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RAPID METHODS FOR ACTINIDE AND STRONTIUM-89,90 DETERMINATION IN URBAN MATRICES

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A dissertation submitted in partial fulfillment
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ABSTRACT

Rapid radiochemical methods are needed to provide fast, reliable analytical measurements on a variety of different sample matrices in the case of a radiological event to protect the public, mitigate dose and protect the environment. If a radiological dispersive device (RDD), an Improvised Nuclear Device (IND) or a nuclear accident occurs, there will be an urgent need for quick analyses of urban matrices materials to support decision-making, dose mitigation and environmental clean-up. Since an incident involving a RDD or IND will likely occur in an urban or metropolitan area, it is very important to employ swift, robust analytical methods that can be effectively applied to urban matrices. These types of sample matrices include soil, concrete, brick, asphalt, limestone, marble, granite and steel. These samples matrices are challenging solid materials that must be effectively digested so that the analytes can be collected, purified and measured quickly. Because there may be refractory particles present in these sample matrices, the analytical methods must utilize robust sample digestion methods. The radiochemical methods need to efficiently remove radiological interferences, so that high quality, defensible measurements can be made. Rapid extraction chromatography techniques can be used to quickly purify actinide elements, ^{89}Sr, ^{90}Sr and ^{226}Ra so that these radioisotopes can be quantified with reliability.

The goal of this work is to develop new, rapid techniques that can be used with a variety of urban matrices and that utilize rapid digestion and preconcentration methods, coupled with fast extraction chromatography techniques. These new methods will need to overcome challenges associated with each sample type. Rugged digestion of refractory particles, that may be present resulting from the intense heat and pressure of a detonation, was tested for a wide range of urban matrices. This research focuses on the rapid measurement of actinides, ^{89}Sr, ^{90}Sr and ^{226}Ra isotopes in limestone, marble, concrete and steel samples. The determination of radium-226 in steel samples is also be included in this work. Alpha spectrometry, gas proportional counting, and liquid scintillation counting instrumentation were all utilized in this study.

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CHAPTER 1: INTRODUCTION

1.1 Motivation

There is a critical need for rapid radiochemical methods that can be used immediately following a radiological emergency such as the detonation of an improvised nuclear device (IND), a radiological dispersive device (RDD) or a nuclear reactor accident like those at Chernobyl (1986) or Fukushima (2011). Hauer describes scenarios whereby terrorists detonate a 10 kiloton (kt) nuclear device and makes persuasively the case that the United States in many ways is not prepared to respond effectively to this type of devastating event. [1] Planning for radiological incidents is complex and presents unique challenges, including management of the physical and psychosocial effects of radiation exposure. Radiological events have the capacity to trigger great anxiety and fear, creating widespread panic. [2, 3] In another study conducted by Redliner and Levin, there was a clear consensus among participants that no American city or region, even with abundant state and federal government and military support, has sufficient health care infrastructure and resources to handle the anticipated injuries and illness from the detonation of a 10-kiloton nuclear device. [4] Following a detonation event, it is critical to know as soon as possible what type of device was detonated and its impact. In particular, it is extremely important to know the scope of the radionuclide contamination and radiation exposure that results.

If an IND detonates, there will be large amounts of remaining nuclear material, activation products and fission products deposited from the blast, including actinides, ^{89}Sr and ^{90}Sr. If an RDD explosion occurs some of the more common radionuclides that can be expected are alpha emitters such as ^{234}U, ^{235}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm, ^{244}Cm and ^{226}Ra and beta/gamma emitters such as ^{57}Co, ^{60}Co, ^{137}Cs, ^{129}I, ^{90}Sr and ^{228}Ra. [5] It is likely that if an IND or RDD detonation occurs, it will be in a major urban area, not in an isolated, unpopulated region of the country. Rapid analytical measurements will be needed on urban material samples to immediately assess the radiological impact, mitigate radiation dose and protect the environment. The availability of proven rapid analytical methods will be essential to allow incident commanders to quickly assess the scope and impact of the event. Rapid identification and quantification of radionuclides present will therefore be essential. A rapid, effective response to a radiological event will also help to reassure the general public and to build trust. Rose et al. note that if an IND detonation occurs, laboratory sample analysis needs to occur in the first 6-24 hours. [6] It is therefore critical that rapid methods are available that can be completed in just a few hours. Solid matrices can however offer significant challenges, and the analytical methods employed must be able to overcome these difficulties.

A full list of possible target radionuclides has been compiled by the US EPA for fission and RDD events. The list includes alpha emitting actinide isotopes, beta/gamma emitters and activation products. [5] Inn et al. have compiled similar lists of radionuclides for which rapid analytical capability is needed, including plutonium isotopes, uranium isotopes, americium and curium isotopes, ^{90}Sr, and ^{226}Ra. [7] Sample matrices of interest will likely include urban building materials such as concrete, brick, limestone, marble, granite and steel.

This work focuses on the rapid measurement of actinide isotopes such as ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{237}Np, ^{234}U, ^{238}U, ^{241}Am and ^{244}Cm, along with the fission products ^{89}Sr and ^{90}Sr, in urban material matrices. U-235 could be added to these analyses by modifying the alpha spectrometry counting protocol to measure ^{235}U alpha decay (4.323 MeV, 3.52%; 4.363 MeV, 18.92%; 4.395 MeV, 57.73%; 4.415 MeV, 3.09%). At environmental levels, these actinide isotopes cannot be quantified with sufficient reliability using non-destructive analytical techniques such as gamma spectrometry. These urban material samples will therefore require rapid digestion and purification to remove interferences and allow fast, reliable measurement of these radionuclides. Strontium-90 is of special interest as it is a pure beta emitter with a relatively long half -life ($t_{1/2}$ = 28.9 years) and may be more difficult to detect at first. It is very radiotoxic, as it follows calcium biologically and deposits in bones.

According to Steinhäusler et al., natural radionuclides can also pose a significant risk for radiological terrorism, as ^{226}Ra has been trafficked repeatedly through different countries. [8] Former Russian intelligence officer Alexander Litvinenko died in a London hospital on November 23, 2006. It was determined that he had been deliberately poisoned with ^{210}Po. Police discovered that those involved in this crime had spread ^{210}Po over many locations in London. [9] The incident caused widespread psychological concern and a heightened political and public health response. This demonstrated that naturally-occurring radionuclides such as ^{226}Ra can also be used as part of a terrorist attack. Analysis of international incident data shows that several acts of murder and terrorism with natural radionuclides have already been carried out in Europe and Russia. [8, 10] Because ^{226}Ra has a high specific activity relative to uranium isotopes and many other naturally occurring radionuclides, the potential is higher for a radiological event leading to a significant committed dose from ^{226}Ra. Radium is very soluble in water and is also very toxic because it follows calcium in the human body and deposits in bones, which can increase the radiation dose to individuals and the probability of different types of cancer. Because of this potential, the work on building material samples was expanded to include the measurement of ^{226}Ra.

The availability of proven rapid methods will be essential to allow incident commanders to assess the scope and impact of the event. If such an emergency occurs, there will be an urgent need for rapid radiochemical analyses for varied types of building materials, including steel from building debris, to support dose mitigation and environmental clean-up. The defensibility of results is very important to not only protect those affected by the blast or accident, but also to maintain the public trust. For example, there were questions about the reliability of ^{90}Sr measurements in seawater samples related to the Fukushima Daiichi release. [11] Having to report later that radiochemical measurements performed by Tokyo Electric Power Company were in error does not foster public confidence following a radiological event. The use of rugged, reliable methods to ensure high quality measurements and to maintain the public confidence is therefore essential.

This work will investigate the development of rapid analytical methods for the urban sample matrices limestone, marble, granite, concrete and steel samples. The goal is to develop new methods for these types of samples that quickly digest the sample matrices, provide high decontamination of potential sample interferences and high quality, defensible results. This work seeks to address challenges associated with rapid total dissolution of these solid matrices, enhanced removal of potential radiological interferences, dissolution of refractory particles and effectiveness, despite the presence of sample matrix components that could interfere with radioanalytical assays.

While there have been significant improvements in radioanalytical methods over the last 15 to 20 years, with a trend toward rapid extraction chromatography (EXC), materials that allow swift sequential separations of analytes, one often still sees tedious, time-consuming methods in the literature. [12, 13, 14] This is not acceptable in the chaotic aftermath of a radiological emergency when immediate, reliable analytical results are essential. The approach in this study was to combine rapid dissolution and preconcentration methods with innovative rapid extraction chromatographic techniques to achieve, reliable results very quickly. The effective use of sample preconcentration methods in concert with rapid sample digestion steps removes sample matrix interferences and facilitates higher chemical yields. High chemical yields are typically an indicator of method ruggedness and thus were deemed important in the method development activities of this work.

1.2 Dissertation Overview

Chapter 1 provides an introduction and background on the need for rapid methods for actinides, ^{89,90}Sr and ^{226}Ra in urban matrices, as well as a description of the challenges faced. Chapter 2 describes aspects of the chemistry of these radionuclides and covers the analytical instrumentation used to perform measurements, including alpha spectrometry, liquid scintillation counting and gas flow proportional counting. The data contained in chapters 3, 4, 6, 7, and 8 have already been published as stand-alone peer-reviewed articles in the Journal of Radioanalytical and Nuclear Chemistry. Chapter 5 describes the study of a new rapid method for plutonium, neptunium, americium and curium in granite samples. Chapter 9 offers some broad conclusions regarding the impact of this work on radiological emergency capabilities, as well as how the analytical challenges were addressed and overcome. In addition, possible directions for future work are given. Appendix A provides a summary of the sample preparation and extraction chromatographic techniques employed in this study, including methods for actinide separations, strontium and radium.

1.3 Urban Sample Matrices

There are many different building materials used in urban areas, such as concrete, brick, asphalt, limestone, marble, granite and steel. Rapid actinide methods have been published for concrete, brick and asphalt previously. [15, 16, 17, 18] One challenge for any radioanalytical method that involves solid sample digestion is to ensure total dissolution of the sample, including refractory particles that may result from the heat and pressure associated with a detonation device. [19] The urban material samples studies in this work require digestion, dissolution and subsequent purification of the respective analytes, including actinides isotopes and $^{89/90}$Sr.

Limestone and marble have been used in many important buildings and monuments in the United States, as well as around the world, including the Pentagon, Lincoln Memorial, Washington Monument and the Empire State Building. Limestone is a sedimentary rock containing calcite and aragonite, which are both forms of calcium carbonate with different crystal systems. Limestone typically also contains skeletal fragments of marine organisms such as coral and mollusks. [20] Marble is chemically similar to limestone, however it is a metamorphic rock, rather than a sedimentary rock deposited over time. Limestone forms when shells, sand, and mud are deposited at the bottom of oceans and lakes and solidify into rock. [20] Marble, however, forms when sedimentary limestone is heated and squeezed by natural processes so that the grains recrystallize. One can usually see fossil fragments in limestone, such as bits of shell, held together by a calcite matrix. Limestone is much more porous than marble, because there are small openings between the fossil fragments in the rock. Marble is usually light colored and is composed of crystals of calcite locked together like the pieces of a puzzle. Marble may contain colored streaks that are inclusions of non-calcite minerals. 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, robust digestion method is required to ensure total digestion of these refractory particles. A radioanalytical method for limestone or marble must also be able to handle the large amounts of calcium present in these solid matrices.

Concrete is a very prevalent urban building material that contains calcium, aluminum, iron and silicates with some variation in mineral composition. There is a significant variation in aggregates used in concrete and cement, and analytical methods employed for this material must be robust. [21, 22, 23] McClain and Sudowe noted in their study of interferences on strontium extraction chromatographic methods for concrete in urban debris that high levels of potassium can adversely impact Sr retention using Sr Resin (Eichrom Technologies, Lisle, IL, USA). [23] Silicates can be particularly troublesome if they precipitate, interfering with extraction chromatography methods used to purify the actinide and strontium isotopes. A rapid method for the analysis of concrete and brick following a radiological emergency has been reported. [16] For this study, large sample aliquots of concrete (5-10g) were processed to achieve lower detection limits for the decommissioning of nuclear facilities and therefore large amounts of calcium and silicates had to be handled successfully during the sample processing. In this study, rapid preconcentration techniques were used so that sample interferences such as potassium and silicates can be quickly and effectively removed. When rapid preconcentration methods are employed that remove interfering matrix elements, there is less concern about adverse effects from variant material composition.

Granite has also been used as a construction material in many important buildings in the United States, including the U.S. Treasury Building and the Vietnam Memorial in Washington, DC. In addition, it has been employed as an important building material for skyscrapers and monuments not only in the United States, but in cities around the world. In a strict sense, granite is an igneous rock with between 20% and 60% quartz by volume, and at least 35% of the total feldspar consisting of alkali feldspar. [24] More commonly, the term "granite" is used to refer to a wider range of coarse grained igneous rocks containing quartz and feldspar. Granite is very hard and tough and has thus been a very popular construction stone. A rugged sample digestion method is required to ensure complete dissolution of this material.

Steel is another urban matrix of interest which contains large amounts of iron. If an incident involving an IND or RDD occurs in an urban area, there will most likely be steel samples from the building debris that need to be analyzed for radionuclide contamination. Samples of 304 stainless steel disks (17.5-20% chromium, 8-11% nickel, <0.08% carbon, <2% manganese, <1% silicon, <0.045% phosphorus, <0.03% sulfur, balance iron), weighing approximately 1g, were used for this study. Bell notes that there are over 3000 types of steel of varying composition. [25] One common characteristic of steel is however a large amount of iron. This could be a potential challenge from an analytical stand point, however, if iron is effectively removed the varied levels of chromium, nickel, carbon and the other constituents would likely not interfere with the separation methods employed, as shown by McClain and Sudowe. [26] Large amounts of iron can cause problems by interfering with actinide retention on some extraction chromatographic resins, and can result in large volumes of dissolved sample to be loaded onto extraction chromatographic columns.

All the solid matrices tested require total dissolution, with complete digestion of refractory particles to give reliable, defensible results. Sodium hydroxide fusion, proven for concrete, brick, asphalt and soil [15, 16, 27] was chosen for limestone, marble and granite. An enhanced acid digestion utilizing fluoride attack was selected for steel, since direct fusion was not an option for the steel matrix. In many cases existing analytical methods reported in the literature are both tedious and time-consuming or they tend to have lower chemical yields. [12, 13, 14] The goal of this work was to develop new rapid methods with total dissolution, high chemical yields and effective removal of samples matrix interferences.

With the success of rapid sodium hydroxide fusion digestion technology in the last 10 years, including use by the US EPA for solid matrices, this digestion approach was chosen for testing with concrete, limestone, marble, and granite. [28] Challenges faced in this study include the high calcium content in limestone and marble, high amounts of calcium and silicates in concrete and the high iron content in steel. Since steel samples could not be fused with sodium hydroxide directly, a rigorous acid digestion was used with an attempt to make it as robust as possible so that refractory particles could be digested effectively. The combination of acid digestion followed by alkaline hydroxide fusion was also explored. In each case the coupling of effective rapid digestion methods with novel rapid purification techniques was key to developing these new methods. The effective digestion of these urban matrices was combined with rapid separations using stacked resin cartridge extraction chromatography and small particle size resin. This multi-stage cartridges allow rapid purification of the radionuclides of interest with speed and effectiveness. Before beginning this study, a thorough review of radiochemical methods reported in the scientific literature was undertaken to assess the best approach to utilize in this study.

