



TIMS

Measuring ^{90}Sr abundances in environmental samples by Thermal Ionization Mass Spectrometry

Authors

Shigeyuki Wakaki¹, Jo Aoki², Ryoya Shimode², Katsuhiko Suzuki³, Takashi Miyazaki⁴, Satoshi Sasaki⁵ and Yoshitaka Takagai^{2,6}, Jenny Roberts⁷, Hauke Vollstaedt⁷

¹ Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan

² Faculty of Symbiotic Systems Science, Fukushima University, Japan

³ Submarine Resources Research Center, JAMSTEC, Japan

⁴ Volcanoes and Earth's Interior Research Center, JAMSTEC, Japan

⁵ Thermo Fisher Scientific, Tokyo, Japan

⁶ Institute of Environmental Radioactivity, Fukushima University, Japan.

⁷Thermo Fisher Scientific, Bremen, Germany

Introduction

There are four stable isotopes of strontium with different isotopic abundances: ^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.0%) and ^{88}Sr (82.58%). In some environments, such as sites that have experienced radioactive contamination from nuclear accidents or weapons testing, radioactive strontium (^{90}Sr) can be found, with a half-life of 28.8 years. The monitoring of ^{90}Sr is important from a human perspective because when contaminated food or water is ingested, ^{90}Sr is concentrated primarily in bones and bone marrow, resulting in bone cancer, cancer of nearby tissues and leukemia.

Typically, the abundance of ^{90}Sr has been measured using radiometric techniques, such as liquid scintillators or gas ionization detectors. The major disadvantage of this technique is the total analysis time (5-20 days)¹. In recent years, mass spectrometry has provided a means to dramatically reduce analysis time, improving sample throughput^{2,3}. However, the peak tailing from the highly abundant ^{88}Sr has limited the ability of conventional mass spectrometry to be able to resolve samples with low radioactivity. Typical abundance sensitivities for the $^{90}\text{Sr}/^{88}\text{Sr}$ ratio (Figure 1) for inductively coupled plasma mass spectrometry with a dynamic reaction cell (ICP-DRC-MS) was on the order of 10^{-9} [3], whereas thermal ionization mass spectrometry (TIMS) was on the order of 10^{-10} [4]. However, in their study, Kavasi et al.⁴, used a TIMS with a WARP energy filter, which has no effect on peak tailing on the high mass side of the peak. Here, we

Keywords

Abundance sensitivity, radioactive strontium, strontium-90, RPQ, strontium isotopes, TIMS

demonstrate the ability of a different technology – the Retarding Quadrupole Lenses (RPQ) of the Triton Series TIMS – to precisely and accurately measure $^{90}\text{Sr}/^{88}\text{Sr}$ ratios of 9.1×10^{-12} . This enables samples with very low activities to be measured. We demonstrate the capability of the Triton Series TIMS to measure low activity samples by measuring a range of environmental samples with a modern activities ranging between 14.8 and 110 Bq/kg. Data shown here is published in Wakaki et al. (2022)⁵.

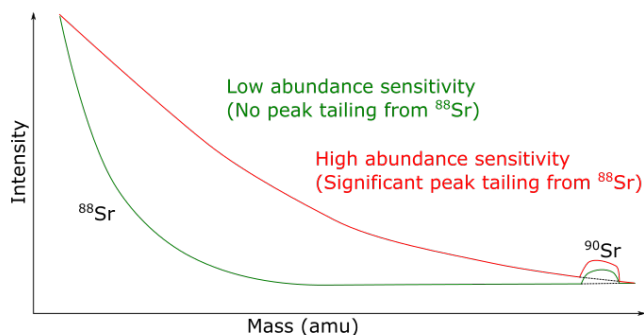


Figure 1. Schematic to illustrate abundance sensitivity. Abundance sensitivity = $^{90}\text{Sr}/^{88}\text{Sr}$ for a non-radioactive sample (i.e. contains no ^{90}Sr).

