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Rapid Method to Determine Sr-89/90 in Large Concrete Samples

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Abstract

A new rapid method has been developed that provides high quality low-level measurements of ^{89,90}Sr in concrete samples with an MDA (Minimum Detectable Activity) of <1 mBq g⁻¹. The new method is fast, meets new decommissioning regulatory limits and is robust even if refractory particles are present. The method utilizes a rapid fusion to ensure total dissolution of samples and rapid preconcentration and separation of ^{89,90}Sr from 5-10 g concrete samples. When, the ⁸⁹Sr/⁹⁰Sr ratio is high, Sr can be isolated from up to 5g concrete samples, total ^{89/90}Sr measured, and then ⁹⁰Sr determined via ⁹⁰Y separated after a period of ingrowth. Another approach allows the immediate determination of ⁹⁰Sr in 10 g concrete aliquots without waiting for ⁹⁰Y ingrowth, in instances where the shorter lived ⁸⁹Sr is unlikely to be encountered.

Introduction

The Savannah River Environmental Laboratory has developed many new rapid methods to facilitate readiness for emergency response to radiological events. Several of these methods were utilized following the nuclear accident at Fukushima Daiichi to provide timely analytical support to the government of Japan and the US Department of Energy. [1, 2, 3] There is a need for rapid, traceable methods to support decommissioning of older nuclear facilities, especially in Europe. A significant reduction in very high decommissioning costs by the development and implementation of new measurement techniques is necessary. [4] Many older analytical methods are tedious and time-consuming, driving up overall facility

decommissioning costs. The assay of radiostrontium ($^{89,90}\text{Sr}$) in decommissioning materials is an important radiochemical measurement for safe disposal of waste. Rapid, efficient analysis of building materials such as concrete for $^{89,90}\text{Sr}$ is therefore very important. For older nuclear facilities, where the short lived ^{89}Sr ($t_{1/2} = 50.55$ days) is unlikely to be found, analysis for only the longer lived ^{90}Sr isotope ($T_{1/2} = 28.9$ years) may be needed. Robust analytical methods with low detection limits are essential. The current disposal limit for ^{90}Sr in soil residues in Germany is 2 mBq g^{-1} , while the limit for ^{90}Sr in concrete residues is 600 mBq g^{-1} . [5] Regulatory limits tend to be lowered over time, and the limit for concrete may be lowered to 2 mBq g^{-1} as well.

There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine radiostrontium in environmental samples. Vajda and Kim provide a very good overview of recent radiostrontium separation and analytical measurement techniques. [6] This review also included more classical methods using fuming nitric precipitation, as reported by Bojanowski et al [7]. Fuming nitric acid presents handling difficulties and can be very tedious and time-consuming. Wang et al. [8] reported a sequential method to determine actinides and strontium in soil samples. A large number of tedious, sequential steps were required in this method.

Acid digestion of soil and concrete samples often leaves undigested residue and may not effectively digest refractory particles. Jurečič et al. studied several soil decomposition techniques and found that alkaline fusion was more effective for the complete digestion of soils than other methods tested. Other techniques, such as conventional wet dissolution with mixtures of HNO_3 , HClO_4 and HF and microwave dissolution using HNO_3 and HF were less effective, with analyte losses of 35-60%. Interestingly, this work found that conventional hot plate acid digestion was more effective than more rapid microwave methods for the digestion of soil samples. The hot plate acid digestion methods, which still had undigested residues, took two days to complete. Only the alkaline fusion digested the samples fully. [9]

New rapid fusion methods that allow rapid assay of actinides and $^{89,90}\text{Sr}$ in many different building material matrices have been recently reported by this laboratory. [10, 11] These methods combine rapid, rugged sample digestion and preconcentration techniques with rapid, innovative column purification methods to analyze building materials and other environmental samples quickly. The rapid fusion technology, which offers speed, simplicity and ruggedness, has also recently been applied to larger soil and concrete sample aliquots for the assay of actinides. The sodium hydroxide fusion and preconcentration steps used in our laboratory take much less time than conventional acid digestion steps, which often require

evaporation of large acid volumes. Faster methods in the laboratory are important not only for emergencies but to reduce analytical labor costs and improve overall operational efficiency.

The regulatory limits for ^{90}Sr in concrete from decommissioning activities can be very low, and 5-10 g aliquots of concrete must typically be digested to achieve detection limits that can meet these low regulatory requirements. Concrete contains large amounts of calcium and silicates, therefore, the analysis of larger sample aliquots can be quite challenging. This new work attempts to apply digestion and separation principles successfully used to measure actinide isotopes in larger concrete samples to the assay of ^{89}Sr and ^{90}Sr .

As a result of this effort to apply new dissolution strategies, a new rapid method for the determination of $^{89,90}\text{Sr}$ in concrete samples has been developed that provides traceable, high quality low-level measurements. The new method has an MDA (Minimum Detectable Activity) of $<1 \text{ mBq g}^{-1}$, with appropriate count times. The new method utilizes a rapid fusion to ensure total dissolution and rapid preconcentration of $^{89,90}\text{Sr}$ from 5-10 g concrete samples. The new method has several options. One preparation method collects and purifies $^{89}\text{Sr} + ^{90}\text{Sr}$ from 5 g concrete aliquots for the analysis of ^{89}Sr and ^{90}Sr , respectively. This method allows a rapid, immediate assay of the total $^{89}\text{Sr} + ^{90}\text{Sr}$. A second count following ^{90}Y ingrowth (typically over 3-10 days) can be employed to determine ^{89}Sr and ^{90}Sr , respectively.

The traditional “two count” method typically has large uncertainties for the ^{90}Sr when the ^{89}Sr activity is very high relative to the activity of ^{90}Sr , since the change in the overall count rate is small during ^{90}Y ingrowth. When the $^{89}\text{Sr}/^{90}\text{Sr}$ ratio is high, another option is to collect and purify ^{90}Y from the initial planchet containing the purified $^{89,90}\text{Sr}$ after ingrowth. A high $^{89}\text{Sr}/^{90}\text{Sr}$ ratio will likely be encountered following a radiological event with a radiological dispersive device (RDD) involving fresh fission products, or in a nuclear power plant accident like at Chernobyl or at Fukushima Daiichi. The collection and measurement of ^{90}Y after purification of $^{89}\text{Sr} + ^{90}\text{Sr}$ may also be of value at low activity levels as well, as it allows the ^{90}Sr to be determined from a single measurement of ^{90}Y , instead of calculating ^{89}Sr and ^{90}Sr from two separate measurements which may will have large counting uncertainties at background levels.

For older facilities, only a ^{90}Sr assay may be needed during decommissioning activities. In this case, the ^{90}Sr daughter, ^{90}Y , is assumed to be in secular equilibrium with ^{90}Sr , a reasonable assumption in a solid matrix like concrete. Ten gram concrete sample aliquots can then be assayed immediately after total dissolution of the concrete and rigorous purification of the ^{90}Y , eliminating the time normally needed for ingrowth of ^{90}Y following isolation of $^{89,90}\text{Sr}$. Gas flow proportional counting was used to count the samples

because of its low background and low MDA, but liquid scintillation or Cerenkov counting could also be used if desired. This new sample preparation method takes < 6 hours. Simultaneous drawer type gas flow proportional counters were used to facilitate longer count times and high sample throughput.

