Rapid Determination of Radiostrontium in Seawater Samples

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Keywords: Strontium, ^{90}Sr, ^{89}Sr, ^{90}Y, seawater, strontium, rapid, Fukushima

Abstract

A new method for the determination of radiostrontium in seawater samples has been developed at the Savannah River National Laboratory (SRNL) that allows rapid preconcentration and separation of strontium and yttrium isotopes in seawater samples for measurement. The new SRNL method employs a novel and effective pre-concentration step that utilizes a blend of calcium phosphate with iron hydroxide to collect both strontium and yttrium rapidly from the seawater matrix with enhanced chemical yields. The pre-concentration steps, in combination with rapid Sr Resin and DGA Resin cartridge separation options using vacuum box technology, allow seawater samples up to 10 liters to be analyzed. The total $^{89}Sr + ^{90}Sr$ activity may be determined by gas flow proportional counting and recounted after ingrowth of ^{90}Y to differentiate ^{89}Sr from ^{90}Sr. Gas flow proportional counting provides a lower method detection limit than liquid scintillation or Cerenkov counting and allows simultaneous counting of samples. Simultaneous counting allows for longer count times and lower method detection limits without handling very large aliquots of seawater. Seawater samples up to 6 liters may be analyzed using Sr Resin for ^{89}Sr and ^{90}Sr with a Minimum Detectable Activity (MDA) of 1-10 mBq/L, depending on count times. Seawater samples up to 10 liters may be analyzed for ^{90}Sr using a DGA Resin method via collection and purification of ^{90}Yonly. If ^{89}Sr and other fission products are present, then ^{91}Y (beta energy 1.55 MeV, 58.5 day half-life) is also likely to be present. ^{91}Y interferes with attempts to collect ^{90}Y directly from the seawater sample without initial purification of Sr isotopes first and ^{90}Y ingrowth. The DGA Resin option can be used to determine ^{90}Sr, and if ^{91}Y is also present, an ingrowth option with using DGA Resin again to collect ^{90}Y can be performed. An MDA for ^{90}Sr of

<1 mBq/L for an 8 hour count may be obtained using 10 liter seawater sample aliquots.

Introduction

There is an increasing need to develop faster analytical methods for emergency response, including emergency environmental samples [1-2]. In light of the nuclear accident at Fukushima Nuclear Power Plant in March, 2011, there is a need for a rapid method for seawater samples which can be applied quickly with high chemical yields and effective removal of interferences. There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine radiostrontium in seawater. Vajda and Kim provide a very thorough overview of recent radiostrontium separation and analytical measurement techniques for a wide range of sample matrices. Only a limited number of seawater methods**,** however, seem to be available. Many methods seem to use older, more tedious sample preparation steps or need improvements in chemical yield. Older methods which use very large cation exchange columns and multiple precipitations, for example, have a very low sample throughput. [3]

This review also included more classical methods for water samples using fuming nitric precipitation as reported by Bojanowski et al [4]. Fuming nitric acid presents safety and handling difficulties and can be very tedious and time-consuming. An additional precipitation step to remove barium as barium chromate is also required and chemical yields for Sr can be ~50-60%.

Butkalyuk et al [5] reported an approach in which ^{90}Y was collected from 1 liter seawater samples using rare earth fluoride columns, with lead sulfide column being used to remove ^{210}Bi, followed by Cerenkov counting. The method seemed to be limited to a 1 liter sample aliquot and the presence of ^{91}Y using this approach would interfere with ^{90}Y measurements.

Grahek et al [6] reported a newer method using Sr Resin (Eichrom Technologies, Inc. Lisle, IL). For one liter seawater samples, an average Sr chemical yield of ~60% was obtained, using a carbonate precipitation and Sr Resin separation. Cerenkov counting was used to avoid problems the method had from residual calcium. The counting efficiency, however, for Cerenkov counting of ^{89}Sr is only about 38%, adversely affecting the MDA. An anion exchange method using alcohol was utilized to separate ^{90}Y with a~70-% chemical yield.

Based on this survey of the literature, a more rapid method to determine radiostrontium in seawater samples is needed. The method would need simple, effective pre-concentration steps and good chemical yields. By also utilizing simultaneous gas flow proportional counters (instead of sequential counters) and extended count times, smaller seawater aliquots (<<50 liters) can be used with much easier handling and faster sample preparation throughput for analyses. This is particularly important in a radiological emergency, but also important to reduce labor costs and analysis times for routine operations.

The recent nuclear accident at Fukushima Nuclear Power Plant in March, 2011 highlights the need to have rapid analyses for radionuclides in environmental samples in the event of a nuclear accident, or even from a terrorist such as a Radiological Dispersive Device (RDD) or Improvised Nuclear Device (IND).

