

High throughput method for Sr extraction from variable matrix waters and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis by MC-ICP-MS

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Natural isotope tracers, such as strontium (Sr), can facilitate the tracking of brine migration caused by CO₂ injection in carbon storage sites and assist in identifying the origin of formation waters associated with oil and gas exploration. However, it might be necessary to analyze tens of samples with complex chemical compositions over a short period to identify subsurface reactions and respond to unexpected fluid movement in the host formation. These conditions require streamlined Sr separation chemistry for samples ranging from pristine groundwaters to those containing high total dissolved solids, followed by rapid measurement of isotope ratios with high analytical precision. Here we describe a method useful for the separation of Sr from energy related geofluids and the rapid measurements of Sr isotopic ratios by MC-ICP-MS. Existing vacuum-assisted Sr separation procedures were modified by using inexpensive disposable parts that also eliminate cross contamination. These improvements will allow an operator to independently prepare samples for Sr isotope analysis using fast, low cost separation procedures and commercially available components. We optimized the elution chemistry by adjusting acid normality and elution rates to provide better separation of Sr from problematic matrices (e.g. Rb, Ca, Ba, K) associated with oilfield brines and formation waters. The separation procedure is designed for high sample throughputs that are ready for immediate Sr isotope measurements by MC-ICP-MS. Precise Sr isotope results can be achieved by MC-ICP-MS with a throughput of 4 to 5 samples per hour. Fluids from a range of geologic environments analyzed by this method yielded results within the analytical uncertainty of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios previously determined by standard column separation and TIMS. This method provides a fast and effective way to use isolate Sr in a variety of geologic fluids for isotopic analysis by MC-ICP-MS.

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1 Introduction

Strontium (Sr) isotopes have long been used to track fluid–rock interaction and the origin of dissolved solids in hydrologic systems.^{1,2} The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio is a highly sensitive natural tracer useful for studying the migration of formation brines into surface and groundwater^{3–8} interaction of coal fly ash and coal mine drainage with natural waters^{9–12} chemical evolution and subsurface fluid flow in oil/natural gas reservoirs,^{3,6,13} and fluid/rock reactions related to geologic storage of carbon dioxide.¹⁴

High sample throughput and rapid analysis is necessary for Sr isotopes to serve as a useful tool for monitoring, verification,

and accounting (MVA) of CO₂ storage or for large-scale, long-term monitoring and/or assessment of fluid flow and water–rock interaction related to oil and natural gas production. Rapid Sr isotope analysis can be achieved by using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), which is an established technique for Sr isotope analysis^{15,16} and is much less time-consuming than traditional thermal ionization mass spectrometry (TIMS).¹⁷ However, as with TIMS, MC-ICP-MS requires the separation of isobaric interferences (mainly Rb) and the removal of matrix elements for accurate and precise Sr isotope measurements.^{17–19}

Strontium is routinely separated from sample matrices using Sr specific extraction resins loaded onto chromatographic columns.^{20,21} Improvements to sample throughput have come with the development of online chromatographic techniques and vacuum assisted methods.^{22–26} Online methods couple either flow injection valves or ion chromatographs directly to a MC-ICP-MS.^{23,24} While these methods are efficient in both sample processing time and acid consumption, their benefit can only be realized in the presence of a MC-ICP-MS. On the

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other hand, vacuum assisted sample purification can be carried out where the only facility requirement is a clean laminar flow hood. More importantly, these vacuum methods can provide flow rates five times faster than gravity flow methods and allow for better matrix separation due to the ability to accommodate smaller resin particle size.²⁵ However, current vacuum assisted Sr extraction methods utilize large volume resin cartridges tailored for extraction of ^{89,90}Sr from radiologically contaminated samples,^{25,26} and are not optimized for ⁸⁷Sr/⁸⁶Sr ratio measurements of natural water, rock, soil and vegetation samples in terms of cost, procedural blanks, and proper analyte concentrations for MC-ICP-MS.

