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Rapid Method to Determine $^{89/90}\text{Sr}$ in Steel Samples

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Abstract

The rapid measurement of $^{89/90}\text{Sr}$ in steel samples is important in the event of a radiological emergency as well as for the characterization of routine nuclear decommissioning samples. A new method for the determination of radiostrontium in steel samples has been developed at the Savannah River Environmental Laboratory. The new method employs a rugged acid digestion that includes hydrofluoric acid, followed by a single preconcentration step to rapidly collect the radiostrontium and remove nearly all of the high iron content. A fusion step can be implemented after the steel dissolution when soil, concrete, or highly refractory particles are present. The $^{89}\text{Sr} + ^{90}\text{Sr}$ and/or ^{90}Y are separated using extraction chromatographic resins and measured radiometrically, either by gas flow proportional counting or liquid scintillation counting. Several approaches for the measurement of $^{89}\text{Sr} + ^{90}\text{Sr}$, ^{90}Sr , and discrimination between ^{89}Sr and ^{90}Sr are discussed. This approach has a sample preparation time for steel samples of 6-8 hours.

Introduction

Rapid analytical methods are needed to support dose mitigation and environmental clean-up in the event of the release of radioactive material, such as a radiological dispersive device (RDD), Improvised

Nuclear Device (IND) or a nuclear accident such as the accident at the Fukushima Nuclear Power Plant in March, 2011. [1,2,3,4] In addition to other environmental samples, steel samples from debris or remaining structures may need to be analyzed quickly to ascertain the radiological content. It has been the approach of the Savannah River Environmental Laboratory (SREL) to combine rapid, rugged sample digestion with rapid, innovative column purification methods to analyze building materials samples for radiological contaminants quickly. The use of vacuum-assisted flow rates and stacked cartridges containing highly selective extractant-coated chromatographic resins allows rapid sequential separations of multiple analytes in an emergency. Recently published methods developed at SREL include analyses for soil, concrete, limestone and marble. [5, 6] All these rapid methods share two key components: 1) rapid complete sample dissolution and matrix removal techniques coupled with 2) rapid innovative, sequential purification techniques. These radiochemical methods are both rapid and reliable, offering highly defensible quality.

There is also an emerging need for rapid, traceable cost-effective 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 vastly improved measurement techniques is necessary. [7] The application of innovative rapid method techniques used for emergency analyses to decommissioning samples or other routine environmental samples can reduce labor costs and facilitate improved efficiencies. Furthermore, the defensibility of results is very important not only in a radiological emergency but also for nuclear decommissioning samples. Effective sample dissolution is paramount. The ruggedness of the dissolution technique used is very important, and it is well-known that acid leaching alone may not completely digest refractory particles, particularly ones dispersed in an explosion. [6] Consistent with this need, a sodium hydroxide fusion method for complete dissolution of 10g concrete samples was recently published by this laboratory. [8] Similar sodium hydroxide fusion methods have been used with great success for soil, concrete, vegetation and other solid samples. However, steel samples cannot be adequately dissolved with sodium hydroxide fusion. Once the steel is effectively dissolved with acid, a sodium hydroxide fusion can be applied to solubilize any remaining soil, concrete or refractory particles that may be present. Therefore, a rigorous acid digestion method for steel was explored, with and without hydrofluoric acid, along with a secondary fusion of the acid digested residue for enhanced ruggedness.

Sample preparation methods for $^{89,90}\text{Sr}$ are described for a wide range of sample matrices in a comprehensive way by Vajda and Kim. [9] Many examples in the literature produce chemical yields that may not be fully optimized, affecting detection limits and perhaps overall reliability. In addition, large acid volumes may be required to perform the analyses, depending on the chemistry used. Grahek et al. [10] reported a method for actinides and $^{89,90}\text{Sr}$ in soil and vegetation samples in which 10g samples were digested and analyzed. Anion exchange separation using a mixed solvent approach was employed using dilute nitric acid plus ethanol and methanol to collect Sr and Y. Cerenkov counting was used to determine ^{89}Sr and ^{90}Sr . While the work appeared to provide useful results and was integrated sequentially with actinides, the chemical yields varied between 53% and 57% and the $^{89,90}\text{Sr}$ measurements were within $\pm 18\%$ of the known values. While this approach certainly offers a viable alternative for environmental assays, improvements in chemical yield would improve detection limits or permit the analysis of smaller sample aliquots, and elimination of the mixed aqueous-organic solvents would alleviate some safety concerns and waste issues.

Other published methods utilize precipitation techniques for matrix removal and preconcentration and extraction chromatography resins for radionuclide separations. Amano et al. used DGA Resin (Eichrom Technologies, Inc.) in combination with Cerenkov counting to determine ^{90}Sr via the assay of ^{90}Y in vegetation samples. [11] Chemical yields in the work by Amano, determined by measurement of stable yttrium carrier by inductively-coupled plasma emission spectrometry, averaged about 99% across multiple vegetation matrices, including Japanese tea leaves. These high yields indicate method robustness. A Hidex SL/SLL liquid scintillation counter was used in Cerenkov mode. The ^{90}Sr recoveries obtained by measuring ^{90}Y with purification using DGA Resin were approximately 107% versus known values, which met the data quality objectives for this study. DGA Resin has an amazing affinity for trivalent actinides and lanthanides, as well as yttrium. [12] For this reason, DGA Resin has also been used in the determination of ^{90}Sr in seawater and concrete in our laboratory as well. [2, 13] This approach can be effective for analyses where ^{90}Sr and ^{90}Y are in equilibrium and short lived fission products (^{89}Sr , ^{91}Y , etc.) are known to be absent. For samples which may contain fresh fission products, separation of radiostrontium followed by multiple sample counts and/or ingrowth and separation of ^{90}Y are required to effectively distinguish between ^{90}Sr , ^{89}Sr and other fission products.

The search for more rapid analyses has also led some to pursue inductively-coupled plasma mass spectrometry (ICP-MS) to measure ^{90}Sr . [14] While ICP-MS offers a simplicity that may be appealing, it suffers from poor detection limits when compared with beta emission measurement methods [8] due to the relatively short half-life of ^{90}Sr (28.9 years). Additionally, the measurement of ^{90}Sr by ICP-MS is affected by the ^{90}Zr isobaric interference and often requires effective matrix removal to produce samples suitable for injection into an ICP-MS instrument. Russell et al [15] studied the measurement of ^{90}Sr using an Agilent 8800 ICP-QQQ-MS in decommissioning wastes. This was studied because of its potential rapid analysis capability and employs O_2 reaction cell techniques to try to further reduce the ^{90}Zr interference by oxidation of Zr to ZrO_2 . The authors note that inclusion of the reaction cell significantly increases the ^{90}Sr detection limit to 5-10 Bq/g. These levels are 500-5000x higher than levels typically achieved in an environmental laboratory using modern radiometric techniques. Therefore, the ICP-MS method may have significant throughput value for high level ^{90}Sr samples but is not currently feasible for decommissioning or low level environmental analyses.