Rapid radiostrontium methods for water and air filter samples have been reported by the SRNL Laboratory in the past, applicable for emergency response samples containing high levels of beta interferences, as demonstrated by good performance on NIST (National Institute of Standards and Technology) NRIP samples containing high levels of gamma isotopes to simulate emergency response samples. [7, 8] These rapid methods employ calcium phosphate precipitation for water samples and accelerated

digestion for air filter samples. Sr Resin cartridges with vacuum- assisted flow rates are used for rapid separations. Radiostrontium results were reported on water and air filter samples within ~3 hours. When very high levels of interferences are present (where decontamination >1000 is needed), a second Sr Resin purification step can be applied by adjusting the purified Sr eluent solution from the first column to ~5-6M HNO_3 and passing the solution through a second Sr Resin cartridge, followed by 8M HNO_3 rinsing, and final Sr elution using 0.05M HNO_3.

This two column approach using Sr Resin cartridges was applied to air samples received from the U. S. Embassy and other sites in Japan following the Fukushima Daiichi event in April, 2011. Gross alpha beta measurements on the filters showed the presence of high levels of beta activity for some air filter samples. It is also important to use 8M HNO_3 rinsing with Sr Resin to effectively remove ^{140}Ba, since the k' of Ba is reduced to <8 free column volumes in 8M HNO_3. Calcium phosphate precipitation, unlike time-consuming water evaporation methods, also reduces the levels of some potential sample interferences such as ^{137}Cs, ^{134}Cs and ^{131}I. [9] It is important to note that Pb isotopes, which may be present in environmental samples, are retained on Sr Resin and remain on the resin when 0.05M HNO_3 is used to elute Sr. [10]

When relatively high levels of Pb are present (higher uranium samples), it is possible for short-lived Bi isotopes to grow-in during the short elution step for Sr while Pb isotopes are retained on the resin. In that case, waiting 2 to 6 hours after elution to allow unsupported Bi isotopes to decay may be warranted.

A new method for the determination of radiostrontium in seawater samples has been developed at the Savannah River National Laboratory (SRNL, Aiken, SC, USA) that allows rapid preconcentration and separation of strontium and yttrium in seawater samples for the measurement of strontium and yttrium isotopes by gas flow proportional

126 counting. While the method can be adapted for use with liquid scintillation or Cerenkov
127 counting, gas flow proportional counting was selected to enable lower MDA and
128 simultaneous counting of samples.

129 While radiostrontium in fresh water samples can be separated quickly and easily
130 using calcium phosphate precipitation and a single 2ml Sr Resin cartridge (Eichrom
131 Technologies, Lisle, IL, USA), seawater samples cab be much more difficult. The
132 seawater matrix offers significant sample matrix challenges due to the high salt content,
133 in particular, the stable strontium (~8 mg L^{-1}), calcium (~400 mg L^{-1}) and magnesium
134 (~1300 mg L^{-1}) ion content. The stable strontium, in particular, limits the size of the
135 seawater aliquot, depending on the amount of Sr Resin used.

136 The new SRNL method employs a rapid pre-concentration step that utilizes a
137 calcium phosphate precipitation (enhanced with iron hydroxide) to collect both strontium
138 and yttrium from the seawater matrix. The iron hydroxide appears to enhance the
139 precipitation of strontium in particular, possibly due to the difficulties associated with
140 achieving excess phosphate ions given the large amounts of calcium and magnesium ions
141 present. The pre-concentration steps, in combination with a rapid Sr Resin separation
142 using vacuum box technology, allow seawater samples up to 10 liters to be analyzed for
143 $^{89,90}Sr$ using gas flow proportional counters. The preconcentration steps can be
144 performed quickly using 500 ml centrifuges tubes with no waiting on settling. Since iron
145 has no adverse impact on Sr Resin or DGA Resin in nitric acid, this enhanced
146 precipitation approach works very well. By using simultaneous gas flow proportional
147 counting and long count times, low detection limits can still be achieved with sample
148 aliquot volumes <<50 liters.

149 Several method approaches were investigated. The total $^{89}Sr + ^{90}Sr$ activity may
150 be determined by gas flow proportional counting and recounted after ingrowth of ^{90}Y to

differentiate ^{89}Sr from ^{90}Sr. Soon after a nuclear accident, the total $^{89}Sr + ^{90}Sr$ detected from a release will be primarily ^{89}Sr. It should be noted that a radiological event, such as a RDD containing ^{90}Sr nuclear waste, for example, would be a predominantly ^{90}Sr. In either case, once the source is identified through early measurements, the total $^{89}Sr + ^{90}Sr$ assay, which can be performed very quickly, has rapid screening value.

