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## Lead and Strontium Isotope Ratio Analysis Using the NexION 5000 ICP-MS

### Introduction

Isotope ratio measurements have been used in many application fields, such as nuclear, geological, geochronological dating, clinical, and others.<sup>1,2,3,4</sup> Depending on the industry, there is interest in measuring natural, depleted, or enriched isotope ratios and exact abundances of all isotopes for the element(s) of interest. Changes in selected isotope ratios are often extremely small, so the techniques used for measurement should be extremely sensitive, selective and stable. Traditionally, multi-collector mass spectrometers are used for accurate isotope ratio analysis, allowing all masses of interest to be measured simultaneously. However, a modern sequential spectrometer, such as the NexION® 5000 Multi-Quadrupole ICP-MS with a very high duty cycle, great sensitivity and technologies for removal of spectral interferences, is the ideal tool not only for quantitative analysis but also for isotope ratio determination.<sup>5,6</sup>

This application note describes the conditions and results for strontium (Sr) and lead (Pb) isotope ratio analysis in a variety of reference materials as well as some environmental samples.

## Experimental

### Samples and Sample Preparation

National Institute of Standards and Technology (NIST) SRM 981 Common Lead Isotopic Standard (NIST, Gaithersburg, Maryland, USA), which is available in the form of a high-purity wire, was dissolved in 5% HNO<sub>3</sub> and diluted to 10 and 20 ppb concentration in 0.5% HNO<sub>3</sub>. Tap water used for Pb ratio analysis was also acidified to 0.5% HNO<sub>3</sub>.

NIST SRM 987 Strontium Carbonate Isotopic Standard was dissolved in 5% HNO<sub>3</sub> and diluted to 2 ppb of Sr in 1% HNO<sub>3</sub>. For seawater Sr isotope analysis, NASS-7 Seawater Certified Reference Material for Trace Metals and Other Constituents (National Research Council Canada - NRC) was used for analysis; a dilution of 10,000 times was required due to the naturally high concentration of Sr in seawater.

Semiconductor-grade nitric acid from TAMA (Moses Lake Industries, Washington, USA) and ultra-pure water were used for standard and sample preparation.

### Instrumental Conditions

The instrument employed for this study was the NexION 5000 Multi-Quadrupole ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA). The NexION 5000's Universal Cell Technology (UCT), while operating in Reaction (DRC) mode, is an extremely effective technique for eliminating atomic and polyatomic interferences.<sup>7,8</sup> The UCT uses a quadrupole mass filter to create dynamic bandpass tuning, wherein only ions of a specific mass range pass through the cell, thus allowing only controlled reactions to take place, preventing undesirable byproduct ions from forming within the cell even

when very reactive gases, such as 100% NH<sub>3</sub> and O<sub>2</sub>, are used. Multi-quadrupole technology in combination with MS/MS or Mass Shift modes permits only isotopes of interest to enter the UCT and undergo desirable reactions.

Instrumental parameters and sample introduction components are shown in Table 1.

Table 1. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Nebulizer	PFA ST3 Self-aspirating
Sample Uptake	~350 µL/min
Nebulizer Flow	1.0 L/min
Spray Chamber	SIQ cyclonic
Torch	SIQ One-piece with 2-mm ID Injector
RF Power	1600 W
Cell Mode	Reaction
Cell Gases	NH <sub>3</sub> and N <sub>2</sub> O

### Optimization Parameters and Method

Pb isotopes 204, 206, 207 and 208 are considered stable, but their natural abundances can differ depending on place of origin, so there is interest in measuring the isotope ratio accurately. One of the Pb isotopes at mass 204 is directly overlapped by Hg 204. Taking advantage of the fact that Hg reacts with NH<sub>3</sub> but Pb does not, the Hg interference can be removed.<sup>9</sup> Another advantage of using pure NH<sub>3</sub> as a reaction gas in the UCT is the enhancement of the signal due to collisional focusing.<sup>10</sup> As shown in Figure 1, sensitivity of Pb can be increased three-fold with 1 mL/min NH<sub>3</sub> in comparison with zero flow.