A new method has been developed in the Savannah River Environmental Laboratory to measure $^{89,90}\text{Sr}$ in steel samples. The method employs preconcentration techniques that effectively manage the high iron content resulting from the dissolution of the steel sample and keep the sample preparation volumes small so that rapid column separation can be achieved. Two options were investigated in this study. In the first method, ^{89}Sr and ^{90}Sr were purified and counted together to determine $^{89}\text{Sr}+^{90}\text{Sr}$, followed by purification and measurement of ^{90}Y after a short ingrowth to determine ^{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. The second option is the collection of ^{90}Y directly from the sample with no waiting for ingrowth to determine ^{90}Sr in the steel sample.

Experimental

Reagents

The extraction chromatography resins employed in this work are DGA Resin, Normal ($\text{N,N,N}',\text{N}'$ -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. ^{90}Sr was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2.96 Bq mL^{-1} . ^{89}Sr was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 8.04 Bq mL^{-1} . Single element standards (10mg/L) for yttrium, strontium, chromium, cobalt, molybdenum, tungsten, copper, nickel and titanium were obtained from High Purity Standards (North Charleston, SC).

Procedures

Measurement of column capacity factors (k'). Column capacity factors (k') for selected elements on Sr Resin and DGA Resin, Normal were measured as previously described. [12] Aqueous solutions (5-10mL) containing the desired acid concentration and 5-100 mg/L of the desired metal ions are equilibrated with a known mass of resin (0.10-0.25 grams) for 1-2 hours at $21(1)^{\circ}\text{C}$ on an orbital plate shaker or tumbling mixer. After equilibration, the aqueous phase is filtered through 0.45mm polypropylene syringe filters to remove resin particles. Stock solutions of the metal ion and solutions that have been equilibrated with resin are then measured using microwave plasma atomic emission spectrometry (MP-AES).

Column preparation. DGA and Sr Resins 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. Flow rates of $\sim 1\text{-}2 \text{ drops sec}^{-1}$ 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 ^{89}Sr and ^{90}Sr in steel samples. Samples of 304 stainless steel disks ($\sim 18\%$ chromium, $\sim 8\%$ nickel), weighing approximately 1g were used for this testing. ^{89}Sr and ^{90}Sr were added to each steel sample to test performance as appropriate. Strontium carrier (6mg) was added to each sample when the Sr Resin separation was employed. When ^{90}Y was collected directly for separation using DGA Resin, 2 mg yttrium was added to determine chemical yield. Y carrier was also added for the combined ^{89}Sr and ^{90}Sr method in which ^{90}Y was collected and purified after an initial total count and short ingrowth time. Initial steel digestion testing was performed with aqua regia in 250 mL glass beakers. While this was successful, subsequent testing was performed in 250 mL Teflon beakers with hydrofluoric acid (HF) added. The addition of HF was found to enhance the steel

dissolution by more rigorously digesting refractory particles.. This was confirmed in parallel testing underway in this laboratory where a small amount of soil containing refractory plutonium was added to the steel sample, with and without HF. [16]

Each sample was placed in a 250 mL Teflon beaker and Sr and/or Y carrier were added to each steel sample. Twenty milliliters of 12M HCl, 5 mL 15.8M HNO₃, and 5 mL 28M HF were added to each beaker, and the samples were digested to dryness on a hot plate on medium heat to avoid any splattering. After the samples were taken to dryness, 10 mL 12M HCl, 1 mL 15.8M HNO₃, and 1 mL 28M HF were added to each beaker and the samples were evaporated to dryness on a hot plate. Finally, 5 mL 12M HCl and 3M HNO₃-0.25M H₃BO₃ were added to each beaker, and samples were evaporated to dryness to remove fluoride. This step was found to facilitate complete removal of the sample residue from the beaker.

To dissolve the sample residue, 25 mL 1M HCl were added to each beaker. Each sample was warmed on a hot plate, and the dissolved sample was transferred to a 225 mL centrifuge tube. The dissolution and transfer with 25 mL 1M HCl were repeated two more times, warming each beaker as needed. Each sample was diluted in the 225 mL tube to 170 mL with 0.01M HCl. To precipitate the Sr/Y from the dissolved sample, 2 mL 1.25M calcium nitrate was added to each 225 mL tube. Twenty-five milliliters 28M HF was added first to each Teflon beaker and warmed slightly on a hot plate to ensure full removal of the sample from the beaker. The addition of HF removes a touch of brown iron color that was sometimes present on the beaker surface. This HF rinse was added to the 225 mL tube to coprecipitate Sr or Y on CaF₂ or CaF₂/YF₃. The high HF concentration is required to effectively precipitate CaF₂ and SrF₂ ($K_{sp} = 5.3E-9$ and $2.5E-9$, respectively). After mixing each sample tube well, the tubes were cooled in ice bath for ~20 minutes to facilitate complete precipitation. Each sample was centrifuged at 3500 rpm for 6 minutes, and the supernate was discarded. Each sample precipitate was redissolved in 5 mL 3M HNO₃-0.25M Boric acid, 5 mL 15.8 HNO₃, and transferred to a 50 mL centrifuge tube. To rinse the 225 mL tube, 5 mL 8M HNO₃, and 5 mL 2M Al(NO₃)₃ were added and transferred to each 50 mL sample tube. Each 50 mL sample tube was mixed well, warmed briefly in a hot bath and centrifuged to check for any solids. The sample liquid was transferred to a new 50 mL tube to remove any small residue of solids.

A fusion option may be used for additional rigor, especially when a steel sample is mixed with soil or concrete or when refractory particles may be present. When using the fusion option, the initial digestion was performed in a 250 mL low form zirconium crucible to digest the steel. Since the fluoride ion will attack Zr metal, only HCl and HNO₃ were used in the initial steel dissolution. Once the digestate was

evaporated to dryness, sodium hydroxide pellets were added, and the sample was fused and processed as described previously [5], except that no additional Fe was added. In this fusion option, an initial precipitation is performed using iron hydroxide enhanced with calcium phosphate to remove the high levels of hydroxide. Following the initial precipitation, the samples are dissolved in dilute HCl and a calcium fluoride precipitation was performed to remove Fe, Ti and silicates.

While this new method will need to be validated for effectiveness on other types of steel, no adverse sample matrix impact from variations in the chromium, nickel, carbon and other constituent content is expected. Iron, the key matrix component in steel, is effectively managed using this method and chromium, nickel, carbon and the other constituents do not interfere with the Sr Resin or DGA Resin separation methods. Figures 3 and 4 shows that there is minimal affinity for these ions in nitric acid on Sr Resin or DGA Resin.