A second option was investigated. ^{90}Y can be collected immediately using Sr Resin +DGA Resin (stacked) and counted to determine if the Sr isotope activity results from ^{90}Sr (^{90}Y) by comparison with the $^{89}Sr + ^{90}Sr$ results, however, ^{91}Y is a problem for this approach. If ^{89}Sr and other fission products are present, then ^{91}Y (beta energy 1.55 MeV, 58.5 day half-life) will also typically be present. ^{91}Y interferes with the collection of ^{90}Y directly from the seawater sample without initial purification of Sr isotopes. Therefore, this stacked approach can simply be used as a confirmatory method, and the presence of ^{91}Y is a problem. Since ^{91}Y interferes, this is not recommended.

A better option seems to rapidly determine the total $^{89}Sr + ^{90}Sr$, wait 1-10 days for ^{90}Y ingrowth, and collect and purify ^{90}Y using DGA Resin or Sr Resin to determine ^{90}Y, and thus ^{89}Sr and ^{90}Sr, respectively. Sr Resin has been used to collect and separate ^{90}Y from the Sr isotopes after in growth, but in that approach it is very important that no ^{89}Sr or ^{90}Sr bleeds through the Sr Resin and is collected with the ^{90}Y. Under circumstances where ^{89}Sr is very high and ^{90}Sr is very low, the slightest bleed through of ^{89}Sr through Sr Resin can change the ^{90}Sr results significantly. This risk can be eliminated by using DGA Resin to purify ^{90}Y. In addition, the DGA Resin separation offers additional removal of high levels of beta emitters that could affect relatively low levels of ^{90}Y using this approach. While Y chemical yield may need to be determined, this may outweigh the risk of some any ^{89}Sr or ^{90}Sr bleeding through the Sr Resin into the ^{90}Y fraction.

The assay of ^{90}Sr in seawater is of interest for oceanographic reasons due to its'

relatively long half -life (28.8 years). A ^{90}Sr only method option was also developed using DGA Resin alone. DGA Resin has a very high retention of yttrium, and it can be easily purified using this resin. In addition, since strontium is not retained under strong nitric acid conditions, the amount of stable Sr in seawater is not a limiting factor.

Seawater samples up to 10 liters may be analyzed for ^{90}Sr using a DGA Resin method via collection and purification of ^{90}Y only. If ^{89}Sr and other fission products are present, then ^{91}Y (beta energy 1.55 MeV, 58.5 day half-life) is also likely to be present. ^{91}Y interferes with attempts to collect ^{90}Y directly from the seawater sample without initial purification of Sr isotopes first and ^{90}Y ingrowth. The DGA Resin option can be used to determine ^{90}Sr with excellent removal of interferences, but if ^{91}Y is present, an ingrowth option using DGA Resin again to collect ^{90}Y can be performed.

The sample preparation steps to obtain purified ^{89}Sr + ^{90}Sr and /or ^{90}Y (present initially in the sample) take <8 hours to complete, and sample aliquots count times and may be adjusted based on MDA requirements. While two count methods after ^{90}Y ingrowth can be applied, this counting method can lead to large uncertainties for the smaller radiostrontium isotope when ratios of ^{89}Sr /^{90}Sr are very large or very small. While the two count method can provide valuable information, there are times where purification of ^{90}Y after ingrowth to differentiate ^{89}Sr from ^{90}Sr offers significant advantages.

Experimental

Reagents

Sr Resin (4, 4', (5') di-t-butylcyclohexane-18-crown-6) and DGA Resin (N,N,N',N' tetraoctyldiglycolamide) cartridges were obtained from Eichrom Technologies, Inc., (Lyle, Illinois, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburgh, PA, USA). All

water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotopes ^{90}Sr were obtained from Eckert & Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate level.

Procedures

Column preparation. Sr Resin and DGA Resin was obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc.. Sr Resin columns stacked to achieve the desired resin volume (4 ml Sr Resin or 6 ml Sr Resin). Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies).

Sample Preparation. Seawater samples were obtained from Isle of Palms, South Carolina, USA. Known amounts of ^{90}Sr were pipetted into each filtered seawater sample aliquot to demonstrate method performance. ^{90}Sr was added to each set of seawater samples to test at the following levels: 148 mBq/L and 74 mBq/L respectively. The uncertainty associated with the known value of ^{90}Sr standard added was ~3 % at the 95% confidence level. The amount of stable strontium in the batches of seawater collected was determined using an inductively-coupled mass spectrometer (ICP-MS) so that stable strontium could be used as a yield tracer. A Perkin Elmer DRC-e (using standard ICP-MS mode) was used to perform the stable Sr and Y measurements. Instrument operating conditions are shown in Table 1. ^{85}Sr could have been used to determine chemical yield, but this requires a separate gamma count of the purified sample, and the simplicity of gravimetric yield determination was preferred.