Here, we report a method for high-throughput Sr separation chemistry and isotopic analysis by MC-ICP-MS optimized for purposes of MVA related to geologic CO₂ storage and for the long-term monitoring of brine migration and fluid/rock reactions related to oil/natural gas production. The motivation for the technique described in this paper is to tailor small, disposable columns for the specific task of separating Sr from water with complex matrices from geologic settings while taking advantage of the increased throughput of vacuum methods. The protocol encompasses five main goals: (i) miniaturize current vacuum assisted Sr extraction configurations to reduce the resin reservoir and reagents used for cost savings; (ii) design columns for disposability to eliminate the concern for residual contaminants; (iii) combine off-the-shelf components for ease of use; (iv) account for potential matrix effects (*e.g.* Ba, Ca, K, Fe) that could influence Sr yields and are common in formation waters and related fluids; and (v) optimize the method to provide adequate concentrations of Sr in the separate for accurate Sr isotopic analysis by MC-ICP-MS with no additional evaporation step.

2 Experimental

2.1 Materials and reagents

All sample handling was done in Class 100 vertical laminar flow hoods at the University of Pittsburgh. Ultrapure *Optima* nitric acid (HNO₃) (Fisher Chemical, USA) was used for sample acidification, resin/column cleaning, and elutions. Milli-Q water (MQW) (Millipore, USA) was used for acid dilution, cleaning, and Sr elution. Sr-Resin®²¹ (50–100 μm particle size) (Eichrom Technologies, Inc., USA) was pre-cleaned prior to use with 8 N HNO₃ and MQW.²⁷ Standard solutions were prepared from the NIST SRM 987 SrCO₃ (National Institute of Standards and Technology, MD) and EN-1 modern carbonate CaCO₃.²⁸ To assess method applicability with samples with complex matrices such as brines and produced waters from oil and gas wells, samples of produced water from natural gas wells were also analyzed. These were filtered to <0.45 μm and acidified with concentrated HNO₃.

The column assembly (Fig. 1) consisted of a 3 mL syringe reservoir (National Scientific Co., part # S7515-3) attached *via* Luer Lock fitting to a 700 μL microcolumn (MoBiTec GmbH, part # M105010S). Sr-Resin® was loaded into the microcolumn and fitted into the inner and outer tips (Eichrom Technologies, Inc., part #AC-1000-IT, OT) that were inserted into the vacuum

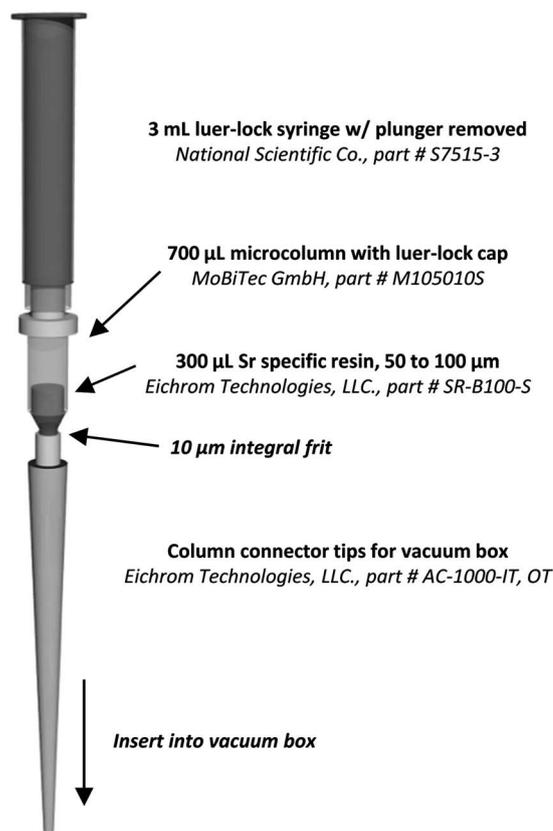


Fig. 1 Column assembly for Sr separation chemistry. Three separately purchased pieces are required, in addition to the SrResin®.

box (Eichrom Technologies, Inc., part #AC-24-BOX). All parts of the column assembly were acid cleaned before use. The polycarbonate vacuum box can accommodate 24 samples and is described in more detail elsewhere.²⁵

2.2 Chemical separation procedure

Table 1 summarizes the Sr chemical separation procedure. To provide sufficient Sr for replicate MC-ICP-MS analysis and to ensure a short washout time, the volume of liquid sample calculated to contain 2 μg of Sr was evaporated in a Teflon beaker. After evaporation, the sample was re-suspended in 250 μL of 8 N HNO₃ to be loaded on the column. While 3 N HNO₃ has been shown to adequately isolate Sr from Rb during column separation,^{21,29} 8 N HNO₃ was selected to maximize the separation of other matrix elements such as Ba that can be present at high concentrations in geologic formation waters.⁵