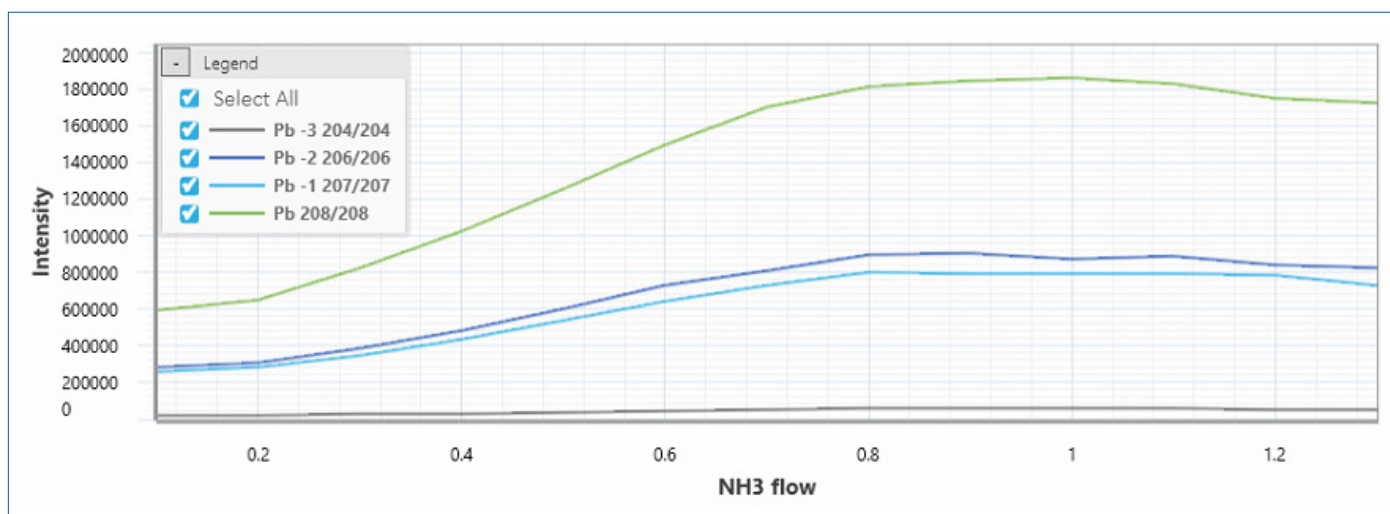


Figure 1. Optimization of NH<sub>3</sub> flow for Pb measurements.

A scan from Syngistix™ for ICP-MS software in Figure 2 shows all four Pb isotopes (from 20 ppb standard) obtained in MS/MS mode with 1 mL/min  $\text{NH}_3$  flow. The green bars correspond to the isotopes' natural abundances and indicate that the measured Pb isotopes match the natural abundances without any mass bias.

Strontium isotope ratios, especially Sr 87/86, are of interest in geochronology and marine science. Different Sr isotopic composition in rock formation and in seawater could be an indication of some geological and nuclear processes occurring over millions of years.<sup>11</sup>

One of the Rb isotopes resides on the same mass as Sr 87. On the NexION 5000 ICP-MS, the power of chemical reactions

combined with multi-quadrupole technology allows Sr isotopes to be effectively resolved from Rb. Here, Sr is oxidized when  $\text{N}_2\text{O}$ , a strong oxidizer, is used in the Universal Cell, while Rb is practically non-reactive. The Mass Shift mode of the NexION 5000 ICP-MS allows the measurement of all Sr isotopes as  $\text{SrO}^+$  in a spectral region where the background is free from any other species (Figure 3). Accuracy of Sr isotopes is not significantly altered by minor O 17 and O 18 isotopes, especially for the Sr 87/86 ratio.

Optimization of the  $\text{N}_2\text{O}$  flow in Mass Shift mode indicates that the maximum signal for  $\text{SrO}^+$  occurs at a flow of 0.5 mL/min (Figure 4). For this test, a 2 ppb Sr isotope standard was used.

