactive isotopes. One of the

most environmentally critical isotopes released was strontium-90 (^{90}Sr), a fission product of uranium and plutonium which has a half-life of 29 years, thus remaining in the environment for a significant amount of time. ^{90}Sr itself decays into yttrium-90 (^{90}Y), followed by decay into stable zirconium-90 (^{90}Zr). When organisms ingest ^{90}Sr , it accumulates in the bones and continues to emit beta radiation. Therefore, assessing ^{90}Sr contamination in the environment is urgently needed for local public health concerns.

Current techniques for ^{90}Sr determination are either time-consuming (days), expensive, or both, and are not capable of the high sample throughput necessary to analyze the large number of samples to determine the extent of ^{90}Sr contamination which originated from the nuclear reactor. Analysis by inductively coupled plasma mass spectrometry (ICP-MS) would overcome these issues, but it suffers from two major challenges: first, ^{90}Sr has the same mass as the major isotope of zirconium (Zr) (51.45% abundant); second, Zr is present at about twelve orders of magnitude higher levels than ^{90}Sr in normal environmental samples (ppm vs. sub-ppq). These challenges must be overcome for the effective ICP-MS measurement of ^{90}Sr in soils.

A sample preconcentration/matrix removal scheme has been developed for reaction-based ICP-MS analysis of ^{90}Sr that can be applied for high throughput sample analysis (patent pending), which is greatly needed for the large number of environmental samples from the vicinity of the Fukushima Daiichi nuclear power plant. This methodology overcomes the challenges of and offers a significant time savings over current ^{90}Sr radiometric analyses: minutes compared to days. This work provides a brief description and overview of the technique, with a more detailed description available elsewhere¹.

Experimental

Samples

Soil samples were collected from areas showing high radiation, 10 and 20 km northwest of the Fukushima Daiichi nuclear power plant. Surface soil samples (100-150 g) were taken at depths up to 2 cm. The samples were collected and stored in plastic containers.

Sample Preparation

One gram of dried soil was placed in each PTFE microwave digestion vessel, followed by 10 mL of 10% (v/v) nitric acid. The vessels were digested following the microwave program shown in Table 1, then allowed to cool at room temperature for 20 minutes. Next, the solutions were transferred to plastic tubes and centrifuged for 10 minutes at 2500 rpm. The supernatant was then filtered through 0.45 μm filters to remove any residue prior to analysis by ICP-MS. It should be noted that multiple samples taken from the same location were prepared at the same time and their filtrates combined to increase the total sample volume.

Table 1. Microwave Digestion Program

Step	Power (W)	Ramp (W/min)	Hold (min)
1	0	90	---
2	900	---	5
3	900	50	---
4	1400	---	15

The upper limits of the microwave were set to 140 °C and 1.0 MPa (10 bar)

Sample Analysis

Because ^{90}Sr levels are so low, the samples were pre-concentrated prior to analysis by passing them through a 50 mm x 4.6 mm column packed with a Sr-specific resin (Eichrom Technology, Lisle, IL, USA) with particle sizes from 50-100 μm . This resin both concentrated the Sr and removed other matrix elements.

All preconcentration was done with a FIAS 400 flow injection system (PerkinElmer, Shelton, CT, USA). The sample was first loaded onto the column at a flow rate of 1.9 mL/min. All isobars at m/z 90, except Sr, were then removed from the column by pumping 20% (v/v) HNO_3 over the column for 90 seconds at a flow rate of 0.75 mL/min. Finally, the Sr was eluted by flushing the column with deionized water at 1.9 mL/min for 90 seconds. Between the matrix removal and Sr elution steps, 20% (v/v) HNO_3 was flushed through the system (but not the column) to rinse/clean the valves. The complete FIAS program is shown in Table 2.

Table 2. FIAS Program for Sr Preconcentration and Matrix Removal

Step	Duration (sec)	Pump #1 (rpm)	Pump #2 (rpm)	Valve Position
Pre-run	60	0	75	2
1	10	120	0	1
2	325	75	30	2
3	90	30	75	2
4	30	75	0	1
5	90	30	75	2
6	30	75	0	1
7	90	30	75	2
8	152	0	75	1
Post-run	---	0	75	1

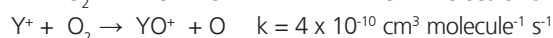
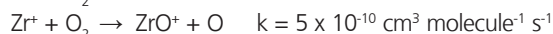
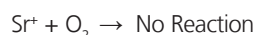
The output from the column was sent directly to an ultrasonic nebulizer (USN; Cetac Technologies, Omaha, NE, USA) to provide greater sensitivity than conventional pneumatic nebulization. The aerosol from the USN entered an ELAN® DRC II ICP-MS (PerkinElmer, Shelton, CT, USA) which measured ^{90}Sr in DRC mode using oxygen as reaction cell gas; instrumental parameters are listed in Table 3. The total run time per sample was 14.6 minutes, the majority of which is spent in the pre-concentration procedure.