1.4 Survey of Current Scientific Literature

There have been a number of improved analytical methods reported for solid matrices over the past several years, including methods for urban matrices such as soil, concrete, brick, and asphalt materials. In some cases, however, these methods did not employ total digestion and the chemical yields reported were lower than desired. Hrnecek et al. [29] reported a method for the determination of plutonium in soil by alpha spectrometry and AMS (accelerator mass spectrometry). In this method, an acid leaching approach with 8M nitric acid was utilized instead of total digestion, which would not fully digest any refractory actinide particles present. Tavčar et al. [14] also reported a method to determine actinides in soil in which plutonium isotopes were separated using a traditional ion exchange process. The chemical yields for plutonium were ~60% and the Np yields were ~40%.

Vajda et al. [30] reported a method for actinides in soil for 0.5 g samples. The samples were fused in platinum crucibles using a lithium metaborate flux to ensure digestion of refractory particles. Actinides were then separated on TRU Resin (Eichrom Technologies, Lisle, IL, USA). The results agreed well with reference values, however, the method appears to be limited to 0.5g soil aliquots, which restricts the detection limits that can be achieved. Although lithium metaborate fusion effectively digests refractory particles, this flux material can sometimes be difficult to remove from a crucible.

Weinreich et al. [17] reported an analytical method for concrete which utilized acid digestion, followed by separation and measurement of plutonium and uranium. Plutonium was separated using a traditional anion resin separation, followed by processing of column effluents through UTEVA Resin (Eichrom Technologies, Lisle, IL, USA) for the separation of uranium isotopes. The uranium chemical yields were greater than 90%, however, plutonium yields were not consistent, perhaps resulting from issues with valence adjustment.

Qiao et al. [18] reported a method for the determination of plutonium in soil and concrete samples. However, this method was optimized for the determination of plutonium fractionation in environmental samples rather than for speed. Samples were digested using aqua regia, followed by two successive iron hydroxide precipitations which were used in combination with anion exchange resin to separate Pu isotopes. No chemical yields were reported. Electrodeposition (4-5 hr. at 0.7A cm^{-2}) was used to prepare the sample test sources for counting, a source preparation technique that is time-consuming and less desirable for emergency response methods.

Eikenberg et al. [31] compared three different separation methods to determine actinide isotopes in soil samples, a similar sample matrix to concrete or brick. Acid leaching of samples does not fully recover uranium and thorium present in a soil matrix and may not effectively digest refractory particles. A traditional ion exchange separation was combined with DGA Resin (Eichrom Technologies, Lisle, IL, USA), which was used to collect Am, Cm, and U. Electrodeposition was used to prepare alpha sources for measurement by alpha spectrometry.

Jia et al. [31] reported a fusion method for the measurement of thorium isotopes in soil by alpha spectrometry. After fusion of the samples with Na_2CO_3 and Na_2O_2 at 600 ˚C, soil samples were leached with HNO_3 and HCl. Thorium was 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. This fusion method provided total digestion of the soil aliquots. A furnace was employed instead of a burner to allow multiple samples to be processed simultaneously. The method seemed to be limited to 0.5 g soil aliquots and required expensive platinum crucibles. Silicon removal via evaporation of an acid leachate was somewhat time-consuming. In an emergency, minimizing time-consuming steps is critical.

Gascoyne et al. [32] reported a lithium metaborate fusion technique for the radiochemical analysis of granite rock samples using alpha spectrometry. Uranium and thorium were separated using 10% tributylphosphate (TBP) in amyl acetate using $Al(NO_3)_3$ as a salting agent, and then back-extracted both U and Th into 1 M H_2SO_4. Uranium was separated from thorium using traditional anion exchange resin. The sample preparation in this study took approximately 8 hours, however, chemical yields were only 20 to 60%. In addition, mixed solvent waste and large volumes of acidic aqueous waste were generated.

Varga et al. [33] reported two improved techniques for the determination of americium and plutonium from environmental samples by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and alpha spectrometry. Both procedures utilized a CaF_2 co-precipitation step for pre-concentration and sample matrix removal followed by extraction chromatographic separations. The average recovery after sample preparation was more than 85 % for americium and plutonium. The methods reported could be performed within 6 hours for one batch of samples.

Jurečič et al. [34] reviewed several soil decomposition techniques and found that alkaline fusion resulted in a complete digestion of uranium in the soils studied. Other analytical digestion techniques, such as conventional wet dissolution with mixtures of HNO_3, $HClO_4$ and HF acids, or microwave dissolution using HNO_3 and HF were less effective, with significant uranium losses. A fast sodium hydroxide fusion can be completed in less than 30 minutes, with preconcentration steps to remove matrix interferences typically taking less than 2 hours. No evaporation steps are needed, and uranium chemical recoveries are very high, even when refractory material is present in the environmental sample.

Ageyev et al. [35] reported a method for environmental samples that included soil. The soil samples were ashed in a furnace at 550˚C, and acid-leached with 8M nitric acid, followed by calcium oxalate precipitation to collect the actinides, redissolution in hydrochloric acid, iron hydroxide precipitation, and a lanthanum precipitation of plutonium, americium and curium. Carbonate, chromate and iron hydroxide precipitations were performed to prepare strontium for assay. Plutonium was separated using a traditional Dowex 1 anion exchange resin loaded under reduced atmosphere. Am and Cm were precipitated as lanthanide hydroxide, redissolved in dilute hydrochloric acid, and separated on Dowex 50 cation exchange resin loaded under reduced pressure. A gradient elution to separate Am and Cm from rare earths was performed using α-hydroxy-iso-butyric acid. Actinides were electrodeposited to prepare sample test sources for alpha counting. Chemical yields were acceptable but not as high as one would typically want: Pu 60-70%, Am and Cm 50-65%, and Sr 50-70%. The method, due to its complexity and time to complete the analyses, would not be considered a fast analytical method.

A review by Hou et al. [36] surveyed a wide range of analytical separation methods for plutonium isotopes in waters and environmental solid samples. These methods included a wide variety of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for plutonium typically varied between 40-85%. Improvements in chemical yield should help to reduce detection limits and improve overall method ruggedness.

A very thorough description of sample preparation methods for ^{89,90}Sr for a wide range of sample matrices was provided by Vajda and Kim. [37] Many techniques published in the literature produce chemical yields that may not be fully optimized, affecting detection limits and in some cases measurement reliability, which is very important to maintain the public trust.

Chabaux used multiple, large cation exchange columns followed by a Sr Resin column to remove sample matrix interferences prior to the assay of ^{226}Ra in volcanic rocks. [38] Larivière [39] tested several different methods, including the large cation resin column method by Chabaux, as well as sulfate precipitation and manganese dioxide approaches. The overall results were good, but the column rinse volumes were very large, requiring long processing times. The chemical yields in some cases were low. Crespo applied a similar ion exchange separation approach to geological samples using ^{225}Ra tracer, with large anion exchange and cation exchange columns followed by electrodeposition. [40]

In a wide-ranging survey of the scientific literature, it was found that the need for fast radiochemical methods for use following a radiological emergency persisted, especially for key urban materials matrices such as limestone, marble, granite and steel. The trends over the last 10-20 years has been toward more rapid, sequential analytical methods and significant advancements have been realized, however further improvements are still needed. The rapid sodium hydroxide fusion technology in combination with extraction chromatography was deemed the best approach to build upon, when considering the need for total dissolution, speed, high chemical yields and reliable results. [15, 16, 44] This was chosen as the foundational analytical development approach with which to move forward for rock and sediment containing samples, in combination with a fast, sequential extraction chromatography approach tailored to meet the specific analytical needs. While sodium hydroxide fusion could not be directly applied to steel samples without initial acid dissolution, it was determined that a rugged acid digestion approach would likely be effective. The survey reinforced the belief that sequential extraction chromatography methods designed to collect and purify multiple analytes would be an essential feature in new emergency response methods for the urban matrices examined in this study, preferably with fast flow rates.

1.5 Extraction Chromatography

Extraction chromatography combines the selectivity of liquid-liquid solvent extraction with the rapid capability of column chromatographic methods. The separation of radionuclides is based on the distribution of the ions of interest between an organic and an aqueous phase. The extractant is adsorbed on the surface of an inert support and corresponds to the organic, stationary phase. The inert support usually consists of porous silica or an organic polymer (such as Amberchrom CG-71, which is an acrylic ester polymer, or Amberlite XAD 4, which is a styrene-divinylbenzene copolymer,) in size from 50 to 150µm in diameter. Liquid extractants, either single compounds or mixtures, are used as the stationary phase in the resin column. The mobile phase is usually an aqueous acid solution, typically nitric or hydrochloric acid. In some cases, complexing ions, such as oxalic or hydrofluoric acids, are used to influence analyte selectivity on the resin or to result in the enhanced elution of strongly retained metal ions from resin columns. Figure 1 is a simplified depiction of a portion of an extraction chromatographic resin bead showing the three key components of an EXC system: the inert support, the stationary phase, and the mobile phase. [41] Vacuum flow rates and smaller particle size (50-100 µm) using a stacked cartridge approach were employed during this study to facilitate rapid flow rates and sequential separations, minimizing analytical processing time.

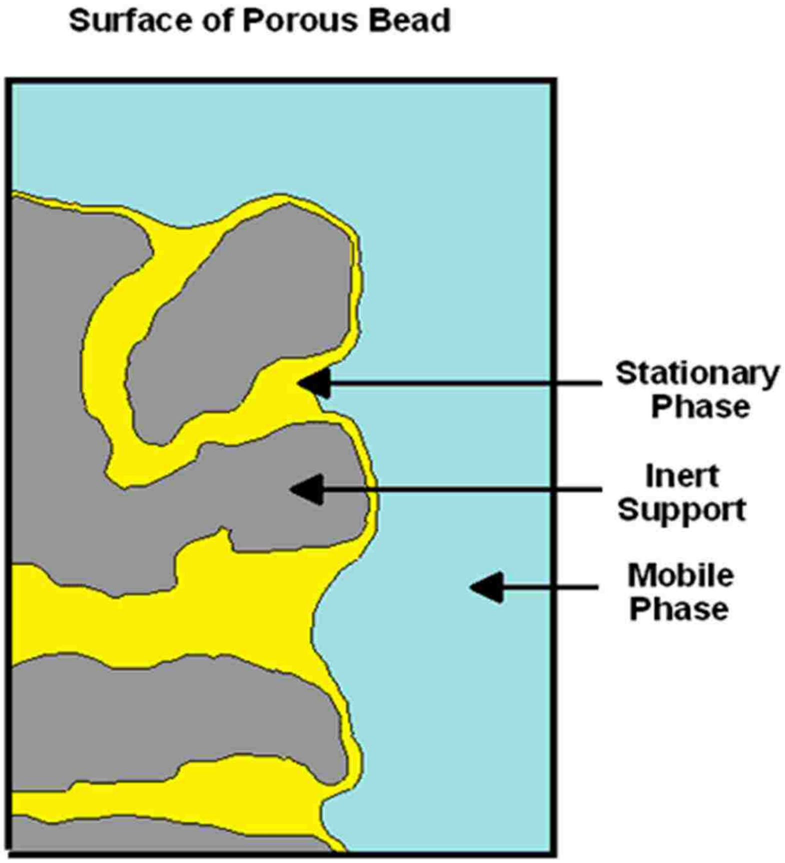

Figure 1: Extraction Chromatography (EXC) Surface of Porous Bead [41]

The free column volumes to peak maximum, k', is an important value in extraction chromatography that can be used to determine analyte retention properties of the resin column. The relationship between the volume distribution ratio (D_v) and the number of free column volumes to peak maximum, k', for the corresponding EXC system is shown below in equation (1):

$$k' = D_v \, x \, \frac{V_s}{V_m} \tag{1}$$

$$D_v = D_w \, x \, (d_{extr} \, x \, V_s)/0.4 \, x \, v_m) \tag{2}$$

where v_s and v_m are the volumes of the stationary and mobile phases, respectively. The volume distribution ratio D_v was calculated using equation (2), where d_{extr} is the density of extractant and the 0.4 factor represents the typical extractant loading in grams of extractant per gram of resin, however this factor may vary. [43] It should be noted that the concentration of extractant is usually much higher in EXC systems where diluents may be absent than in conventional SX systems. D_v and k' are not usually measured directly for EXC systems, but calculated from D_w, the weight distribution ratio, which can be easily measured. The weight distribution ratio, D_w, is obtained by measuring the amount of a given metal ion taken up by a measured weight of resin from a given volume of aqueous solution. The weight distribution ratio is then calculated using the following equation:

$$D_w = \frac{A_0 - A_s}{A_s} \quad x \ \frac{mL}{g} \tag{3}$$

where A_o - A_s = activity absorbed on a known weight of resin, g, and As = the activity in a known volume, mL, of solution. The volume distribution ratio D_v is calculated from the volume of stationary phase per gram divided into D_w. The volume of stationary phase is obtained from its weight percent retained on the inert support and its density. The number of free column volumes to peak maximum, the capacity factor, k', is then calculated from equation (1). The quantities, v_s and v_m, are measured from the weight of resin required to fill a column to a known volume and the density of the EXC resin.

The coupling of rapid digestion, preconcentration and multistage extraction chromatographic techniques is the common thread among the new methods developed in this study. The fast EXC separation techniques used in this study are covered in the respective chapters that describe the rapid methods developed, however, in addition, a detailed summary of the separation chemistry may also be found summarized in Appendix A.

CHAPTER 2: EXPERIMENTAL APPROACH

2.1 Urban Materials

Urban material samples require rigorous sample digestion, dissolution and subsequent purification of the respective analytes, including actinide isotopes, ^{89,90}Sr and ^{226}Ra to allow rapid quantification following a radiological event. Chapter 1 discussed various sample matrix challenges associated with each type of urban material studied.

2.1.1 Dissolution

In this work limestone, marble, concrete and granite samples were digested using a rapid sodium hydroxide fusion, with adjustments made as appropriate to address sample matrix challenges [15, 16, 43] The alkaline fusion method used can be performed in about 15 minutes at relatively low temperature (600°C) due to its lower melting point, without a burner, and multiple samples can be processed simultaneously in furnaces. The ability to process multiple samples simultaneously is key following a radiological emergency. Acid leaching can result in incomplete digestion of refractory particles due to incomplete digestion. Total dissolution is very important for the analysis of building materials, where refractory particles may be present following a radiological event or nuclear detonation. [44] The sodium hydroxide fusion is rapid, rugged and can be performed using relatively inexpensive 250 mL zirconium crucibles, which resist attack from sodium hydroxide.

Flux materials such as sodium carbonate require much higher temperatures and are typically performed one at a time over a propane burner. [45] This is much less efficient in an emergency when analytical processing time is critical. Lithium metaborate fusion may be used for solid samples, however, it has a relatively high melting point and requires either more expensive platinum crucibles, or graphite crucibles, and often is performed one sample at a time over a burner. Unlike fusion using lithium metaborate, the sodium hydroxide fusion cake comes out of the zirconium crucible easily, with water dissolution followed by acid rinsing. This approach allows LaF_3 and CaF_2 preconcentration steps to effectively remove iron, titanium and silicates, which can interfere with extraction chromatographic separations.