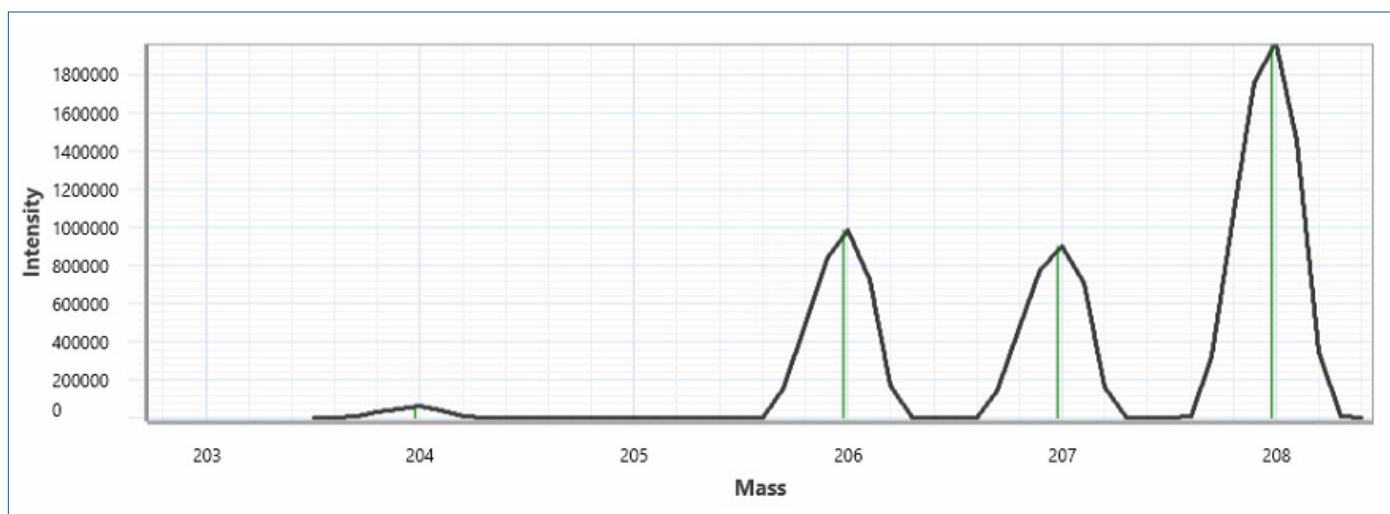


Figure 2. MS/MS scan in Reaction- $\text{NH}_3$  mode for Pb isotopes.

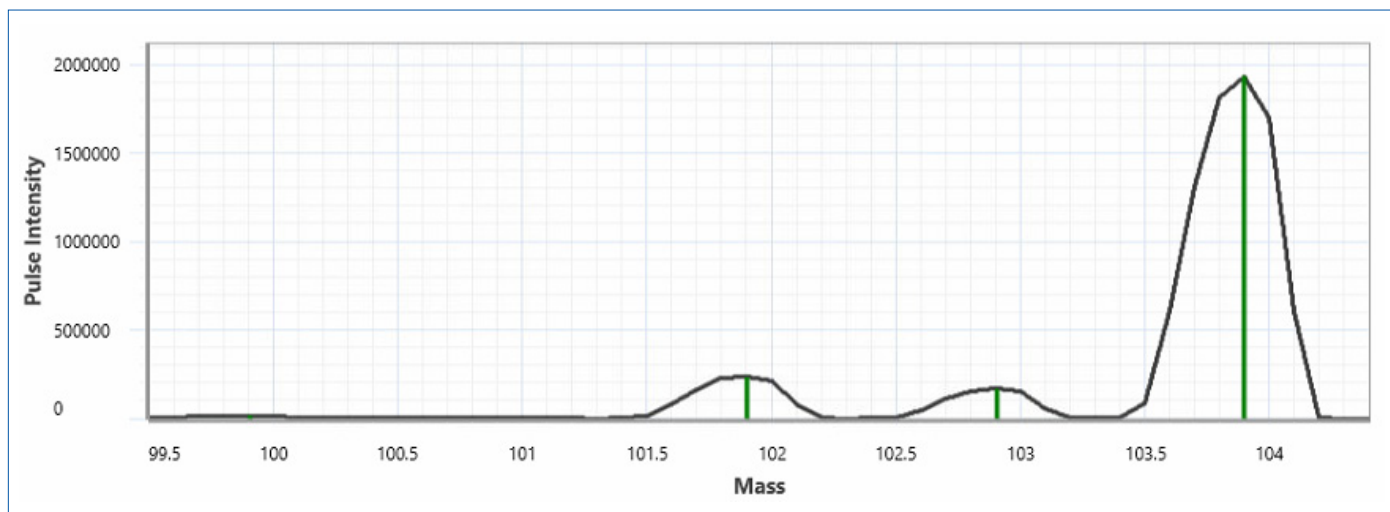


Figure 3. Mass Shift scan in Reaction- $\text{N}_2\text{O}$  mode for  $\text{SrO}$  isotopes.