The columns were packed with 300 μL of Sr-Resin® suspended in MQW, and the luer-lock cap with reservoir was screwed into place. When loading the resin into the microcolumn, the vacuum must draw at near capacity (~50 Pa) to ensure that the resin forms an intact bed. Air bubbles often develop during the loading process if the resin is settled by gravity without suction, resulting in channelization and poor Sr retention. After the columns were packed, the resin was cleaned and rinsed two times, alternating between 3 mL of 8 N HNO₃ and 3 mL of MQW, and then conditioned with 5 mL of 8 N

Table 1 Sr separation procedure

Protocol	Materials
(1) Evaporate sample aliquot containing 2 µg of Sr. Add acid when dry	0.25 mL 8 N HNO ₃
(2) Attach microcolumn to connector tips and insert into the vacuum box	
(3) With vacuum drawing at maximum suction, slowly load Sr specific resin directly into the microcolumn to form a compact bed	300 µL of clean Sr-Resin®, 50–100 µm, in H ₂ O
(4) Attach luer lock cap and 3 mL reservoir to microcolumn	
(5) Supplemental resin cleaning	3 mL 8 N HNO ₃
(6) Supplemental resin cleaning	3 mL MQ H ₂ O
(7) Repeat steps 5 and 6	
(8) Resin conditioning, calibrate flow rate to ≤1 mL min ⁻¹	5 mL 8 N HNO ₃
(9) Load sample into reservoir	Sample in 0.25 mL 8 N HNO ₃
(10) Matrix rinsing. Discard eluent or save for other elements	3.5 mL 8 N HNO ₃
(11) Sr elution. Collect in 15 mL centrifuge tube	4 mL MQ H ₂ O

HNO₃. During this time, the flow rate was adjusted from maximum suction to a pressure that results in a flow rate of ≤1 mL min⁻¹ (generally <17 Pa). Faster flow rates during sample loading, matrix rinsing, and Sr elution result in variable Sr retention and poor yields. During cleaning and all subsequent elutions, the column was allowed to run dry between additions of eluent.

Once the flow rate was calibrated and the resin was conditioned, the sample in 8 N HNO₃ was carefully pipetted into the syringe reservoir. After the sample was loaded, the resin was suctioned dry, and 3.5 mL of 8 N HNO₃ was added to the reservoir to rinse the matrix from the resin. The pump was shut off and the waste containers were replaced by 15 mL acid-washed polypropylene centrifuge tubes to collect the Sr fraction. With the pump on, 4 mL of MQW was added to the reservoir and the eluent was collected in the centrifuge tube. The eluent was acidified by the addition of 0.08 mL of concentrated nitric acid to preserve the sample while obtaining

a 2% v/v solution that was ready for immediate Sr isotope analysis by MC-ICP-MS.

2.3 Matrix separation experiments

To demonstrate that the column method can achieve proper separation of Rb from Sr, a sample consisting of 2 µg Sr and 1 µg Rb was loaded onto the column and eluent fractions were collected and analyzed for Rb and Sr content. The Rb fraction was collected after addition of 4 mL of 8 N HNO₃ and the Sr fraction was recovered with the addition of 4 mL of MQW.

In addition to proper Rb separation, it is important that the Sr separation procedure can effectively isolate Sr from matrix elements common to energy related geofluids (Table 2) that are known to interfere with column yield^{20,21} or MC-ICP-MS analysis. We loaded columns with 2 µg Sr, 1 µg Rb, and a range of Ca, K, Ba, and Fe concentrations to give molar ratios similar to what is observed in fluids such as fly ash impoundment waters, acid mine drainage, formation brines, Marcellus shale produced