2.1.2 Preconcentration

Preconcentration of the actinides, strontium or radium is required following urban matrix sample dissolution to collect the analytes from the fusion cake or acid digest matrix and to remove interfering sample matrix components. Iron hydroxide coprecipitation has been used for years to preconcentrate actinides from aqueous solutions or digested solid samples. It is very effective to coprecipitate most trivalent and tetravalent actinides. However, hexavalent actinides such as uranium present as uranyl ion UO_2^{+2}can be more difficult to coprecipitate. To facilitate higher chemical yields, titanium (III) is typically added to reduce U(VI) to U(IV) and enhance its chemical recovery across the preconcentration steps. In addition, calcium phosphate, which effectively coprecipitates both U(IV) and U(VI) ions, has also been used to increase uranium chemical yields. However, iron (III) can interfere with actinide retention on some extraction chromatographic resins. In addition, large iron hydroxide precipitates can require fairly large acid volumes to dissolve, resulting in a large column load solution, necessitating much larger resin columns, flow times and acid waste. [46] In this study, lanthanum fluoride combined with calcium fluoride coprecipitation was utilized to remove Fe, Ti, and silicates in the supernate, reducing interferences, and enabling smaller column load solutions and resin volumes. The approach used in this study minimized separation time and column effluent waste volumes. Silicates can cause extraction chromatographic resin flow problems through gel formation in the column load solution.

Therefore, the elimination of silicates is very important in the development of a rugged, rapid method for urban matrices. Fast flow rates are essential to achieve analyte purification for measurement very quickly, so a column load solution free of particulates is critically important to avoid delays and low chemical yields.

2.2 Extraction Chromatography

In this study rapid sequential extraction chromatography methods were used to separate actinide isotopes, $^{89/90}$Sr and ^{226}Ra after the various urban sample matrices were quickly digested. Historically, ion exchange or liquid-liquid solvent extraction has been used to separate actinides and strontium isotopes. Solvent extraction (SX) can be performed in batch or continuous multistage mode. While SX is more selective than ion exchange processes, there are potential problems and difficulties with this approach. Aqueous and solvent entrainment may occur, which lowers the efficiency of each extraction stage. Third phase formation can also occur, and there can be problems with back-extraction and solvent cleanup [47].

In some cases fuming nitric acid has been used to precipitate strontium from aqueous solutions as strontium nitrate; however, there are safety considerations and handling issues associated with that approach and chemical yields are often less than desired. [48] Ion exchange has been used historically to separate plutonium, neptunium and thorium isotopes as anionic nitrate complexes. Under these conditions, the selectivity for these isotopes in the tetravalent valence state is very good, since only very few other metals form anionic complexes with nitrate. [49, 50] The effectiveness of solvent extraction and ion-exchange processes in nitric acid, for example, depends strongly on the stoichiometry, stability, molecular geometry and molecular charge of nitrate complexes. Nitrate tends to bind plutonium in a bidentate fashion to retain its planar molecular geometry, similar to carbonate. [49]. Figure 2 shows the Pu(IV) hexanitrate complex with six nitrate ions, $[Pu(NO_3)_6]^{-2}$, resulting in an anionic complex with a net negative charge of 2.

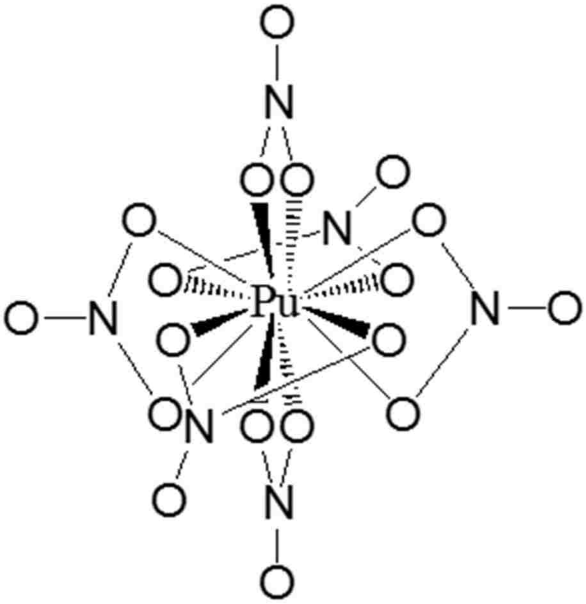

Figure 2: Pu(IV) Hexanitrate Anion Complex [49]

The adjustment and control of actinide isotope valence states has played a key role in actinide separations for many years, and continues to do so. The chemical differences between various oxidation states of a single actinide are larger than those of different actinides in the same oxidation states. The ability of the various species to form complexes is dependent on the charge density. For example, the complexation strength tendency of Pu decreases in the order:

$$\text{Pu (IV)} > \text{Pu(VI)}O_2^{+2} > \text{Pu(III)} > \text{Pu(V)}O_2^{+} \qquad (4)$$

Choppin further notes that an effective charge of +3.2 has been assigned to plutonium in $Pu(VI)O_2^{+2}$ and this supports its position in the series. [51] Actinide nitrates are well-studied. It should also be noted that uranium, plutonium, neptunium isotopes can also be separated by ion exchange as anionic chloride complexes of the An(IV) or An (VI) valence states.

Uranium, plutonium, and thorium can also be extracted as neutral complexes using tributylphosphate in nitric acid. This approach has been utilized for SX and EXC. For example, the hexavalent actinide ion, An(VI), forms a neutral extracted TBP complex $AnO_2\,(NO_3)_2(TBP)_2$ in nitric acid, as shown in Eq 2:

$$An(VI) + 2NO_3^- + 2TBP \rightleftharpoons AnO_2\,(NO_3)_2(TBP)_2 \qquad (5)$$

The variable oxidation states of actinide isotopes are very useful in facilitating the separation of actinide isotopes. Plutonium and neptunium both have multiple valence states, and effective valence control chemistry must be applied to achieve quality results. Plutonium and neptunium both have valence states ranging from (III) through (VII), however in aqueous solution Pu is more commonly Pu(III), Pu(IV), Pu(V), or Pu(VI) depending on the oxidation reduction conditions, while Np exists more typically as Np(IV), Np(V), or Np(VI). While uranium ions in acid solution are typically present as U(VI) in the form of the uranyl ion, UO_2^{+2}, uranium can be adjusted to U(IV) using reductants such as Ti(III). Americium and curium typically exist in aqueous solution as Am(III) and Cm(III), while the alkaline earth elements strontium and radium are present as Sr(II) and Ra(II) ions respectively.

The lack of selectivity of ion exchange compared with solvent extraction can present difficulties. Extraction chromatography resins have been developed in the last 25 years that have improved the toolkit of radioanalytical methods that can be used to separate actinides, strontium and radium isotopes. These resins offer improved selectivity, greater separation efficiency, less acid waste, and the ability to stack resins in a multistage column to provide rapid sequential analyses. The use of vacuum boxes and small particle size resin facilitates time savings, critical for emergency response methods.

2.2.1 TEVA Resin

In the study, the first resin used for actinide separations is TEVA Resin, which is an Aliquat 336 (trialkyl, methylammonium nitrate or chloride) extractant coated resin. Figure 3 shows the trialkyl, methylammonium nitrate or chloride structure. [52]

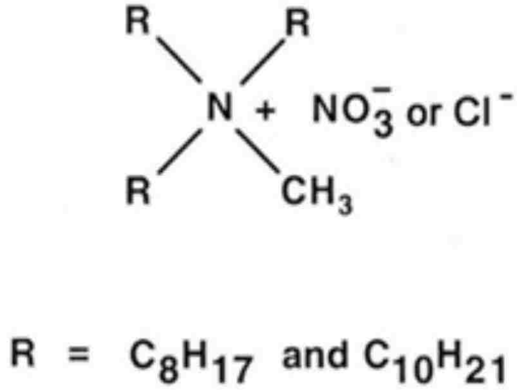

Figure 3: TEVA, Aliquat 336, trialkyl, methylammonium nitrate (or chloride)

Plutonium (IV), neptunium (IV) and thorium (IV) ions can be separated as anionic nitrate complexes at lower nitrate concentrations than has been used in more traditional anion exchange separations, for example, in 3M HNO_3 instead of 8M HNO_3. [52] Thorium exists as Th(IV) in aqueous solution, while plutonium and neptunium have multiple valence states: An (III), An(IV), An(V), An(VI), and under certain conditions An(VII). For the TEVA Resin separation employed in this study, the plutonium and neptunium were adjusted to Pu(IV) and Np(IV) valence states by reduction with ferrous ion, Fe(II), and the oxidation of Pu(III) to Pu(IV) with sodium nitrite, $NaNO_2$. Fe(II) has very fast reduction kinetics with both Pu and Np in solution. Table 1 shows the electrochemical potentials associated with the oxidation reduction of plutonium and neptunium. [53]

Table 1: Relevant Electrochemical Potentials for Pu and Np

$Pu^{+4} + e = Pu^{+3}$	E=0.92 V (in 1M HNO_3 at 25C)
$PuO_2^{+2} + 2e = Pu^{+4}$	E=1.054 V (in 1M HNO_3 at 25C)
$PuO_2^{+2} + 3e = Pu^{+3}$	E=1.18 V (in 1M HNO_3 at 25C)
$PuO_2^{+} + e = Pu^{+4}$	E=1.006 V (in 1M HNO_3 at 25C)
$NpO_2^{+2} + 2e = Np^{+4}$	E=0.94 V (in 1M HNO_3 at 25C)
$NpO_2^{+} + e = Np^{+4}$	E=0.66 V (in 1M HNO_3 at 25C)

The Pu^{+3}/Pu^{+4} redox couple involved only electron transfer and therefore is much faster than ones involving formation or rupture of Pu-O bonds (as exist in PuO_2^{+2}). [51, 54]. Equation 4 shows the electrochemical potential for the $Fe^{3+/2+}$ couple.

$$Fe^{+3} + e = Fe^{+2} \qquad E = 0.77 \text{ volts} \tag{4}$$

Reduction of plutonium to Pu(III) is accomplished conveniently by adding Fe(III) as iron nitrate, followed by the addition of ascorbic acid to reduce Fe(III) to Fe(II). This eliminates the need to prepare fresh Fe(II) reagent every few days, since Fe(II) will oxidize to Fe(III) over time due to air oxidation. Pu is reduced to Pu(III) and Np is reduced to Np(IV) by Fe(II). Ascorbic acid ($C_6O_8H_6$) not only reduces Fe(III) to Fe(II) but also will reduce Pu to Pu(III) directly. After reduction to Pu(III), sodium nitrite was added to oxidize Pu(III) to Pu(IV) very rapidly, so that Pu(IV) will be retained on TEVA Resin. [55]

Fortunately, the kinetics of Np(IV) oxidation to Np(V) with nitrite ions are extremely slow so Pu(IV) and Np(IV) can be effectively separated together. [56] By using ^{236}Pu, a tracer that does not interfere with the Np alpha spectrometry measurements, Pu and Np can be measured using alpha spectrometry in the same purified test source.

$$UO_2{}^{2+}(aq) + 4\ H+(aq) + 2\ e- \rightarrow U^{4+}\ (aq) + 2\ H_2O\ (l)\ E = +0.27\ V \quad (7)$$

While it appears that U(VI) reduction to U(IV) by ferrous ion is not favored, [57] there is evidence that this reduction process in the column load solution can occur to a certain extent, based on the retention and loss of U on TEVA Resin as U(IV). This retention of U(IV) reduces the amount available for collection and separation on a resin placed below TEVA Resin. This seems to be exacerbated by the presence of traces of Ti(III) in the column load solution, resulting from the preconcentration steps used. [24] Uranium (VI) is removed from TEVA Resin in nitric acid with much less tailing than with anion exchange resin. [52] TEVA Resin is well-suited for tetravalent actinide separations as many commonly encountered metal cations are not retained under the conditions used. The retention of Pu(IV) is very high on TEVA Resin, and high chemical yields may be obtained providing the digestion and preconcentration steps are effective. [52]

Some methods have used UTEVA Resin (Diamyl, amylyphosphonate-DAAP coated resin) coupled in tandem with TRU Resin to separate U on UTEVA Resin and Pu on TRU Resin. [58] Figure 4 shows the diamyl, amylyphosphonate extractant structure.

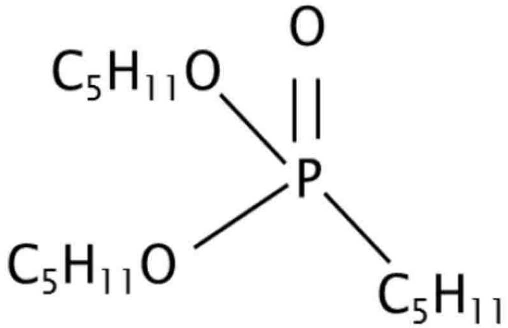

Figure 4: UTEVA Resin Extractant Diamyl, amylyphosphonate

Uranium and thorium are retained on UTEVA Resin, placed above TRU Resin, while Pu passes through that UTEVA Resin as Pu(III) and is collected on TRU Resin under reducing conditions in nitric acid. One potential disadvantage to this approach is that if any of the plutonium present in the column load solution is not reduced to Pu(III) or if some fraction of the Pu(III) reoxidizes to Pu(IV), Pu will be retained on UTEVA Resin instead and potentially interfere with U and/or Th. This can sometimes occur in nitric acid solutions with total nitrate levels (e.g. 6M total NO_3) that are somewhat oxidizing (>3M NO_3), such as in 3M HNO_3-1M $Al(NO_3)_3$ solution, which is often used as the column load solution.

In this study, a stacked TEVA Resin plus TRU Resin column was used to separate Pu, Np and U. Pu and Np were retained on TEVA Resin as Pu (IV) and Np(IV) anionic nitrate complexes.

Uranium (VI) was collected on TRU Resin as a neutral uranium nitrate extractant complex. TRU Resin employs octylphenyl-N,N- diisobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) to retain trivalent, tetravalent and hexavalent actinides, shown in Figure 5.

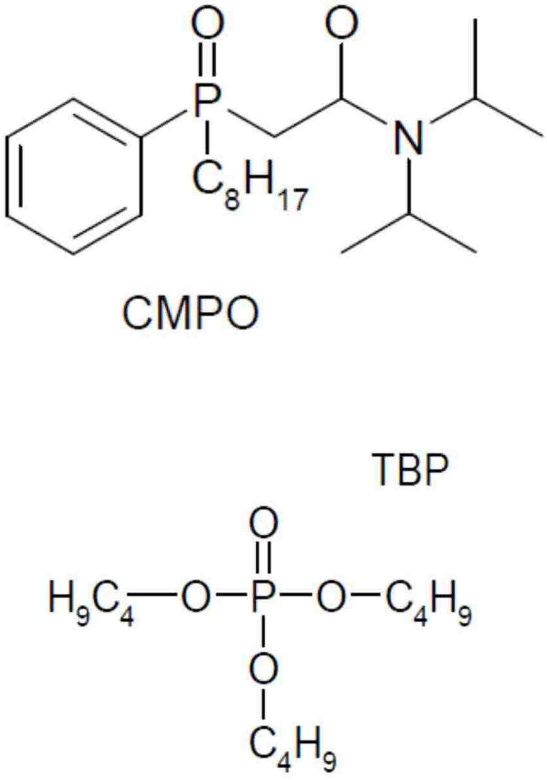

Figure 5: TRU Resin Extractants Octylphenyl -N, N- diisobutyl carbamoylphosphine oxide (CMPO) Dissolved in Tributylphosphate (TBP)

UTEVA Resin can also be utilized below TEVA Resin instead of TRU Resin, however the k’ capacity factor is much higher for U(VI) on TRU Resin than for UTEVA Resin. For a given ion on TRU Resin, the k’ value is typically 100-1000 times higher than UTEVA Resin. Am and Cm can also be separated for measurement using TRU Resin, which retains trivalent actions with a k' of approximately 100 in 3M HNO_3. [26] Fe(III) can interfere with Am/Cm retention on TRU Resin. The preconcentration strategy used in this study removes all but traces of Fe(III). This allows the use of TEVA Resin plus TRU Resin under the oxidizing conditions whereby Pu is oxidized to Pu(IV), and Fe, if in that load solution, is present as Fe(III). The preconcentration steps eliminates all but a small amount of Fe(III) so that U can be recovered effectively on TRU Resin without the adverse impact of Fe(III) retention. The coupling of effective preconcentration steps and rapid multistage extraction chromatography is a very powerful approach, and was of great benefit during this study.