This method offers much lower detection limits than the direct measurement of ^{90}Sr using inductively-coupled plasma mass spectrometry (ICP-MS) methods. The measurement of ^{90}Sr by ICP-MS also does not require waiting on ^{90}Y ingrowth. However, ICP-MS methods require thorough removal of the isobaric interference ^{90}Zr , and there is typically a very low number of ^{90}Sr atoms present in environmental samples for mass measurement due to the relatively short half-life of ^{90}Sr ($T_{1/2}=28.9$ yr). This results in an MDA that is unacceptable for low level environmental assay of ^{90}Sr . For example, an MDA of ~ 1.5 Bq L $^{-1}$ has been reported for ^{90}Sr in water. [12]

Experimental

Reagents

The extraction chromatography resins employed in this work are DGA Resin (N,N,N',N'-tetraoctyldiglycolamide), and Sr Resin (4, 4', (5') di-t-butylcyclohexane-18-crown-6), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2TM water purification system. All other materials were ACS (American Chemical Society) reagent grade. Sr-90 was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2.96 Bq mL $^{-1}$.

Procedures

Column preparation. Sr Resin and DGA Resin were obtained as 2 mL cartridges. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). The small particle size coated support, with enhanced surface area, improves column separation efficiencies and removal of interferences. Flow rates of $\sim 1\text{-}2$ mL min $^{-1}$ were typically used for this work, slower on sample loading and final elution steps, faster for the rinses used to remove sample matrix interferences. To facilitate enhanced removal of interferences, column reservoirs and connector tips in the lid were changed after sample loading and prior to final elution of analytes.

Sample Preparation. Figure 1 shows the sample preparation flowchart for the measurement of $^{89,90}\text{Sr}$ in 5 g concrete samples. Concrete samples were pulverized, homogenized and passed through a 20 mesh sieve prior to sampling so that representative samples could be taken. For testing purposes, ^{90}Sr was

added to concrete samples, but the method can also be tailored to measure ^{89}Sr as well. MAPEP 32 soil was added to test the method to assess the removal of potentially interfering radionuclides, such as ^{137}Cs . The MAPEP soil samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA.

Rapid Method for Sr-89,90 in 5 g Concrete Aliquots Stable strontium carrier (6.1 mg) was added to each concrete aliquot in 250 mL zirconium crucibles as a carrier to determine chemical yield. After drying the crucibles briefly on a hotplate, 30 grams of NaOH pellets were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600°C for ~30 minutes. The crucibles were removed from the furnace, cooled for about 10 minutes, and transferred to a hot plate. Water was added and the crucibles were heated on a hot plate to dissolve the fusion cake. The dissolved fusion cake was transferred to 500 mL centrifuge tubes, and residual solids were removed from the crucibles by adding water and heating the crucibles on the hot plate as needed. A final rinse of 10 mL 3M HNO_3 was added to each crucible, and heated until very hot on the hot plate to ensure complete removal of strontium from the crucible surface.

Fifty milligrams of Fe (added as $\text{Fe}(\text{NO}_3)_3$) were added to each 500 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 450 mL with water and the tubes were cooled in an ice bath to room temperature. For the processing of batches where reagent blank and laboratory control samples (LCS) are also included (no concrete), approximately 200 mg Ca may be added to simulate the high Ca matrix for the blank and LCS samples. Eight and one-half milliliters of 3.2M ammonium hydrogen phosphate were added to each tube. Tubes were capped, mixed well and cooled in an ice bath for 10 minutes. Addition of phosphate improves strontium recovery during the initial precipitation step, where Sr precipitation using iron hydroxide alone tends to yield low Sr recoveries. The tubes were centrifuged at 3500 rpm for ~6 minutes, and the supernate was discarded. The precipitates were partially dissolved by adding 200 mL of 1.5 M HCl and 50 mL of 0.01M HCl to each tube, mixing well with each addition. Fifteen to twenty milliliters of 28M HF were added to each tube, and the samples were mixed well, dissolving any remaining Fe hydroxide solids and forming a CaF_2 precipitate which carries the strontium. The tubes were allowed to stand for ~15 minutes and centrifuged for ~6 minutes at 3500 rpm. The CaF_2 precipitation step effectively removes almost all of the Fe, as well as silicates that can adversely affect column flow by forming gel-like solids. It was found that the calcium fluoride precipitate was difficult to redissolve in a column load solution if too much 28M HF was

added, apparently due to formation of a hard fluorosilicate crystal structure when contacted by the nitric acid. By reducing the volume of 28M HF added from 30-40 mL to 15-20 mL, this problem was avoided and the precipitates dissolved relatively quickly in the nitric acid load solution.

The supernate was discarded, and the precipitate containing the strontium was dissolved in 7 mL of 3M HNO₃-0.25M H₃BO₃, mixed, and transferred to 50 mL tubes. The 500 mL tubes were rinsed with 7 mL of 15.8 M HNO₃, 7 mL of 2 M Al(NO₃)₃ and 7 mL 8 M HNO₃, respectively, transferring the rinses to the 50 mL centrifuge tubes. The goal was to have a high nitric acid load solution (8-9M HNO₃), which is ideal for retaining ^{89,90}Sr on Sr Resin, while eluting key interferences. [13] The samples were mixed using a vortex stirrer and heated 2 to 5 minutes in a hot block heater at 105°C. The 50 mL tubes were centrifuged to test for any traces of solid particulates, which were removed if needed. Typically, the sample load solutions were very clear.

Total ⁸⁹Sr + ⁹⁰Sr was separated using a method similar to what was published for ⁹⁰Sr in large soil samples. [16] The sample load solutions were loaded onto 4 mL Sr Resin (2 x 2 mL cartridges) at approximately 1 drop per second, with applied vacuum. After the sample was loaded, a tube rinse of ~ 5 mL 8M HNO₃ was transferred to the Sr Resin column and allowed to pass through the resin at ~1-2 drops per second. The following column rinses were performed at ~2 drops per second: 20 mL 8M HNO₃ (removes Ca, Ba, Cs), 5 mL 3M HNO₃ - 0.05M oxalic acid (removes tetravalent metal ions), and 10 mL 8M HNO₃. After the final rinse, the column reservoirs and connector tips were changed out to maximize decontamination from potential interferences.

Sr was eluted from the resin with 18 mL 0.05M HNO₃ at ~1 drop per second. This eluent solution was transferred to preweighed planchets and evaporated on a hot plate with consistent, medium heat to dryness. Two milliliters 0.05M HNO₃, used to rinse each tube, was transferred to each planchet, and evaporated to dryness on a hot plate. After dryness was reached, the planchets were heated ~10-15 minutes on the hot plate. The dried planchets were allowed to cool and weighed to determine gravimetric carrier recovery. The planchets were counted by simultaneous gas flow proportional counting for 60 minutes. It is important that direct stable strontium carrier standardization on planchets (7-10 replicates) be heated on the hot plate at the same temperature for the same time as the samples to minimize gravimetric yield errors. Strontium carrier yields may also be measured using instrumental techniques, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ICP-MS.