When comparing a mass spectrum of Sr isotopes in diluted seawater measured in Standard mode with a mass spectrum obtained in Mass Shift mode with  $N_2O$  converting  $Sr^+$  into  $SrO^+$  (Figure 5), it is observed that all Sr isotopes are quantitatively mass-shifted to mass range 100-104, away from any spectral interferences, and that sensitivity is enhanced.

One more experiment was performed to check the relation of precision (expressed as RSD of Pb 207/208 ratio) to measuring time per replicate (in Figure 6 - blue line). As expected, with a longer measurement time, more counts were collected, and

the precision improved. However, when the time per replicate reached 60 seconds, the curve flattened, indicating that due to system noise, there are some limitations with regard to RSD improvement.<sup>11</sup> For this point, the total measurement time with 10 replicates and two isotopes was 10 minutes and the precision of the Pb ratio for 10 ppb reached 0.06%. An orange line indicating theoretical ratio RSDs was constructed based on a counting statistic from collected counts. It can be seen that the agreement between the two lines is very good, with a small positive bias in the experimental plot.

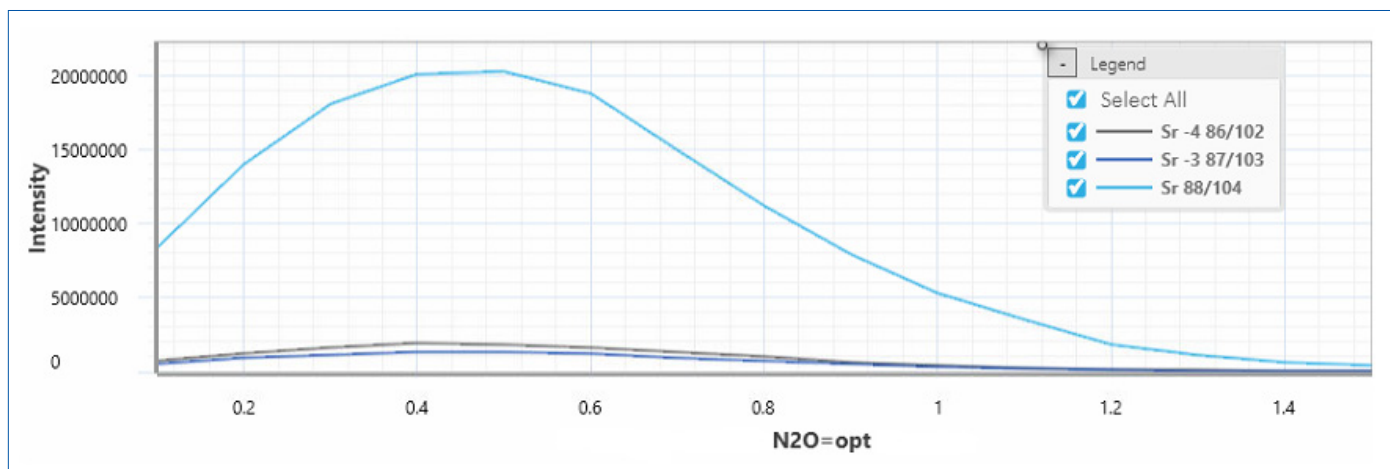


Figure 4. Optimization of  $N_2O$  flow for  $SrO^+$  isotopes.