Figure 1 provides a flow chart of the initial sample preparation method for seawater. It was found that handling of the seawater sample aliquots was much easier if

aliquots were limited to 2 liters of seawater. Two liter aliquots can be processed as replicates and recombined after purification to facilitate handling of larger aliquots. Up to ~6 liters of seawater can be processed in this manner using Sr Resin for ^{89}Sr, ^{90}Sr analysis and up to 10 liters to determine ^{90}Sr (^{90}Y) using DGA Resin, with a single 2ml DGA cartridge for each 2 L replicate.

For a 2 liter seawater aliquot, 200 mg of Fe^{3+} as iron nitrate, 1 mg stable yttrium (if ^{90}Y was determined immediately using DGA Resin) and 25 ml 3.2M ammonium hydrogen phosphate were added. The pH was adjusted to ~ 10 by adding 30 ml 14.5 M ammonium hydroxide and stirring to mix well.

The samples were centrifuged using 500 ml centrifuge tubes, splitting the samples between two 500 ml tubes and centrifuging for ~6 minutes @3400 rpm. The supernatant was discarded. The rest of the 2 liter seawater aliquot was centrifuged using the same two 500 ml tubes. The calcium phosphate/iron hydroxide mixed precipitate was redissolved in a total of 25 ml 15.8M HNO_3 (15 ml, then 10 ml volumes), transferring dissolved solids from one of the replicate tubes to the next tube and then into a 600 ml glass beaker. The tubes were rinsed with a total of 8 ml 2M aluminum nitrate and ~5 ml 3M HNO_3, which was used to rinse the replicate centrifuge tubes and then transferred into the 600 ml glass beaker. Each dissolved sample precipitate was evaporated to a volume of ~25 ml on a hot plate and transferred to a 50 ml centrifuge tube. The glass beaker was rinsed with two 5 ml volumes of 1M HNO_3, which were added to the 50 ml tube. Each sample tube was warmed slightly in a hot block and centrifuged ~ 5 minutes to remove any residual solids. If any residual solids remained, these were rinsed with ~3 to 5 ml 8M HNO_3, centrifuged to remove the solids and this rinse was added to the load solution.

It should be noted that smaller volume seawater aliquots (200 ml, 500 ml, etc.) can be processed in the same way even more quickly, if a higher MDA is still sufficient to meet measurement quality objectives.

Column separation. Figure 2 provides a flow chart of the rapid column separation method using two 2 ml Sr cartridges (~1.4 g Sr Resin total) for a 2 liter sample aliquot. Sr Resin columns were conditioned with 10 ml 8M HNO_3 .The sample solution was loaded onto the Sr Resin column at approximately ~1 drop per second. After the sample was loaded, a tube rinse of ~ 5 mL 8M HNO_3 was transferred to the Sr Resin column and allowed to pass through the resin at ~2 drops per second. The following column rinses were performed at ~2-3 drops per second: 15 ml 8M HNO_3, 10 ml 3M HNO_3 - 0.05M oxalic acid, and 8 ml 8M HNO_3. Sr was eluted from the resin with 20 ml 0.05M HNO_3 at ~1 drop per second. It is possible to combine purified eluents on a single planchet to increase the sample aliquot and lower the MDA.

This solution was transferred to preweighed planchets and evaporated on a hot plate with medium heat to dryness. Two milliliters 0.05M HNO_3 were used to rinse each tube and then was transferred to each planchet, and evaporated to dryness on a hot plate. The dried planchets were allowed to cool and then were weighed to determine gravimetric carrier recovery. The planchets were counted by simultaneous gas flow proportional counting (Tennelec LB 4100) for 120 minutes. Longer count times to significantly lower MDA can be performed. The detectors were calibrated using NIST Traceable $^{90}Sr/^{90}Y$ sources matching the sample geometry. Detector backgrounds are determined and subtracted from the sample counts. A mass attenuation correction factor was determined experimentally using prepared mounts containing $^{90}Sr/^{90}Y$ (>167 Bq) and a nominal amount of Sr carrier.