Am and Cm typically exist as trivalent ions in aqueous solution, and the valence adjustment steps described above to adjust the valence states of Pu and Np do not affect Am (III) and Cm (III). The electrochemical reduction potential for Am^{+4}/Am^{+3} is shown in equation (5).

$$Am^{+4} + e = Am^{+3} \quad E=2.3\text{ V (in 1M HNO3 at 25C)} \quad [59] \qquad (5)$$

Am(III) can be oxidized to higher oxidation states with very strong oxidants such as sodium bismuthate, ozone or peroxydisulfate. [60] There is no need, however, to separate Am and Cm from each other for this work. In fact, separating Am and Cm together is preferred for environmental assays as this allows ^{243}Am to be used as a yield monitor for both Am and Cm through the analytical method. Am and Cm can be collected and purified on TRU Resin or DGA Resin (N, N, N', N'-tetraoctyldiglycolamide), however the k' factor for DGA Resin is approximately 500 times greater for Am(III) than on TRU Resin in 3M HNO_3. [61] The extractant N, N, N', N'-tetraoctyldiglycolamide is shown in Figure 6.

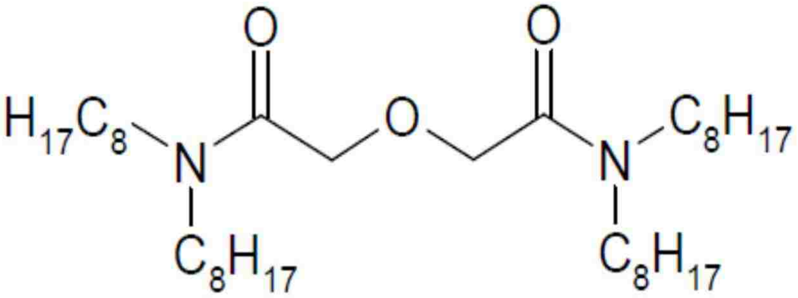

Figure 6: Structure of N, N, N’, N’-tetra-n-octyldiglycolamide, where R is a straight chain 8-carbon group

Figure 7 shows the similar affinities that Am(III) and Cm (III) have for DGA Resin in both nitric and hydrochloric acid solutions. Cf(III) has a slightly higher affinity for DGA Resin than Am and Cm due to its higher charge density. [62]

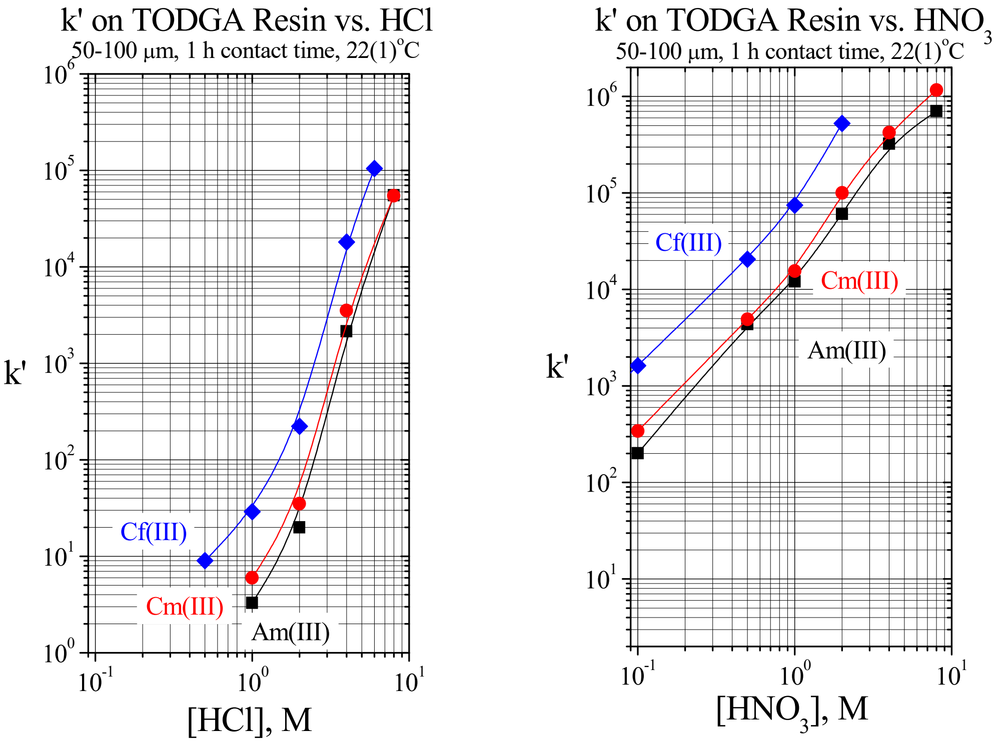

Figure 7: Retention of Am, Cm and Cf on DGA Resin

In addition, it is very advantageous that Fe(III) is not retained on DGA Resin in nitric acid and therefore does not interfere with the Am and Cm retention by the extractant. This is particularly important in the processing of steel samples, which are very high in iron content. Despite the steel sample matrix removal step using the LaF_3 preconcentration, a small amount of Fe(III) remains. TRU Resin can be used to separate both Am(III) and Cm(III) for less demanding sample matrices such as water or air filters. DGA Resin, however, is needed to recover and purify Am and Cm for more challenging matrices such as urban building materials due to its much higher affinity for trivalent actinides.

2.2.2 TEVA Resin and DGA Resin (Pu, Np, Am, Cm)

For the Am/Cm work in this study TEVA Resin and DGA Resin were coupled together in tandem so that sequential Pu, Am, and Cm separations could be carried out. Even if Pu separation and measurement is not needed, TEVA Resin is still required to remove any Pu, Np and Th and prevent their collection and potential interference with the Am/Cm purification using DGA Resin. While TEVA Resin effectively removes Th under these the acid conditions utilized, some residual Th may pass through TEVA Resin and be retained on DGA Resin. Rinse steps were therefore utilized to remove any U and Th from DGA Resin.

2.2.3 Sr Resin and DGA Resin (^{89}Sr, ^{90}Sr, ^{90}Y)

In this study Sr Resin (4, 4', (5') di-t-butylcyclohexane-18-crown-6) was employed to separate strontium, which allows for the measurement of both ^{89}Sr and ^{90}Sr. [63] Figure 8 shows the 4,4'(5')-di-t-butylcyclohexano 18-crown-6.

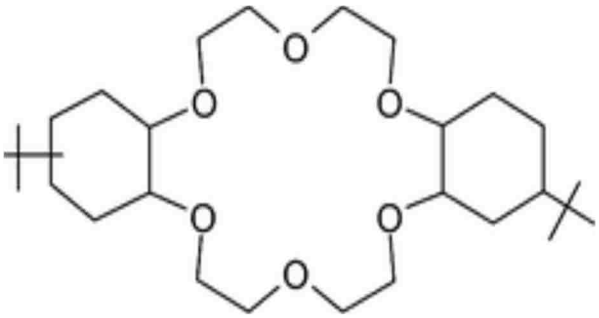

Figure 8: Sr Resin Extractant 4,4'(5')-di-t-butylcyclohexano 18-crown-6

In one option that worked very well in this study for high ^{89}Sr/^{90}Sr ratios, following separation on Sr Resin and a total ^{89}Sr + ^{90}Sr measurement, DGA Resin was used to collect and purify the ^{90}Sr daughter, ^{90}Y, after a few days ingrowth period. This allows the determination of ^{90}Sr as well as ^{89}Sr by difference. In another option further developed in this work, ^{90}Y was collected and purified directly from a sample using DGA Resin to determine ^{90}Sr without waiting on daughter ingrowth. Sr^{+2} nitrate ion fits into the 4, 4', (5') di-t-butylcyclohexane-18-crown-6 cavity.

$$Sr^{+2} + 2NO_3^- + \overline{\boldsymbol{Crown}} \rightleftharpoons \overline{\boldsymbol{Sr(NO3)2\ Crown}} \qquad (9)$$

Dietz and Jensen [64] applied extended X-ray absorption fine-structure (EXAFS) measurements to examine the coordination environment of strontium ion extracted from aqueous nitric acid solutions on resin containing di-t-butylcyclohexane-18-crown-6 on a polymeric support. The x ray absorption results for the metal ions retained onto the resin was consistent with a 1:1:2 strontium: crown ether: nitrate stoichiometry. The strontium ion is enveloped in the crown ether ring and the two nitrate anions are coordinated to the strontium as bidentate ligands. [64]

2.2.4 Cation Exchange Resin and DGA Resin (Ra)

In this new method for radium on steel samples, Ra is initially separated from Ca and other sample matrix interferences using cation exchange resin, AG50 X8 (Eichrom Technologies, LLC), a polystyrene divinylbenzene polymer containing sulfonic acid groups. After Ca and other matrix components are removed, DGA Resin is employed to remove potential alpha emitting interferences such as actinides isotopes and polonium. The cation exchange resin typically has a higher capacity and tolerance for calcium than extraction chromatography resins and thus it was utilized to initially collect and separate Ra from the Ca present. Calcium was added in the steel work described in chapter 8 to coprecipitate Ra as RaF_2, so subsequent Ca removal was required.

2.3 Source Preparation

Following the respective sample digestion and purification methods, rapid measurements were made to enable identification and quantitation of the analytes present. Sample test source preparation depended on the measurement instrumentation used. Further sample preparation details are given in Appendix A. Rare earth microprecipitation was used to prepare the alpha sources for counting by alpha spectrometry. Rapid source preparation is critical in a rapid method, and electrodeposition was not utilized due to the time associated with this technique. Both evaporation and microprecipitation were used for source preparation for gas flow proportional counting, depending on the analyte measured and the column separation employed. The measurement times employed following a radiological event can be tailored to the detection limits required.

2.4 Alpha Spectrometry

Alpha spectrometry was used to measure actinide isotopes in this study, while gas flow proportional counting and liquid scintillation counting were used to measure the beta emitters ^{89}Sr, ^{90}Sr and ^{90}Y. Alpha spectrometry is an effective tool to distinguish between various alpha-emitting radionuclides and determine the actinide isotopic composition. The alpha spectrometer is made up of a series of vacuum chambers that contain solid-state semiconductor detectors, in this case PIPS (Passivated Implanted Planar Silicon) detectors. The alpha particles emitted from a sample placed in a detector traverse the short distance from the source under vacuum and deposit their energy within the active depleted region of the detector. The energy deposited by each alpha particle is converted to a charge which is collected, amplified, and binned by a multi-channel analyzer (MCA). The MCA converts the electronic signal to a digital signal and the resulting spectra can be processed to determine the number of counts associated with the respective energy ranges across the energy spectrum.

Plutonium, neptunium, uranium, americium and curium isotopic measurements were performed by alpha particle pulse height measurements using a Canberra Alpha Management System (AMS) with Passivated Implanted Planar Silicon (PIPS) detectors. The PIPS detectors used 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. Alpha spectrometry counting using silicon semiconductor diode detectors offers excellent sensitivity, energy resolution and low detection limits. This is ultimately related to the number of charge carriers, electron-hole pairs, created in silicon semiconductor materials, which are much greater than the charge carriers created in gas proportional counting or liquid scintillation counting. Whereas in gas flow proportional counting it takes about 30 kiloelectron volts (keV) to create an ion pair in the detector chamber, it only takes about 3 keV in a silicon detector used for alpha spectrometry, so about 10 times the number of charge carriers are generated in alpha spectrometry. A more detailed description of alpha spectrometry can be found in [65].

2.5 Gas Flow Proportional Counting

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}Sr/^{90}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}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. The annealing process 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.

Gas proportional counting offers lower detection limits than liquid scintillation counting. [65]. Gas proportional counting is a technique where radioactive particles are measured in a chamber where gas molecules are ionized as a result of the interaction with charged particles to form ion pairs. A cascade of gas multiplication, called a "Townsend Avalanche", occurs in the gas proportional counter. This cascade of electron multiplication occurs through the creation of free electrons, ionization of gas molecules and acceleration of the free electrons in the electric field to ionize additional gas molecules. An electric field of at least 10^6 V/m is applied, and the positive ions drift to a cathode and electrons are collected at a thin wire anode in a cylindrical geometry. A gas multiplication factor of typically 10^2-10^4 is achieved, using the appropriate voltage to achieve linearity in the detector response relative to the original number of ion pairs formed. A quench gas, usually a polyatomic gas such as methane, is added to a fill gas such as argon to prevent photon-induced excitation of gas molecules, which will de-excite and emit UV radiation that can ionize additional gas molecules, creating additional avalanches not proportional to the original ion pars. [66]

2.6 Liquid Scintillation Counting

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 – 1400 CH) ROI (region of interest) allowing for reducing background and increasing sensitivity (expressed as Efficiency^2/Background) allowing for a reduction in the calculated MDA.

The detection of light emission via scintillation counting is one of the oldest radioanalytical techniques known. It can be used for the detection and measurement of alpha and beta particles, as well as neutrons. Pulse shape measurements can be used to identify the radioactive particles present. [66] In liquid scintillation counting (LSC), the sample is placed in a scintillation cocktail, containing an organic solvent, which typically consists of an aromatic solvent and organic scintillator. Since most samples are measured in an aqueous form, an emulsifier is also present in the cocktail to disperse aqueous samples in very small micelles (~10 nm), or droplets. This dispersal facilitates close contact with the organic solvent so that the radioactive particles can excite the organic solvents molecules. The energy can be transferred from solvent molecule to molecule by collisions, until it is transferred to the organic scintillator, or fluor molecule. The electrons in the scintillator are excited and then de-excite through prompt fluorescence, phosphorescence or delayed fluorescence. A secondary scintillator, or waveshifter, can be included in the scintillation cocktail to absorb light form the primary scintillator and shift the emitted light to a longer wavelength. This approach can be employed to better match the sensitivity of the photomultiplier tubes used. Chemical quenching, non-radiative processes that impact the transfer of energy between the solvent and organic scintillator, which do not result in the emission of light, can occur. In addition, color quenching can occur, where color in the sample absorbs or scatters the emitted light and reduces the photons prior to measurement by the photomultiplier tubes. Instruments utilize various techniques to develop quench curves correct for sample quenching, which affects sample counting efficiency. 66[] Photomultiplier tubes are used to convert a weak light signal in an electrical pulse, which can carry information about the particle measured. The emitted fluorescence is measured using coincidence circuitry electronics to minimize background counts. Pulse height and multichannel analyzers are employed to perform spectral analysis of the light emitted from the sample. Many liquid scintillation counters utilize two photomultiplier tubes, with gated coincidence circuitry to minimize background and interferences. [65, 66]

2.7 Inductively-Coupled Plasma Mass Spectrometry

This work also utilized inductively couple plasma – mass spectrometry (ICP-MS) to determine stable yttrium chemical yields. ICP-MS uses a nebulizer to aerosol liquid samples and a inductively coupled plasma to atomize and excite analytes of interest for analysis. After the yttrium is ionized in the high temperature plasma, the sample is injected into a mass separator, which uses a magnetic field to selectively allow ions through to the detector based on their mass to charge (m/z) ratio. If the ICP-MS is tuned such that each analyte is only ionized to the +1 charge, it is then possible to segregate between individual isotopes of elements. Stable yttrium recoveries in the ^{90}Y tests were measured with a Perkin Elmer model DRC-e inductively coupled plasma-mass spectrometer operated with 1400W RF power, 5.5 mm torch depth, 15L/min plasma gas, 1L/min carrier gas, 0.98L/min nebulizer gas, 6.25V E1 lens voltage, 0.0165 E1 lens slope, 4.413 E1 lens intercept, -12 CPV cell path voltage, -17V cell rod offset, and -4V Q-pole rod offset. The quadrupole utilizes four rods arranged in parallel with a radiofrequency (RF) voltage and a direct current offset voltage applied to opposing rods. The oscillation frequency of the radiofrequency (RF) voltage selectively allows ions of a certain m/z to pass through the quadrupole to the detector. By varying the RF frequency, it is then possible to scan through various m/z and quantify different isotopes.

