Rapid Method to Determine Actinides and Sr-89/90 in Limestone and Marble Samples

Sherrod L. Maxwell[1], Brian Culligan[1], Jay B. Hutchison[1], Robin C. Utsey[1]

Ralf Sudowe[2] and Daniel R. McAlister[3]

[1]Savannah River Nuclear Solutions, LLC, Building 735-B, Aiken, SC 29808, USA
[2]University of Nevada Las Vegas, Las Vegas, NV 89154
[3]PG Research Foundation, Inc. Lisle, IL 60532

Author for correspondence (email: sherrod.maxwell@srs.gov)

phone   803-952-7473

fax   803-952-7881

Abstract

A new method for the determination of actinides and radiostrontium in limestone and marble samples has been developed that utilizes a rapid sodium hydroxide fusion to digest the sample. Following rapid pre-concentration steps to remove sample matrix interferences, the actinides and $^{89/90}$Sr are separated using extraction chromatographic resins and measured radiometrically. The advantages of sodium hydroxide fusion versus other fusion techniques will be discussed. This approach has a sample preparation time for limestone and marble samples of <4 hours.

Introduction

Limestone and marble have been used in many important buildings and monuments in the United States, including the Pentagon, the Lincoln Memorial, the Washington Monument, Washington National Cathedral in Washington, DC, and the Empire State Building in New York City. If 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 occurs that affects these monuments or buildings, there will be an urgent need for rapid analyses of limestone and marble materials to support dose mitigation and environmental clean-up. It has been the approach of the Savannah River Environmental Laboratory to combine rapid, rugged sample digestion and preconcentration techniques with rapid, innovative column

purification methods to analyze building materials samples 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. This includes recently published methods for soil, concrete and brick, and asphalt. [1, 2, 3]

Limestone is sedimentary rock containing calcite and aragonite, which are different forms of calcium carbonate. Most limestone also contains skeletal fragments of marine organisms such as coral and mollusks. According to the US Geological Survey, "The main difference between limestone and marble is that limestone is a sedimentary rock, typically composed of calcium carbonate fossils, and marble is a metamorphic rock. Limestone forms when shells, sand, and mud are deposited at the bottom of oceans and lakes and over time solidify into rock. Marble forms when sedimentary limestone is heated and squeezed by natural rock-forming processes so that the grains recrystallize. If you look closely at a limestone, you can usually see fossil fragments (for example, bits of shell) held together by a calcite matrix. Limestone is more porous than marble, because there are small openings between the fossil fragments. Marble is usually light colored and is composed of crystals of calcite locked together like pieces of a jigsaw puzzle. Marble may contain colored streaks that are inclusions of non-calcite minerals." [4] The sample composition of limestone and marble is very similar, with large amounts of calcium and carbonate present. Limestone or marble samples taken after a RDD or IND may be contaminated with refractory particles containing actinide isotopes, ^{89}Sr and ^{90}Sr. A rapid, rugged digestion is required to ensure total digestion of these refractory particles. Rapid, reliable measurement of these radionuclides is very important to maintain the public trust.

Vajda et al. [5] reported a method for actinides in soil in which 0.5 g soil samples were fused using lithium metaborate in platinum crucibles. After preconcentration of actinides using calcium fluoride precipitation, actinides were separated on TRU extraction chromatographic resin. The use of lithium metaborate fusion ensured that refractory particles were digested. The results agreed well with reference values, however, the method appears to be limited to 0.5g soil aliquots and requires very expensive platinum crucibles. While lithium metaborate fusion can be very effective, it can also be somewhat difficult to remove from the crucible. In addition, when this fusion is not combined with calcium fluoride or

lanthanum fluoride precipitation to remove silicates, the acidified fusion cake may need treatment with polyethylene glycol (PEG) to flocculate silica in the sample. If gel-like silicates are not removed, they can cause resin column clogging or loss or radionuclides on the residual solids.

Jia et al. [6] reported a fusion method for determination of thorium isotopes in soil by alpha-spectrometry. After fusion with Na_2CO_3 and Na_2O_2 at 600 ˚C, soil samples were leached with HNO_3 and HCl. Thorium was coprecipitated together with iron (III) as hydroxides and/or carbonates at pH 9, separated from uranium and other alpha-emitters by a Microthene-TOPO (tri-octyl-phosphine oxide) chromatographic column, electrodeposited on a stainless steel disk, and measured by alpha-spectrometry. It was noted in this work that leaching of uranium and thorium from soil sample with only mineral acids (dilute or concentrated), such as HCl, HNO_3, $HClO_4$, HF, etc., may be incomplete. The method also addressed the common problem of resulting silicates, which interfere with subsequent method steps, by evaporation and precipitation of the silicate solids. This method provided total digestion of the soil aliquots by fusion, use of a furnace instead of a burner to allow multiple samples to be processed simultaneously, and a way to address silicates, at least for relatively small sample aliquots. The method also seems to be limited to 0.5 g soil and requires expensive platinum crucibles. The removal of silica required evaporation of a 150 mL leachate following the fusion, precipitation and washing of insoluble silicates, and filtration of remaining residue after final dissolution of an iron hydroxide precipitate.

The U.S EPA published a rapid carbonate fusion method for soil [7] that also requires an additional pre-digestion with hydrofluoric acid to remove silica, then fusion of one sample at a time over a burner using expensive platinum crucibles. The EPA soil fusion method, however, does direct that a rapid sodium hydroxide fusion, used in the EPA rapid method for concrete and brick, may also be used for soil. This fusion method can be performed in relatively inexpensive zirconium crucibles. [8] The ability to digest many samples at the same time in a furnace with inexpensive crucibles, instead of heating one at a time over a burner, would seem to be advantageous not only in an emergency, but also for routine laboratory processing.