Figure 3 shows the DGA Resin only option using a single 2 ml DGA Resin

cartridge for each 2 liter volume of seawater processed. Ca, Sr, and Pb isotopes are removed during the 8M HNO_3 rinse step. Bi isotopes are also removed using DGA Resin, as Bi isotopes are retained on the resin during the nitric acid rinsese and stay on the resin during the 0.25M HCl elution of yttrium. U and Th isotopes are removed using 3M HNO_3-0.25M HF rinse steps, and lighter rare earths such as La and Ce are removed with the 1.75M HCl rinsing. [11] The DGA Resin option can be used to determine ^{90}Sr with excellent removal of interferences, but if ^{91}Y is present, an ingrowth option using DGA Resin again to collect ^{90}Y can be performed.

Apparatus

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

Planchets were annealed for ~4 hours in a furnace at 550 ˚C prior to use. This provides chemical resistance to the planchets so that iron oxide does not form during evaporation of the nitric acid, which would cause error in the gravimetric weights.

Results and Discussion

Table 1 shows the measured values for ^{90}Sr in a set of eleven 1 liter seawater samples spiked at the 148 mBq L^{-1} level. The average ^{90}Sr result was 149.8 mBq L^{-1} ± 11 mBq (1SD, standard deviation) with an average bias of 1.2%. The average stable Sr carrier recovery was 88.8% (1 SD =5.3%), indicating very good chemical yield. The stable Sr level in the seawater used was determined by ICP-MS to be 7.66 mg Sr L^{-1}. The uncertainty in this ICP-MS assay is ~1.5% at 1 SD.

Table 2 shows the measured values for ^{90}Sr in a set of eleven 1 liter seawater samples spiked at the 148 mBq L^{-1} level. The average ^{90}Sr result was 152.6 mBq L^{-1} ± 3.1 mBq L^{-}

^{1} (1 SD). The average stable Y carrier recovery was 95.0% (1 SD =1.6%) with an average bias of 3.1%. The Y yield measurements were very consistent and rapid using the ICP-MS in a single element assay mode.

Table 3 shows the measured values for ^{90}Sr in a set of four 2 liter seawater samples spiked at the 148 mBq L^{-1} level. The average ^{90}Sr result was 154.2 mBq L^{-1} ± 4.2 mBq L^{-1} (1 SD), with an average bias of 4.2%. The stable Sr level in the seawater used was determined by ICP-MS to be 7.70 mg Sr L^{-1}**.** The uncertainty in this ICP-MS assay is ~1.5% at 1 SD.

The average stable Sr carrier recovery was 81.9% (1 SD =4.1%), indicating very good chemical yield, despite increasing the sample aliquot to 2 liters.

Table 4 shows the measured values for ^{90}Sr in a set of four 2 liter seawater samples spiked at the 148 mBq L^{-1} level. The average ^{90}Sr result was 157.8 mBq L^{-1} ± 6.9 mBq L^{-1} (1 SD), with an average bias of 6.6%. The average stable Y carrier recovery was 89.1% (1 SD =2.8%), indicating very good chemical yield, despite increasing the sample aliquot to 2 liters.

Table 5 shows the measured values for ^{90}Sr in a set of five seawater samples spiked at 740 and 74 mBq L^{-1}, respectively. The average bias in the ^{90}Sr results was only -2.0% The average stable Y carrier recovery was 91.9% (1 SD =2.5%). The Y carrier added was split between the two liter replicate aliquots and recombined in the final purified solution for counting so that up to 10L of seawater could be processed.

The tests indicate that radiostrontium can be measured very well using Sr Resin, and that ^{90}Sr can be analyzed using DGA Resin only (a single 2 ml cartridge per 2 liter sample replicate). The sample pre-concentration steps to remove the seawater matrix worked very well. Chemical yields were very good and no column flow issues were observed. The use of iron hydroxide along with calcium phosphate to enhance the precipitation was

effective, and tests demonstrate that up to 10 liters of seawater can be analyzed by combining purified replicates, working with 2 liter aliquots. When calcium phosphate alone was tested Sr yields were only 60-70%.

Due to the Sr capacity limitations of Sr Resin and the large amounts of stable Sr in seawater, the two liter samples required 6 ml of Sr Resin to separate ^{89}Sr and ^{90}Sr. Three 2 liter aliquots of seawater can be processed using 6 ml of Sr Resin be combining purified replicates. Larger aliquots would require and inordinate amount of Sr Resin to perform the separation.

The MDA (Minimum Detectable Activity) for the ^{90}Sr using this method with gas flow proportional counting were calculated according to equations prescribed by Currie: [12]

$$MDA = [3+4.65\sqrt{B}]/ (CT*R*V*Eff*0.060)$$

Where B = Total Background counts, = BKG (rate) * BKG Count time

CT = sample count time (min)

R = Chemical Recovery

V = Sample aliquot (g)

EFF = Detector Efficiency

0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

The MDA for the results can be adjusted as needed, depending on the sample aliquot and count time. For a 2 L sample aliquot, the method MDA for ^{89}Sr and /or ^{90}Sr with a 120 minute count time is 9.1 mBq L^{-1}. For a 6 L sample aliquot, the method MDA for ^{89}Sr and /or ^{90}Sr with a 1000 minute count time is 1 mBq L^{-1}. For a 10 L sample

aliquot (DGA only option), the method MDA for ^{90}Sr with a 1000 minute count time is 0.61 mBq L^{-1}.