Instrumentation

Two thermal ionization mass spectrometers were used, the Triton™ XT (Thermo Scientific™) at Thermo Fisher Scientific, Bremen, Germany, and the Triton™ Plus (Thermo Scientific™) at Fukushima University, Japan. Both instruments were equipped with a Retarding Potential Quadrupole lens (RPQ) in front of the central Secondary Electron Multiplier (SEM) to reduce peak tailing from more abundant masses.

Sample preparation

The IAEA reference material's certified ^{90}Sr activity values were calculated using their dry weight. Therefore, these materials were weighed and digested as they were. Concentrated HNO_3 and HClO_4 acids were used to digest IAEA 156 and IAEA 330. The ashed crayfish and smallmouth bass samples were weighed and digested successively using 2.4 M HCl and conc HNO_3 . All the samples were dissolved in 3 M HNO_3 . Sr was separated from the other elements, including Zr, using extraction chromatography with Sr Resin (Eichrom Technologies Inc., USA) using a handmade PTFE column of 0.2 mL volume⁶. After sample solution loading, the column was rinsed with 2 mL of 6 M HNO_3 and 0.5 mL of 3 M HNO_3 successively, and Sr was eluted with 2 mL of 0.05 M HNO_3 . Finally, the separated Sr fraction was reacted with one drop of concentrated HNO_3 to decompose resin-derived organics. The total yield of the Sr separation chemistry was approximately 94%⁶. After the Sr separation chemistry, the Zr/Sr ratio was reduced to 1.2×10^{-5} times the original ratio of the sample.

The dried separated sample was re-dissolved in 2% HNO_3 solution and loaded in 100–400 ng Sr samples onto rhenium zone-refined (Re-ZR) filaments. The Re-ZR had previously been degassed at 5.5 A for 30 min under vacuum. This current was chosen to significantly reduce the ^{90}Zr interference, which appears at higher filament temperatures (Figure 2). When the filament temperature is increased to 1790 °C (ca. 3.5 A filament current), the ^{90}Zr peak can be observed, however at this temperature Sr is almost entirely consumed. For measurements of ^{90}Sr , it is recommended to measure at filament temperatures in the range of 1500–1600 °C.

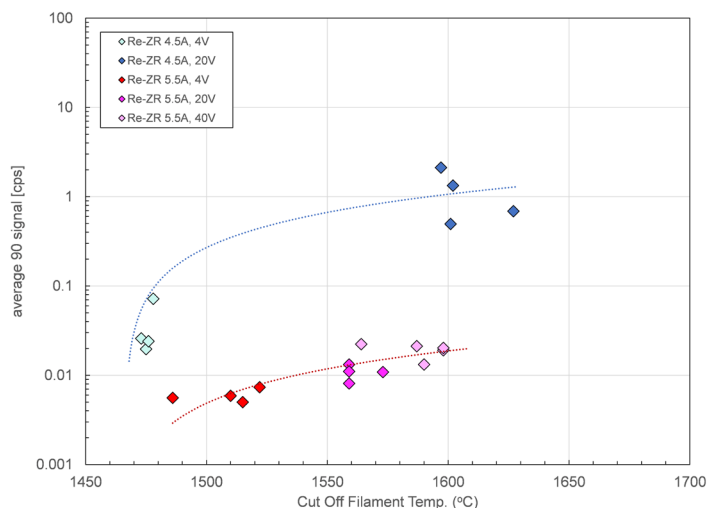


Figure 2. Comparison of Re-ZR filaments that have been degassed at 4.5 A (blue points) and 5.5 A (red points). A non-radioactive sample (SRM® 987) was loaded onto the filaments and measured using the conventional measurement mode (at 4 V, 20 V or 40 V ^{88}Sr) for 1 hour. The x-axis shows the final filament temperature at the end of the 1 hr measurement. Note that these data have not been dark noise corrected.

Mass spectrometry methods and discussion

In Bremen, filaments were heated to 2400 mA at a rate of 300 mA/min. During this time, a 5 minute baseline was measured. After which, the filament temperature was increased to 3000 mA at 100 mA/min to achieve a 20 V signal on ^{88}Sr . After a wait of 1 minute and re-adjustment of the filament temperature to achieve 20 V, the measurement was started. Samples were measured using conventional measurement mode at 20 V (^{88}Sr) for 1 hour (10 blocks, 86 cycles/block, 4.194 s integration time). A lens focusing was carried out every 3rd block. The filament temperature was modulated to keep the ^{88}Sr signal within 20 ± 4 V.