Table 2 Geochemistry and Sr isotope ratios of energy related fluids

Source	(M/M)					TIMS ^a		MC-ICP-MS		(TIMS) – (MC-ICP-MS)
	µS cm ⁻¹	Ca/Sr	Ba/Sr	K/Sr	Fe/Sr	⁸⁷ Sr/ ⁸⁶ Sr ^b	±2 (SE)	⁸⁷ Sr/ ⁸⁶ Sr ^b	±2 (SE)	⁸⁷ Sr/ ⁸⁶ Sr
Coal ash storage impoundment	533	267	—	53	3.2	0.712927 (ref. 12)	07	0.712942	15	–0.000015
Coal ash storage impoundment	561	301	—	45	—	0.712771 (ref. 12)	08	0.712766	09	0.000005
Abandoned natural gas well	1275	633	0.08	38	913	0.715864 (ref. 11)	10	0.715861	13	0.000003
Coal mine drainage (acidic)	1441	953	0.11	37	20	0.714503 (ref. 11)	11	0.714516	13	–0.000013
Coal mine drainage (net alkaline)	—	136	0.04	3.6	31.18	0.712056 (ref. 30)	10	0.712057	11	–0.000001
Formation brine	173 438	154	0.02	2.0	0.03	0.717022 (ref. 11)	16	0.717017	11	0.000005
Hydraulic fracturing produced water	240 625	7	5.13	0.1	0.04	0.710742 (ref. 5)	06	0.710733	14	0.000009
Hydraulic fracturing produced water	294 063	9	2.23	0.3	0.02	0.711173 (ref. 5)	09	0.711165	13	0.000008
High CO ₂ natural analog	1868	147	0.02	14	0.07	0.709566	10	0.709557	12	0.000009
High CO ₂ natural analog	1692	152	0.02	14	0.01	0.709544	07	0.709536	13	0.000008

^a Source of TIMS data indicated by reference superscript. ^b TIMS and MC-ICP-MS values are normalized to SRM 987 = 0.71024.

waters, and fluids associated with geologic analogs for carbon storage (Table 2). The Sr + Rb mixture was spiked with 442 μg Ca, 4 μg K, 4 μg Ba, and 830 μg Fe, which represent the highest element/Sr ratio in the samples from Table 2. To further test the influence of matrix elements on Sr recovery during the separation procedure, columns were loaded with a solution containing 2 μg Sr, 1 μg Rb, and varying amounts of a single matrix element, including Ca (200–75 000 μg), K (10–4000 μg), Ba (2–400 μg), and Fe (300–50 000 μg). The highest matrix element : Sr ratio of these solutions greatly exceed ratios measured in typical brine and produced water samples, in order to demonstrate the range of effectiveness of the column procedure to adequately separate Sr from a complex matrix, including brines.

2.4 Instrumentation and data handling

Elemental concentrations for calibration standards and yield tests were obtained by ICP-MS (Perkin Elmer NexION 300X) and ICP-OES (Spectroflame EOP). Strontium isotope ratios were analyzed on a Thermo Scientific Neptune Plus double-focusing MC-ICP-MS (Thermo Scientific, Bremen, Germany). Acidified solutions were introduced into a stable introduction system (SIS) spray chamber *via* a 100 $\mu\text{L min}^{-1}$ PFA-nebulizer. Instrument parameters and cup configuration for Sr isotope ratio determination are summarized in Table 3. For comparison of Sr isotope results with standard TIMS analysis of samples, we used the method described in this note to chemically separate and

Table 3 MC-ICP-MS running parameters

Thermo Scientific Neptune Plus MC-ICP-MS	
Running parameter	Typical setting
RF power	1200 W
Cooling gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	0.7 L min^{-1}
Sample gas flow rate	1.0 to 1.1 L min^{-1}
Extraction voltage	2000 V
Focus voltage	725 V
Sample cone	Standard, Ni
Skimmer cone	Standard, Ni
Spray chamber	SIS
Nebulizer	PFA-ST, 100 $\mu\text{L min}^{-1}$
Sample uptake rate	65 $\mu\text{L min}^{-1}$
Uptake mode	Free aspiration
Instrument resolution	400 (low)
Analyzer pressure mbar	1×10^{-8} mbar
Minimum sensitivity for ^{88}Sr ($10^{11} \Omega$ resistors)	16 V ppm^{-1}
Blocks	1
Cycles/block	45
Integration time	8.41 s
Baseline on peak, 2% HNO_3	60 s
Cup configuration	
Collection mode	Static
L3	$^{82}\text{Kr}^+$
L2	$^{84}\text{Sr}^+ / ^{84}\text{Kr}^+$
L1	$^{85}\text{Rb}^+$
C	$^{86}\text{Sr}^+ / ^{86}\text{Kr}^+$
H1	$^{87}\text{Sr}^+ / ^{87}\text{Rb}^+$
H2	$^{88}\text{Sr}^+$

analyze by MC-ICP-MS samples that were previously measured using a multidynamic method on a Finnigan-MAT 262 thermal ionization mass spectrometer (Table 2). Details of sample preparation and analysis of those samples are discussed elsewhere.^{5,11,12,30}