CHAPTER 3: RAPID METHOD TO DETERMINE ACTINIDES AND ^{89,90}SR IN LIMESTONE AND MARBLE SAMPLES

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3.1 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.

3.2 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 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. [15, 16, 43]

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." [67] 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. [30] 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. [31] 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 [68] 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. [69] 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. [34] 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. [44, 56] 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. [16] 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.

3.3 Experimental

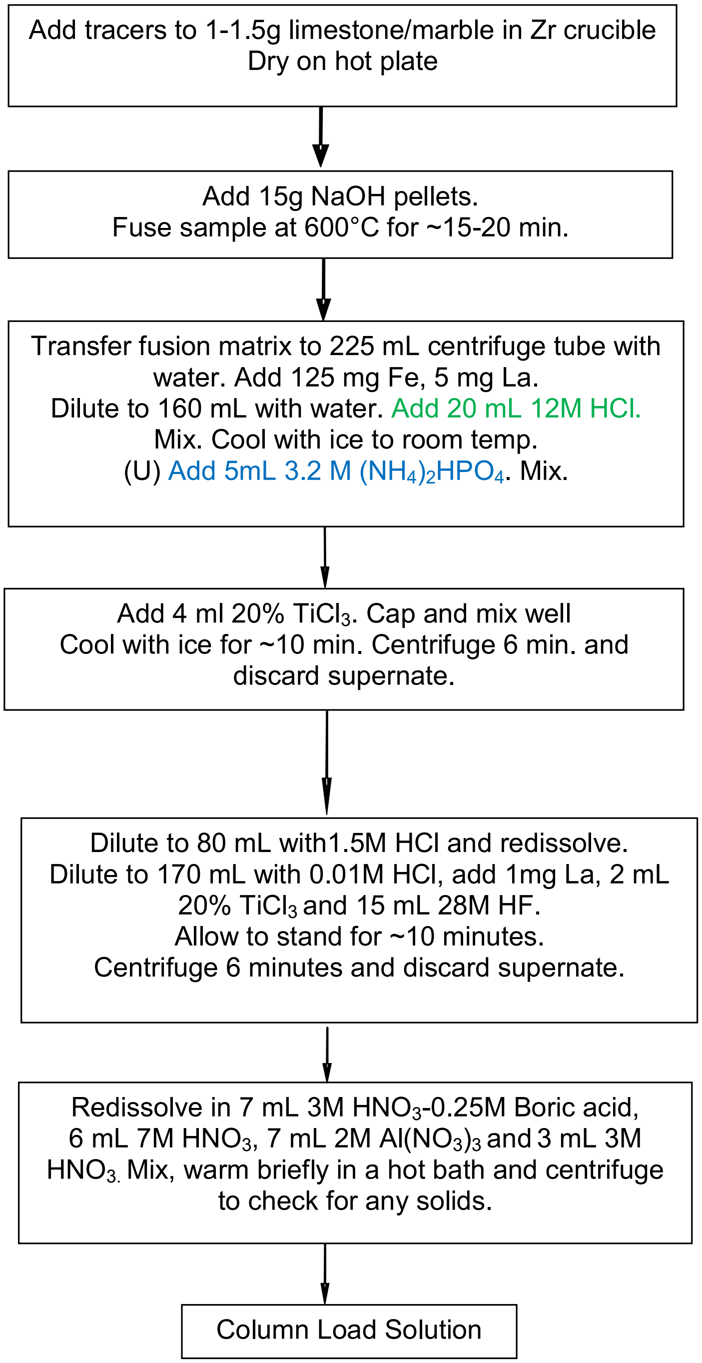
3.3.1 Reagents

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 [70].

3.3.2 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. [71, 72] 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 9 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.



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 9: Sample Preparation for Actinides in Limestone and Marble

Tracers were added to each crucible, and the crucibles were dried briefly on a hotplate. Figure 9 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 10 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.

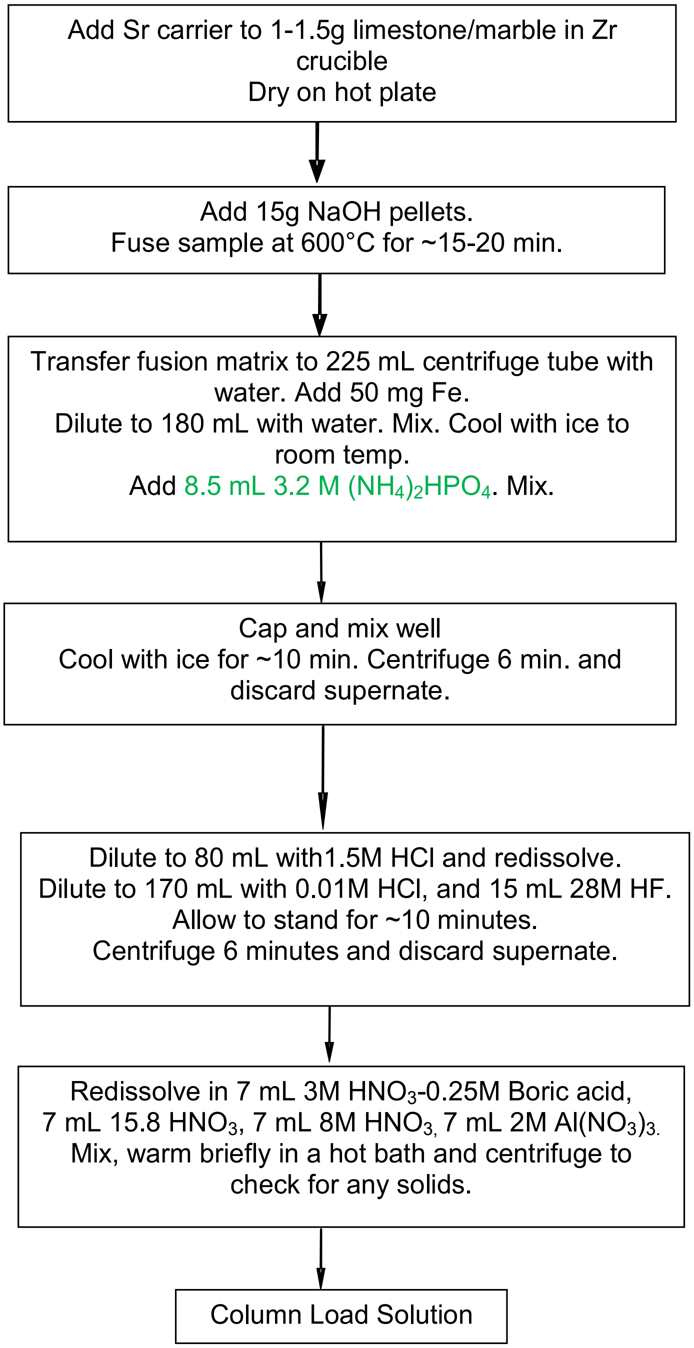


Figure 10: Sample Preparation for Radiostrontium in Limestone and Marble

Column separation for Actinides and Strontium-89,90. Column separation techniques previously reported were used to separate and purify actinides. [15, 16, 43, 44, 56] 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 11 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+1 mL 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. [73]

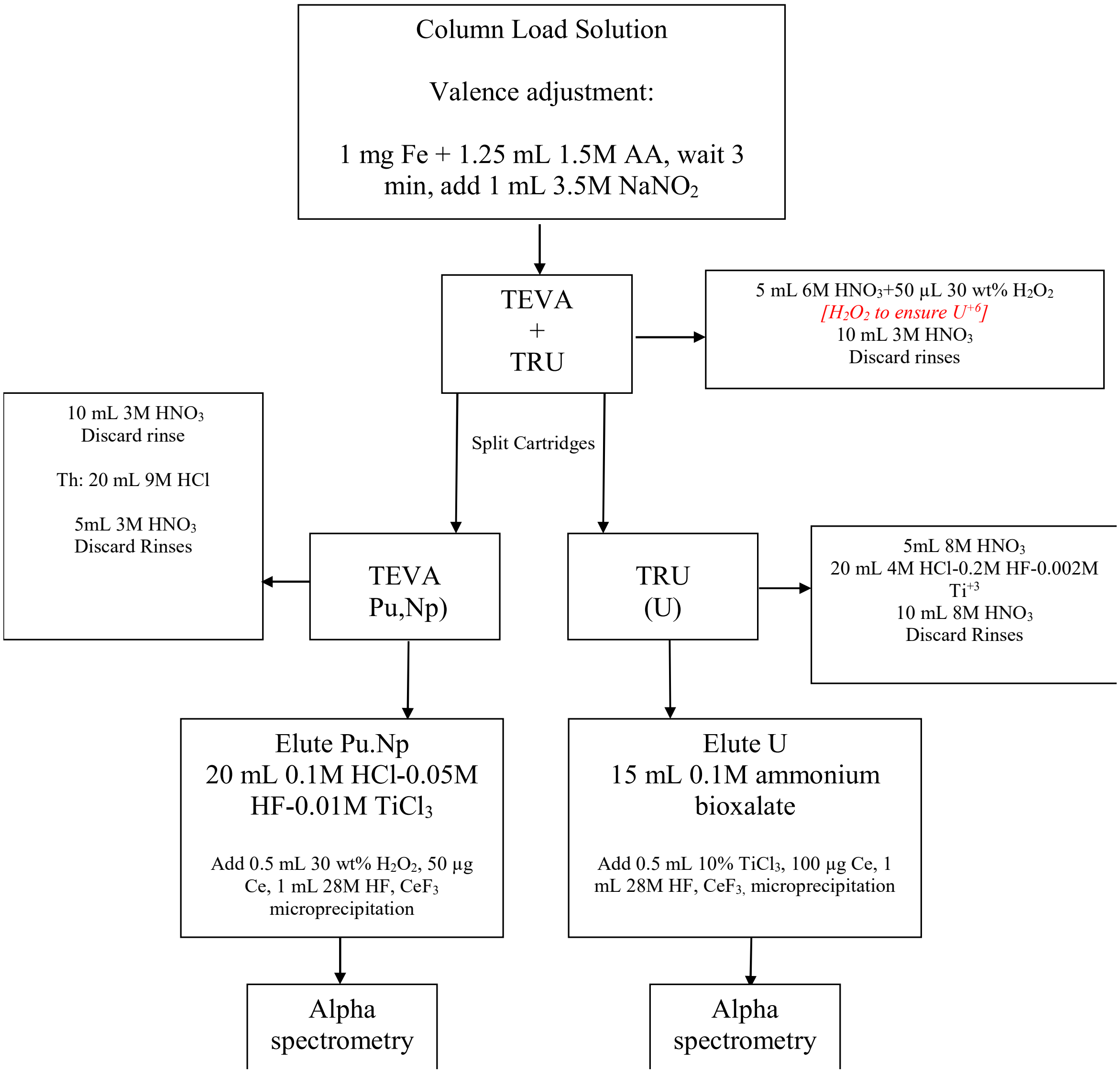


Figure 11: Rapid Column Separation for Pu, Np, and U isotopes in Limestone and Marble

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 12 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. [74] 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.

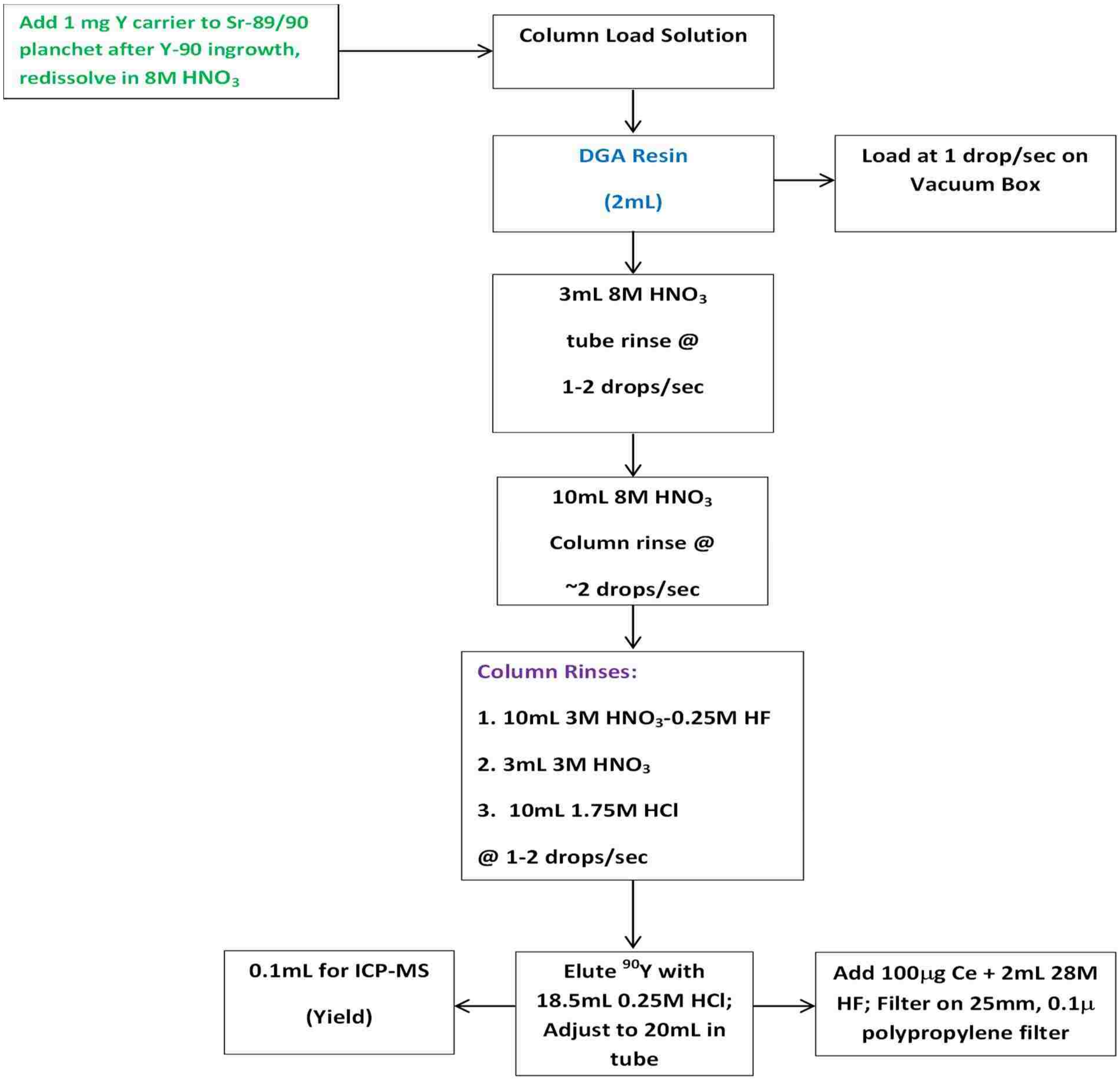


Figure 12: Column Separation for ^{90}Y after Ingrowth in Limestone and Marble Samples with High ^{89}Sr to ^{90}Sr Ratio

3.3.3 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.