In Fukushima, filaments were preheated at 2250 mA for 30 min before the measurement. During the measurement, filaments were heated to 1500 mA at a rate of 1500 mA/min and then to 2250 mA at a rate of 214 mA/min.⁵ The filament

current was increased at 100 mA/min until an ^{88}Sr signal of 25 V was achieved. Samples were measured using conventional measurement mode at 25 V (^{88}Sr) for 1 hour (22 blocks, 10 cycles/block, 16.777 s integration time). During the measurement, the inter-block filament current adjustment kept the ^{88}Sr signal at ± 2.5 V.

The collector configuration for both setups is shown in Table 1.

Table 1. Collector configuration for the measurement of radioactive strontium.

Cup	L3	L2	L1	C
Isotope	^{86}Sr	^{87}Sr	^{88}Sr	^{90}Sr (89.878 amu)
Detector (R)	F ($10^{11} \Omega$)	F ($10^{11} \Omega$)	F ($10^{11} \Omega$)	RPQ-SEM

Results

Abundance sensitivity

Samples of the non-radioactive NIST strontium carbonate isotopic standard SRM[®] 987 were measured to determine the abundance sensitivity on ^{90}Sr of the Triton Series TIMS equipped with an RPQ.

The effect of the RPQ on peak tailing was observed by scanning across the mass range 88-90.075 amu of a non-radioactive sample SRM 987 for 2 hours (a total measurement time of 1.5 minutes on each data point) (Figure 3). It is clear that the tailing from the ^{88}Sr is effectively removed by 89.878 amu (the axial mass during static measurement). Slightly higher backgrounds observed in the SEM between 89.1-89.7 are caused by scattering of ions as the ions are not falling into a cup. Across the range 89.7-90 amu, all ions are collected in cups and the background signal measured in the SEM is extremely low (< 0.01 cps). By contrast, the signal on ^{88}Sr is > 11 orders of magnitude greater.

The abundance sensitivity ($^{90}\text{Sr}/^{88}\text{Sr}$) achieved by the Triton Series TIMS equipped with RPQ during static measurements of SRM 987 at 20 V ^{88}Sr was $9.1 \times 10^{-12} \pm 2.6 \times 10^{-12}$ (2 SD, $n=34$) (Figure 4). Note that this value is not dark noise corrected.

The limit of detection (LOD) is defined as $3 \cdot \sigma$ ($^{90}\text{Sr}/^{88}\text{Sr}$ ratio (dark noise corrected ratio)) = 2.9×10^{-12} . Using this LOD, it is possible to determine the minimum activity for environmental samples with varying concentrations of stable strontium (Figure 5):

$$\text{Min. } ^{90}\text{Sr} \text{ resolvable} = \frac{\text{LOD} \cdot [\text{Sr}] \cdot ^{88}\text{Sr}/\text{Sr}_{\text{TOT}} \cdot 0.001}{\text{Ar}_{\text{Sr}}}$$

$$\text{Min. Activity Resolvable} = \frac{\text{Min. } ^{90}\text{Sr} \text{ resolvable} \cdot N_A \cdot \ln(2)}{T_{1/2, \text{Sr}}}$$

Where “min. ^{90}Sr resolvable” is in mol/kg, LOD is 2.9×10^{-12} , [Sr] is in mg/kg, $^{88}\text{Sr}/\text{Sr}_{\text{TOT}}$ is 0.8258, Ar_{Sr} is 87.62 u, “Min. Activity Resolvable” is in Bq/kg, N_A is $6.022 \times 10^{23} \text{ mol}^{-1}$, $T_{1/2, \text{Sr}}$ is 28.79 yr $\times 3.15 \times 10^7 \text{ s/yr}$.