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was corrected for instrumental mass discrimination using an exponential law^{31,32} as well applying an interference correction for $^{87}\text{Rb}^+$ and $^{86}\text{Kr}^+$.³³

2.5 Chemistry procedural blank analysis

Procedural blanks for the vacuum box separation method described here were determined by evaporating solution aliquots containing 0.17 picomoles (pM) of ^{84}Sr to dryness and putting them through the complete column procedure. The resultant separated Sr solutions were dried down in Teflon vials and loaded on Re filaments for isotope dilution analysis by TIMS. The $^{84}\text{Sr}/^{88}\text{Sr}$ ratio was measured using a secondary electron multiplier to a precision of $\pm 5\%$ or better. This procedure yielded a range of sample processing Sr blank values from 40 to 320 picograms (pg), with an average of 160 pg ($n = 4$); even the highest blank measured would have a negligible effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a 2 μg Sr sample.

3 Results and discussion

3.1 Separation chemistry and matrix effects on Sr yields

Our matrix separation experiments demonstrated that the column method can achieve proper separation of Rb from Sr. Rb was $\sim 100\%$ eluted after 2 mL of 8 N HNO_3 , and an additional 2 mL of 8 N HNO_3 was added to ensure that the tail of the Rb elution curve returned to background. Fig. 2 shows the elution curves for one experiment with an 88% Sr yield. Strontium yields of $<100\%$ can occur with Sr-Resin®, and recoveries as low

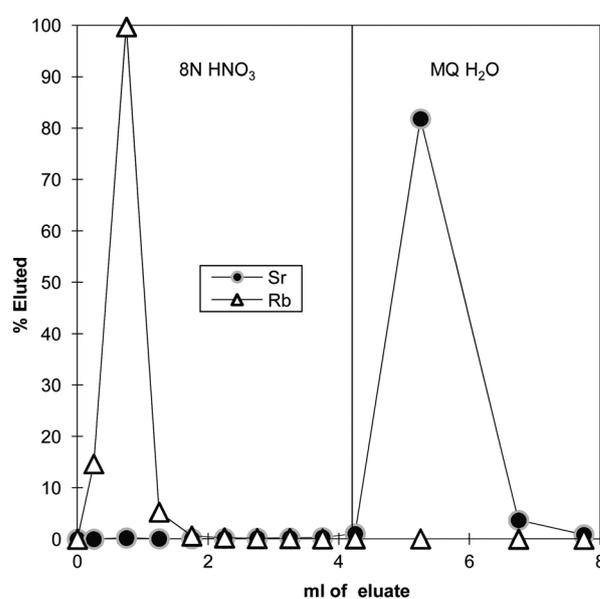


Fig. 2 Typical column elution curves showing the separation of Rb from Sr in an otherwise clean matrix.

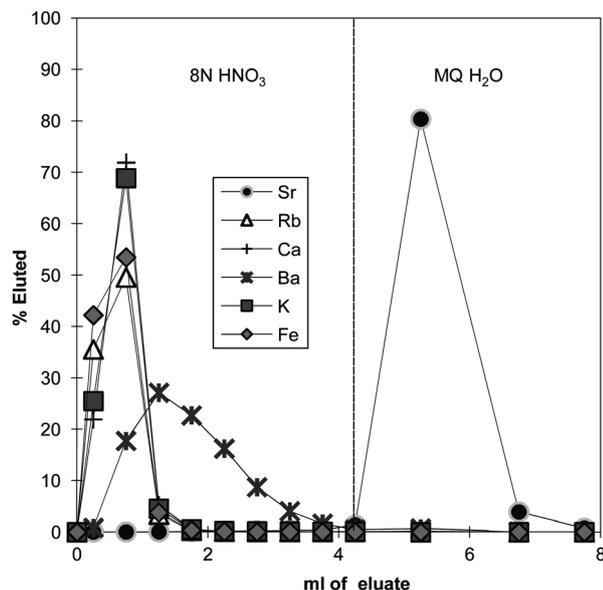


Fig. 3 Elution curves showing the separation of Rb (1 μg) and other elements from Sr (2 μg) with a complex matrix of Ca, K, Ba, and Fe (at 871, 47, 4.7 and 1147 μg , respectively).

as 70% in standard gravity-fed columns have been reported.²⁹ However, any fractionation that might occur in the column and during isotopic analysis is corrected for by using an exponential law correction. We have found that to obtain optimum signal intensity on the MC-ICP-MS, a yield of at least a 50% of Sr from the column is required for a 2 μg load.