Table 3. ELAN DRC II Parameters

Parameter	Condition
Nebulizer Gas Flow	1.08 L/min
RF Power	1400 W
Sweeps/Reading	5
Readings/Replicate	320
Replicates	1
Dwell Time	15 ms
Reading Time	152 sec
Cell Gas	O_2
Cell Gas Flow	1.2 mL/min
RPq	0.70

Results and Discussion

The reaction rates of Sr, Zr, and Y are shown below²:



These reactions demonstrate that Sr^+ does not react with oxygen, while both Zr^+ and Y^+ react rapidly, which demonstrates that oxygen is an effective gas for removing the $^{90}\text{Zr}^+$ and $^{90}\text{Y}^+$ interferences from $^{90}\text{Sr}^+$. (Although ^{89}Y is the only naturally occurring yttrium isotope, ^{90}Y is formed through nuclear processes.) While these reaction schemes appear to resolve the interferences without the need for matrix separation, the significant differences between the ^{90}Zr and ^{90}Sr levels present in the soils (6.5-11 $\mu\text{g/g}$ Zr vs. ppq levels of ^{90}Sr) presents a challenge: when enough O_2 is used in the cell to remove all of the $^{90}\text{Zr}^+$, a small amount of $^{90}\text{Sr}^+$ is lost due to collisional scattering with the O_2 molecules. Given the low levels of $^{90}\text{Sr}^+$, this scattering loss is enough to make $^{90}\text{Sr}^+$ undetectable.

To overcome this limitation, matrix separation/Sr preconcentration was used. However, significant Zr signal remained after the matrix separation step. Further investigation showed that 0.23% Zr remained on the column, along with the Sr. Therefore, a mixture of Zr and Sr were eluted and analyzed. However, this lower level of Zr could be easily removed with oxygen without causing ⁹⁰Sr sensitivity loss. Therefore, the combination of matrix removal/Sr preconcentration along with oxygen in the reaction cell proved to be the ideal solution.

To further increase sensitivity, an ultrasonic nebulizer was used to aspirate the sample into the ICP-MS. The ultrasonic nebulizer provided at 21.8-fold improvement in detection limits relative to conventional nebulization.

Before analyzing real samples, the method was characterized. Based on the 3σ criteria, ⁹⁰Sr detection limits were determined to be 0.46 pg/L in solution and 0.77 pg/kg in soils. The ⁹⁰Sr linearity was found to range from 1.39 pg/L to 0.83 μg/L, being limited by the preconcentration column. The analysis time for each sample (from injection to detection) is 14.6 minutes. This is significantly shorter than the accepted method for measuring ⁹⁰Sr (with a gas flow detector and sample pretreatment), which requires at least 14 days. (Details of the accepted procedure are given in Reference 1).

Table 4 shows the results for the analysis of three soil samples (average of four measurements each) taken from 10-20 km northwest of the Fukushima nuclear power plant. The samples were split for analysis both with the method described here and by the accepted method for ⁹⁰Sr determination. The results of both techniques agree within a 95% confidence level. The reason there was not a stronger agreement between the methods is due to sample partitioning and the inhomogeneous distribution of ⁹⁰Sr within the soils.

The mass concentration can be converted to radioactivity with the following equation:

$$A = \left(\frac{\ln 2}{t_{1/2}} \times \frac{m}{M_n} \times N_A \right) / 1 \text{ kg}$$

A = activity concentration (Bq kg⁻¹)

t_{1/2} = half-life (seconds)

m = mass of nuclide (pg) per kg of sample

M_n = mass number of nuclide

N_A = Avogadro's number

Using this equation, the ICP-MS results (in ppq) were converted to their activity concentrations (Bq kg⁻¹), as shown in Table 4.

Table 4. ⁹⁰Sr Results from Soils

Sample	⁹⁰ Sr Concentration Bq kg ⁻¹ (ppq)	
	ICP-MS Method	Conventional Method
1	73.5 (14.5)	74.0 (14.6)
2	68.6 (13.5)	45.0 (8.9)
3	52.1 (10.2)	62.9 (12.4)

Conclusion

This work has demonstrated the ability of ICP-MS to measure ⁹⁰Sr in soils, a challenging analysis due to the low levels of ⁹⁰Sr and the high levels of Zr present in soils. A matrix separation/pre-concentration step was used to remove the majority of the matrix elements and pre-concentrate the ⁹⁰Sr. Despite this step, matrix interferences remained, which were removed with a Dynamic Reaction Cell. Results in soil samples compared well to those obtained with the conventional ⁹⁰Sr analytical method. Initial studies have also demonstrated this method is applicable to sample types, including water and food.

Although this work was performed on an ELAN DRC II, equivalent or better results would be expected on a NexION® 350 ICP-MS (PerkinElmer, Shelton, CT, USA). The ICP-MS approach reduces the analysis time from 14 days to 14 minutes, which is vitally important when monitoring a large number of samples following a nuclear incident to ensure the health and safety of the environment.

References

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Acknowledgements

The authors gratefully acknowledge funding by JSPS Grant-in-Aid for Young Scientists (B) Grant #25870083, the New Chemical Technology Research Encouragement Award and Foundation from the Japan Association for Chemical Innovation (JACI). In addition, we thank Mr. Mitsuyuki Konno from Environmental Radioactivity Monitoring Center of Fukushima Prefecture for useful discussions and radioactivity measurements.