Column separation for Strontium-89,90. Sr is separated using Sr Resin (3 mL Sr Resin, using stacked 2 mL+1 mL resin cartridges) using a method similar to that previously published for the determination of ^{89}Sr and ^{90}Sr in limestone and marble samples. [5] The sample load solutions were added to the Sr Resin at approximately 1 drop per second. After the sample was loaded, the sample tube was rinsed with 5 mL 8M HNO_3 , which 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 then performed at ~2 drops per second: 15 mL 8M HNO_3 , 5 mL 3M HNO_3 - 0.05M oxalic acid, and 10 mL 8M HNO_3 .

Sr-89,90 was eluted from 3 mL Sr Resin with 15 mL 0.05M HNO_3 at ~1 drop per second. This eluent was transferred to preweighed planchets and evaporated on a hot plate with medium heat to dryness. Two milliliters 0.05M HNO_3 , used to rinse each tube, were also 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 to determine $^{89/90}\text{Sr}$. To minimize gravimetric yield errors, the direct stable strontium carrier standardization on planchets (7-10 replicates) should be heated on the hot plate at the same temperature for the same time as.

Sr Resin also retains Pb isotopes, while Bi and its other daughter isotopes are eluted during the column rinse steps. During the short elution step, Bi daughters may grow in and be eluted with the ^{89}Sr and ^{90}Sr . This will typically be of 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. This may be less important for steel samples than soil samples, for example, where Pb isotopes are more likely to occur.

When ^{89}Sr is known to be absent, the ^{90}Sr can be determined using a single Sr Resin purification and count. It should be noted, however, 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 after ^{90}Y ingrowth. High levels of ^{89}Sr may cause significant errors in the ^{90}Sr measurements, which are based on a second count after ingrowth of ^{90}Y and calculations to account for the ingrowth of ^{90}Y and decay of ^{89}Sr . When the ^{89}Sr is high, the change in activity upon ^{90}Y ingrowth may be relatively small and hard to measure and calculate precisely.

For samples with relatively high ^{89}Sr to ^{90}Sr ratios, purification and measurement of ^{90}Y following the initial separation and measurement of $^{89/90}\text{Sr}$ and suitable ingrowth period, can offer a much more reliable assay of ^{90}Sr . The ^{89}Sr can then be calculated by difference by subtracting the appropriate amount of ^{90}Sr (plus ^{90}Y ingrowth) from the initial total $^{89}\text{Sr} + ^{90}\text{Sr}$ count. In this method, yttrium carrier is added to the planchet containing the purified $^{89}\text{Sr}/^{90}\text{Sr}$ after a 2-3 days (or longer) ^{90}Y ingrowth period. The residues from the planchets were dissolved in 8M HNO_3 , warming on a hot plate, and the planchet was rinsed 3 or 4 times with ~5 ml 8M HNO_3 . All aliquots were transferred to a 50 mL tube, and the 8M HNO_3 solution was loaded onto DGA Resin column to rapidly purify ^{90}Y . ^{89}Sr and ^{90}Sr are effectively removed using this separation. After ^{90}Y elution in 0.25M HCl, a small volume of the final purified eluent was taken for ICP-MS assay to determine the Y chemical yield. The ^{90}Y separation time used is the midpoint of the time required for the sample loading step.

Column separation for Strontium-90 (using ^{90}Y). Figure 4 shows the DGA Resin method used when ^{90}Y was collected directly from the steel sample for rapid purification without waiting for ingrowth. This method is applicable when ^{89}Sr and other short lived fission products are known to be absent and assumes equilibrium between ^{90}Sr and ^{90}Y . After collecting ^{90}Y from the steel samples, the samples were loaded onto DGA Resin cartridges. The DGA Resin was rinsed with 8M HNO_3 to remove Ca and Pb isotopes, and with 0.05M HNO_3 to remove any U isotopes that may be present. A 20 mL rinse of 3M HNO_3 -0.25M HF was used to remove any Th isotopes. 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. Sample results were corrected for the removal of 0.5% of the ^{90}Y eluent solution.

Counting methods. Two different measurement techniques were tested, gas flow proportional

counting and liquid scintillation counting. Gas flow proportional counting was used to count the planchets containing purified ^{90}Sr + ^{89}Sr or ^{90}Sr prepared using the Sr Resin separation method. To count ^{90}Y by gas flow proportional counting, 25 mm polypropylene filters used to collect the filtered YF_3 microprecipitate were counted. In each case a 0.1 mL volume of purified sample (0.5% of sample) was taken to determine the yttrium yield by ICP-MS.

For measurement by LSC counting, the 25 mm filter was placed in a plastic LSC vial. Two milliliters of 0.25M HCl—0.05M boric acid were added to each LSC vial and mixed well to dissolve the fluoride microprecipitate. Following this dissolution of the YF_3 , 17 mL Ecolite liquid scintillation cocktail was added to each vial and mixed well. Cerenkov counting could have been also used on the final purified eluent. However, the counting efficiency using Cerenkov counting is only 60-70% relative to the LSC measurement using cocktail. It was found that that collection of YF_3 on a filter took less time than evaporation of the eluent on a hot plate to reduce the volume and acid for LSC counting.

Gas flow proportional counting and LSC gave very good results. However, a key difference is that proportional counting allows for simultaneous counting of multiple samples using a drawer based system. While the drawer system detector backgrounds may be slightly higher than sequential instruments (~ 1.3 cpm vs. ~ 1 cpm), longer count times may be used to achieve even lower detection limits, in contrast to the sequential counting done in a liquid scintillation counter. Liquid scintillation counting does allow the sample spectrum to be examined for potential interferences, which may be resolved by selecting the appropriate counting window. However, typical modern sample preparation approaches offer effective removal of most impurities, which reduces this advantage somewhat. Lower detection limits are often a key requirement for environmental analyses, but may not be as important for emergency response or higher activity nuclear process or waste samples.

Cerenkov Counting Option. While Cerenkov counting was not tested in this study, it is widely used and this approach can be adapted to this steel sample preparation method to count ^{89}Sr and ^{90}Y . [10, 17, 18] Cerenkov radiation is electromagnetic radiation emitted when a charged particle (such as an electron) passes through a dielectric medium at a speed greater than the phase velocity of light in that medium. Cerenkov counting relies on the Cerenkov radiation being detected directly by the photomultiplier tubes without the addition of LSC cocktail. Cerenkov radiation from high-energy beta emitters, such as ^{90}Y and ^{89}Sr (2280 and 1463 keV beta endpoint energy, respectively) can be counted in a scintillation counter. The beta emission from ^{90}Sr (546 keV) is below the threshold for Cerenkov counting. Chung et al [18] reported

a method using Cerenkov counting to determine ^{89}Sr and ^{90}Sr in milk. Using Cerenkov counting, the counting efficiency for ^{90}Y is about 65-70%, while ^{90}Y counting efficiency in liquid scintillation cocktail is 90-100%. One advantage of Cerenkov counting for radiostrontium measurements is that ^{89}Sr may be determined immediately, without waiting on ^{90}Y ingrowth, as the beta decay energy of ^{90}Sr is too low to cause Cerenkov radiation to be emitted. Additionally, Cerenkov counting does not suffer from the quench effects that can limit application of LSC and can eliminate low level beta interferences that may be encountered in some samples. Gas flow proportional counting has the ability to eliminate very low energy particles as well, as it has an avalanche threshold, such that charged particles must have sufficient energy to result in pulse formation and subsequent gas multiplication.