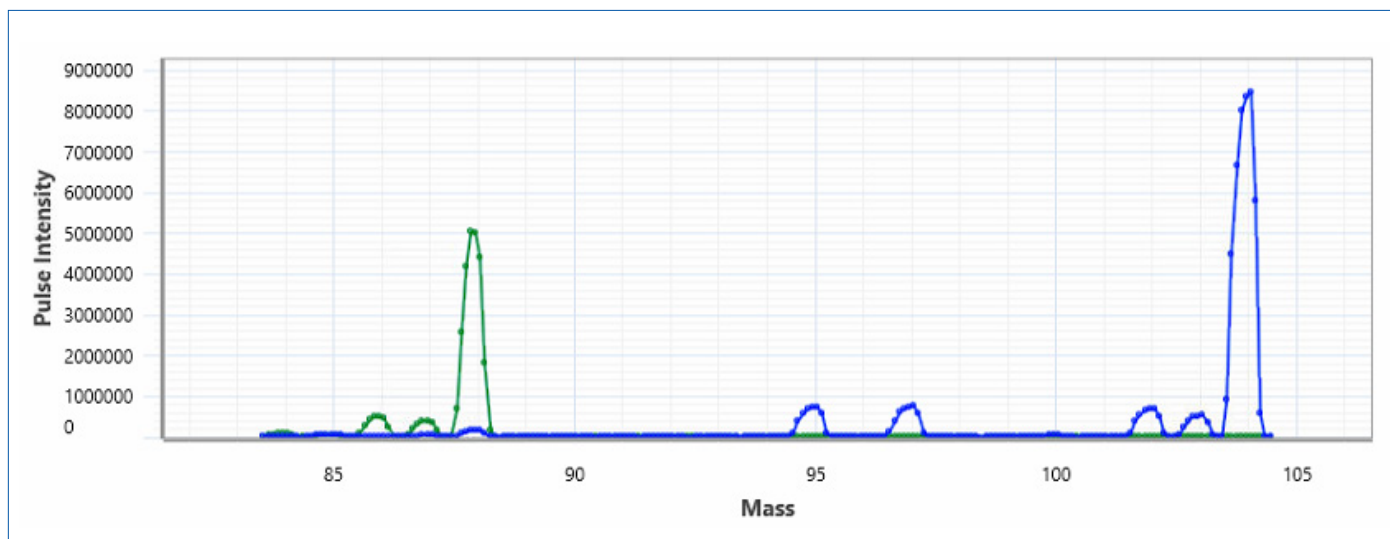


Figure 5. Overlain Sr spectra in Standard mode (green line) and  $SrO$  in Reaction- $N_2O$  (blue line) in diluted seawater.

The method parameters for both Pb and Sr isotopic analysis are listed in Table 2. For each element, all four isotopes were analyzed with dwell times dependent on the natural isotope abundances (meaning a longer dwell for the less abundant isotopes). Pb analysis was conducted in MS/MS mode with NH<sub>3</sub> and Sr analysis in Mass Shift mode with N<sub>2</sub>O as a reaction gas. On the NexION 5000 ICP-MS, an extremely short electronics' settling time (0.2 ms) between isotopes is possible, and despite short dwell times, the duty cycles for both analyses are extremely high. This high percentage of the duty cycle means that the instrument spends most of its time measuring isotopes (over 96%) and only 4% of the total sample analysis time is idle. With 10 replicates, the measurement time per sample was close to 600 seconds, which delivers good precision in a fairly short time for relatively low concentrations.

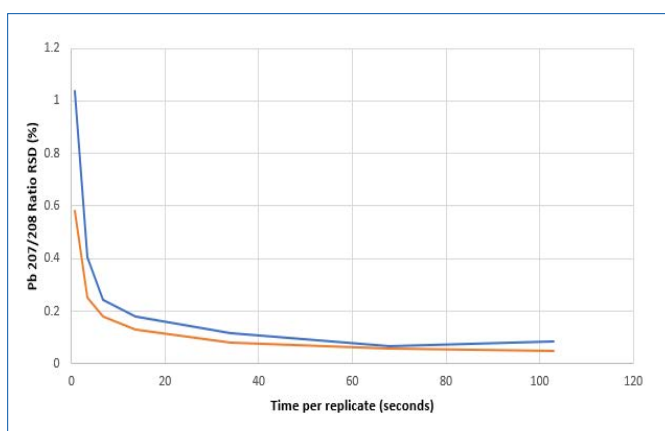


Figure 6. Effect of time per replicate (s) on ratio RSD (%) of Pb 207/208. Blue line: experimental ratio RSD; orange line: theoretical ratio RSD (average statistical error).