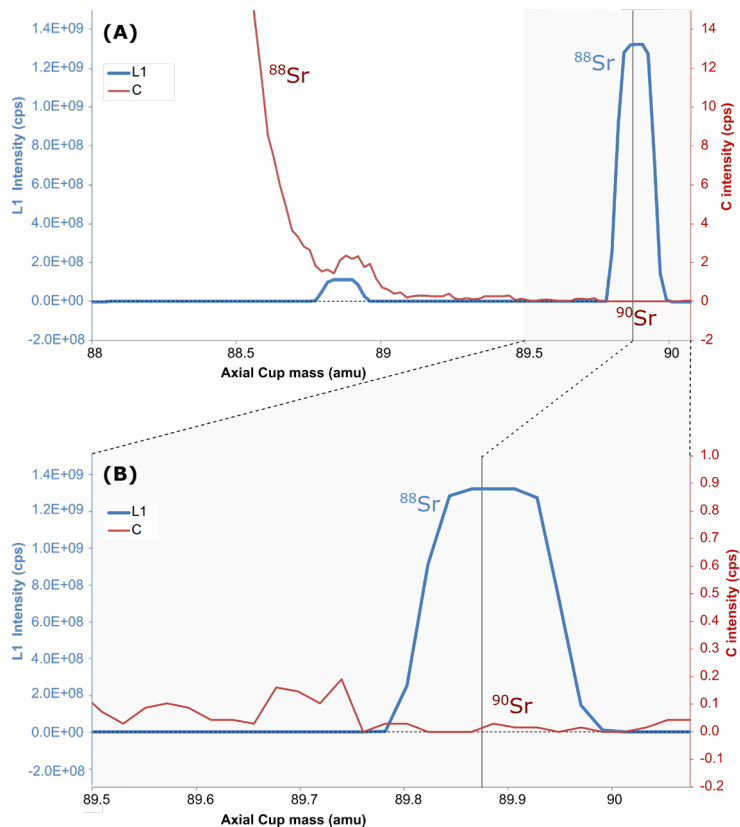


Figure 3. (A) Mass scan of non-radioactive Sr (SRM 987) integrating the signal in C and L1 for 2 hours. Black vertical line shows the magnet position during static measurements. (B) Zoom in of same mass scan between 89.5 and 90.075 amu (axial mass) shows absence of ^{88}Sr peak tailing at 89.878 amu (position of ^{90}Sr signal).

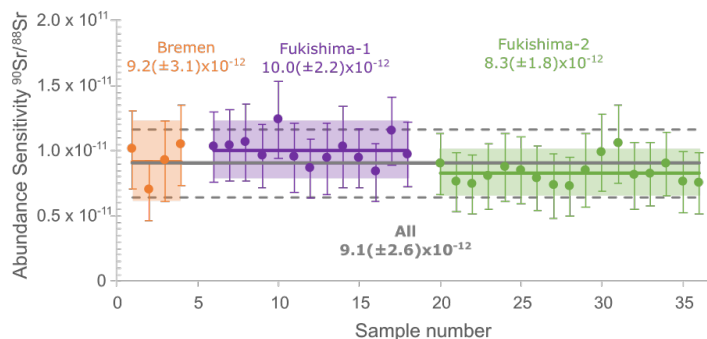
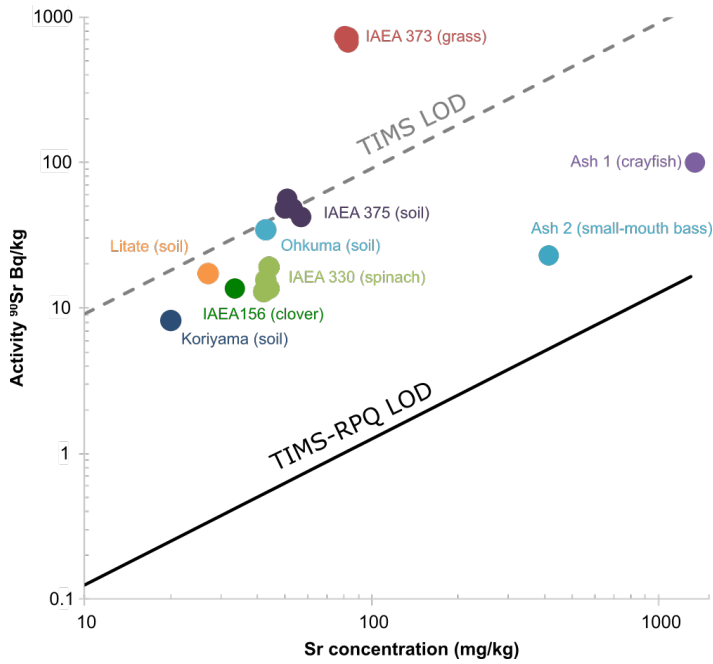