Rugged soil dissolution methods are essential to accurately determine actinide isotopes in soil. The recent failure by ~80% of participating labs in the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP) Session 30 was traced to incomplete dissolution of refractory particles in the samples by acid digestion and points to the need for the implementation of robust sample digestion of soil

samples and other solid matrices. Labs that did not utilize total dissolution methods typically reported [234]U and [238]U results that were ~60% lower than the soil reference values, even when digesting this soil with hydrofluoric acid.

Jurečič et al [9] studied several soil decomposition techniques and found that alkaline fusion digested uranium in the soils studied completely. Other techniques, such as conventional wet dissolution with mixtures of HNO_3, $HClO_4$ and HF acids, microwave dissolution using HNO_3 and HF were less effective, with uranium losses of 35-60%. Two reference materials, including NIST-4353a Rocky Flats Soil, and six soil samples from near a former uranium mine were investigated. It is interesting that the authors found more residual, undissolved uranium using microwave techniques than the conventional wet dissolution methods tested. Relatively long digestion and evaporation times (up to 2 days) were cited in this work. The rapid sodium hydroxide fusion can be completed in < 30 minutes, with subsequent preconcentration steps typically taking < 2 hours. No evaporation steps are required, and uranium recoveries are nearly quantitative, even when refractory material is present.

Rapid sodium hydroxide fusion methods have been reported by this laboratory for many different sample matrices, including soil, concrete, brick and asphalt. The ruggedness of these methods has been validated by analyzing soil containing refractory Pu or U. [10, 11] Application of the sodium hydroxide fusion to limestone and marble, and optimization of the subsequent matrix removal and separation steps has led to a new method to determine actinides and radiostrontium in these building materials. The method, developed in the Savannah River Environmental Laboratory, effectively digests refractory actinide and strontium isotopes and allows a sample preparation for batches of 12 limestone or marble samples of <4 hours. Several samples are fused simultaneously at 600˚C in zirconium crucibles in muffle furnaces. Rapid sodium hydroxide fusion offers advantages over acid dissolution (which usually takes longer and may not be as rugged), as well as other fusion techniques. The preconcentration techniques effectively eliminate sample matrix interferences, and result in high chemical yields. Total dissolution is very important for the analysis of building materials such as limestone or marble, where refractory particles may be present following a radiological event. The sodium hydroxide fusion is rapid, rugged and can be performed using relatively inexpensive zirconium crucibles. The fusion can be performed at low temperature (600°C), without a burner, and multiple samples can be processed simultaneously in furnaces. Unlike lithium metaborate fusion, the fusion cake comes out of crucible easily. This approach allows LaF_3 and CaF_2

preconcentration steps to remove iron, titanium and silicates, which can interfere with rapid column separations.

Once the sample is digested, there are many different stacked cartridge options, depending on which analytes are desired. Plutonium and neptunium are separated quickly and efficiently using TEVA Resin cartridges. Uranium can be collected and purified using TEVA plus TRU Resin cartridges, while Am/Cm can be separated using TEVA plus DGA Resin cartridges. A combination of TEVA+TRU+DGA Resin may also be used.[2] Rapid flow rates achieved using vacuum box technology, and stacked resin cartridges with highly selective extraction chromatographic resins significantly reduce separation times and waste volumes. Alpha spectrometry sources were prepared by cerium fluoride microprecipitation, however, electrodeposition can also be used with slight adjustments to some eluents. Other measurement techniques such as inductively-coupled plasma mass spectrometry (ICP-MS) can also be employed.

Experimental

Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336), TRU-Resin® (tri-n-butylphosphate (TBP) and octyl (phenyl) N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), 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-Q2™ water purification system. All other materials were ACS (American Chemical Society) reagent grade. Radiochemical isotope tracers ^{236}Pu, ^{242}Pu ^{,243}Am, and ^{232}U were obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1} to enable yield corrections. ^{90}Sr was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2.96 Bq mL^{-1}. Np-237 and ^{244}Cm were obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1}.   U-232 tracer was prepared to be self-cleaning, removing its ^{228}Th daughter using barium sulfate precipitation [12].

Procedures

Column preparation. TEVA , TRU, 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 ~1-2 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. It has been demonstrated that reduced separation times can be achieved using higher flow rates by increasing the applied vacuum without significant loss of analytes. [13, 14] 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 actinides in limestone and marble samples. Limestone and marble samples were pulverized, homogenized and passed through a 20 mesh sieve prior to sampling so that representative samples could be taken. One gram aliquots of limestone and marble were analyzed for actinides, while 1.5 g aliquots were used for ^{90}Sr measurements. For testing purposes, ^{90}Sr was added but the method can also be tailored to measure ^{89}Sr. MAPEP 30 soil aliquots (~0.25 g) were also placed into 250 mL low form zirconium crucibles along with the limestone or marble sample aliquots. The MAPEP soil samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. MAPEP 24 soil standard was chosen because the soil contains refractory ^{239}Pu in the soil. Successful analysis would indicate analytical method ruggedness and applicability when refractory particles are present. Reference activities were calculated based on the activity added per mass of limestone or marble analyzed, excluding the mass of the MAPEP soil added.

Tracers were added to each crucible, and the crucibles were dried briefly on a hotplate. Figure 1 shows the sample preparation flowchart for actinides in limestone and marble samples. After removing crucibles from the hotplate, 15 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 ~ 15-20 minutes. The crucibles were removed from the furnace, cooled for about 10 minutes, and transferred to a hot plate. Water was added to dissolve the fusion cake on the hot plate and transfer the sample to 225 mL centrifuge tubes. 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 the crucibles, and heated until very hot on the hot plate to ensure complete removal of actinides and strontium from the crucible.

Sample Preconcentration for Actinides. The actinide preconcentration and matrix removal steps are described below. One hundred and twenty-five milligrams of Fe (added as Fe $(NO_3)_3$) and 5 mg of La (as lanthanum nitrate standard) were added to each 225 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 160 mL with water, 20 mL 12M HCl was added, and the tubes were cooled in an ice bath to room temperature.