Apparatus

A Tennelec LB 4100 gas flow proportional counter was used to count the ^{89}Sr and ^{90}Sr spiked samples. The detectors were calibrated using NIST Traceable $^{90}\text{Sr}/^{90}\text{Y}$ and ^{89}Sr sources to match the sample geometry. Detector backgrounds were 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.

A Beckman Coulter LS 6500 liquid scintillation counter was used to perform the liquid scintillation measurements of ^{90}Y . The liquid scintillation counting of these samples in this study utilizes full window (0-1400 CH) and partial window (50-1400 and 100 - 1400CH) ROI (region of interest) allowing for reducing background and increasing sensitivity (expressed as E^2/B) allowing for a reduction in the calculated MDC.

Multi-element analysis for the determination of column capacity factors were performed on an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES) equipped with an SPS 3 autosampler.

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.

Results and Discussion

Table 1 shows the individual results for the determination of ^{90}Sr in ten 2 g steel samples spiked with ^{90}Sr using the Sr Resin separation option and gas flow proportional counting. The results were corrected for stable Sr carrier yield. The average ^{90}Sr result was 1.41 Bq g^{-1} , with a -0.4% bias and SD (standard deviation) of 0.04 Bq g^{-1} . The average Sr carrier recovery was $90.1\% \pm 2.4\%$ (SD). The high Sr chemical yields and excellent results for ^{90}Sr versus known values indicate the ruggedness of the sample preparation and measurement steps. The uncertainties for the individual ^{90}Sr results were typically $\pm 3\text{-}4\%$ (1 SD), with a 60 minute count time. Approximately 37 Bq of ^{137}Cs was added to test for the removal of this fission product interference. The results show there was no adverse impact due to the presence of this level of ^{137}Cs in the samples. The fluoride preconcentration step provides a factor of ~ 1000 decontamination from ^{137}Cs and the column separation typically provides another factor of ~ 1000 . This approach enhances the ruggedness of this method significantly, providing a decontamination factor for ^{137}Cs of approximately 10^6 .

Table 2 shows the individual results for the determination of ^{90}Sr in eight 1 g steel samples spiked with ^{90}Sr using the DGA Resin separation option for direct separation of ^{90}Y and gas flow proportional counting. The results were corrected for stable Y carrier yield. Four 1g steel samples were spiked with $1.415 \text{ Bq } ^{90}\text{Sr}$ and 4 steel samples were spiked with $2.83 \text{ Bq } ^{90}\text{Sr}$. The average bias versus the known values was -2%. The average Y carrier recovery was $96.9\% \pm 3.7\%$ (SD). The high Y carrier yields and excellent results for ^{90}Sr versus known values indicate the effectiveness of the sample preparation and illustrates the strong affinity of DGA Resin for Y(III). The uncertainties for the individual ^{90}Sr results were typically $\pm 3\text{-}4\%$ (1 SD), with a 60 minute count time.

Table 3 shows the individual results for the determination of ^{90}Sr in six 1 g steel samples spiked with ^{90}Sr using the DGA Resin separation option for direct isolation of ^{90}Y and liquid scintillation counting. The results were corrected for stable Y carrier yield. The average of ^{90}Sr result was 1.45 Bq g^{-1} , with a -1.8% bias and SD (standard deviation) of 0.03 Bq g^{-1} . The average Y carrier recovery was $93.7\% \pm 1.7\%$ (SD). The high Y carrier yields and excellent results for ^{90}Sr versus show that the method can be effectively coupled with liquid scintillation counting. The uncertainties for the individual ^{90}Sr results were typically $\pm 3\text{-}4\%$ (1 SD), with a 60 minute count time. Approximately 51 Bq of ^{137}Cs were added to each sample for this test, with no discernable adverse impact on the ^{90}Sr results.

Table 4 shows the individual results for the determination of $^{89}\text{Sr} + ^{90}\text{Sr}$ in eight 1 g steel samples spiked with ^{89}Sr and ^{90}Sr using Sr Resin to separate $^{89/90}\text{Sr}$ and gas flow proportional counting, followed by

ingrowth and separation of ^{90}Y . The results were corrected for stable Sr carrier yield. The average of total $^{89}\text{Sr} + ^{90}\text{Sr}$ result was 3.97 Bq g^{-1} , with a 4.1% bias and SD (standard deviation) of 0.09 Bq g^{-1} . The average Sr carrier recovery was $94.1\% \pm 2.8\%$ (SD). The high Sr carrier yields and excellent results for ^{90}Sr versus known values are indicative of the robust nature of the method. The uncertainties for the individual ^{90}Sr results were typically $\pm 4\%$ (1 SD), with a 60 minute count time. Yttrium-90 was collected from these planchets after about 5 days of ^{90}Y ingrowth and purified using DGA Resin.

Table 5 shows the individual results for the determination of ^{90}Sr via ^{90}Y in the eight 1 g steel samples after the initial count to determine $^{89}\text{Sr} + ^{90}\text{Sr}$ in (Table 4). Following DGA Resin separation, the ^{90}Y was measured on 25mm filters by gas flow proportional counting. The results were corrected for initial Sr carrier yield and stable Y carrier yield. The average ^{90}Sr result was 0.556 Bq g^{-1} , with a -1.8% bias and SD (standard deviation) of 0.051 Bq g^{-1} . It is not known why sample #3 showed a -16% bias, but it should be noted that without this atypical result that the average bias is 0.2%. The average Y carrier recovery was $97.5\% \pm 2.9\%$ (SD). The uncertainties for the individual ^{90}Sr results were typically $\pm 3\text{-}4\%$ (1 SD), with a 60 minute count time.

Table 6 illustrates that ^{89}Sr can be calculated by difference after the determination of ^{90}Sr via ^{90}Y . The average ^{89}Sr result for this set of data was calculated to be 3.425 Bq g^{-1} , with a 4.73% bias. The SD (standard deviation) for these results was 0.099 Bq g^{-1} . The total $^{89}\text{Sr} + ^{90}\text{Sr}$ measurement was adjusted for the slight variation in counting efficiencies between ^{89}Sr , ^{90}Sr and ^{90}Y , based on the separate ^{90}Sr assay using ^{90}Y .