Even with a complex matrix typically found in energy related geofluids (Table 2), Rb and Sr were separated effectively, with nearly all the Rb removed after addition of 2 mL of 8 N HNO_3 (Fig. 3). Calcium, K, and Fe behaved similarly to Rb and were rinsed from the resin with 2 mL of 8 N HNO_3 . Barium, on the other hand, had a wider elution band and was retained on the resin even when as much as 4 mL of 8 N HNO_3 was added. However, this behavior did not affect the elution of Rb or Sr. In fact, the Sr yield in the presence of Ca, K, Ba and Fe was similar (87% recovery) to the simple elution curve with just Sr + Rb (Fig. 2).

Strontium yields using this method are generally unaffected by increasing amounts of Fe and K. The result of the Fe experiment is not surprising as the binding efficiency of Fe on the resin is relatively low.²⁰ However, high concentrations of K and Ca have been shown to reduce Sr retention.²⁰ We hypothesize that the higher nitric acid concentration (8 N compared to 3 N used in Horwitz *et al.*²⁰) in our method allows for better retention of Sr in the presence of these two elements. The Sr yield does begin to decrease with excessive amounts of Ca. However, this effect is observed when the Ca : Sr exceeds 20 000, roughly 20 times the ratio observed in our samples.

An increased amount of Ba in the matrix does result in a reduction in Sr retention. The effect of Ba, however, occurs on these columns when the Ba : Sr is >100 : 1. Even though produced waters from the Marcellus Shale have high Ba content (Table 2), the Ba:Sr ratio is <6 : 1 indicating that our column method can effectively separate typical geological samples.

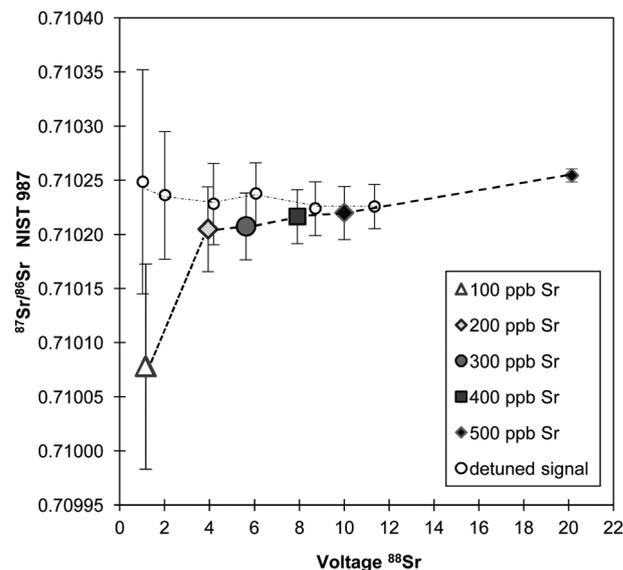


Fig. 4 Measured value of NIST SRM 987 plotted against the voltage of ^{88}Sr . Error bars indicate the in-run standard error of NIST 987 $^{87}\text{Sr}/^{86}\text{Sr}$ at various solution concentrations and instrument settings. Solution of NIST 987 with [Sr] of 100 ppb, 200 ppb, 300 ppb, 400 ppb, and 500 ppb were run using the same instrument settings. NIST 987 solutions of 400 and 500 ppb were run while detuning the instrument (lowered sample gas).