Due to the high calcium content in limestone and marble, no additional calcium was added to the limestone or marble aliquots. For processing of batches where reagent blank and laboratory control samples (LCS) are also included (no limestone or marble is added), 200 mg Ca may be added to simulate the high Ca matrix for the blank and LCS. Five milliliters of 3.2M ammonium hydrogen phosphate were added to each tube, and each tube was capped and mixed well. The phosphate and 4 mL 20% $TiCl_3$ (added to each tube to reduce U(VI) to U(IV)), help improve uranium recovery during the precipitation steps. The samples were mixed and cooled in an ice bath for ~10 minutes. The tubes were centrifuged at 3500 rpm for ~5 minutes and the supernate was discarded. The precipitates were partially dissolved by adding 1.5 M HCl to a total volume of 80 mL in each tube and diluting to 170mL with 0.01M HCl, mixing well with each addition. After dilution, 1 mg of La (as lanthanum nitrate standard) was added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, 3 mL 20% titanium chloride were added to each sample. Ten milliliters of 28M HF were added to each tube. The samples were mixed well, dissolving any remaining Fe-Ti hydroxide solids and forming a La-Ca-fluoride precipitate. The tubes were cooled briefly in an ice bath for ~5 minutes, removed, allowed to stand for ~5 minutes and centrifuged for 5 minutes at 3500 rpm. The LaF_3 removal step effectively removes almost all of the Fe and Ti, as well as silicates that can affect column flow.

The supernate was discarded, and the precipitate containing the actinides was dissolved in 7 mL of 3M HNO_3-0.25M H_3BO_3, mixed, and transferred to 50 mL tubes. The 225 mL tubes were rinsed with 6 mL of 7M HNO_3, 7 mL of 2 M $Al(NO_3)_3$ and 3 mL 3M HNO_3, respectively, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed using a vortex stirrer and heated 2-5 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 are very clear. If gel-like solids are observed in the sample load solutions or flow problems are encountered for more difficult sample types, that particular sample may require slightly less titanium chloride added or a slightly larger load solution volume to facilitate total dissolution.

Sample Preconcentration for Strontium-89,90. Figure 2 shows the preconcentration steps for radiostrontium in limestone and marble samples. The method is very similar to the actinide method, however, no 12M HCl was added, since the collection of alkaline earth elements such as Ca/Sr is desired. Additional phosphate was added to ensure effective precipitation of the strontium. Following the iron hydroxide and calcium fluoride precipitations, the supernate was discarded and the precipitate containing the strontium 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 225 mL tubes were rinsed with 7 mL of 8M HNO_3 and 7 mL of 2 M $Al(NO_3)_3$, respectively, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed using a vortex stirrer and heated 2-5 minutes in a hot block heater at 105°C. The 50 mL tubes containing the load solutions were centrifuged, and ant traces of solids were discarded.

Column separation for Actinides and Strontium-89,90. Column separation techniques previously reported were used to separate and purify actinides. [1, 2, 3, 10, 11] Depending on the desired analytes, several separation schemes can be employed. Pu and Np isotopes were separated rapidly using a single TEVA Resin cartridge, while U isotopes are separated using a stacked TEVA + TRU Resin cartridge approach. Figure 3 shows how TEVA+TRU Resin as stacked cartridges can be used to rapidly separate Pu, Np and U using this method. Am and Cm are separated from interferences using TEVA + DGA Resin, while ^{90}Sr is separated using Sr Resin (3mL Sr Resin, using stacked 2 mL+1mL resin cartridges). The Sr Resin method used is similar to what was published for ^{90}Sr in large soil samples, except that volumes were scaled back slightly for 3 mL Sr Resin instead of 4 mL Sr Resin. The sample load solutions were loaded onto 3 mL Sr Resin 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 ~1-2 drops per second. The following column rinses were 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 was eluted from the resin with 15 mL 0.05M HNO_3 at ~1 drop per second. [15]

Cerium fluoride microprecipitation was used to prepare the purified actinide samples for alpha spectrometry counting. After adding 50 μg Ce, 0.5 mL 30 wt% H_2O_2 and 1 mL 28 M HF to the Pu eluent solution and waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 μm pore size disposable Resolve™ filter funnel). 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. A similar approach was used for the Am/ Cm and U eluents. For Am/Cm, 40 μg Ce, 0.2 mL 30 wt% H_2O_2

and 1 mL 28 M HF were added. To prepare the U eluents, 100 µg Ce, 0.5 mL 10% $TiCl_3$ and 1 mL 28 M HF were added. The additional Ce added for U eluents is needed to ensure effective precipitation of U even when higher levels of U are present in the samples. The filtering protocol as described above was followed after a 15 minute wait time. Adding hydrogen peroxide to the Pu and Am/Cm precipitation steps provides additional decontamination from uranium by ensuring the U is U(VI), which does not carry on the CeF_3 precipitate. $TiCl_3$ is added during the uranium microprecipitation steps to reduce U(VI) to U(IV), which will carry with the CeF_3.

Sr was eluted from 3 mL Sr Resin with 15 mL 0.05M HNO_3 at ~1 drop per second. This eluent solution 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, 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 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. Sr Resin also collects Pb isotopes while Bi 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.

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 after ^{90}Y ingrowth. In that case, 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 to determine ^{89}Sr and [90]Sr. When the ^{89}Sr is high, the ^{90}Y ingrowth fraction is very small and hard to measure precisely. In cases such as these, 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 by subtracting the appropriate amount of [90]Sr (plus ^{90}Y ingrowth) from the initial total [89]Sr+[90]Sr count. Figure 3 shows a DGA Resin separation method previously reported for seawater that may also be used for limestone, marble and other solid samples to purify [90]Y. [16] This DGA Resin method has also been successfully used for high ^{89}Sr, low ^{90}Sr air filter samples from the MAPEP program. In this method, yttrium carrier is added to the

planchet containing the purified ^{89}Sr/ ^{90}Sr after a 2-3 day (or longer) ^{90}Y ingrowth period. The planchet

solids are dissolved in 8M HNO_3 and transferred to a 50 mL tube. This 8M HNO_3 solution is loaded onto

DGA Resin column to 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

chemical yield.