In a similar test, $^{89}\text{Sr} + ^{90}\text{Sr}$ were added to 1g steel + 0.5g concrete. After an initial acid digestion to dissolve the steel sodium hydroxide fusion in a Zr crucible was applied. Similar results to the data in Tables 4 and 5 were obtained. For the initial Sr Resin separation assay of total $^{89}\text{Sr} + ^{90}\text{Sr}$, the average result was 3.38 Bq g^{-1} , with a 1.8% bias and SD (standard deviation) of 0.045 Bq g^{-1} . The average Sr carrier yield was 89.7%. The average ^{90}Sr result, determined by measuring ^{90}Y using DGA Resin and gas flow proportional counting after about 5 days of ^{90}Y ingrowth, was 0.533 Bq g^{-1} , with a -4.8% bias and SD (standard deviation) of 0.054 Bq g^{-1} . The average Y carrier recovery was $97.1\% \pm 2.7\%$ (SD).

The MDA (Minimum Detectable Activity) for the radiostrontium using this method with measurement was calculated according to equations prescribed by Currie: [19]

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

where B = Total Background counts, = $BKG \text{ (rate)} * \text{sample count time}$; CT = sample count time (min)
 R = Chemical Recovery; V = Sample aliquot (g) ; EFF = Detector Efficiency ; A = Isotopic abundance (in most cases this will be ~ 1) ; 0.060 = conversion from dpm to mBq.

The MDA (minimum detectable activity) for the gas flow proportional counts results can be adjusted as needed, depending on the sample aliquot and count time. For ^{89}Sr or ^{90}Sr in steel samples, the MDA is $\sim 25 \text{ mBq g}^{-1}$ for a 1 g sample aliquot, 60 minute count time, 90% chemical recovery, 54% detector efficiency and 1.5 count per minute background using gas flow proportional counting. For a 1g steel aliquot, the method MDA for the Sr isotopes with a 4 hour count time is $\sim 12 \text{ mBq g}^{-1}$.

For ^{89}Sr or ^{90}Sr in steel samples using liquid scintillation counting, the MDA is $\sim 60\text{-}80 \text{ mBq g}^{-1}$ for a 1 g sample aliquot, 60 minute count time, 90% chemical recovery, $\sim 100\%$ detector efficiency using liquid scintillation counting. The MDA varies slightly depending on whether a full window is used or slightly smaller windows are used to reduce background and increase sensitivity (expressed as E^2/B), allowing for a slight reduction in the calculated MDC. Regarding detection limits of LSC counting, Ultra low level LSC counters such as the Quantulus Ultra Low Level LSC (Perkin Elmer, Waltham, MS, USA) can achieve lower MDAs than noted here. There continues to be significant improvements in instrument technology, where lowering the background in liquid scintillation counting is of particular interest. Douglas et al [20] at Pacific Northwest National Laboratory (Richland, WA, USA) have been evaluating ways to lower backgrounds in a LSC system, critical for low level environmental measurements. This includes optimization of coincidence counting electronics, construction with low background materials and perhaps even a shallow underground location.

Conclusions

A new rapid method to determine ^{89}Sr and ^{90}Sr isotopes in steel samples has been developed that effectively digests steel samples (or steel plus concrete). The new method offers rapid separation of these isotopes with high chemical yields and effective removal of interferences such as ^{137}Cs . The method digests the samples with ruggedness and is very flexible, allowing several different measurement options depending on which Sr isotopes are needed. Both gas flow proportional counting and liquid scintillation counting may be used.

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References

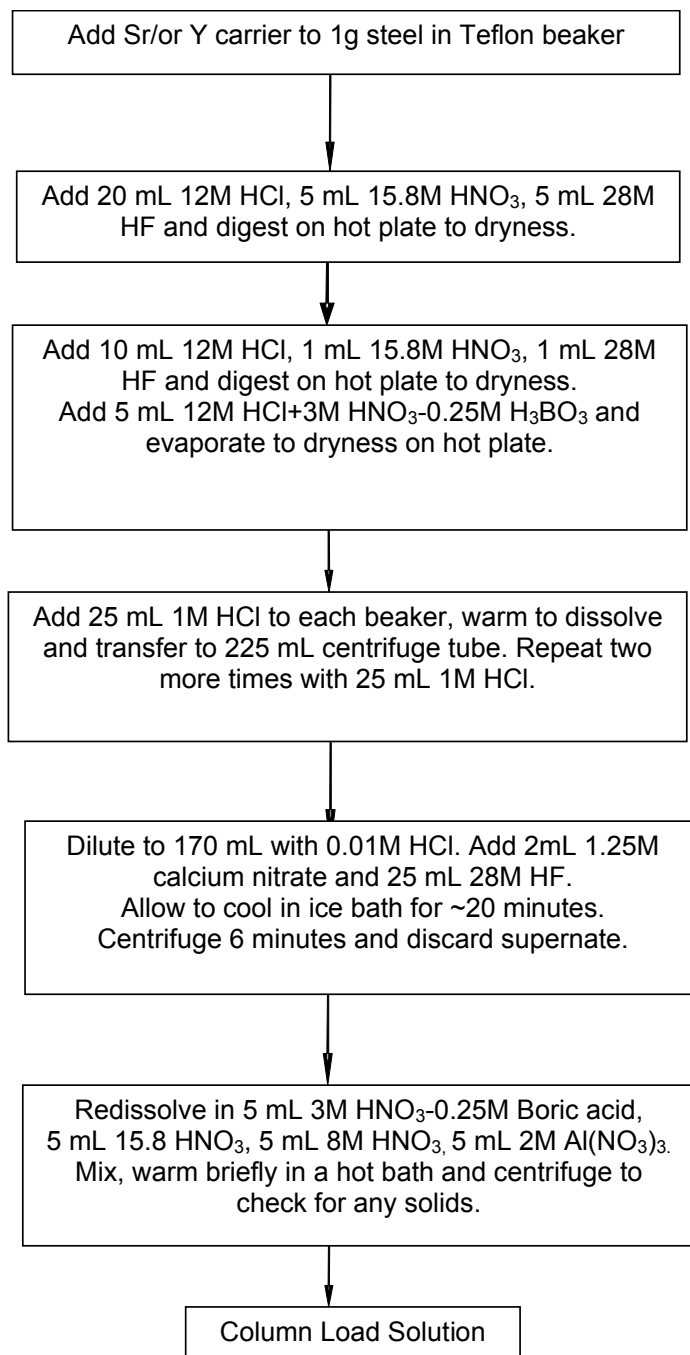
- [1] Stricklin, D.L., Tjarnhage, A., and Nygren, U. (2002) Application of low energy gamma-spectrometry in rapid actinide analysis for emergency preparedness, *J. Radioanal. Nucl. Chem.* 251 (1), 69
- [2] Maxwell S, Culligan B, and Wall A. G. (2011) Rapid radiochemical method for determination of actinides in emergency concrete and brick samples. *Analytica Chimica Acta* 701: 112-118
- [3] A Procedure for the Rapid Determination of Plutonium Isotopes and Am-141 in Soil and Sediment Samples by Alpha Spectrometry, http://www-pub.iaea.org/MTCD/publications/PDF/IAEA-AQ-11_web.pdf, Accessed 3/22/17
- [4] Vajda N, Törvényi A, Kis-Benedek G., Kim C.K., Bene B., and Mácsik Z. (2009) Rapid method for the determination of actinides in soil and sediment samples by alpha spectrometry, *Radiochim. Acta* 97, 395-401
- [5] Maxwell, S, Culligan, B. , Utsey, R. , Hutchison, J., McAlister, D and Sudowe, R. Rapid Method to Determine Actinides and Sr-89/90 in Limestone and Marble Samples, *J Radioanal Nucl Chem* October 2016, Volume 310, Issue 1, pp 377–388
- [6] Maxwell S, Hutchison, J and McAlister, D. (2015) Rapid Fusion Method for the Determination of Refractory Thorium and Uranium Isotopes in Soil Samples, *Journal of Radioanalytical and Nuclear Chemistry* Vol. 305, pp 631-641
- [7] European Metrology Research Programme, JRP ENV 09, metrology for Radioactive Waste Management, http://www.radwaste-emrp.eu/?page_id=10
- [8] Maxwell, S, Culligan, B. , Utsey, R. , Hutchison, J., McAlister, D and Sudowe, R., Rapid method to determine $^{89}\text{Sr}/^{90}\text{Sr}$ in large concrete samples, *J Radioanal Nucl Chem* , October 2016, Volume 310, Issue1, pp 399–411
- [9] Vajda N and Kim C. (2010), Determination of radiostrontium isotopes: A review of analytical methodology, *Applied Radiation and Isotopes*, Volume 68, Issue 12, pages 2306–2326