Figure 4. Abundance sensitivity of non-radioactive Sr (SRM 987) across three different analytical sessions. Each data point represents a 1 hour measurement at 20 and 25 V on ^{88}Sr . Error bars show internal precision (2 SE). Note that these data are not dark noise corrected).



Environmental samples

A number of different radioactive environmental samples of known activity were measured to determine the $^{90}\text{Sr}/^{88}\text{Sr}$ ratio (Figure 6). These measurements were made on both the Bremen and Fukushima instruments across 3 analytical sessions (2 years apart).

There is good correlation between the measured $^{90}\text{Sr}/^{88}\text{Sr}$ of the samples and the decay-corrected reference value. The variability of the $^{90}\text{Sr}/^{88}\text{Sr}$ in the IAEA-330 samples might be reflective of the larger variability in the $^{90}\text{Sr}/^{88}\text{Sr}$ of the reference material.

When converting the internal precision of each measurement to RSD, it is clear that IAEA-330 has one of the lowest RSDs of all the samples measured (Figure 7). For all samples, the internal precision is very close to the theoretical limit based on counting statistics, demonstrating the excellent precision obtainable with the Triton Series TIMS.

Figure 5. Determination of the minimum activity resolvable with a Triton XT with RPQ (black line) for varying strontium concentrations. The $^{90}\text{Sr}/^{88}\text{Sr}$ detection limit of the previous TIMS studies⁴ (grey dashed line) and typical environmental samples⁷ (decay corrected to January 2020) are shown for comparison.

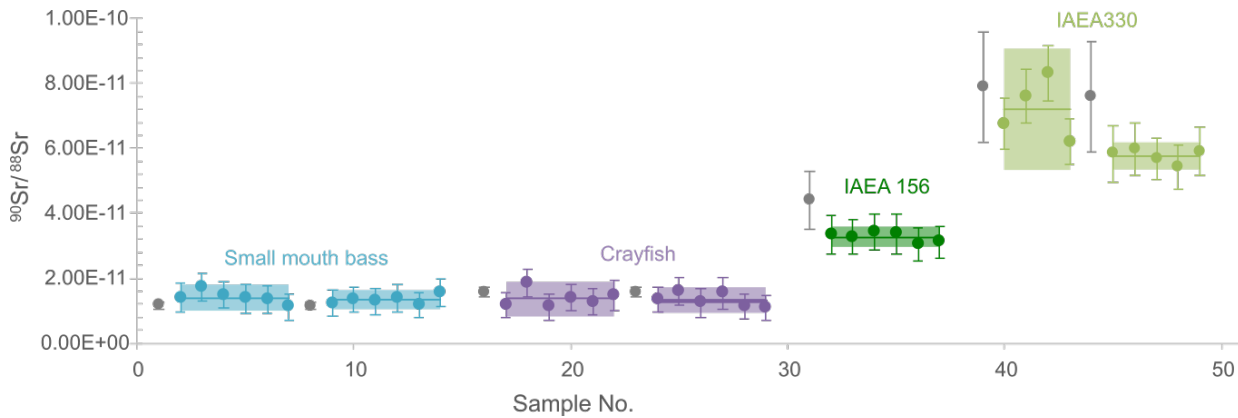


Figure 6. Determination of the $^{90}\text{Sr}/^{88}\text{Sr}$ ratio for a range of environmental samples. The decay corrected reference value (corrected to the measurement date) is shown in grey. Different analytical sessions are separated here due to the difference in the $^{90}\text{Sr}/^{88}\text{Sr}$ owing to radioactive decay over time.