Apparatus

Plutonium, neptunium, uranium, americium and curium isotopic measurements were performed by

alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. The

PIPS detectors have an active surface of 450 mm^2. The nominal counting efficiency for these detectors is

28-30%. The distance between the sample and detector surface is ~3 mm.

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}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. 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.

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 $^{239/240}$Pu in six 1 g limestone samples

spiked with a small amount of MAPEP 24 soil using this rapid separation method and alpha spectrometry.

The results were corrected for ^{242}Pu tracer yield. The average $^{239/240}$Pu result was 29.6 mBq g^{-1}, with a 0.6%

bias and SD (standard deviation) of 2.2 mBq g^{-1}. The average tracer recovery for ^{242}Pu was 100% ± 4.9%

(SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the

ruggedness of the sample preparation and measurement steps, even for refractory Pu isotopes. The Full

Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show acceptable alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time. Shorter count times may be used in a radiological emergency, with higher tracer activity levels added to minimize counting uncertainty for the tracer used.

Table 2 shows the individual results for the determination of $^{239/240}$Pu in six 1 g limestone samples spiked with MAPEP 30 soil samples. The results were corrected for ^{236}Pu tracer yield. Pu-236 tracer was added so that ^{237}Np could also also be measured, since ^{242}Pu interferes with the assay of ^{237}Np, due to overlapping alpha particle energies. The average $^{239/240}$Pu result was 23.7 mBq g^{-1}, with a 3.0% bias and SD (standard deviation) of 1.3 mBq g^{-1}. The average tracer recovery for ^{236}Pu was 93.1% ± 6.1% (SD). The Full Width Half Maximum (FWHM) results for the ^{236}Pu tracer peaks show acceptable alpha peak resolution. The uncertainties for the individual $^{239/340}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 3 shows the individual results for the determination of ^{238}Pu in six 1 g limestone sample spiked with 0.25g MAPEP 30 soil sample. The average ^{238}Pu result was 29.1 mBq g^{-1}, with a 1.0% bias and SD (standard deviation) of 1.8 mBq g^{-1}. Table 4 shows the results for ^{237}Np in the same set of samples, also corrected for ^{236}Pu tracer yield. The average ^{237}Np result was 38.8 mBq g^{-1}, with a 4.9% bias and SD (standard deviation) of 2.7 mBq g^{-1}. Without the second replicate sample which was biased high at 15%, the overall bias for the set would have been only 2.9%. The overall bias of <5% was still acceptable, however.

Table 5 shows the individual results for the determination of $^{239/240}$Pu in four 1 g marble samples spiked with a small amount of MAPEP 24 soil. The results were corrected for ^{242}Pu tracer yield. The average $^{239/240}$Pu result was 30.0 mBq g^{-1}, with a 2.0% bias and SD (standard deviation) of 2.1 mBq g^{-1}. The average tracer recovery for ^{242}Pu was 96.0% ± 2.9% (SD). The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show acceptable alpha peak resolution. The uncertainties for the individual $^{239/340}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 6 shows the individual results for the determination of ^{241}Am in four 1 g marble samples spiked with a small amount of MAPEP 32 soil. The results were corrected for ^{243}Am tracer yield. The average ^{241}Am result was 28.7 mBq g^{-1}, with a -1.3% bias and SD (standard deviation) of 1.1 mBq g^{-1}. The average tracer recovery for ^{243}Am was 88.8% ± 3.7% (SD). The Full Width Half Maximum (FWHM) results for the ^{243}Am tracer peaks show acceptable alpha peak resolution. The uncertainties for the individual ^{241}Am results

were typically ± 7-8% (1 SD), with a 16 hour count time. Cm-244 was also determined from the Am alpha spectrum, using [243]Am tracer to correct the [244]Cm results. Table 7 shows that the average [244]Cm result was 34.5 mBq g^{-1}, with a 0.7% bias and SD (standard deviation) of 2.5 mBq g^{-1}.

Table 8 shows the individual results for the determination of [238]U in eight 1 g limestone samples spiked with a small amount of MAPEP 32 soil. The results were corrected for [232]U tracer yield. The average [238]U result was 48.4 mBq g^{-1}, after correction for a native [238]U content of 8.5 mBq/g. with a -3.6% bias and SD (standard deviation) of 1.5mBq g^{-1}. The average tracer recovery for [232]U was 92.8% ± 6.0% (SD). The Full Width Half Maximum (FWHM) results for the [232]U tracer peaks show acceptable alpha peak resolution. The uncertainties for the individual [238]U results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 9 shows the individual results for the determination of ^{90}Sr in seven 1 g limestone samples spiked with 1.415 Bq g^{-1} [90]Sr. The ^{90}Sr results were corrected for chemical yield using a stable strontium gravimetric method, with an average value of 73.8%. The average ^{90}Sr result was 1.40 Bq g^{-1}, with an average bias of -0.79%, and SD (standard deviation) of 0.04 Bq g^{-1}. Adjustments were made in the phosphate level added in the initial preconcentration step to see if phosphate was a limiting reagent and the chemical yield would increase. This was tested because of the high level of calcium in the samples. Table 10 shows that the increased phosphate (8.5 mL 3.2M ammonium phosphate added instead of 7 mL .2M ammonium phosphate) did not increase the chemical yield. Though the chemical yield did not increase significantly, the ^{90}Sr results were still excellent, with an average bias of only -0.12%. Table 11 shows the results when the fluoride level across the final CaF$_2$ precipitation step was increased. The volume of 28M HF added was increased from 10 mL to 15 mL and the average chemical yield increased to 84.6%, a significant increase in yield. This test showed that the fluoride ion level was limiting the calcium and strontium precipitation efficiency and that a higher level was needed to enhance chemical yields. The average bias for the ^{90}Sr measurements was only -0.85%. The MDA (Minimum Detectable Activity) for actinide isotopes using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie: [17]

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

where   B = Total Background counts, = BKG (rate) * 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 alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. For a 1g limestone or marble aliquot, the method MDA for the actinide isotopes with a 16 hour count time is ~500 uBq g^{-1}, assuming a detector efficiency of ~28%, 1 count background per 16 hours and a chemical recovery of 90%. Samples counted for only 4 hours are estimated to have an MDA of ~1.4 mBq g^{-1}.