- 419 [10] Grahek Z and Nodilio M (2012) Continuous separation of Sr, Y and some actinides by mixed
420 solvent anion exchange and determination of Sr-89, Sr-90, Pu-238, Pu-239 and Am-241 in soil and
421 vegetation samples 293(3); p. 815-827
- 422 [11] Amano H, Sagamoto H, Shiga N (2016) Suzuki K Method for rapid screening analysis of Sr-90 in
423 edible plant samples collected near Fukushima, Japan. Appl Radiat Isot. 2016 Jun;112:131-5.
- 424 [12] Horwitz E. P, McAlister D, Bond A, Barrans Jr. A B (2005) Novel extraction chromatographic
425 resins based on tetraalkyldiglycolamides: characterization and potential applications. Solv.
426 Extr. Ion Exch. 23 No.3: 319-344
- 427 [13] Maxwell S, Culligan B and Utsey R. (2013) Rapid Determination of Radiostrontium in Seawater
428 Samples, Journal of Radioanalytical and Nuclear Chemistry Vol. 298, pp 867-875
- 429 [14] Innovative Technology to Provide Faster Results on Water Quality at Fukushima,
430 http://www.tepco.co.jp/en/press/corp-com/release/2014/1244484_5892.html, accessed 12/28/15
- 431 [15] Russel B, Garcia-Miranda M, and Ivanov P. (2017) Development of an optimised method for
432 analysis of ^{90}Sr in decommissioning wastes by triple quadrupole inductively coupled plasma mass
433 spectrometry, Appl Radiat Isot. Online, 2017 Jan 24
- 434 [16] Maxwell S, Culligan, B, Hutchison J, McAlister D and Sudowe R., (2017) Rapid Method to
435 Determine Plutonium Isotopes in Steel Sample, J Radioanal Nucl Chem , in press
- 436 [17] Günther, K, Lange, S and Veit, M. (2009) A rapid method for determining ^{89}Sr and ^{90}Sr by
437 Cerenkov counting. Applied Radiation and Isotopes, Volume 67, Issue 5
- 438 [18] Chung, K H, Lim J M, Ji YY, Choi G S, and Kang, M J (2015) Rapid determination of
439 radiostrontium in milk using automated radionuclides separator and liquid scintillation counter, J
440 Radioanal Nucl Chem Volume 304, Issue 1, pages 293-300
- 441 [19] Currie, LA (1968) Limits for qualitative and quantitative determination. Anal. Chem. 40: 586-593
- 442 [20] Douglas M et al. (2016). Liquid scintillation counting of environmental radionuclides: a review of
443 the impact of background reduction, J Radioanal Nucl Chem March 2016, Volume 307, Issue 3, pp
444 2495-2504

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450 Figure 1 Steel Dissolution with ^{89}Sr , ^{90}Sr / ^{90}Y Preconcentration Method

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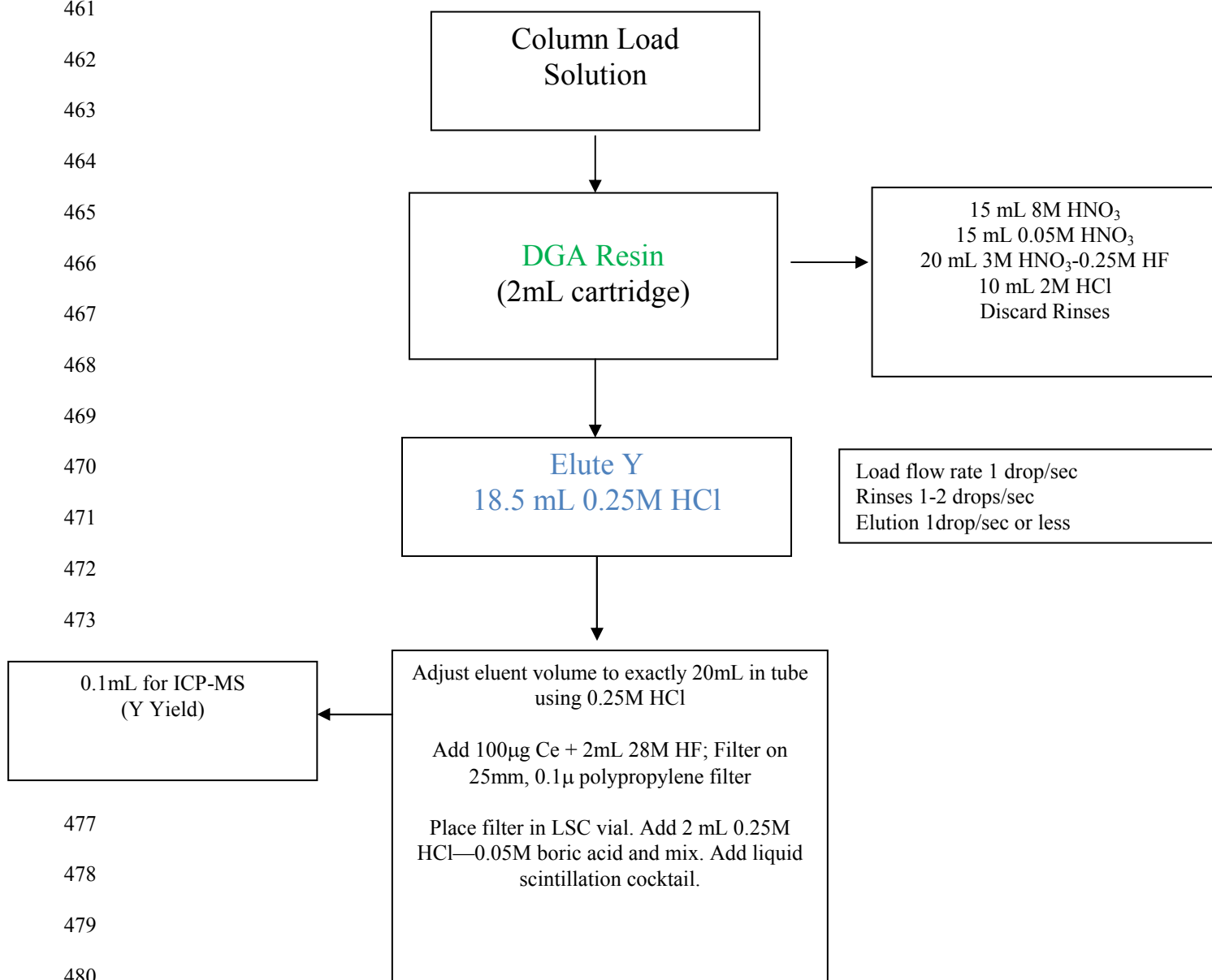
Figure 2 DGA Resin Separation for ^{90}Y in Steel