Table 2. Method Parameters.

Parameter	Pb Analysis	Sr Analysis
Method Type	Isotope Ratio	Isotope Ratio
Sweeps per Reading	200	200
Readings per Replicate	10	10
Replicates	10	10
Dwell Time	Pb 204/204 - 25 ms	Sr 84/SrO 100 - 20 ms
	Pb 206/206 - 2 ms	Sr 86/SrO 102 - 5 ms
	Pb 207/207 - 2 ms	Sr 87/SrO 103 - 5 ms
	Pb 208/208 - 1 ms	Sr 88/SrO 104 - 0.5 ms
Duty Cycle	96.8%	97.4%
Sample Analysis Time	620 sec	630 sec
Reaction Gas	NH <sub>3</sub> 1.0 mL/min	N <sub>2</sub> O 0.5 mL/min

## Results and Discussion

Depending on the concentrations of analytes and the abundances of individual isotopes, measurements in the same method can be done in both the pulse and analog portions of the detector. Therefore, to ensure good accuracy of results, it is very important that the calibration of the detector is up to date. In the following examples, relatively low concentrations of Pb and Sr standards were used, allowing all measurements to be conducted in the pulse portion of the detector.

Table 3 shows the results for the SRM 981 Common Lead Isotopic Standard. The SRM was analyzed five times after a ratio calibration standard was run to correct for mass discrimination. The accuracy of the measurement and external precision were excellent for all Pb isotopes, demonstrating the great stability of the NexION 5000 ICP-MS during a one-hour analysis.

Table 3. Isotopic Analysis of SRM 981 Common Lead Isotopic Standard (5 measurements).

Sample No.	Pb 204 Abundance (%)	Pb 206 Abundance (%)	Pb 207 Abundance (%)	Pb 208 Abundance (%)
1	1.4232	24.1113	22.0902	52.3753
2	1.4198	24.1107	22.1031	52.3663
3	1.4166	24.0936	22.0645	52.4254
4	1.4157	24.0604	22.0522	52.4717
5	1.4156	24.0872	22.0658	52.4314
<b>Average Abundance (%)</b>	1.4182	24.0926	22.0751	52.4140
<b>Certified Abundance (%)</b>	1.4255	24.1442	22.0833	52.3470
<b>Accuracy (%)</b>	-0.51	-0.21	-0.04	0.13
<b>External Precision RSD (%)</b>	0.23	0.09	0.09	0.08

Tap water was also analyzed for the Pb isotopes (Table 4). Although the Pb concentration was very low – less than 20 ppt – the external precision for five measurements of all isotopes was below 0.75%. Abundances differed slightly from those in the SRM. To be sure that these values are real, Pb had to be pre-concentrated to obtain more counts per replicate.

Similar to the Pb tests, measurements were done for four Sr isotopes in SRM 987. The measurements were conducted in Mass Shift mode with N<sub>2</sub>O in the UCT, converting Sr<sup>+</sup> into SrO<sup>+</sup> and moving all isotopes to masses 16 amu higher. The SRM

was analyzed five times after the calibration. The accuracy of the measurement and external precision were excellent for all Sr isotopes, demonstrating once again the exceptional stability of the NexION 5000 ICP-MS during a one-hour analysis (Table 5).

As a sample, diluted seawater was analyzed for all Sr isotopes (Table 6). A dilution factor of 10,000 times was required due to the high natural concentration of Sr in seawater. The external precision of five measurements for all isotopes was below 0.3% and abundances differed very little from those in the SRM.

Table 4. Isotopic Analysis of Pb in Tap Water (5 measurements).

Sample No.	Pb 204 Abundance (%)	Pb 206 Abundance (%)	Pb 207 Abundance (%)	Pb 208 Abundance (%)
1	1.3808	24.7367	21.8234	52.0591
2	1.3632	24.4757	21.5026	52.6586
3	1.3766	24.5907	21.9136	52.1192
4	1.3646	24.4285	21.6633	52.5436
5	1.3846	24.2894	21.8033	52.5227
<b>Average Abundance (%)</b>	1.3740	24.5042	21.7412	52.3806
<b>External Precision RSD (%)</b>	0.70	0.69	0.74	0.52

Table 5. Isotopic Analysis of SRM 987 Strontium Carbonate (5 measurements).