For ^{89}Sr or ^{90}Sr in limestone and marble samples, the MDA is ~ 18 mBq g^{-1} for a 1.5g sample aliquot, 60 minute count time, 90% chemical recovery, 54% detector efficiency and 1.5 count per minute background using gas flow proportional counting. The count time may be increased to lower the MDA if desired.

Conclusions

A new rapid fusion method to determine actinide isotopes, ^{89}Sr and ^{90}Sr in 1 g -1.5 g limestone and marble samples has been developed that allows the separation of these isotopes with high chemical yields and effective removal of interferences. It has been validated by adding MAPEP 24 soil standards containing refractory [239]Pu isotope to the limestone and marble samples. The sodium hydroxide fusion technique is fast and rugged. The stacked cartridge approach offers many options, depending on the analytes required. The new method is rapid, effective and has been optimized for chemical yields and removal of interferences.

Acknowledgment

References

[1]   Maxwell S, Culligan B, and Noyes G (2010) Rapid separation method for actinides in emergency soil samples**.** Radiochim. Acta 98: 1–8

[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]   Maxwell, S, Culligan, B and Hutchison, J (2014) Rapid determination of actinides in asphalt

        samples, Journal of Radioanalytical and Nuclear Chemistry Vol. 299, No 3, pp 1891-1901

[4]   How do you recognize limestone and marble? Accessed 12/1/15

        http://pubs.usgs.gov/gip/acidrain/4.html

[5]   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

[6]   Jia G, Torri G, Ocone R, Di Lullo, A, Boshcetto (2008) Determination of thorium isotopes in

        mineral and environmental water and samples by a-spectrometry and the fate of thorium in water

        Applied Radiation and Isotopes 66, 1478– 1487

[7]   "Rapid method for Fusion of Soil and Soil-Related Matrices prior to Americium, Plutonium, and

        Uranium Analyses for Environmental Remediation Following Radiological Incidents",

        http://www2.epa.gov/sites/production/files/2015-

        06/documents/soil_dissolution_by_fusion_for_am_pu_u_09-17-12_epa-600-r-12-636637638.pdf

[8]   "Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices prior to Americium,

        Plutonium, Strontium, Radium and Uranium Analyses for Environmental Remediation Following

        Radiological Incidents", http://www2.epa.gov/sites/production/files/2015-

        06/documents/concrete_and_brick_dissolution_by_fusion_rev_0_402r14004.pdf

[9]   Jurečič S, Benedik L, Planinšek P, Nečemer M, Kump, P, Pihlar B. (2014) Analysis of uranium

        in the insoluble residues after decomposition of soil samples by various techniques, Applied

        Radiation and Isotopes, Volume 87, pp 61–65

[10]   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

[11]   Maxwell S, Culligan B, Hutchison, J and McAlister, D. (2015) Rapid Fusion Method for the

        Determination of Pu, Np, and Am in Large Soil Samples, Journal of Radioanalytical and Nuclear

        Chemistry Vol. 305, pp 599-608

[12]   Sill, C. (2004) "Purification of Radioactive Tracers for Use in High Sensitivity Alpha

        Spectrometry", Analytical Chemistry, Vol. 46, No. 11, 1426-1431

[13]   Gostic, J. (2009) "Evaluation of extraction chromatography resins for rapid actinide analysis",

          Doctoral Thesis at University of Nevada Las Vegas,

          http://digitalscholarship.unlv.edu/cgi/viewcontent.cgi?article=1103&context=thesesdissertations

[14]   Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid separation method for actinides in

          emergency air filter samples, Appl. Radiation and isotopes, December 2010, Pages 2125-2131

[15]   Maxwell S, and Culligan B. (2013) Rapid Determination of Radiostrontium in Large Soil Samples,

          Journal of Radioanalytical and Nuclear Chemistry Vol. 295, pp 965-971

[16]   Maxwell S, Culligan B and Utsey R. (2013) Rapid Determination of Radiostrontium in Seawater

          Samples , Journal of Radioanalytical and Nuclear Chemistry Vol. 298, pp 867-875

[17]   Currie, LA (1968) Limits for qualitative and quantitative determination. Anal. Chem. 40: 586-593

Table 1 Pu-239/240 Results for Limestone Spiked with MAPEP 24 Soil

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	104.6	40.5	29.4	0.747	27.64	-6.0
2	98.9	50.1	29.4	0.803	29.71	1.1
3	104.5	27.1	29.4	0.819	30.30	3.1
4	92.1	34.4	29.4	0.731	27.05	-8.0
5	97.4	46.9	29.4	0.796	29.45	0.2
6	102.7	58.3	29.4	0.900	33.30	13.3
Avg. Spiked Smps	100.0			0.80	29.6	0.6
SD	4.9			0.06	2.2	7.5
% RSD	4.9			7.5	7.5	
			16 hour count	MAPEP 24 contains refractory Pu		

Table 2 Pu-239/240 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	91.3	32.5	23.0	0.682	25.23	9.5
2	87.8	70.8	23.0	0.604	22.35	-3.0
3	101.2	60.8	23.0	0.683	25.27	9.7
4	98.9	59.9	23.0	0.651	24.09	4.5
5	93.9	49.9	23.0	0.611	22.61	-1.9
6	85.7	82.7	23.0	0.618	22.87	-0.8
Avg. Spiked Smps	93.1			0.64	23.7	3.0
SD	6.1			0.04	1.3	5.7
% RSD	6.5			5.6	5.6	
			16 hour count			