Figure 3 Affinity for Steel Components for Sr Resin In Nitric Acid

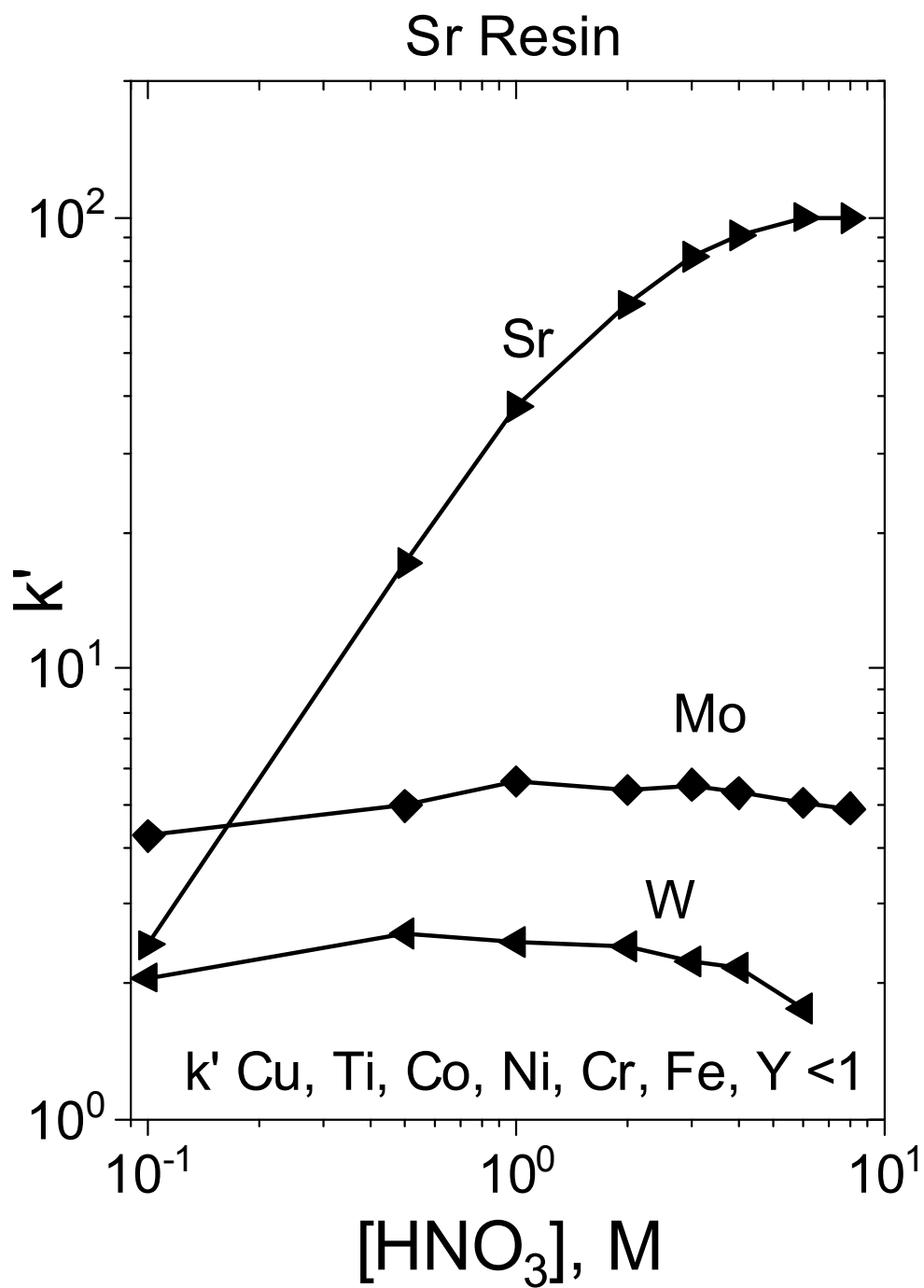


Figure 4 Affinity for Steel Components for DGA Resin In Nitric Acid

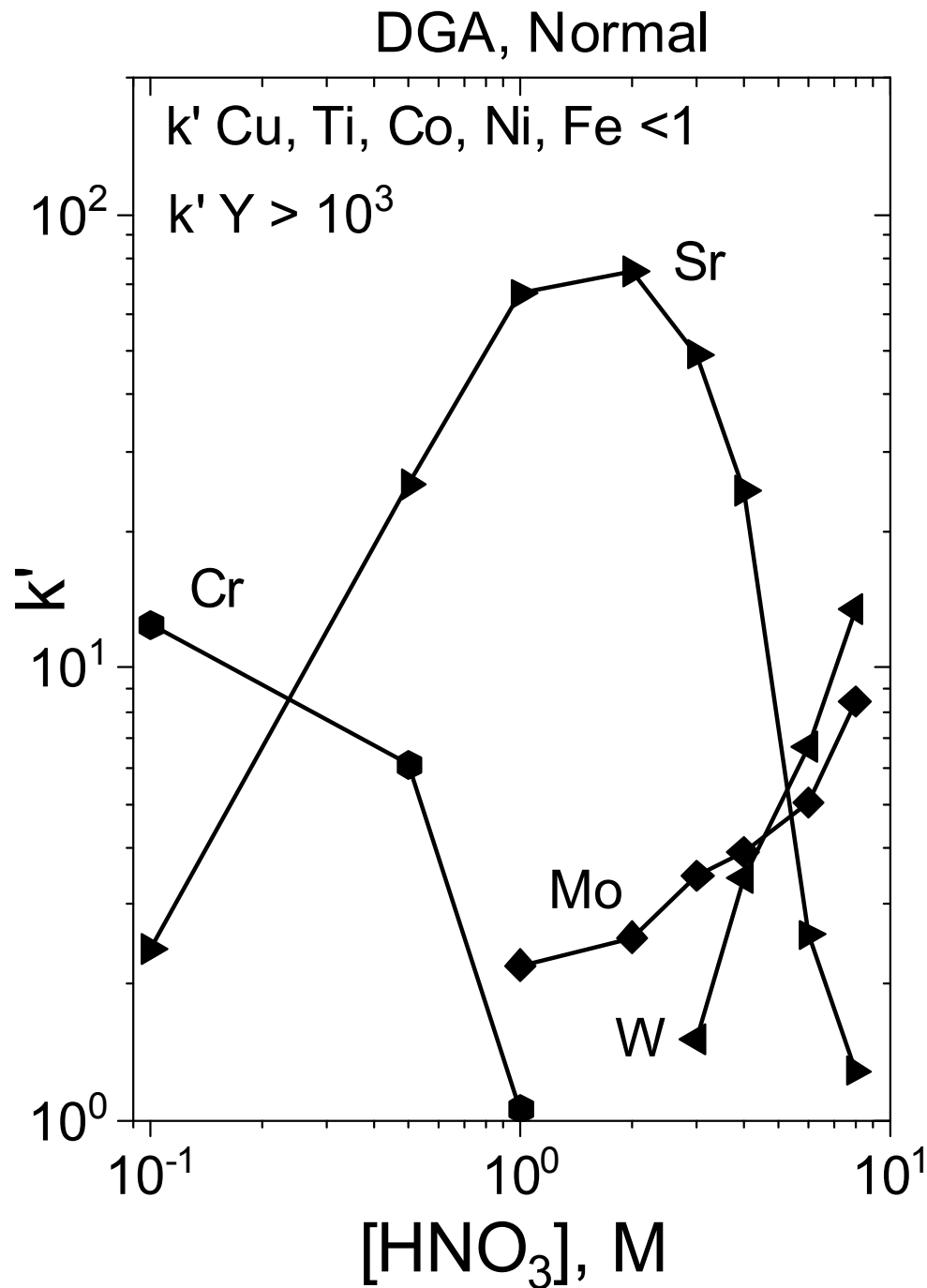


Table 1 Steel Sample Results: Sr Resin Method for ⁹⁰Sr (Gas Proportional Counting)

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	87.5	1.415	38.72	1.432	1.2
2	88.5	1.415	39.58	1.464	3.5
3	87.5	1.415	38.94	1.441	1.8
4	91.6	1.415	37.76	1.397	-1.3
5	87.5	1.415	38.91	1.440	1.7
6	88.5	1.415	37.57	1.390	-1.8
7	91.6	1.415	38.05	1.408	-0.5
8	91.6	1.415	36.17	1.338	-5.4
9	92.6	1.415	38.08	1.409	-0.4
10	93.6	1.415	37.22	1.377	-2.7
Avg. Spiked Smpls	90.1		38.1	1.41	-0.39
SD	2.4		1.0	0.04	2.6
% RSD	2.6		2.6	2.6	
		60 minute count			

Table 2 Steel Sample Results: DGA Resin Method for ^{90}Sr (^{90}Y) (Gas Proportional Counting)

Sample	Y 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	96.5	1.415	37.74	1.396	-1.3
2	98.5	1.415	37.38	1.383	-2.3
3	95.6	1.415	37.65	1.393	-1.6
4	89.4	1.415	36.30	1.343	-5.1
5	100.0	2.830	76.29	2.822	-0.3
6	101.9	2.830	74.29	2.748	-2.9
7	96.6	2.830	78.50	2.904	2.6
8	97.1	2.830	72.31	2.675	-5.5
Avg. Spiked Smpls	96.9				-2.0
SD	3.7				2.6
% RSD	3.8				
		60 minute count			

Table 3 Steel Sample Results: DGA Resin Method for ^{90}Sr (^{90}Y) (Liquid Scintillation Counting)

Sample	Y 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	94.8	1.447	37.13	1.374	-5.0
2	92.1	1.447	39.04	1.444	-0.2
3	91.6	1.447	39.10	1.447	0.0
4	93.6	1.447	38.38	1.420	-1.8
5	93.8	1.447	38.62	1.429	-1.2