The method can be applied to smaller seawater sample aliquots (even more rapidly) if slightly higher MDA levels are adequate for emergency response measurements, depending on the measurement quality objectives following an incident. The option to perform a second Sr Resin separation when a decontamination factor of greater than ~1000 is needed to ensure sufficient removal of high levels of beta interferences is also a recommended.

The combination of Sr Resin to assay total ^{89}Sr + ^{90}Sr, followed by DGA Resin to collect and purify ^{90}Y is a powerful combination and avoids any breakthrough of high levels of ^{89}Sr into the ^{90}Y fraction when high levels of ^{89}Sr are present. The ingrowth time for ^{90}Y may only need to be a 3-5 days, depending on levels present and MDA needs to facilitate more rapid results.

Conclusions

A new method to determine ^{89}Sr and ^{90}Sr has been developed that allows the rapid separation of radiostrontium in seawater samples with high chemical yields and effective removal of interferences. The simple matrix removal steps and rapid column separation steps resulted in reliable measurements of radiostrontium isotopes at very low levels from 1 to 10 liter sample aliquots. Simultaneous gas flow proportional counters with longer count times can be used to reduce the amount of seawater samples processed.

Acknowledgment

This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500.

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Table Captions

Table 1 Operating Conditions for Perkin Elmer DRC-e

Table 2 ^{90}Sr in Seawater Results using Sr Resin (1 liter samples)

Table 3 ^{90}Sr in Seawater Results using DGA Resin (^{90}Y-1 liter samples)

Table 4 ^{90}Sr in Seawater Results using Sr Resin (2 liter samples)

Table 5 ^{90}Sr in Seawater Results using DGA Resin (^{90}Y-2 liter samples)

Table 6 ^{90}Sr in Seawater Results using DGA Resin Only (^{90}Y)

Table 1 Operating Conditions for Perkin Elmer DRC-e

Plasma Conditions	
RF Power	1400 W
Torch Depth	5.5 mm
Plasma Gas	15 L/min
Carrier Gas	1 L/min
Nebulizer Gas	0.98 L/min
Sample Pump	5 rps
Ion Lens/Quadrupole	
E1 Lens Voltage	6.25 V
E1 Lens Slope	0.0165
E1 Lens Intercept	4.413
Cell Path Voltage	-12 CPV
Cell Rod Offset	-17 V
Q-pole Rod Offset	-4 V
Detector	
Discriminator	17 V
Analog HV	-1550 V
Pulse HV	900 V
Typical Tune	
Counts	>300,000 cps In-115 at 10 ug/L
RSD%	< 5%
Oxide 156/140	< 5%
Background	< 10 cps at Mass 220; <10 cps at Mass 8.5 (Vacant mass for noise detection only)
Resolution	0.60 - 0.80 amu at 10% peak height
Data Acquisition	
Integration	1000 msec Dwell time 50 msec
Replicates	3 with 20 sweeps/reading

Table 2 ^{90}Sr in Seawater Results using Sr Resin (1 liter samples)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	94.1	4.0	148.0	150.6	1.8
2	91.4	4.0	148.0	138.5	-6.4
3	86.5	4.0	148.0	146.4	-1.1
4	96.2	4.0	148.0	127.0	-14.2
5	83.3	4.0	148.0	146.4	-1.1
6	86.2	4.0	148.0	153.7	3.9
7	82.9	4.0	148.0	161.1	8.9
8	90.5	4.0	148.0	159.9	8.0
9	89.4	4.0	148.0	134.2	-9.3
10	87.3	4.0	148.0	170.5	15.2
11	88.9	4.0	148.0	159.8	8.0
Avg	88.8			149.8	1.2
SD	5.3			11.0	
% RSD	5.9			7.3	
Seawater assay by ICP-MS		7.66 mg Sr/L			
I liter sample aliquot					
2 hour count time					

Table 3 ^{90}Sr in Seawater Results using DGA Resin (^{90}Y -1 liter samples)