Table 3 Pu-238 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq g^{-1})	^{238}Pu Measured Value (pCi g^{-1})	^{238}Pu Measured Value (mBq g^{-1})	Difference (%)
1	91.3	32.5	28.8	0.852	31.53	9.5
2	87.8	70.8	28.8	0.750	27.75	-3.7
3	101.2	60.8	28.8	0.808	29.90	3.8
4	98.9	59.9	28.8	0.809	29.93	3.9
5	93.9	49.9	28.8	0.711	26.29	-8.7
6	85.7	82.7	28.8	0.786	29.07	0.9
Avg. Spiked Smps	93.1			0.79	29.1	1.0
SD	6.1			0.05	1.8	6.4
% RSD	6.5			6.3	6.3	
			16 hour count			

Table 4 Np-237 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{237}Np Reference Value (mBq g^{-1})	^{237}Np Measured Value (pCi g^{-1})	^{237}Np Measured Value (mBq g^{-1})	Difference (%)
1	91.3	40.5	37.0	1.06	39.22	6.0
2	87.8	50.1	37.0	1.15	42.55	15.0
3	101.2	27.1	37.0	1.10	40.52	9.5
4	98.9	34.4	37.0	0.98	36.26	-2.0
5	93.9	46.9	37.0	1.06	39.04	5.5
6	85.7	58.3	37.0	0.96	35.34	-4.5
Avg. Spiked Smps	93.1			1.05	38.8	4.9
SD	6.1			0.07	2.7	7.2
% RSD	6.5			6.9	6.9	
			16 hour count			

Table 5 Pu-239/240 Results for Marble Spiked with MAPEP 24 Soil

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	93.4	61.2	29.4	0.728	26.9	-8.4
2	93.6	50.9	29.4	0.860	31.8	8.2
3	98.7	46.9	29.4	0.814	30.1	2.4
4	98.5	39.2	29.4	0.839	31.0	5.6
Avg. Spiked Smps	96.0			0.81	30.0	2.0
SD	2.9			0.06	2.1	7.3
% RSD	3.0			7.2	7.2	
			16 hour count	MAPEP 24 contains refractory Pu		

Table 6 Am-241 Results for Marble Spiked with MAPEP 32 Soil

Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{241}Am Reference Value (mBq g^{-1})	^{241}Am Measured Value (pCi g^{-1})	^{241}Am Measured Value (mBq g^{-1})	Difference (%)
1	89.7	39.4	29.1	0.742	28.8	-0.9
2	92.3	35.8	29.1	0.742	28.8	-0.9
3	89.7	43.3	29.1	0.770	29.9	2.8
4	83.7	49.5	29.1	0.703	27.3	-6.1
Avg. Spiked Smps	88.8			0.74	28.7	-1.3
SD	3.7			0.03	1.1	3.7
% RSD	4.1			3.7	3.7	
			16 hour count			

Table 7 Cm-244 Results for Marble Spiked with MAPEP 32 Soil

Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{244}Cm Reference Value (mBq g^{-1})	^{244}Cm Measured Value (pCi g^{-1})	^{244}Cm Measured Value (mBq g^{-1})	Difference (%)
1	89.7	39.4	34.8	0.908	33.6	-3.5
2	92.0	35.8	34.8	0.912	33.7	-3.0
3	89.7	43.3	34.8	1.032	38.2	9.7
4	82.4	49.5	34.8	0.882	32.6	-6.2
Avg. Spiked Smps	88.4			0.93	34.5	-0.7
SD	4.2			0.07	2.5	7.1
% RSD	4.7			7.2	7.2	
			16 hour count			

Table 8 U-238 Results for Marble Spiked with MAPEP 30 Soil

Sample ID	^{232}U Yield (%)	Tracer Peak (FWHM)	^{238}U Reference Value (mBq g^{-1})	^{238}U Measured Value (pCi g^{-1})	^{238}U Measured Value (mBq g^{-1})	Corrected for Native U (mBq g^{-1})	Difference (%)
1	86.9	67.6	50.2	1.58	58.5	50.0	-0.5
2	91.8	61.9	50.2	1.59	58.8	50.3	0.3
3	88.7	83.1	50.2	1.50	55.5	47.0	-6.4
4	100.5	32.7	50.2	1.54	57.0	48.5	-3.4
6	87.6	38.0	50.2	1.48	54.8	46.3	-7.8
7	101.5	40.0	50.2	1.54	57.0	48.5	-3.4
8	92.3	58.9	50.2	1.53	56.6	48.1	-4.2
Avg. Spiked Smps	92.8					48.4	-3.6
SD	6.0					1.5	2.9
% RSD	6.5					3.0	
			16 hour count		Native ^{238}U = 0.23 pCi/g (8.5 mBq/g)		

Table 9 Sr-90 Results for Spiked Limestone - Initial

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq g^{-1})	^{90}Sr Measured Value (pCi g^{-1})	^{90}Sr Measured Value (Bq g^{-1})	Difference (%)
1	78.0	1.415	38.1	1.41	-0.5
2	69.2	1.415	38.3	1.42	0.1
3	71.9	1.415	37.4	1.38	-2.3
4	74.6	1.415	37.3	1.38	-2.5
5	76.7	1.415	36.8	1.36	-3.8
6	71.9	1.415	37.3	1.38	-2.5
7	74.0	1.415	40.2	1.49	5.1
Avg. Spiked Smps	73.8		37.9	1.4	-0.89
SD	3.0		1.13	0.04	2.95
% RSD	4.1		2.98	2.98	
		60 minute count			
		7 mL 3.2M PO4, 10 mL 28 M HF			

Table 10 Sr-90 Results for Spiked Limestone – More Phosphate Added

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq g^{-1})	^{90}Sr Measured Value (pCi g^{-1})	^{90}Sr Measured Value (Bq g^{-1})	Difference (%)
1	77.3	1.415	37.6	1.39	-1.6
2	76.0	1.415	38.6	1.43	1.0
3	74.6	1.415	38.3	1.42	0.2
Avg. Spiked Smps	76.0		38.20	1.41	-0.12
SD	1.4		0.50	0.02	1.32
% RSD	1.8		1.32	1.32	
		60 minute count			
		8.5 mL 3.2M PO4, 10 mL 28 M HF			