3.2 Optimizing Sr concentrations in solutions for MC-ICP-MS

Our goal in the column procedure was to obtain samples that were preserved and ready for immediate isotopic analysis, without an evaporation step. Through a set of experiments on solutions of different Sr concentrations, we determined the optimal range of concentrations in the post-column solutions that yield accurate and precise Sr isotope measurements by MC-ICP-MS. We varied the concentration of the NIST 987 Sr standard (100–500 ppb) to assess the effect of signal intensity (monitored by ^{88}Sr) on accuracy and precision (Fig. 4). When instrument parameters remained constant and only the solution concentration varied, a clear decrease in measurement precision and a deviation in the accuracy of the measurement were observed with the 100 ppb solution (run at approximately 1 V ^{88}Sr). This result is consistent with a previous study that showed similar deviation in the accuracy with low signal intensity during MC-ICP-MS analysis,³⁴ but the authors could not attribute the deviation in accuracy exclusively to low signal intensity. Surprisingly, there is little affect on accuracy when the signal is detuned to a lower voltage as opposed to when the analyte concentration is reduced (Fig. 4). This result underscores the importance of designing the column method to produce a solution with consistent and adequate Sr concentrations. Overall, these results suggest that in order to achieve accurate and precise Sr isotope ratio measurements with the Neptune MC-ICPMS, the ^{88}Sr signal should be ≥ 8 V (and <50 V with 10^{11} Ω resistors). This can be achieved with 400 to 500 ppb Sr solutions using standard operating procedures. Optimal tuning of the instrument usually produces a higher ^{88}Sr signal strength (15–30 volts). This indicates that solutions taken directly from the column procedure described in Section 2.2,

even if Sr yields are as low as 50%, have adequate concentrations of Sr to achieve good accuracy and precision.

We conducted similar tests of accuracy and precision of the NIST 987 Sr standard using various data acquisition methods (e.g. varied signal integration time, number of sampling blocks, and number of cycles per block). We found the ideal balance between precision and sample throughput occurred with signal integration times of ~ 8 seconds and 1 block of 45 measurements (or cycles per block). Table 3 describes the optimal instrument parameters for the Neptune MC-ICPMS based on our experiments.

To assess long term variability of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, we analyzed the NIST 987 Sr standard over the course of a month using the instrument parameters shown in Table 3. The average $^{87}\text{Sr}/^{86}\text{Sr}$ value ($n = 99$) is 0.710265 ± 0.000014 (2σ). These values are consistent with other measurements of NIST 987 by MC-ICP-MS.^{34,35}

3.3 Comparison of MC-ICP-MS and TIMS

We compared Sr isotopes measurements performed on by MC-ICP-MS to TIMS on a variety of samples with a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ (Table 2). All of these samples had been previously processed through gravity-fed Sr-Resin® columns and analyzed by TIMS.^{5,11,12,30} We obtained unseparated aliquots of the same samples and processed them through the entire chemical separation and MC-ICP-MS procedure described in this paper. When measured by TIMS or MC-ICP-MS, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NIST SRM 987 standard can vary significantly and therefore the measured value of this standard is routinely reported to allow inter-laboratory comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. As a result, we normalized all measured ratios to a common value of 0.710240 for the NIST SRM 987 standard by applying the offset between our standard measurements and this value to all measured ratios. To assess the agreement of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured by TIMS and MC-ICP-MS, we used the Bland-Altman test (Table 2).³⁶ The average difference of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured by TIMS and MC-ICP-MS is 1.7×10^{-6} . While this indicates that, for the ten samples that we measured, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured to be slightly higher using TIMS, this value is smaller than the average standard error of sample measurements by TIMS (8.0×10^{-6}). Therefore, we can conclude that any bias related to the average difference $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured by TIMS and MC-ICP-MS is within the error of the measurement. Furthermore, difference between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured TIMS and MC-ICP-MS is no greater than 1.8×10^{-5} . This variability is close to the long term precision (2σ) of standard measurements by TIMS (1.7×10^{-5}). These results suggest that Sr isotopic measurements with a precision and accuracy comparable to routine measurements made by TIMS are achievable using this method.

4 Conclusions

We developed a high throughput Sr separation procedure for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis by MC-ICP-MS, based in part on previously existing vacuum box methods for measurement of

$^{89,90}\text{Sr}$ by counting methods.²⁵ Our procedure is optimized for accurate and precise $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of fluids related oil/gas production and geologic storage of carbon. The chemical separation procedure can effectively isolate Sr from complex sample matrices and from solutions that have excess Ca, K, Ba, and Fe. This separation procedure uses off-the-shelf parts, and is designed with the option to be carried out without the direct need for a mass spectrometry facility. Samples can be processed in a filtered workstation and saved for subsequent MC-ICP-MS analysis. The low cost of the column and resin assembly allows use of a new column and fresh resin for each sample to minimize contamination. This paper also describes optimal parameters for MC-ICP-MS analysis to achieve routine accuracy with precision of $\pm 1.4 \times 10^{-5}$. Column processing time is approximately five times faster than traditional methods using standard columns. The results of this high throughput method demonstrate that Sr isotopes analysis could be a viable tool for MVA and long term geochemical monitoring of oil/gas reservoirs.

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