Sample ID	Y carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	93.8	4.0	148	160.0	8.1
2	95.9	4.0	148	166.4	12.4
3	94.0	4.0	148	153.9	4.0
4	96.5	4.0	148	155.1	4.8
5	92.1	4.0	148	149.4	0.9
6	96.0	4.0	148	157.7	6.6
7	96.0	4.0	148	142.5	-3.7
8	95.2	4.0	148	150.0	1.4
9	95.0	4.0	148	153.2	3.5
10	96.3	4.0	148	139.5	-5.7
11	94.1	4.0	148	151.1	2.1
Avg	95.0			152.6	3.1
SD	1.6			7.6	
% RSD	1.7			5.0	
	Y carrier by ICP-MS				
	I liter sample aliquot				
	2 hour count time				

Table 4 ^{90}Sr in Seawater Results using Sr Resin (2 liter samples)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	80.6	4.0	148	154.8	4.6
2	84.9	4.0	148	151.1	2.1
3	85.5	4.0	148	150.0	1.4
4	76.7	4.0	148	160.7	8.6
Avg	81.9			154.2	4.16
SD	4.1			4.8	
% RSD	5.0			3.1	
Seawater assay by ICP-MS		7.70 mg Sr/L			
2 liter sample aliquot					
2 hour count time					

Table 5 ^{90}Sr in Seawater Results using DGA Resin (^{90}Y-2 liter samples)

Sample ID	Y carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	87.0	4.0	148	148.1	0.1
2	93.2	4.0	148	157.9	6.7
3	88.0	4.0	148	163.8	10.7
4	88.0	4.0	148	161.5	9.1
Avg	89.1			157.8	6.6
SD	2.8			6.9	
% RSD	3.2			4.4	
	Y carrier by ICP-MS				
	2 liter sample aliquot				
	2 hour count time				

Table 6 ^{90}Sr in Seawater Results using DGA Resin Only (^{90}Y)

Sample ID	Smp. Vol. (L)	Y carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	4	91.6	20.0	740	725	-2.0
2	4	88.7	2.0	74	74	0.0
3	10	94.3	2.0	74	74	0.0
4	10	94.5	2.0	74	66	-10.8
5	10	90.2	2.0	74	76	2.7
Avg		91.9				-2.0
SD		2.5				
% RSD		2.8				
	Y carrier by ICP-MS					
	2 hour count time					

Figure 1 Rapid Sample Preparation Method for $^{89}Sr + ^{90}Sr$ in Seawater

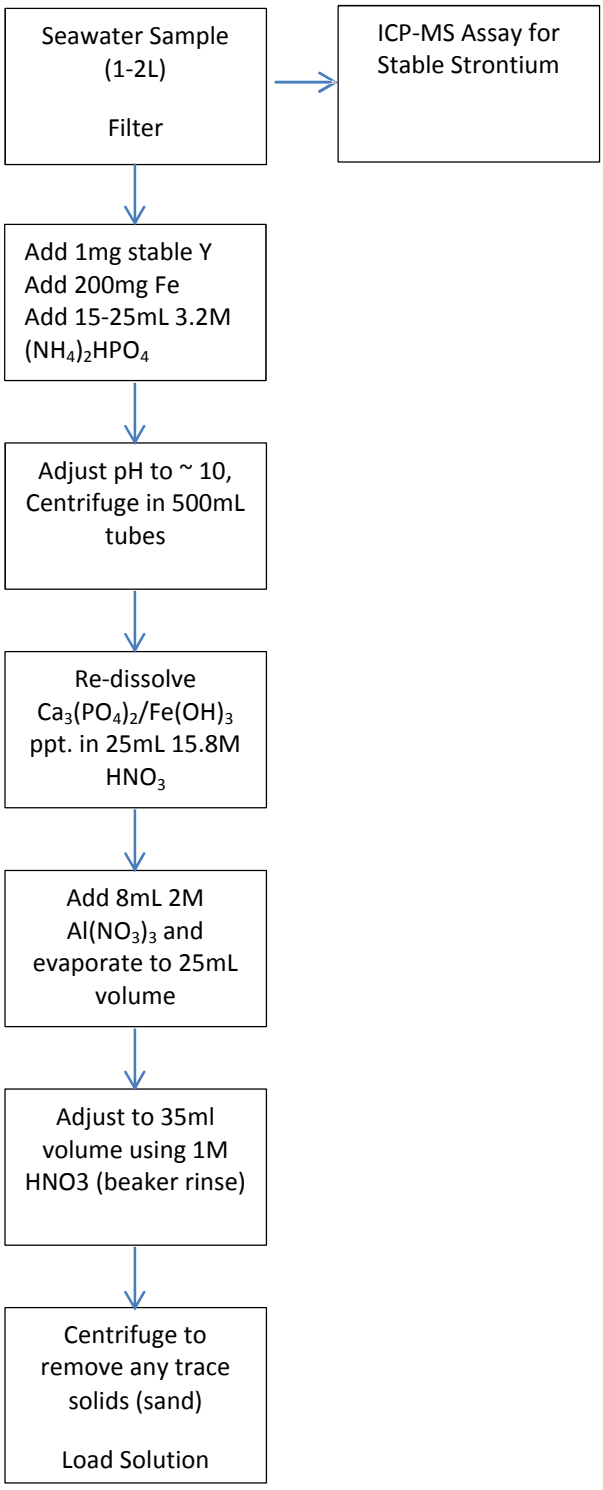

Figure 2 Rapid Separation Method for ^{89}Sr + ^{90}Sr in Seawater (^{90}Y ingrowth option)