6	96.1	1.447	38.13	1.411	-2.5
Avg. Spiked Smpls	93.7			1.42	-1.8
SD	1.7			0.03	1.8
% RSD	1.8				
		60 minute count			

Table 4 Steel Sample Results: Sr Resin Method for $^{89}\text{Sr} + ^{90}\text{Sr}$ (Gas Proportional Counting)

Sample	Y Carrier Yield	$^{89}\text{Sr} + ^{90}\text{Sr}$ Reference Value	$^{89}\text{Sr} + ^{90}\text{Sr}$ Measured Value	Difference
ID	(%)	(Bq smp ⁻¹)	(Bq smp ⁻¹)	(%)
1	91.41	3.816	4.013	5.2
2	90.72	3.816	4.118	7.9
3	97.59	3.816	3.942	3.3
4	94.16	3.816	3.957	3.7
5	92.10	3.816	3.957	3.7
6	92.78	3.816	3.784	-0.8
7	96.22	3.816	4.013	5.2
8	97.59	3.816	3.998	4.8
Avg. Spiked Smpls	94.1		3.97	4.1
SD	2.8		0.09	
% RSD	2.9			
		60 minute count		

Table 5 Steel Sample Results: ^{90}Sr via ^{90}Y Assay after short ingrowth

Sample	Y Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	99.80	0.566	0.523	-7.6
2	98.90	0.566	0.618	9.2
3	99.80	0.566	0.476	-16.0
4	91.82	0.566	0.618	9.2
5	96.21	0.566	0.581	2.7
6	95.41	0.566	0.562	-0.7
7	100.00	0.566	0.511	-9.7
8	98.40	0.566	0.557	-1.5
Avg. Spiked Smps	97.5		0.556	-1.8
SD	2.9		0.051	
% RSD	2.9			
		60 minute count		

Table 6 Steel Sample Results: ^{89}Sr Calculated by Difference After ^{90}Sr Assay

Sample	Sr Carrier Yield	^{89}Sr Reference Value	^{89}Sr Measured Value	Difference
ID	(%)	(Bq smp $^{-1}$)	(Bq smp $^{-1}$)	(%)
1	91.41	3.270	3.51	7.2
2	90.72	3.270	3.50	7.0
3	97.59	3.270	3.47	6.1
4	94.16	3.270	3.35	2.3
5	92.10	3.270	3.38	3.5
6	92.78	3.270	3.23	-1.3
7	96.22	3.270	3.51	7.4
8	97.59	3.270	3.45	5.5
Avg. Spiked Smpls	94.1		3.425	4.7
SD	2.8		0.099	