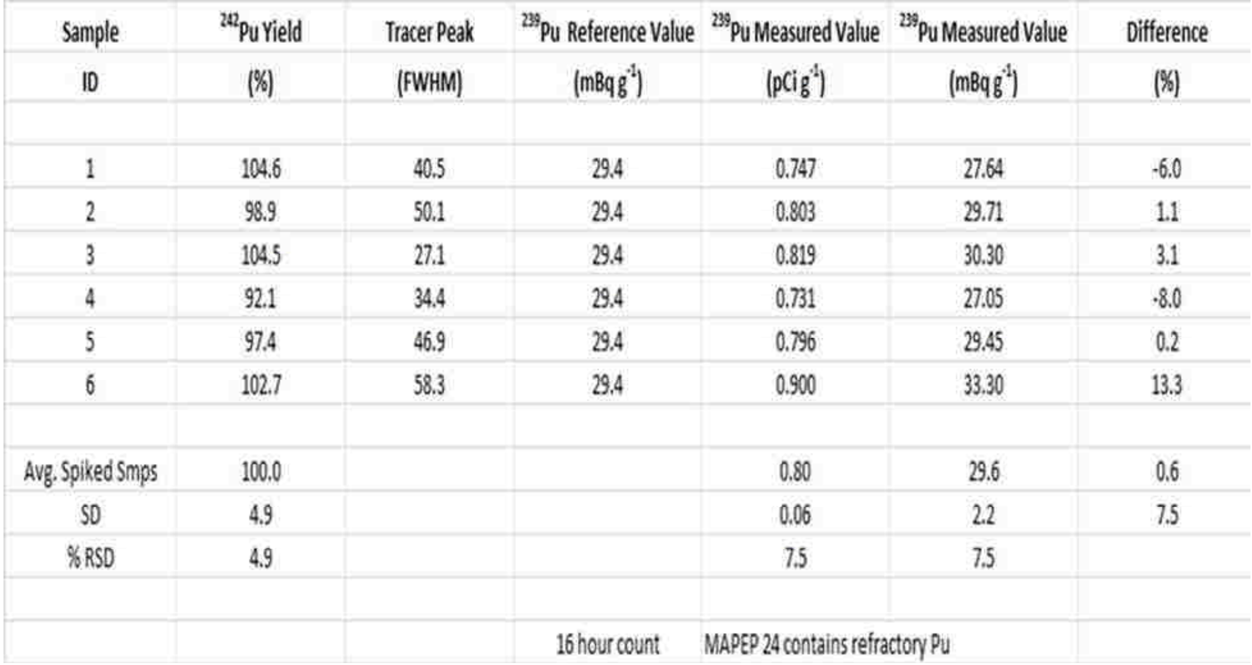
A Tennelec LB 4100 gas flow proportional counter was used to count the ^{90}Sr spiked samples. The detectors were calibrated using NIST Traceable $^{90}Sr/^{90}Y$ sources matching the sample geometry. Detector backgrounds are determined and subtracted from the sample counts. A mass attenuation correction 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.

3.4 Results and Discussion

Table 2 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: Pu-239/240 Results for Limestone Spiked with MAPEP 24 Soil

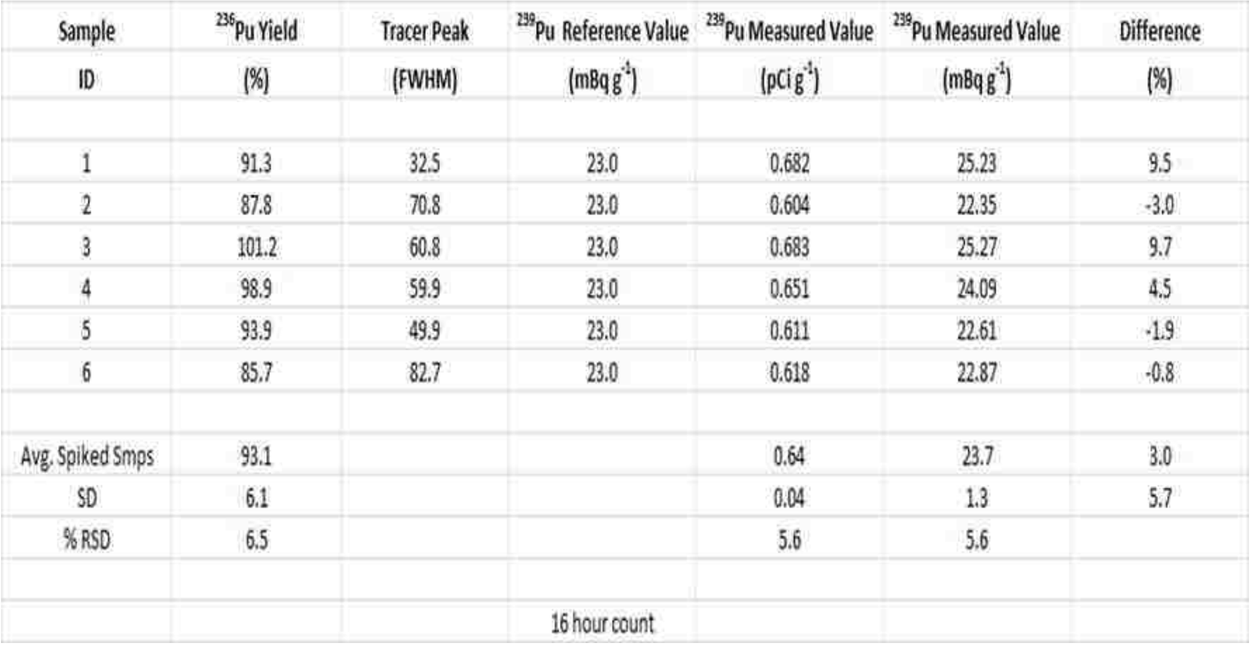


Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	104.6	40.5	29.4	0.747	27.64	-6.0
2	98.9	50.1	29.4	0.803	29.71	1.1
3	104.5	27.1	29.4	0.819	30.30	3.1
4	92.1	34.4	29.4	0.731	27.05	-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 3 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.

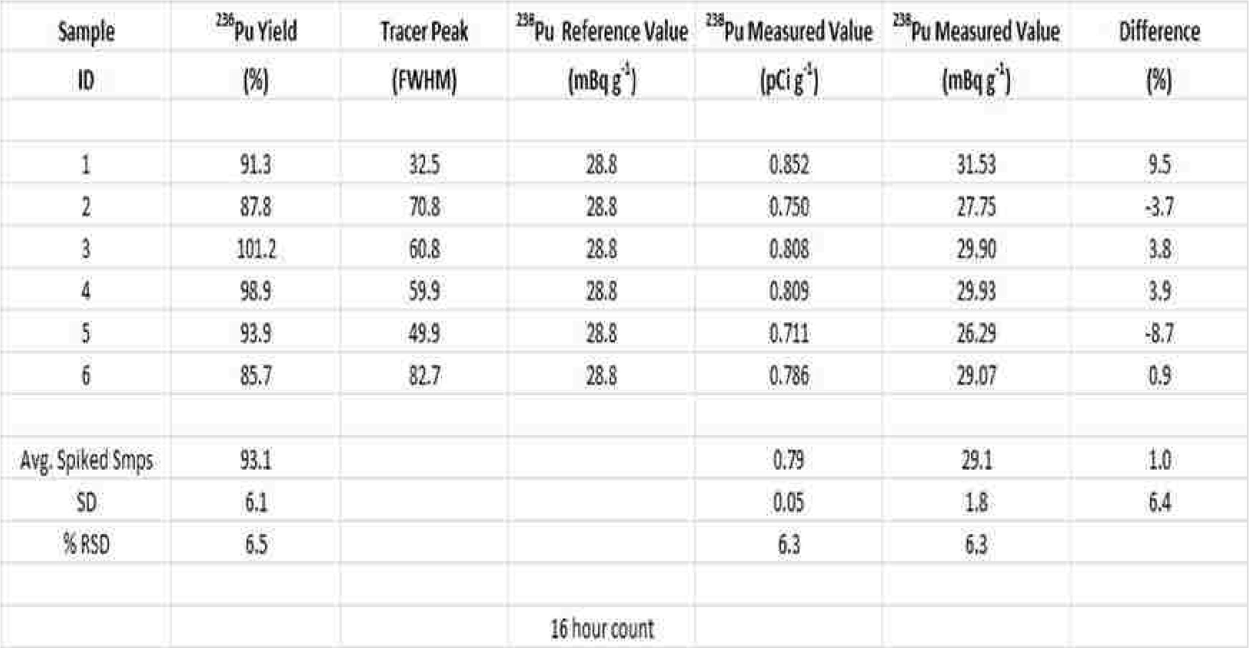
Table 3: Pu-239/240 Results for Limestone Spiked with MAPEP 30 Soil



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			

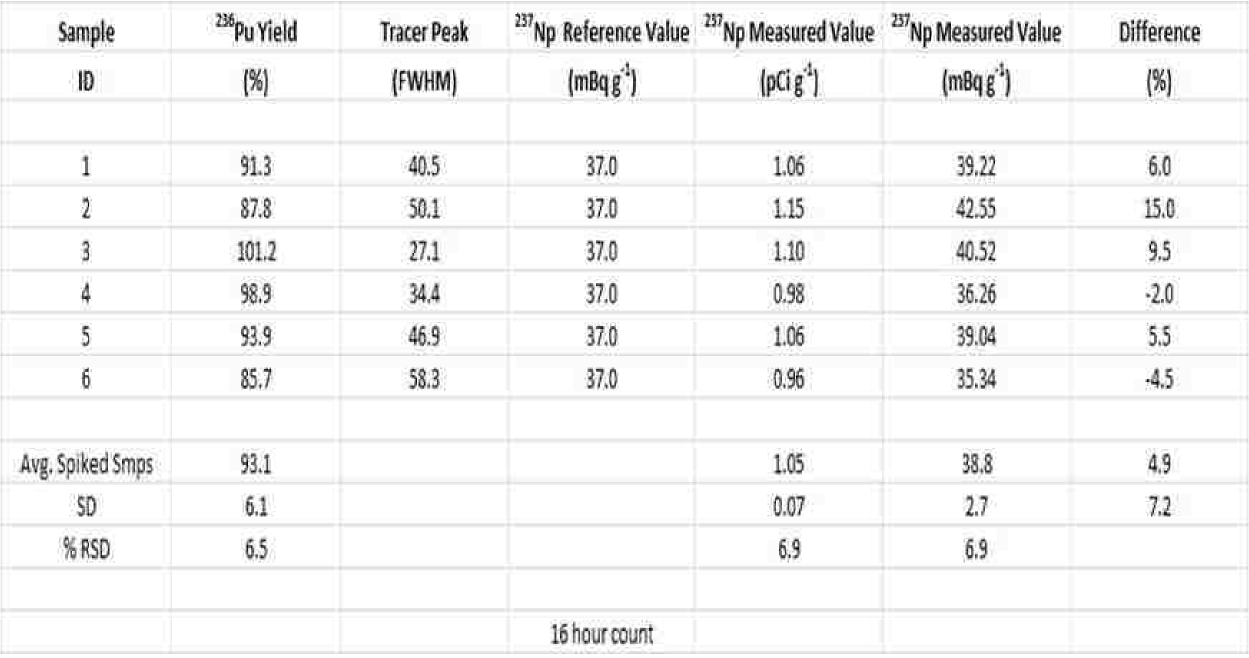
Table 4 shows the individual results for the determination of ^{238}Pu in six 1 g limestone sample spiked with 0.25g MAPEP 30 soil sample. The average ^{238}Pu result was 29.1 mBq g^{-1}, with a 1.0% bias and SD (standard deviation) of 1.8 mBq g^{-1}. Table 5 shows the results for ^{237}Np in the same 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 4: 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			

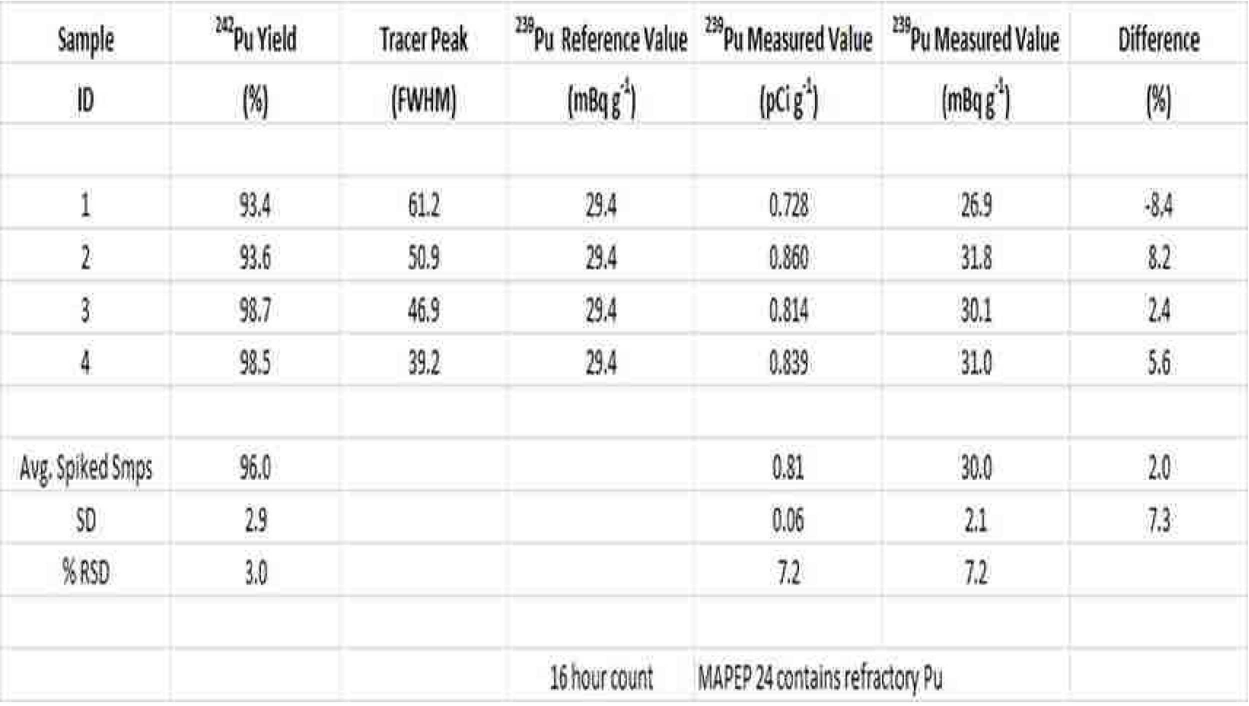
Table 5: Np-237 Results for Limestone Spiked with MAPEP 30 Soil



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 6 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.