Sr Resin also collects Pb isotopes while Bi daughter isotopes are eluted during the column rinse steps. During the short elution step, however, Bi daughter isotopes may grow in and be eluted with the ^{89}Sr and ^{90}Sr . This will typically have little impact if relatively high levels of ^{89}Sr and ^{90}Sr are present in the samples, however, waiting 2 to 6 hours to allow unsupported Bi isotopes to decay may be advisable. Longer count times may be used if needed to meet data quality objectives.

In cases where ^{89}Sr is known to be absent or when the total $^{89}\text{Sr}+^{90}\text{Sr}$ total assay is less than regulatory levels, no additional processing to differentiate $^{89}\text{Sr}+^{90}\text{Sr}$ may be needed. In this case the total measurement of $^{89}\text{Sr}+^{90}\text{Sr}$ may be sufficient. The rapid fusion of 5 g concrete sample, combined with rapid Sr Resin separation and initial measurement by gas flow proportional counting would meet the data quality objectives. In other cases, this will not suffice. Some labs use a second count approach after adequate ingrowth of ^{90}Y (7-21 days) to determine ^{89}Sr and ^{90}Sr . This method, however, can have significant errors under certain conditions.

It should be noted that samples with high levels of fresh fission products, present following a radiological event, may cause large uncertainties in the ^{90}Sr measurement when using a “two count” approach to determine ^{89}Sr and ^{90}Sr . High levels of ^{89}Sr may cause significant errors in the ^{90}Sr measurements, which are based on a second count of the sample planchet after ingrowth of ^{90}Y . When the ^{89}Sr is very high relative to ^{90}Sr , the ^{90}Y ingrowth fraction is very small compared to the total count rate and therefore hard to measure precisely. In these cases, purification of ^{89}Sr and ^{90}Sr , followed by collection and purification of ^{90}Y , can offer a much more reliable assay of ^{90}Sr . The ^{89}Sr can then be calculated by difference, subtracting the appropriate amount of ^{90}Sr (plus ^{90}Y ingrowth) from the initial total $^{89}\text{Sr}+^{90}\text{Sr}$ count.

Figure 3 shows a DGA Resin separation method previously reported for seawater samples that may also be used for concrete samples to purify ^{90}Y after ingrowth. [14] In this method, yttrium carrier was added to the planchet containing the purified $^{89}\text{Sr}/^{90}\text{Sr}$ after an initial count of $^{89}\text{Sr}+^{90}\text{Sr}$, followed by a 2-3 day (or longer) ^{90}Y ingrowth period. The planchet solids were dissolved in 8M HNO_3 and transferred to a 50 mL tube. This 8M HNO_3 solution was loaded onto DGA Resin column to purify ^{90}Y . ^{89}Sr and ^{90}Sr are effectively removed using this separation on DGA Resin, as they have no significant retention in 8M HNO_3 . After ^{90}Y elution with 18.5 mL 0.25M HCl , and adjustment of each volume to 20.0 mL, a small volume of the final purified eluent was taken for ICP-MS assay to determine chemical yield.

Cerium fluoride microprecipitation was used to prepare the purified ^{90}Y samples for gas flow

proportional counting by adding 100 μg Ce and 2 mL 28 M HF to the ^{90}Y eluent solution. After waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (disposable Resolve™ filter funnel, Eichrom Technologies, Inc.). Each tube was rinsed with ~5 mL deionized water, followed by ethanol to facilitate drying. The filters were heated briefly under a heat lamp to ensure dryness. Cerium was not required to precipitate YF_3 , but was added just in case Y carrier was inadvertently omitted from the sample. It is likely the cerium is not needed, but it was added anyway for this work.

If liquid scintillation counting (LSC) or Cerenkov counting is desired, the purified ^{90}Y eluent can be evaporated to dryness or near dryness, redissolved in a very dilute HNO_3 or HCl solution. The redissolved sample can be transferred to a liquid scintillation vial with scintillation cocktail added for LSC counting or without scintillation cocktail for Cerenkov counting. In this work, however, gas flow proportional counting was used to demonstrate the method with the counting technique capable of the lowest MDA. The YF_3 filter geometry was found to give a convenient, reproducible, stable geometry for counting. In contrast, traditional yttrium oxalate precipitate geometries can be quite challenging to use, typically requiring highly reproducible drying conditions to attempt to create consistent counting sources, often with very inconsistent results. The YF_3 filter counting geometry has proven to be much more robust and reproducible in this laboratory.

It should be noted that some labs have reused Sr Resin to repass purified sample aliquots back through Sr Resin after ^{90}Y ingrowth, to retain ^{89}Sr and ^{90}Sr , and collect the ^{90}Y for measurement. It should be noted, however, that any loss of ^{89}Sr or ^{90}Sr through Sr Resin will end up in the ^{90}Y fraction using this approach. This presents a high risk condition when high levels of ^{89}Sr are present following a nuclear accident, where even a 0.5% of ^{89}Sr would bias the ^{90}Y measurements tremendously. The use of DGA Resin, where ^{89}Sr and ^{90}Sr can be more effectively rinsed through the resin, eliminates this risk.

Rapid Method for Y-90 in 10 g Concrete Aliquots Figure 2 shows the sample preparation method for the determination of ^{90}Sr by the direct separation of ^{90}Y from 10 g sample aliquots, eliminating the time for ^{90}Y ingrowth. Stable yttrium carrier (2 mg) was added to each concrete aliquot in 250 mL zirconium crucibles, and the crucibles were dried briefly on a hotplate. After removing crucibles from the hotplate, 40 grams of NaOH pellets were added to each crucible. For a 5 gram aliquot, only 30 g NaOH is needed. The crucibles were covered with a zirconium lid and placed into a furnace at 600°C for ~30 minutes. The crucibles were removed from the furnace, cooled for about 10 minutes, and transferred to a hot plate. The fusion cakes were transferred to 500 mL tubes as described earlier.

The preconcentration steps for ^{90}Y in 10 g concrete samples allow for the immediate assay of ^{90}Sr via ^{90}Y (assumed to be in secular equilibrium). The ^{90}Y preconcentration and matrix removal steps are described below. One hundred twenty-five milligrams of Fe (added as $\text{Fe}(\text{NO}_3)_3$) were added to each 500 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 450 mL with water. The samples were mixed and cooled in an ice bath for ~10 minutes. The tubes were centrifuged at 3500 rpm for ~6 minutes, and the supernate was discarded. The iron hydroxide precipitate was rinsed twice with 150 mL of water (pH of 8.8-8.9).