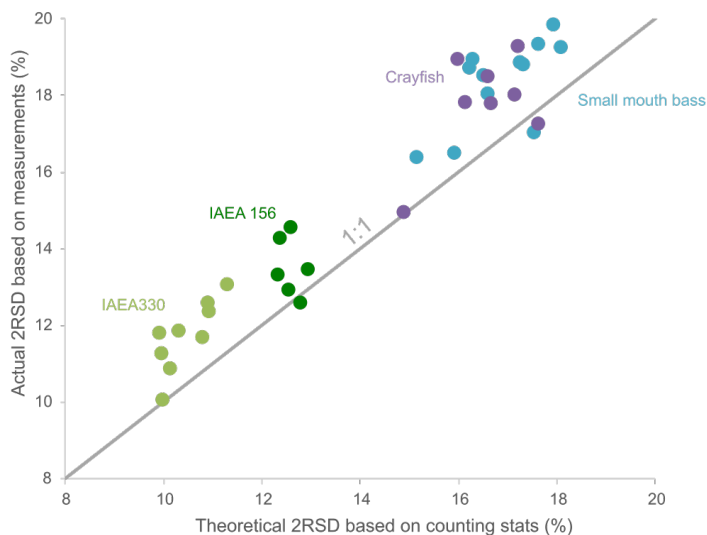


Figure 7. Cross-plot of relative standard deviation of $^{90}\text{Sr}/^{88}\text{Sr}$ ratio for each filament against the theoretical limit based on counting statistics.

Conclusion

The RPQ feature of the Triton Series TIMS improves the abundance sensitivity by reducing peak tailing on both the high and low mass side of the peak. Replicate measurements of non-radioactive Sr demonstrate that an abundance sensitivity ($^{90}\text{Sr}/^{88}\text{Sr}$) of 9.1×10^{-12} can be achieved. This theoretically enables samples with a low ^{90}Sr activity to be measured with a detection limit of 2.9×10^{-12} ($^{90}\text{Sr}/^{88}\text{Sr}$ ratio).

The ability of the Triton Series TIMS coupled with the RPQ to measure low levels of ^{90}Sr has been demonstrated through measurements of a range of environmental samples. These experiments show that the ^{90}Sr can be accurately and precisely determined, with precisions close to the limit of counting statistics.

References

- Hou, X. & Roos, P. Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. *Analytica Chimica Acta* vol. 608 105–139 (2008).
- Bu, W. et al. The role of mass spectrometry in radioactive contamination assessment after the Fukushima nuclear accident. *Journal of Analytical Atomic Spectrometry* vol. 33 519–546 (2018).
- Feuerstein, J., Boulyga, S. F., Galler, P., Stingeder, G. & Prohaska, T. Determination of ^{90}Sr in soil samples using inductively coupled plasma mass spectrometry equipped with dynamic reaction cell (ICP-DRC-MS). *Journal of Environmental Radioactivity* 99, 1764–1769 (2008).
- Kavasi, N. & Sahoo, S. K. Method for ^{90}Sr Analysis in Environmental Samples Using Thermal Ionization Mass Spectrometry with Daly Ion-Counting System. *Analytical Chemistry* 91, 2964–2969 (2019).
- Wakaki, S. et al. A part per trillion isotope ratio analysis of $^{90}\text{Sr}/^{88}\text{Sr}$ using energy-filtered thermal ionization mass spectrometry. *Sci Rep* 12, 1151, 1–10 (2022).
- Wakaki, S., Obata, H., Tazoe, H. & Ishikawa, T. Precise and accurate analysis of deep and surface seawater Sr stable isotopic composition by double-spike thermal ionization mass spectrometry. *Geochemical journal* 51, 227–239 (2017).
- Ohno, T., Hirono, M., Kakuta, S. & Sakata, S. Determination of strontium 90 in environmental samples by triple quadrupole ICP-MS and its application to Fukushima soil samples. *Journal of Analytical Atomic Spectrometry* 33, 1081–1085 (2018).

Learn more at thermofisher.com/tims