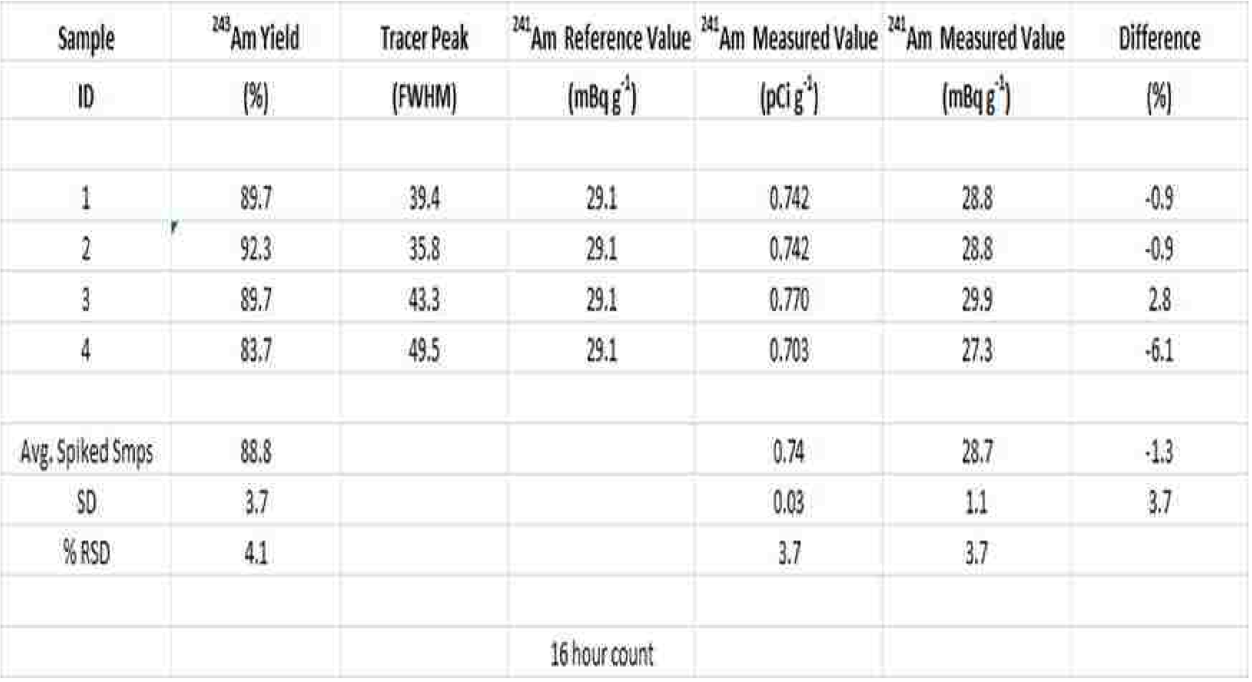
Table 6: Pu-239/240 Results for Marble Spiked with MAPEP 24 Soil



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		

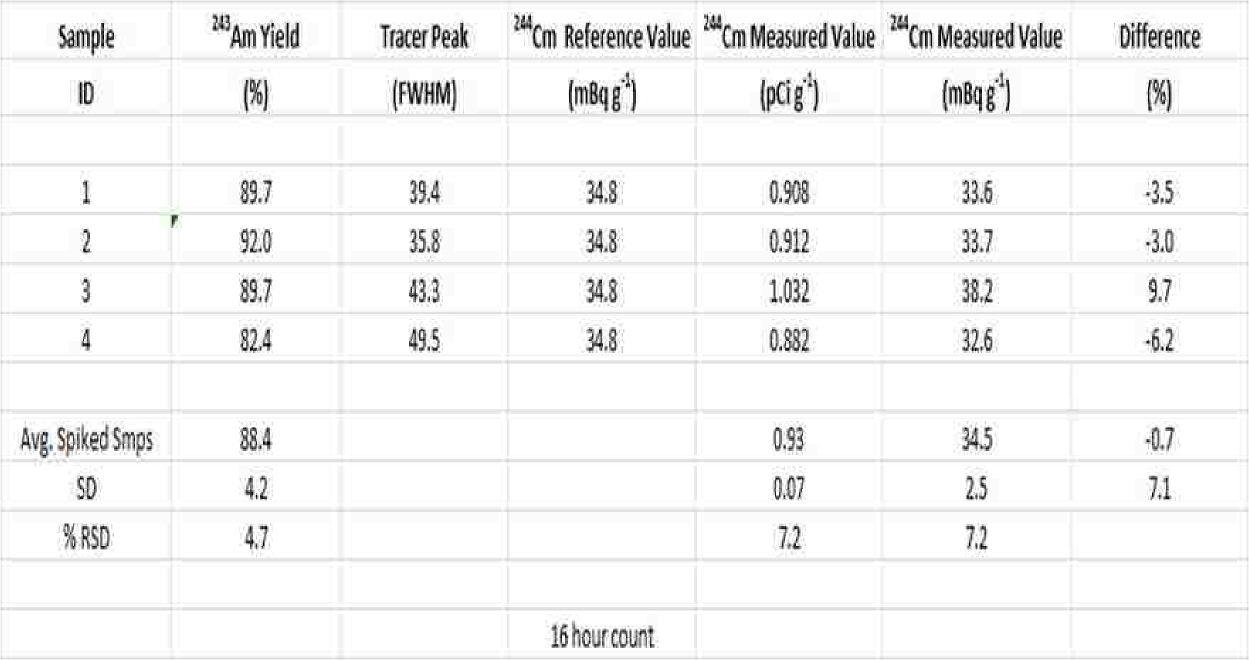
Table 7 shows the individual results for the determination of ^{241}Am in four 1 g marble samples spiked with a small amount of MAPEP 32 soil. The results were corrected for ^{243}Am tracer yield. The average ^{241}Am result was 28.7 mBq g^{-1}, with a -1.3% bias and SD (standard deviation) of 1.1 mBq 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 8 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 7: Am-241 Results for Marble Spiked with MAPEP 32 Soil



Sample	^{243}Am Yield	Tracer Peak	^{241}Am Reference Value	^{241}Am Measured Value	^{241}Am Measured Value	Difference
ID	(%)	(FWHM)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
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			

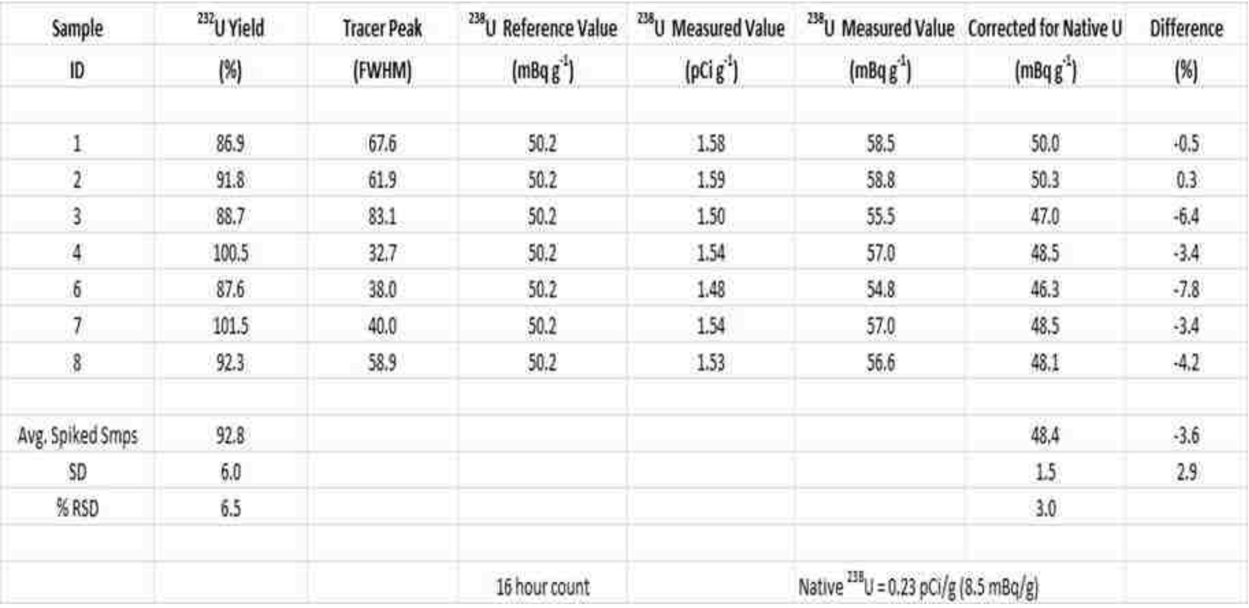
Table 8: Cm-244 Results for Marble Spiked with MAPEP 32 Soil



Sample	^{243}Am Yield	Tracer Peak	^{244}Cm Reference Value	^{244}Cm Measured Value	^{244}Cm Measured Value	Difference
ID	(%)	(FWHM)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
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 9 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.

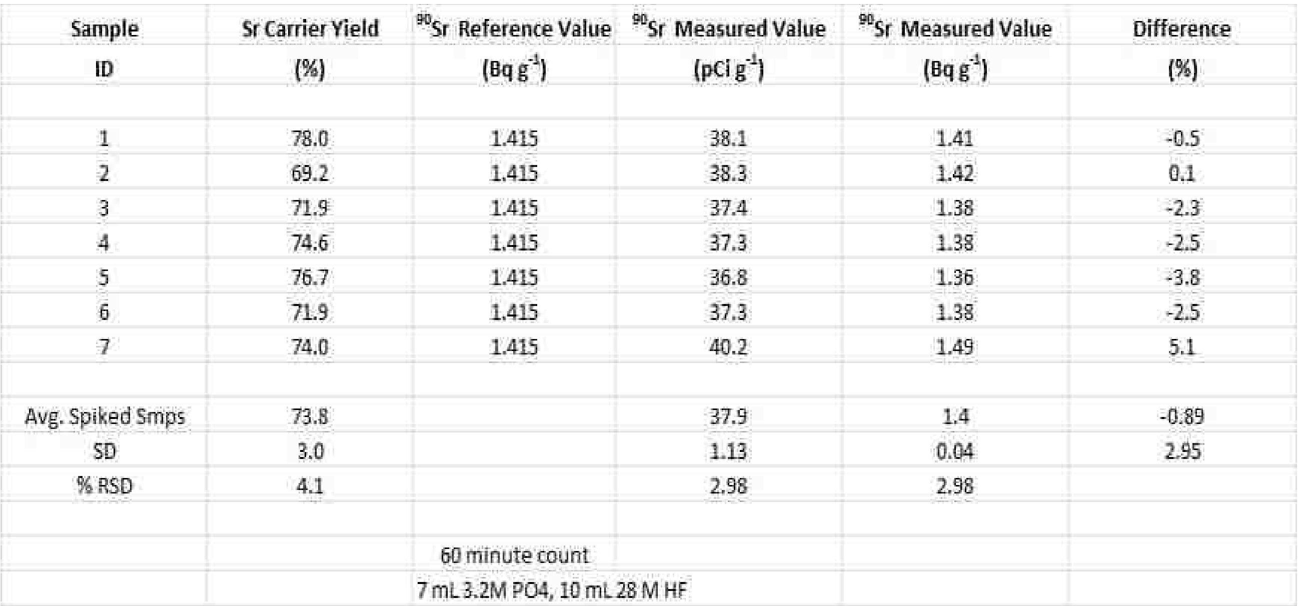
Table 9: U-238 Results for Marble Spiked with MAPEP 30 Soil



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)		

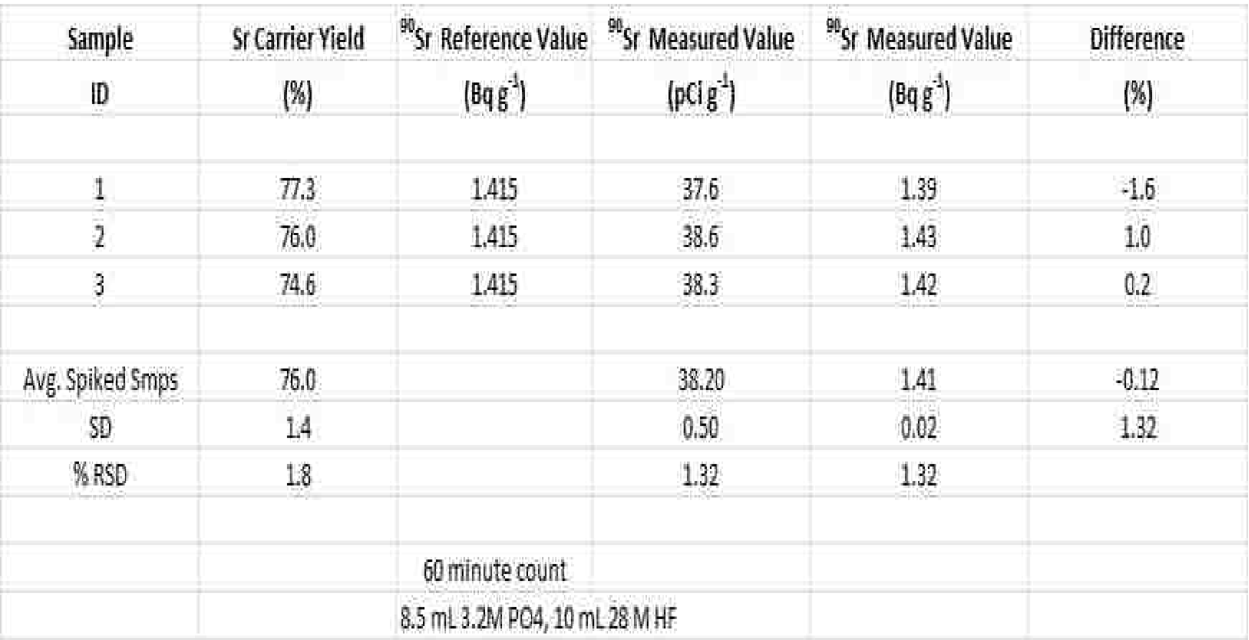
Table 10 shows the individual results for the determination of ^{90}Sr in seven 1 g limestone samples spiked with 1.415 Bq g^{-1} ^{90}Sr. The ^{90}Sr results were corrected for chemical yield using a stable strontium gravimetric method, with an average value of 73.8%. The average ^{90}Sr result was 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 11 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 12 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%.