After centrifuging and pouring off the water rinse, 200 mL 1.5 M HCl was added to each tube to partially dissolve the precipitate. The sample was diluted with 50 mL 0.01M HCl, and 15 mL of 28M HF were added to each sample. The samples were mixed well, allowed to stand for ~15 minutes and centrifuged for 6 minutes at 3500 rpm. Although not tested in this work, it is likely that an equivalent amount of fluoride added as sodium fluoride instead of hydrofluoric acid could be used for laboratories with restrictions on the use of hydrofluoric acid. The YF_3/CaF_2 precipitation step effectively removes iron from the initial precipitation and any silicates that may have coprecipitated. It is essential to eliminate silicate solids to prevent column flow problems and potential analyte loss.

This ^{90}Y preconcentration method is very similar to the $^{89,90}\text{Sr}$ sample preparation method, however, no phosphate was added and additional iron was therefore utilized, since the goal was to remove Ca and Sr. Water rinses of the iron hydroxide precipitate with pH 8.8-8.9 water were performed to ensure effective removal of Ca, as well as the ^{90}Sr parent. The completion of the water rinse of the iron hydroxide precipitate was used as the ^{90}Sr parent separation time to start the ^{90}Y decay calculation for this method. Following the iron hydroxide and yttrium fluoride precipitations, the supernate was discarded and the precipitate containing the YF_3 (plus CaF_2 from a small amount of any residual calcium present) was dissolved in 7 mL of 3M HNO_3 -0.25M H_3BO_3 and 7 mL of 15.8M HNO_3 , mixed, and transferred to 50 mL tubes. The 500 mL tubes were rinsed with 7 mL of 8M HNO_3 and 7 mL of 2 M $\text{Al}(\text{NO}_3)_3$, respectively, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed using a vortex stirrer and heated 2 to 5 minutes in a hot block heater at 105°C. The 50 mL tubes containing the load solutions were centrifuged, and any traces of solids were discarded. The column load solutions for Y separation on DGA Resin were prepared in ~8M nitric acid solution to enhance DGA Resin affinity for Y^{+3} and remove Ca^{+2} ions effectively. The volume of YF_3 precipitate is typically <10 mL and dissolves easily. If the YF_3/CaF_2 precipitate is much larger than ~10 mL, a second rinse with 100mL of 1.5M HCl and 3 mL 28M HF may be

added to reduce the amount of CaF_2 remaining.

Figure 4 shows the column method used when ^{90}Y was collected directly from the concrete sample for rapid purification. A TRU Resin + DGA Resin separation method is used for ^{90}Y collected immediately from 10 g concrete sample aliquots. TRU Resin was added to provide additional removal of U, Th and Bi isotopes which could bias the ^{90}Y measurement. After collecting ^{90}Y from the concrete samples, the samples were loaded onto stacked TRU Resin + DGA Resin cartridges. Pu, U and Th isotopes are strongly retained on TRU Resin. The stacked resin cartridges were rinsed with 6M HNO_3 and 3M HNO_3 , respectively. Twelve milliliters of 4M HCl were added to the stacked TRU Resin + DGA Resin to ensure all Y has been moved to the DGA Resin cartridge. The TRU Resin cartridge was discarded. The DGA Resin was rinsed with 8M HNO_3 to remove Ca and Pb isotopes, and with 0.1M HNO_3 to remove any U isotopes that have bled through from TRU Resin onto DGA Resin. A 25 mL rinse of 3M HNO_3 -0.25M HF was used to remove any residual Th isotopes that may have made it through to TRU Resin. After ^{90}Y elution in 0.25M HCl, a small volume of the final purified eluent was taken for ICP-MS assay to determine chemical yield. The ^{90}Y was then determined by gas flow proportional counting after the CeF_3 microprecipitation source preparation described above. Sample results were corrected for the removal of 0.5% of the Y eluent solution.

It should be noted that ^{90}Y decay is about 1% per hour from the point at which ^{90}Sr is removed. For example, after 12 and 24 hours, ^{90}Y has decayed to about 88% and 78% of its secular equilibrium value, respectfully. This decay must be factored into activity calculations and delays should be minimized. Fortunately, the sample processing from the point of ^{90}Sr removal using rapid preconcentration with vacuum-assisted TRU Resin + DGA Resin separation, is very fast, minimizing ^{90}Y decay. The drawer system gas flow proportional counters allow simultaneous counting of multiple samples.

Apparatus

A Tennelec LB 4100 gas flow proportional counter was used to count the ^{90}Sr spiked samples. The detectors were calibrated using NIST Traceable $^{90}\text{Sr}/^{90}\text{Y}$ 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 $^{90}\text{Sr}/^{90}\text{Y}$ (>167 Bq) and a nominal amount of Sr carrier. Planchets were annealed for ~1.5 hours in a furnace at 450°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. Annealing the planchets for only 90 minutes at 450°C was found to provide improved corrosion resistance. Longer, hotter furnace times previously reported, 3.5 hours at 550°C, apparently oxidizes the planchet surface too much and can lead to iron oxide solids during sample evaporation.

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 mL plastic tubes were used for cartridge separations and CeF_3 precipitation filter preparations. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box. Waste liners were used in the vacuum box to collect rinses to facilitate handling, while collection racks were added to collect final eluents in 50 mL tubes.

Results and Discussion

Table 1 shows the individual results for the determination of ^{90}Sr in four 5 g concrete samples spiked with ^{90}Sr using the rapid fusion method plus Sr Resin, with gas flow proportional counting to measure ^{90}Sr . In this test, no additional phosphate was added to enhance yields across the iron hydroxide preconcentration step. As expected, the average Sr carrier recovery was only $48.8\% \pm 4.4\%$ (1SD, standard deviation). The low chemical yields without the addition of phosphate illustrate why phosphate was used in this new method. The average ^{90}Sr result was $1.57 \text{ mBq sample}^{-1}$, with a 11.1% bias and SD (standard deviation) of $0.1 \text{ Bq sample}^{-1}$. The bias may be attributed to errors associated with the Sr carrier yield. The ^{90}Sr activity added to each 5 g aliquot was 1.416 Bq (283.2 mBq g^{-1}).

Table 2 shows the measured values for six 5 g concrete aliquots spiked with $0.283 \text{ Bq } ^{90}\text{Sr}$ (56.6 mBq g^{-1}). In this case, $5 \text{ mL } 3.2 \text{ M } \text{PO}_4^{3-}$ was added to enhance chemical yields during the initial precipitation with iron hydroxide from the alkaline matrix. With phosphate added, the average Sr carrier yield increased to $64.1\% \pm 3.5\%$ (SD), but this average yield was still lower than desired. The average bias for the ^{90}Sr measurements was 2.1%, with an SD of 4.1%. In this case, $20 \text{ mL } 28\text{M HF}$ was added to facilitate the calcium fluoride precipitation. Since concrete contains high levels of Ca, an additional test was performed to determine whether fluoride might be a limiting reagent in the calcium fluoride step, adversely affecting chemical yield.