Table 11 Sr-90 Results for Spiked Limestone – More HF Added

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq g^{-1})	^{90}Sr Measured Value (pCi g^{-1})	^{90}Sr Measured Value (Bq g^{-1})	Difference (%)
1	84.1	1.415	38.2	1.41	-0.2
2	84.8	1.415	38.4	1.42	0.3
3	84.8	1.415	37.2	1.38	-2.7
Avg. Spiked Smps	84.6		37.92	1.40	-0.85
SD	0.4		0.61	0.02	1.60
% RSD	0.5		1.61	1.61	
		60 minute count			
		8.5 mL 3.2M PO4, 15 mL 28 M HF			

Figure 1 Sample Preparation for Actinides in Limestone and Marble

Add tracers to 1-1.5g limestone/marble in Zr crucible
Dry on hot plate

Add 15g NaOH pellets.
Fuse sample at 600°C for ~15-20 min.

Transfer fusion matrix to 225 mL centrifuge tube with water. Add 125 mg Fe, 5 mg La.
Dilute to 160 mL with water. Add 20 mL 12M HCl.
Mix. Cool with ice to room temp.
(U) Add 5mL 3.2 M $(NH_4)_2HPO_4$. Mix.

Add 4 ml 20% $TiCl_3$. Cap and mix well
Cool with ice for ~10 min. Centrifuge 6 min. and discard supernate.

Dilute to 80 mL with1.5M HCl and redissolve.
Dilute to 170 mL with 0.01M HCl, add 1mg La, 2 mL 20% $TiCl_3$ and 15 mL 28M HF.
Allow to stand for ~10 minutes.
Centrifuge 6 minutes and discard supernate.

Redissolve in 7 mL 3M HNO_3-0.25M Boric acid,
6 mL 7M HNO_3, 7 mL 2M $Al(NO_3)_3$ and 3 mL 3M HNO_3. Mix, warm briefly in a hot bath and centrifuge to check for any solids.

Column Load Solution

Figure 2 Sample Preparation for Radiostrontium in Limestone and Marble

```
┌─────────────────────────────────────────────────┐
│    Add Sr carrier to 1-1.5g limestone/marble in Zr │
│                    crucible                        │
│                Dry on hot plate                    │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│              Add 15g NaOH pellets.                 │
│      Fuse sample at 600°C for ~15-20 min.          │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│  Transfer fusion matrix to 225 mL centrifuge tube with │
│                water. Add 50 mg Fe.                │
│    Dilute to 180 mL with water. Mix. Cool with ice to │
│                    room temp.                      │
│        Add 8.5 mL 3.2 M (NH₄)₂HPO₄. Mix.           │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│                 Cap and mix well                   │
│   Cool with ice for ~10 min. Centrifuge 6 min. and │
│                discard supernate.                  │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│    Dilute to 80 mL with1.5M HCl and redissolve.    │
│  Dilute to 170 mL with 0.01M HCl, and 15 mL 28M HF. │
│             Allow to stand for ~10 minutes.        │
│       Centrifuge 6 minutes and discard supernate.  │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│    Redissolve in 7 mL 3M HNO₃-0.25M Boric acid,    │
│ 7 mL 15.8 HNO₃, 7 mL 8M HNO₃, 7 mL 2M Al(NO₃)₃.    │
│    Mix, warm briefly in a hot bath and centrifuge to │
│              check for any solids.                 │
└─────────────────────────────────────────────────┘
                        │
                        ▼
          ┌───────────────────────────┐
          │    Column Load Solution    │
          └───────────────────────────┘
```

The flowchart boxes contain:

Add Sr carrier to 1-1.5g limestone/marble in Zr crucible
Dry on hot plate

Add 15g NaOH pellets.
Fuse sample at 600°C for ~15-20 min.

Transfer fusion matrix to 225 mL centrifuge tube with water. Add 50 mg Fe.
Dilute to 180 mL with water. Mix. Cool with ice to room temp.
Add 8.5 mL 3.2 M $(NH_4)_2HPO_4$. Mix.

Cap and mix well
Cool with ice for ~10 min. Centrifuge 6 min. and discard supernate.

Dilute to 80 mL with1.5M HCl and redissolve.
Dilute to 170 mL with 0.01M HCl, and 15 mL 28M HF.
Allow to stand for ~10 minutes.
Centrifuge 6 minutes and discard supernate.

Redissolve in 7 mL 3M HNO_3-0.25M Boric acid,
7 mL 15.8 HNO_3, 7 mL 8M HNO_3, 7 mL 2M $Al(NO_3)_3$.
Mix, warm briefly in a hot bath and centrifuge to check for any solids.