Sample No.	Sr 84 -> SrO 100 Abundance (%)	Sr 86 -> SrO 102 Abundance (%)	Sr 87 -> SrO 103 Abundance (%)	Sr 88 -> SrO 104 Abundance (%)
1	0.5567	9.8675	7.0172	82.5093
2	0.5592	9.8784	7.0405	82.5219
3	0.5583	9.8528	7.0167	82.5723
4	0.5584	9.8668	7.0026	82.5722
5	0.5583	9.8790	7.0148	82.5093
<b>Average Abundance (%)</b>	0.5582	9.8689	7.0187	82.5447
<b>Certified Abundance (%)</b>	0.5574	9.8566	7.0015	82.5845
<b>Accuracy (%)</b>	0.14	0.12	0.24	-0.05
<b>External Precision RSD (%)</b>	0.16	0.11	0.20	0.03

Table 6. Isotopic Analysis of Sr in 10,000x Diluted Seawater (5 measurements).

Sample No.	Sr 84 -> SrO 100 Abundance (%)	Sr 86 -> SrO 102 Abundance (%)	Sr 87 -> SrO 103 Abundance (%)	Sr 88 -> SrO 104 Abundance (%)
1	0.5504	9.8317	6.9739	82.6439
2	0.5510	9.8313	6.971	82.6468
3	0.5512	9.8234	6.976	82.6494
4	0.5522	9.8384	6.9901	82.6193
5	0.5548	9.8598	6.9748	82.6106
<b>Average Abundance (%)</b>	0.5519	9.8369	6.9772	82.6340
<b>External Precision RSD (%)</b>	0.31	0.14	0.11	0.02

To find out if the difference in isotope distribution between SRM and seawater was real, the ratio of Sr 87 to Sr 86 was plotted (Figure 7). Each matrix was measured five times. The average ratio for the seawater sample is 0.709, slightly lower than the ratio in the SRM, but in good agreement with the number reported in the literature.<sup>12</sup>

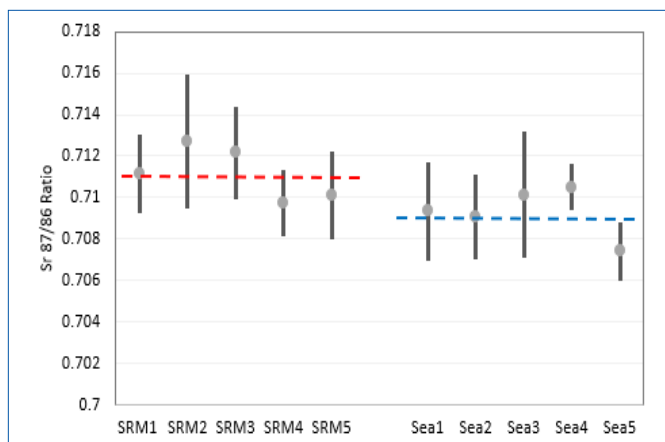


Figure 7. Comparison of measured Sr 87/86 ratios in SRM 987 and in seawater sample. Red line is the average Sr 87/86 ratio in SRM 987 and blue line in seawater for five measurements per sample. The error bar is  $\pm$  SD of 10 replicates of each measurement.

## Conclusion

The results presented in this study demonstrate the ability of the NexION 5000 Multi-Quadrupole ICP-MS to accurately measure isotope ratios and abundances. A unique way of removing spectral interferences combined with the Universal Cell's ability to enhance sensitivity and control the reaction within the cell, the instrument's stability and a very high duty cycle allow for high precision isotope ratios to be achieved without the need to use excessively long measurement times.

## References

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## Consumables Used

Component	Part Number
PFA-ST Nebulizer	N8152378
SilQ Spray Chamber	N8152539
SilQ One-Piece Torch with 2 mm Injector	N8152428
Self-Aspirating Probe, 0.3 mm	N8152513