Table 3 shows the measured values for four replicates of 5 g concrete spiked with $1.416 \text{ Bq } ^{90}\text{Sr}$ (283.2 mBq g^{-1}). The same amount of phosphate was used, but additional 28 M HF was added. The Sr carrier chemical yields were still lower than desired, with an average yield of $62.9\% \pm 5.9\%$ (SD). The average ^{90}Sr

result, however, was $1.49 \text{ Bq sample}^{-1}$, with a 5.4% bias and SD (standard deviation) of $0.1 \text{ Bq sample}^{-1}$.

The Sr carrier yields indicate that the HF was not a limiting reagent under these test conditions.

Table 4 shows the results for ^{90}Sr in concrete when the phosphate was increased even further. The amount of phosphate added in the initial preconcentration step was increased from 5 mL to 7.5 mL 3.2M PO_4^{-3} . The average Sr carrier yield increased significantly to $74.6\% \pm 12.6\%$ (SD). Several of the individual Sr carrier recoveries were $> 80\%$, indicating the increase in phosphate was beneficial. The average ^{90}Sr result was $1.44 \text{ Bq sample}^{-1}$, with an average bias of 1.9%.

Table 5 shows the results for ^{90}Sr in 5 g concrete samples when the phosphate added in the initial preconcentration step was increased to an even higher level, from 7.5 mL to 8.5mL 3.2M PO_4^{-3} . The average Sr carrier yield was $74.8\% \pm 8.4\%$ (SD). These results indicate that the additional increase in phosphate was neither beneficial nor harmful. The average ^{90}Sr result was $1.44 \text{ Bq sample}^{-1}$, with an average bias of 1.9%. Despite variations in chemical yield with the different conditions employed, the ^{90}Sr results were typically very good.

Table 6 shows results for the ^{90}Sr method that measures ^{90}Y in the sample with no waiting for ^{90}Y ingrowth. This method employed the ^{90}Y sample preparation steps shown in Figure 3, coupled with ^{90}Y purification using the TRU Resin + DGA Resin column method shown in Figure 4. In this test, 0.5 g MAPEP 32 soil was added to 10 g concrete aliquots. MAPEP 32 soil contains ^{90}Sr and potentially interfering radionuclides. To test the ruggedness of the method even further, a relatively high level of ^{137}Cs (18.5 Bq) was added to each sample aliquot to test for the removal of this potential interference. Due to its relatively long half-life ($T_{1/2}=30.17 \text{ yrs}$), it would not be surprising to encounter ^{137}Cs fission product activity in decommissioning samples. Y carrier (2 mg) was used to determine the Y chemical yield. Four 10 g aliquots were analyzed, with an average Y chemical yield of $83.9\% \pm 1.9\%$ (SD). The average ^{90}Sr result was -2.5%, with SD $\pm 3.2\%$, showing excellent results. The high, consistent Y yields indicate that the sample preparation method is very rugged. The effective removal of MAPEP 32 soil radionuclides, despite the presence of 18.5 Bq ^{137}Cs and other interferences indicate that the method removes other beta-emitting interferences very well.

Stable yttrium carrier was added to enhance ^{90}Y precipitation during the sample preconcentration steps and to determine chemical yield. Initial testing with 1 mg stable Y was successful, but the stable Y amount was increased to 2 mg to reduce potential errors in the Y chemical yield associated with native Y in the concrete. A correction of approximately 7% was made in the chemical yield for the native Y, which was

measured to be ~150 ug in the 10 g concrete aliquot. Up to 4 mg Y carrier was tested to further minimize any contribution from native Y, but with this much Y added the amount of YF_3 solids on the final sample test source was larger than desired. Initially La was added as a carrier to enhance Y recovery, as was reported for ^{90}Sr in seawater [14], but it was found that La was not required to enhance chemical yields. The $\text{Fe}(\text{OH})_3$ precipitation appears to be highly effective for preconcentration of Y and the combination of a small amount of Y and Ca appears to work very well to collect Y as a fluoride precipitate, without the addition of La. Y^{+3} ions are retained much more strongly than La^{+3} on DGA Resin, however La is still retained. [15] Eliminating La reduced the risk of Y loss on DGA Resin, and allowed for an increase in the amount of Y carrier to at least 2 mg Y. Native Y levels in concrete may be determined by digestion and analysis of an aliquot by ICP-MS. An alternate approach, perhaps less disruptive to the laboratory, is to process a representative number of the concrete samples through the method without the addition of Y carrier to determine the native content in that way. Employing a native Y correction gives the best possible ^{90}Y results. It may also be possible, however, to minimize the impact of native Y in the samples and not make a native Y correction. By analyzing slightly smaller aliquots of concrete, and increasing the Y carrier to 3-4 mg, for example, the impact would likely be < 5%.

The sample preparation can be performed in <6 hours. The rapid sample preconcentration steps make the method more robust. Not only are sample matrix components such as iron and silicates removed, radionuclide interferences are also reduced across these steps. For example, ^{137}Cs does not precipitate during the sample preconcentration steps, as a hydroxide or fluoride, so extremely high decontamination factors can be achieved, when coupled with ^{137}Cs removal using DGA Resin. Samples may be counted for much longer count times to lower MDA. This is feasible with gas flow proportional counters using a drawer system that allows simultaneous counting of multiple samples.

A recount may be needed to verify the ^{90}Y decay profile, when ^{91}Y ($T_{1/2} = 58.5$ days) could be encountered. For older concrete samples where ^{89}Sr has decayed away and only ^{90}Sr assay is needed, the presence of the fission product ^{91}Y is also unlikely. Though not presented here, it is feasible that recounts of the YF_3 filters, when both ^{90}Y and ^{91}Y are present, would allow for the calculation of ^{90}Y in spite of the presence of ^{91}Y by solving simultaneous equations.

The MDA (Minimum Detectable Activity) for ^{90}Sr and ^{89}Sr using this method with gas flow proportional counting was calculated according to equations prescribed by Currie: [17]

$$\text{MDA} = [2.71 + 4.65\sqrt{B}] / (\text{CT} * \text{R} * \text{V} * \text{Eff} * 0.060)$$

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

CT = sample count time (min)

R = Chemical Recovery

V = Sample aliquot (L)

EFF = Detector Efficiency

0.060 = conversion from dpm to mBq

Figure 5 shows the MDA for these methods plotted vs. count time for 5 g and 10 g aliquots using ~54% efficiency gas flow proportional detectors, assuming ~80% chemical yield and 1.35 cpm (counts per minute) average background count rate. The MDA (minimum detectable activity) for the method can be adjusted as needed, depending on the sample aliquot and count time.

For ^{89}Sr or ^{90}Sr in concrete samples, the MDA is $\sim 1.4 \text{ mBq g}^{-1}$ for a 5 g sample aliquot, 1000 minute count time, 75% chemical recovery, 54% detector efficiency and 1.35 count per minute background using gas flow proportional counting. For the 10 g concrete aliquot using the ^{90}Y preconcentration method to collect and measure ^{90}Sr with no waiting, an MDA of $\sim 700 \text{ uBq g}^{-1}$ can be obtained with 1000 minute count time.