Column Load Solution
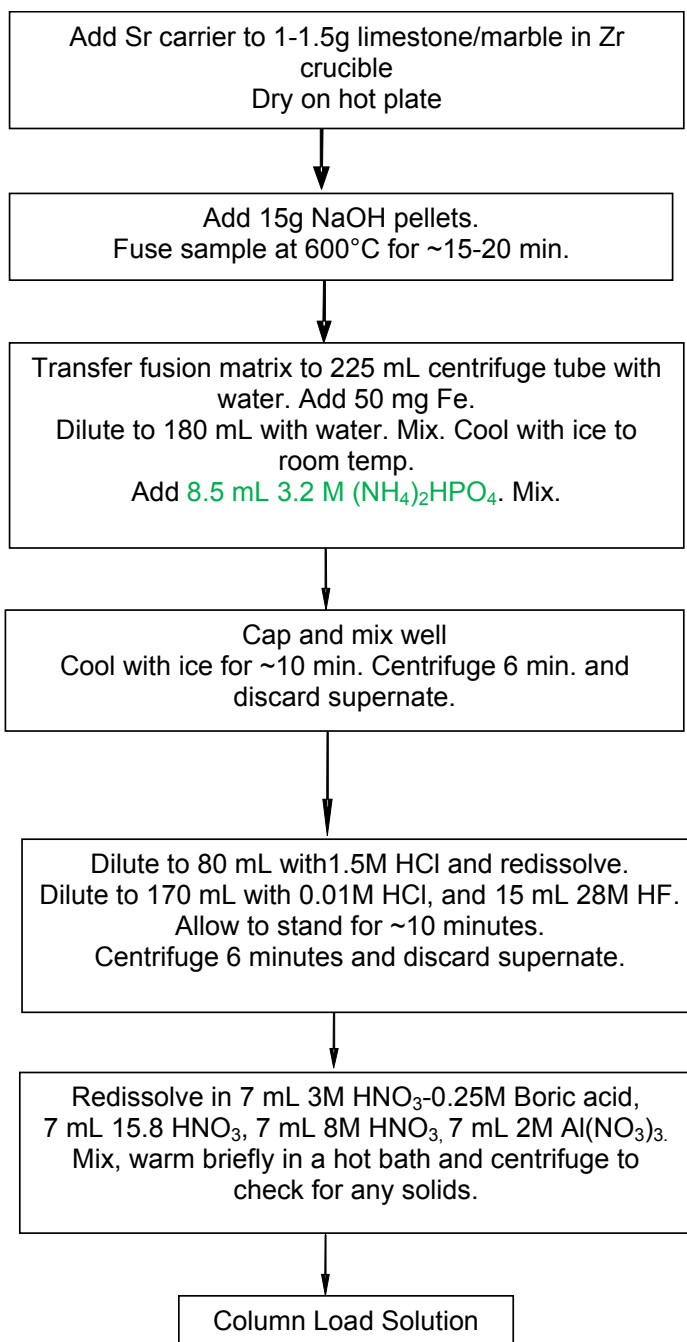
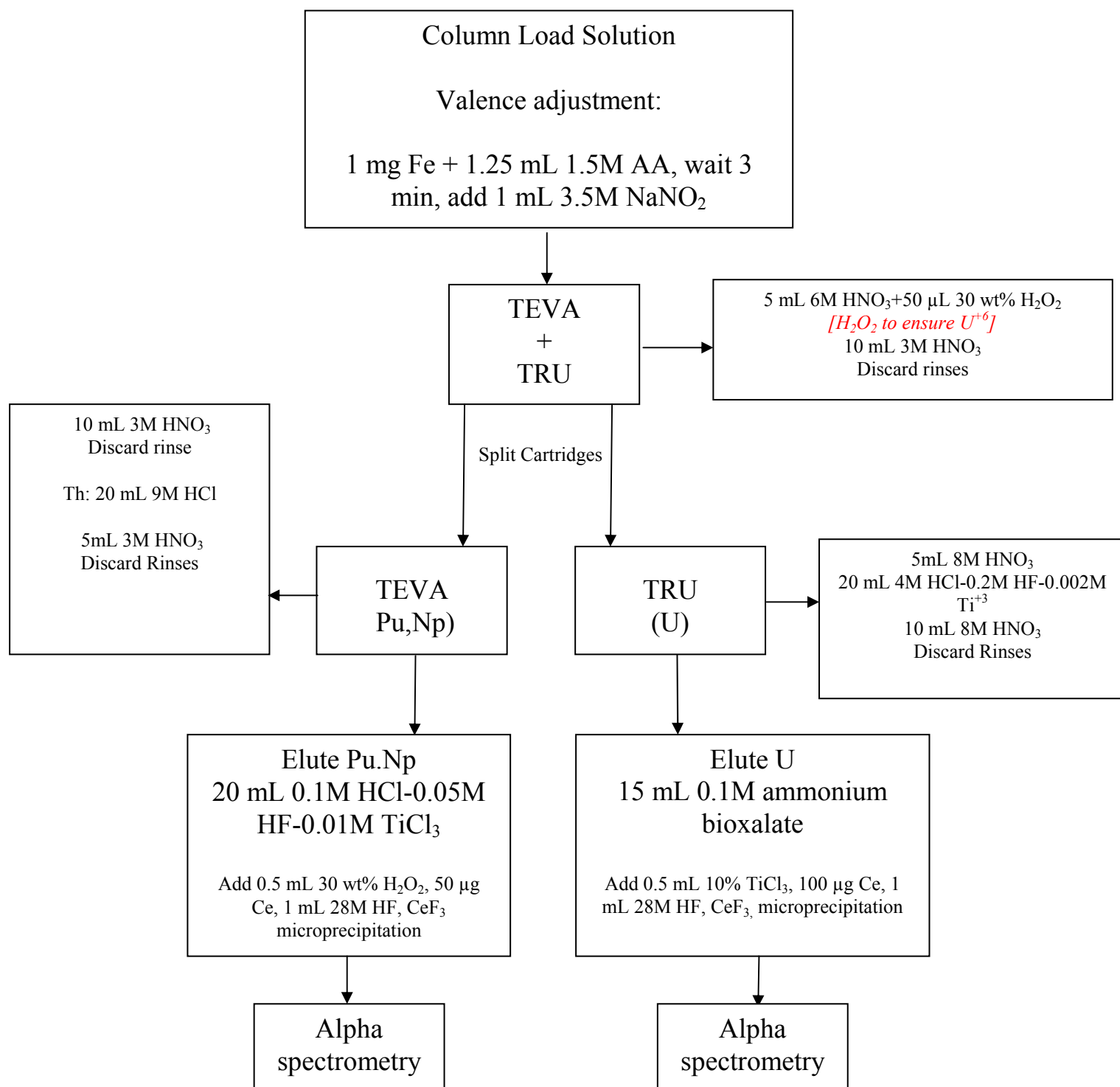Figure 3 Rapid Column Separation for Pu, Np, and U isotopes in Limestone and Marble

Figure 4 Column Separation for ^{90}Y after Ingrowth in Limestone and Marble Samples with High ^{89}Sr to ^{90}Sr Ratio