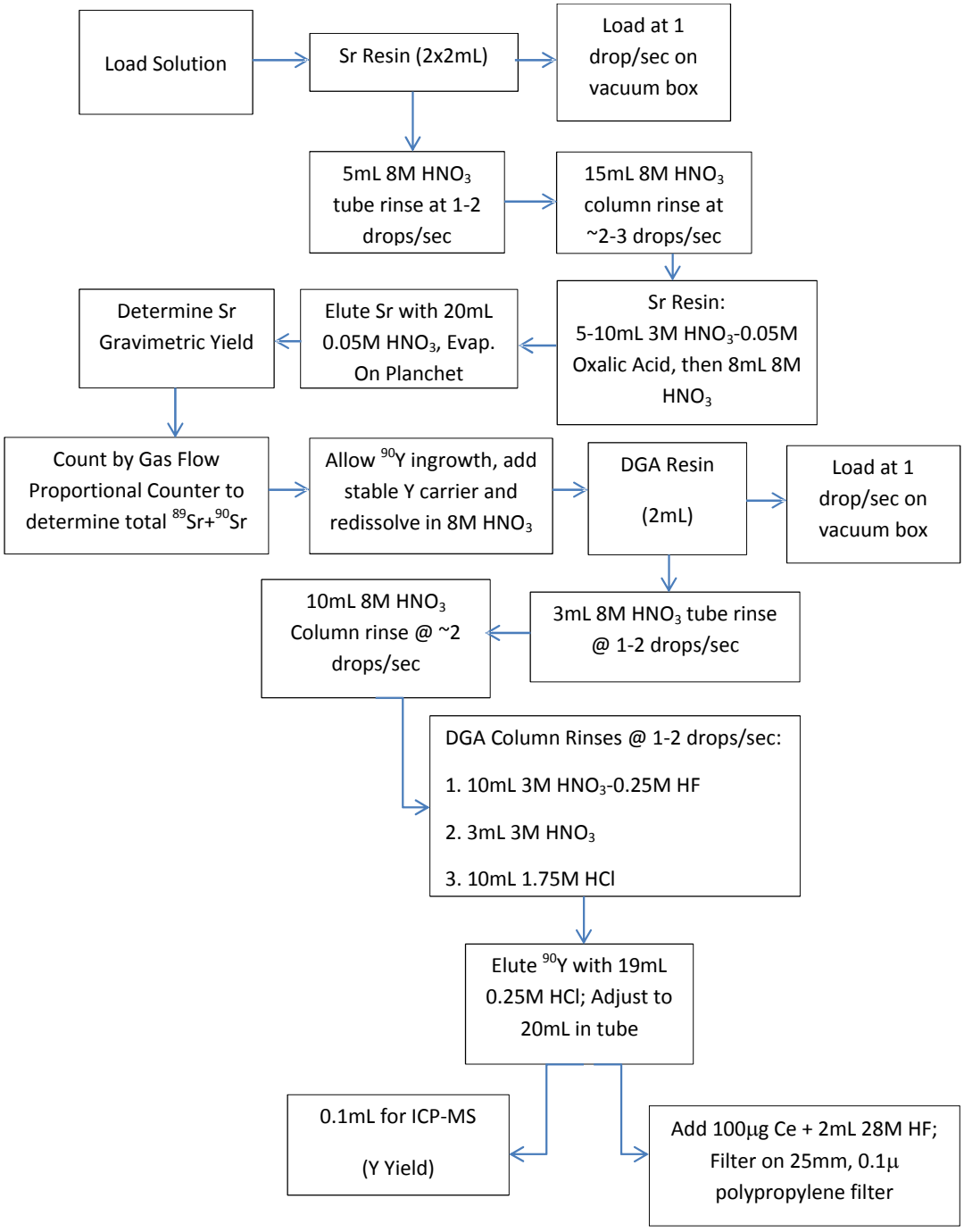

Figure 3 Rapid Separation Method for ^{90}Sr in Seawater (DGA Resin only)