For the 10 g concrete fusion method to measure ^{90}Sr via ^{90}Y with no waiting, the ^{90}Y decay during assay is not significant for ~ 24 hours or longer. Even with ^{90}Y decay at $\sim 1\%$ per hour following the removal of the ^{90}Sr parent, the decay during measurement (10-20%) is still minimal for a relatively long count time. In addition, the smaller diameter 25 mm YF_3 filter geometry has a higher counting efficiency ($\sim 20\%$) in the gas flow proportional counter than the ~ 50 mm planchets used for the $^{89,90}\text{Sr}$ counting. Decay correction for ^{90}Y is made from the midpoint of the count time to the separation time. The ^{90}Y decay does not significantly affect the MDA even with 1000 minute sample count time for at least 24 hours.

Conclusions

A new rapid fusion method to determine ^{89}Sr and ^{90}Sr in 5 g -10 g concrete samples has been developed that allows the separation of Sr isotopes with high chemical yields and effective removal of interferences. Several analytical options were presented that offer significant method flexibility, depending on which Sr isotopes are required. One method collects, purifies and measures $^{89,90}\text{Sr}$ in 5 g concrete aliquots. Another approach allows the immediate determination of ^{90}Sr in 10 g concrete aliquots with no waiting for ^{90}Y

ingrowth. The total digestion and separation method is not only rapid (< 6 hrs), but it provides ruggedness that can help maintain the public trust regarding the quality of the measurements. Count times may be adjusted depending on the MDA and uncertainty requirements, and detection limits below 1 mBqg⁻¹ can be achieved to meet new, lower regulatory limits.

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Table 1 Sr-90 in Concrete: 5 g Aliquots using Sr Resin; No PO_4^{-3}

Sample	Sr Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(pCi smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	43.2	1.416	43.68	1.616	14.1
2	50.7	1.416	41.66	1.541	8.9
3	47.9	1.416	43.67	1.616	14.1
4	53.4	1.416	41.01	1.517	7.2
Avg. Spiked Smpls	48.8		42.5	1.57	11.1
SD	4.4		1.4	0.1	3.6
% RSD	8.9		3.2	3.2	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq g $^{-1}$		
		No PO_4^{-3}			
		15 mL 28 M HF			

Table 2 Sr-90 in Concrete: 5 g Aliquots using Sr Resin Using PO_4^{-3}

Sample	Sr Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(pCi smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	62.2	0.283	7.814	0.289	2.2
2	66.9	0.283	8.364	0.309	9.4
3	66.3	0.283	7.744	0.287	1.2
4	58.1	0.283	7.869	0.291	2.9
5	64.2	0.283	7.645	0.283	0.0
6	67.0	0.283	7.419	0.275	-3.0
Avg. Spiked Smpls	64.1		7.81	0.289	2.1
SD	3.5		0.31	0.012	4.1
% RSD	5.4		4.0	4.0	
		120 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 56.6 mBq g $^{-1}$		
		5 mL 3.2M PO_4^{-3}			
		20 mL 28 M HF			

Table 3 Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Increased HF

Sample	Sr Carrier Yield	⁹⁰ Sr Reference Value	⁹⁰ Sr Measured Value	⁹⁰ Sr Measured Value	Difference
ID	(%)	(Bq smp ⁻¹)	(pCi smp ⁻¹)	(Bq smp ⁻¹)	(%)
1	62.9	1.416	41.53	1.537	8.5
2	68.3	1.416	37.02	1.370	-3.3
3	54.7	1.416	41.42	1.533	8.2
4	65.6	1.416	41.36	1.530	8.1
Avg. Spiked Smpls	62.9		40.3	1.49	5.4
SD	5.9		2.2	0.08	5.8
% RSD	9.4		5.5	5.5	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq g ⁻¹		
		5 mL 3.2M PO ₄ ⁻³			
		50 mL 28 M HF			

Table 4 Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Increased PO_4^{-3}

Sample	Sr Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(pCi smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	71.0	1.416	38.64	1.430	1.0
2	85.9	1.416	39.44	1.459	3.1
3	83.9	1.416	38.22	1.414	-0.1
4	86.6	1.416	38.86	1.438	1.5
5	62.2	1.416	40.73	1.507	6.4
6	58.1	1.416	38.09	1.409	-0.5
Avg. Spiked Smpls	74.6		39.0	1.44	1.9
SD	12.6		1.0	0.04	2.6
% RSD	16.9		2.5	2.5	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq g $^{-1}$		
		7.5 mL 3.2M PO_4^{-3}			
		30 mL 28 M HF			

Table 5 Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Even Higher PO_4^{-3}

Sample	Sr Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(pCi smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	78.5	1.416	40.80	1.510	6.6
2	77.8	1.416	36.50	1.351	-4.6
3	80.5	1.416	38.35	1.419	0.2
4	62.2	1.416	40.27	1.490	5.2
Avg. Spiked Smpls	74.8		39.0	1.44	1.9
SD	8.4		2.0	0.07	5.1
% RSD	11.3		5.0	5.0	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq g $^{-1}$		
		8.5 mL 3.2M PO_4^{-3}			
		15 mL 28 M HF			

Table 6 Sr-90 in Concrete: 10 g Aliquots using TRU+DGA Resin (Y-90)

Sample	Sample Aliquot	Y carrier	⁹⁰ Sr Reference Value	⁹⁰ Sr Reference Value	⁹⁰ Sr Measured Value	Difference
ID	(g)	(%)	(Bq smp ⁻¹)	(pCi smp ⁻¹)	(Bq smp ⁻¹)	(%)
1	10	81.7	0.327	8.36	0.309	-5.4
2	10	83.3	0.327	8.94	0.331	1.2
3	10	83.7	0.327	8.40	0.311	-5.0
4	10	86.3	0.327	8.78	0.325	-0.6
Avg		83.8		Y carrier by ICP-MS		-2.5
SD		1.9				3.2
% RSD		2.3				
				120 minute count	added 500 pCi Cs-137	
		yield corrected for native Y		10 g concrete		
		added 0.5 g MAPEP 32		2 mg Y carrier, no La		

Figure 1 Sample Preparation for Radiostrontium in 5g Concrete Samples

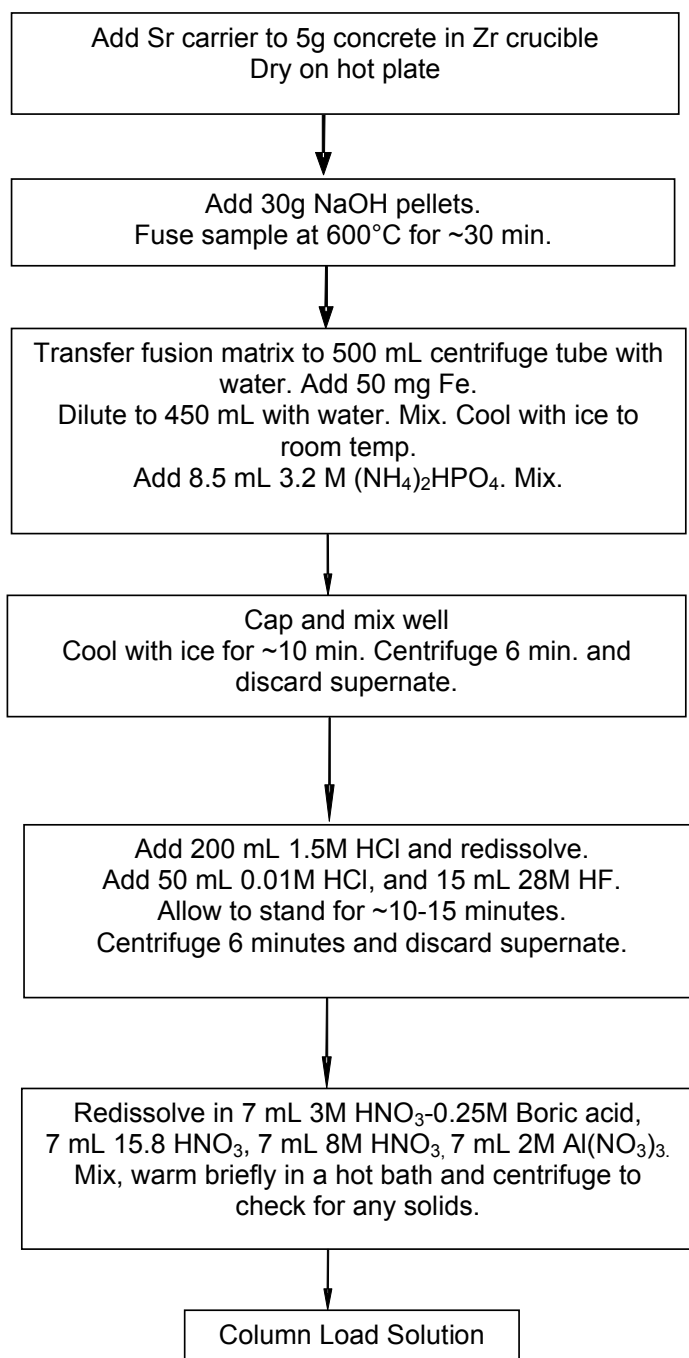


Figure 2 Sample Preparation for Yttrium-90 in 10g Concrete Samples

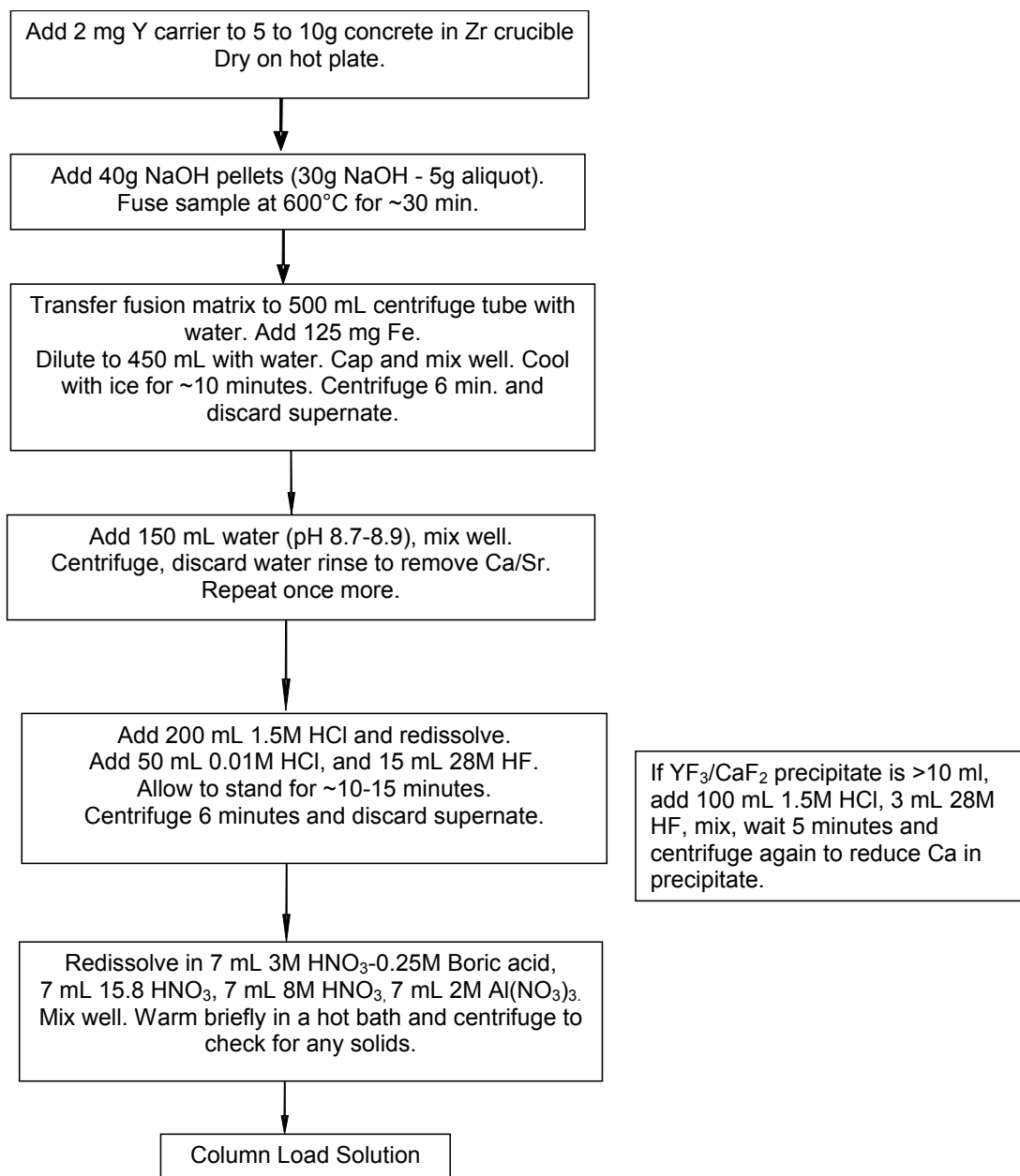


Figure 3 Column Separation for ^{90}Y after Ingrowth on $^{89}\text{Sr} + ^{90}\text{Sr}$ Planchets

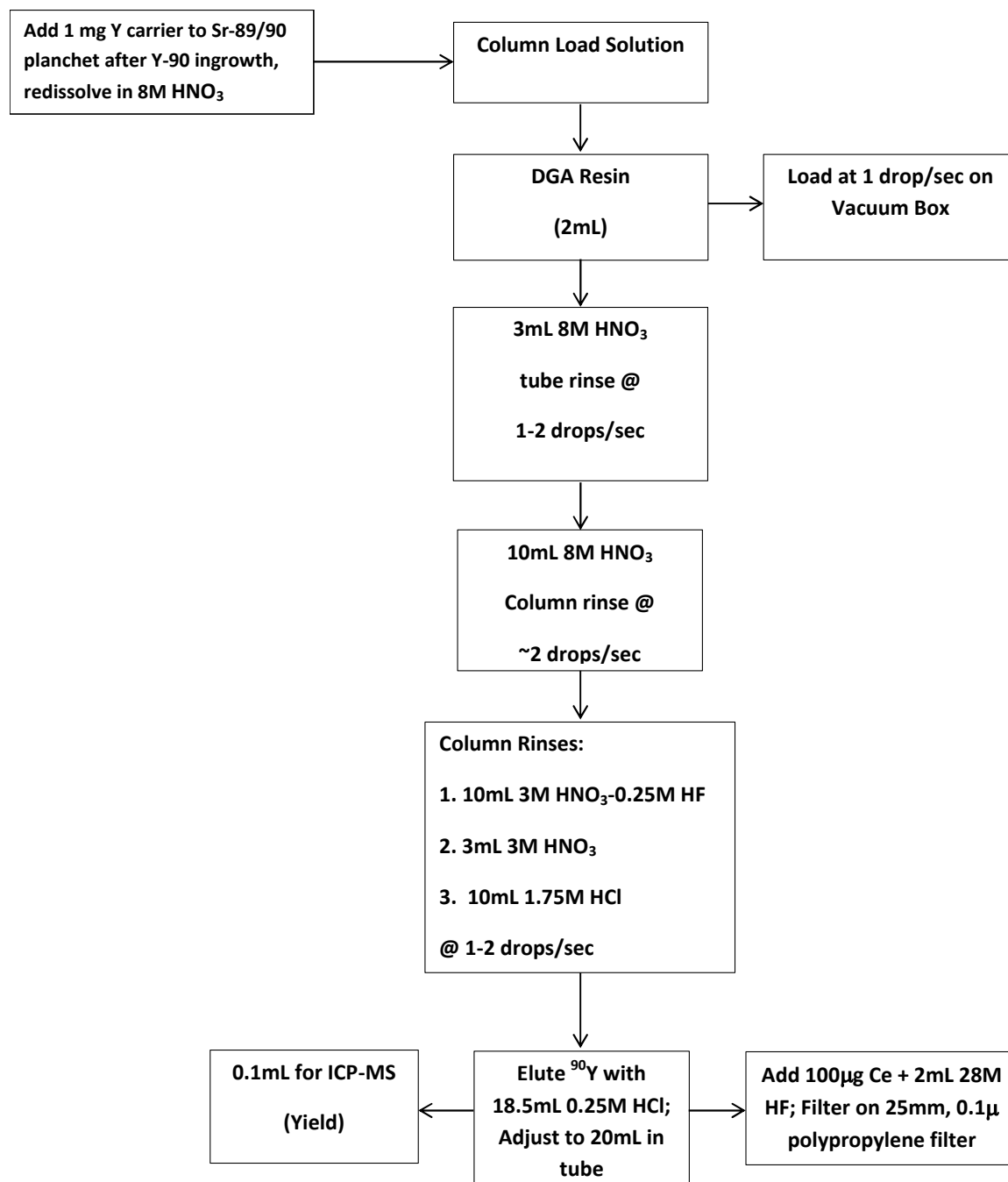


Figure 4 TRU+DGA Resin Y-90 Separation Method for Concrete

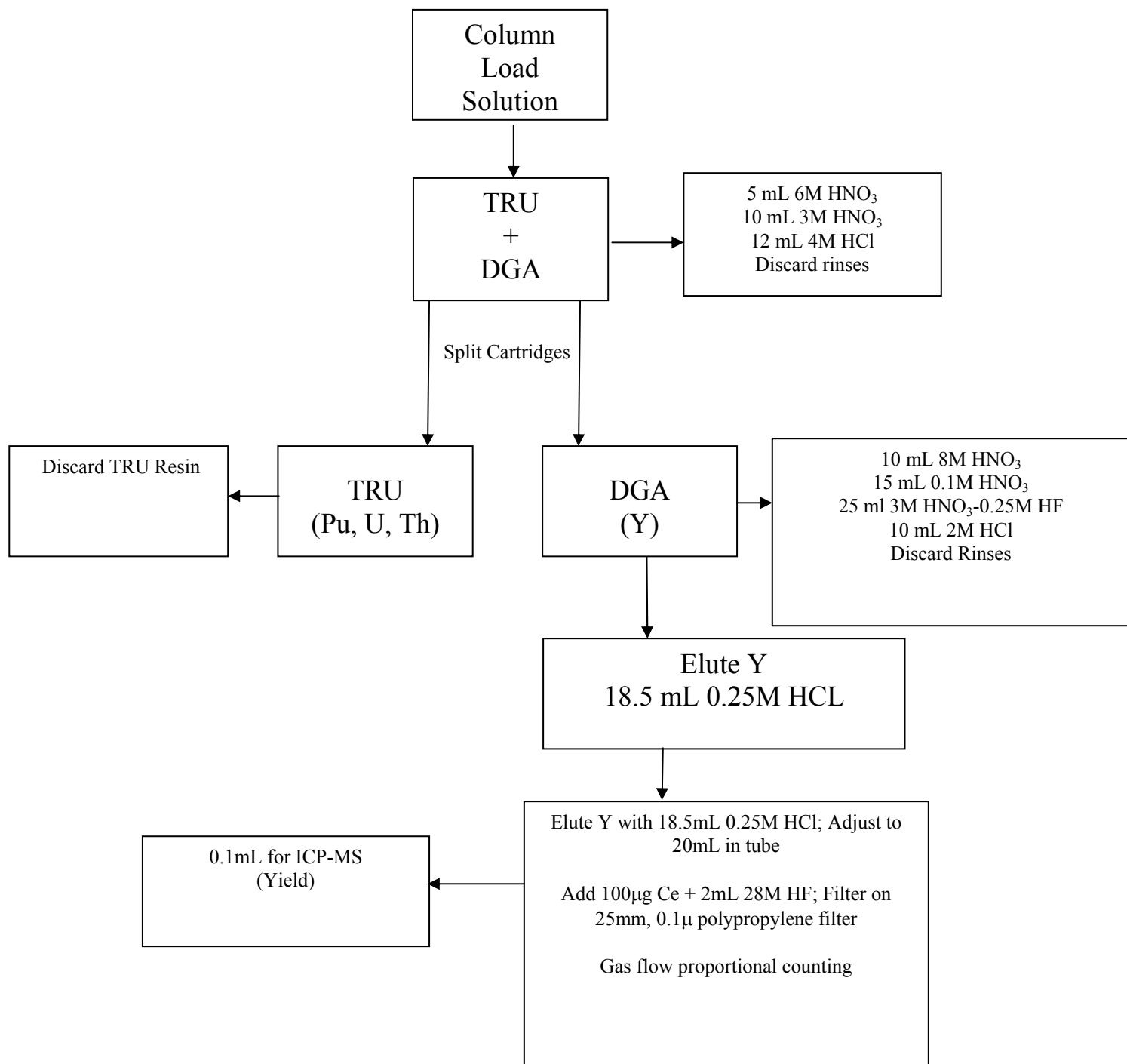


Figure 5 MDA for 5g and 10 g Aliquots vs. Count Time