Table 10: Sr-90 Results for Spiked Limestone – Initial



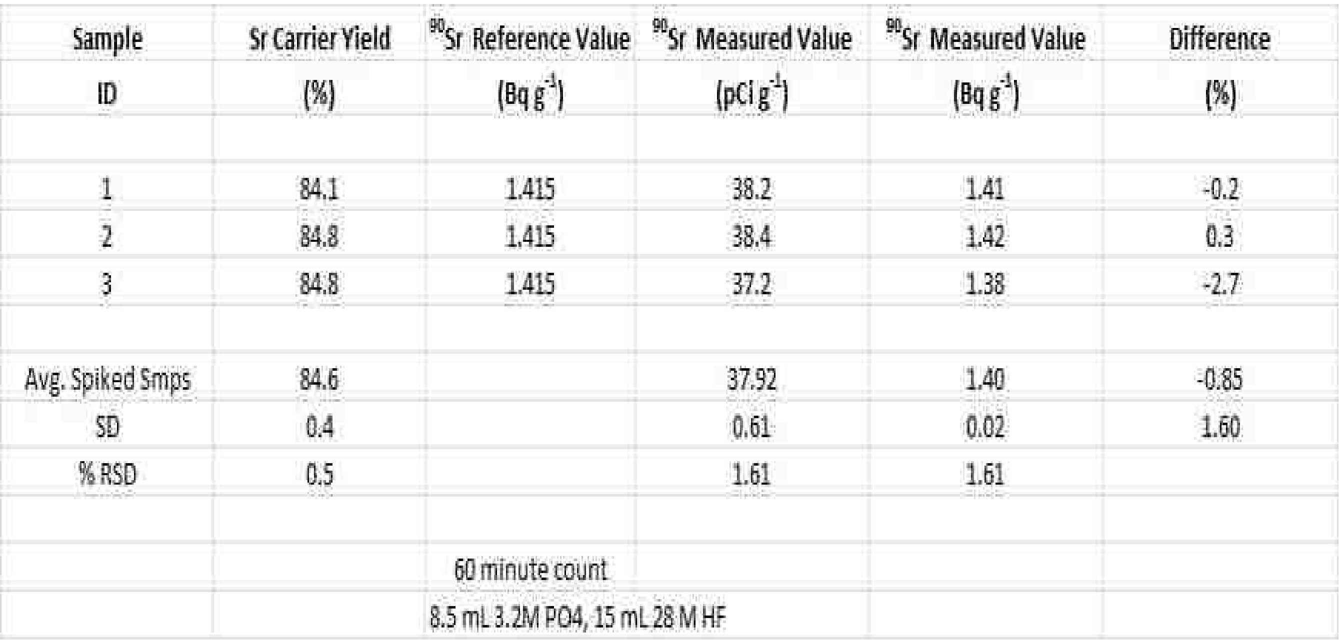
Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq g^{-1})	^{90}Sr Measured Value (pCi g^{-1})	^{90}Sr Measured Value (Bq g^{-1})	Difference (%)
1	78.0	1.415	38.1	1.41	-0.5
2	69.2	1.415	38.3	1.42	0.1
3	71.9	1.415	37.4	1.38	-2.3
4	74.6	1.415	37.3	1.38	-2.5
5	76.7	1.415	36.8	1.36	-3.8
6	71.9	1.415	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 11: 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 12: 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			

The MDA (Minimum Detectable Activity) for actinide isotopes using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie shown in equation (6): [75]

$$\text{MDA} = [2.71+4.65\sqrt{\text{B}}\ ]/\ (\text{CT*R*V*Eff*}\mathbf{A}\text{*0.060}) \tag{6}$$

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.

3.5 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.

3.6 Acknowledgment

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CHAPTER 4: RAPID METHOD TO DETERMINE ^{89}SR/^{90}SR IN LARGE CONCRETE SAMPLES

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4.1 Abstract

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

4.2 Introduction

The Savannah River Environmental Laboratory has developed many new rapid methods to facilitate readiness for emergency response to radiological events. Several of these methods were utilized following the nuclear accident at Fukushima Daiichi to provide timely analytical support to the government of Japan and the US Department of Energy. [16, 43, 76] There is a need for rapid, traceable methods to support decommissioning of older nuclear facilities, especially in Europe. A significant reduction in very high decommissioning costs by the development and implementation of new measurement techniques is necessary. [77] Many older analytical methods are tedious and time-consuming, driving up overall facility decommissioning costs. The assay of radiostrontium (^{89,90}Sr) in decommissioning materials is an important radiochemical measurement for safe disposal of waste. Rapid, efficient analysis of building materials such as concrete for ^{89,90}Sr is therefore very important. For older nuclear facilities, where the short lived ^{89}Sr ($t_{1/2}$ = 50.55 days) is unlikely to be found, analysis for only the longer lived ^{90}Sr isotope ($T_{1/2}$ = 28.9 years) may be needed. Robust analytical methods with low detection limits are essential. The current disposal limit for ^{90}Sr in soil residues in Germany is 2 mBq g^{-1}, while the limit for ^{90}Sr in concrete residues is 600 mBq g^{-1}. [78] Regulatory limits tend to be lowered over time, and the limit for concrete may be lowered to 2 mBq g^{-1} as well.

There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine radiostrontium in environmental samples. Vajda and Kim provide a very good overview of recent radiostrontium separation and analytical measurement techniques. [79] This review also included more classical methods using fuming nitric precipitation, as reported by Bojanowski et al. [80]. Fuming nitric acid presents handling difficulties and can be very tedious and time-consuming. Wang et al. [13] reported a sequential method to determine actinides and strontium in soil samples. A large number of tedious, sequential steps were required in this analytical method.

Acid digestion of soil and concrete samples often leaves undigested residue and may not effectively digest refractory particles. Jurečič et al. studied several soil decomposition techniques and found that alkaline fusion was more effective for the complete digestion of soils than other methods tested. Other techniques, such as conventional wet dissolution with mixtures of HNO_3, $HClO_4$ and HF and microwave dissolution using HNO_3 and HF were less effective, with analyte losses of 35-60%. Interestingly, this work found that conventional hot plate acid digestion was more effective than more rapid microwave methods for the digestion of soil samples. The hot plate acid digestion methods, which still had undigested residues, took two days to complete. Only the alkaline fusion digested the samples fully. [34]

New rapid fusion methods that allow rapid assay of actinides and $^{89,90}Sr$ in many different building material matrices have been recently reported. [15, 43, 44, 81] These methods combine fast, rugged sample digestion and preconcentration techniques with rapid, innovative column purification methods to analyze building materials and other environmental samples quickly. The rapid fusion technology, which offers speed, simplicity and ruggedness, has also recently been applied to larger soil and concrete sample aliquots for the assay of actinides. [56] The sodium hydroxide fusion and preconcentration steps used in our laboratory take much less time than conventional acid digestion steps, which often require evaporation of large acid volumes. Faster methods in the laboratory are important not only for emergencies but to reduce analytical labor costs and improve overall operational efficiency.

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

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

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

For older facilities, only a ^{90}Sr assay may be needed during decommissioning activities. In this case, the ^{90}Sr daughter, ^{90}Y, is assumed to be in secular equilibrium with ^{90}Sr, a reasonable assumption in a solid matrix like concrete. Ten gram concrete sample aliquots can then be assayed immediately after total dissolution of the concrete and rigorous purification of the ^{90}Y, eliminating the time normally needed for ingrowth of ^{90}Y following isolution of $^{89/90}$Sr. Gas flow proportional counting was used to count the samples because of its low background and low MDA, but liquid scintillation or Cerenkov counting could also be used if desired. This new sample preparation method takes < 6 hours. Simultaneous drawer type gas flow proportional counters were used to facilitate longer count times and high sample throughput.

This method offers much lower detection limits than the direct measurement of ^{90}Sr using inductively-coupled plasma mass spectrometry (ICP-MS) methods. The measurement of ^{90}Sr by ICP-MS also does not require waiting on ^{90}Y ingrowth. However, ICP-MS methods require thorough removal of the isobaric interference ^{90}Zr , and there is typically a very low number of ^{90}Sr atoms present in environmental samples for mass measurement due to the relatively short half-life of ^{90}Sr ($T_{1/2}$=28.9 yr). This results in an MDA that is unacceptable for low level environmental assay of ^{90}Sr. For example, an MDA of ~1.5 Bq L^{-1} has been reported for ^{90}Sr in water. [82]

4.3 Experimental

4.3.1 Reagents

The extraction chromatography resins employed in this work are DGA Resin (N,N,N’,N’-tetraoctyldiglycolamide), and Sr Resin (4, 4’, (5’) di-t-butylcyclohexane-18-crown-6), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA) and Triskem International

(Bruz, France). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS (American Chemical Society) reagent grade. Sr-90 was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2.96 Bq mL^{-1}.

4.3.2 Procedures

Column preparation. Sr Resin and DGA Resin were obtained as 2 mL cartridges. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). The small particle size coated support, with enhanced surface area, improves column separation efficiencies and removal of interferences. Flow rates of ~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. 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 13 shows the sample preparation flowchart for the measurement of ^{89,90}Sr in 5 g concrete samples. Concrete samples were pulverized, homogenized and passed through a 20 mesh sieve prior to sampling so that representative samples could be taken. For testing purposes, ^{90}Sr was added to concrete samples, but the method can also be tailored to measure ^{89}Sr as well. MAPEP 32 soil was added to test the method to assess the removal of potentially interfering radionuclides, such as ^{137}Cs. The MAPEP soil samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA.

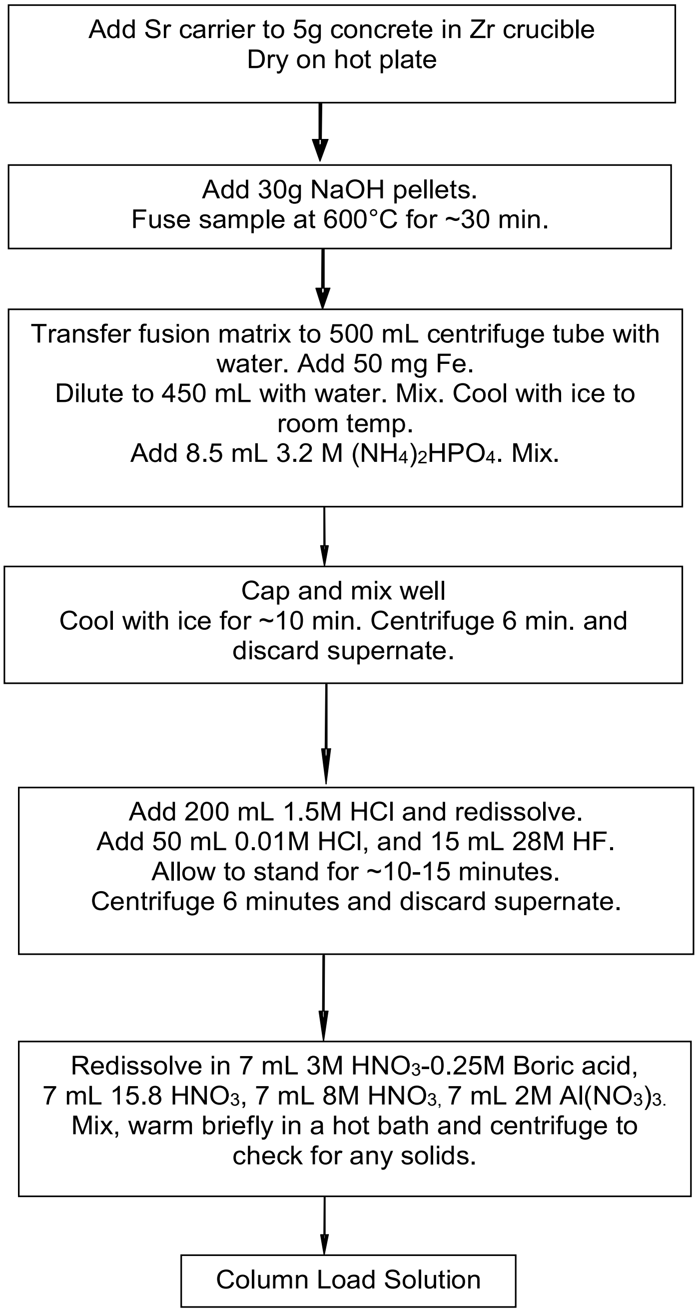


Figure 13: Sample Preparation for Radiostrontium in 5g Concrete Samples

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

Fifty milligrams of Fe (added as $Fe(NO_3)_3$) were added to each 500 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 450 mL with water and the tubes were cooled in an ice bath to room temperature. For the processing of batches where reagent blank and laboratory control samples (LCS) are also included (no concrete), approximately 200 mg Ca may be added to simulate the high Ca matrix for the blank and LCS samples. Eight and one-half milliliters of 3.2M ammonium hydrogen phosphate were added to each tube. Tubes were capped, mixed well and cooled in an ice bath for 10 minutes. Addition of phosphate improves strontium recovery during the initial precipitation step, where Sr precipitation using iron hydroxide alone tends to yield low Sr recoveries. The tubes were centrifuged at 3500 rpm for ~6 minutes, and the supernate was discarded. The precipitates were partially dissolved by adding 200 mL of 1.5 M HCl and 50 mL of 0.01M HCl to each tube, mixing well with each addition. Fifteen to twenty milliliters of 28M HF were added to each tube, and the samples were mixed well, dissolving any remaining Fe hydroxide solids and forming a CaF_2 precipitate which carries the strontium. The tubes were allowed to stand for ~15 minutes and centrifuged for ~6 minutes at 3500 rpm. The CaF_2 precipitation step effectively removes almost all of the Fe, as well as silicates that can adversely affect column flow by forming gel-like solids. It was found that the calcium fluoride precipitate was difficult to redissolve in a column load solution if too much 28M HF was added, apparently due to formation of a hard fluorosilicate crystal structure when contacted by the nitric acid. By reducing the volume of 28M HF added from 30-40 mL to 15-20 mL, this problem was avoided and the precipitates dissolved relatively quickly in the nitric acid load solution.

The supernate was discarded, and the precipitate containing the strontium was dissolved in 7 mL of 3M HNO_3-0.25M H_3BO_3, mixed, and transferred to 50 mL tubes. The 500 mL tubes were rinsed with 7 mL of 15.8 M HNO_3, 7 mL of 2 M $Al(NO_3)_3$ and 7 mL 8 M HNO_3, respectively, transferring the rinses to the 50 mL centrifuge tubes. The goal was to have a high nitric acid load solution (8-9M HNO_3), which is ideal for retaining ^{89,90}Sr on Sr Resin, while eluting key interferences. [73] The samples were mixed using a vortex stirrer and heated 2 to 5 minutes in a hot block heater at 105°C. The 50 mL tubes were centrifuged to test for any traces of solid particulates, which were removed if needed. Typically, the sample load solutions were very clear.

Total ^{89}Sr + ^{90}Sr was separated using a method similar to what was published for ^{90}Sr in large soil samples. [73] The sample load solutions were loaded onto 4 mL Sr Resin (2 x 2 mL cartridges) at approximately 1 drop per second, with applied vacuum. After the sample was loaded, a tube rinse of ~ 5 mL 8M 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: 20 mL 8M HNO_3 (removes Ca, Ba, Cs), 5 mL 3M HNO_3 - 0.05M oxalic acid (removes tetravalent metal ions), and 10 mL 8M HNO_3. After the final rinse, the column reservoirs and connector tips were changed out to maximize decontamination from potential interferences.

Sr was eluted from the resin with 18 mL 0.05M HNO_3 at ~1 drop per second. This eluent solution was transferred to preweighed planchets and evaporated on a hot plate with consistent, medium heat to dryness. Two milliliters 0.05M 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 and weighed to determine gravimetric carrier recovery. The planchets were counted by simultaneous gas flow proportional counting for 60 minutes. It is important that direct stable strontium carrier standardization on planchets (7-10 replicates) be heated on the hot plate at the same temperature for the same time as the samples to minimize gravimetric yield errors. Strontium carrier yields may also be measured using instrumental techniques, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ICP-MS.

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

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

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

Figure 14 shows a DGA Resin separation method previously reported for seawater samples that may also be used for concrete samples to purify ^{90}Y after ingrowth. [74] In this method, yttrium carrier was added to the planchet containing the purified ^{89}Sr/ ^{90}Sr after an initial count of ^{89}Sr+^{90}Sr, followed by a 2-3 day (or longer) ^{90}Y ingrowth period. The planchet solids were dissolved in 8M HNO_3 and transferred to a 50 mL tube. This 8M HNO_3 solution was loaded onto DGA Resin column to purify ^{90}Y. ^{89}Sr and ^{90}Sr are effectively removed using this separation on DGA Resin, as they have no significant retention in 8M HNO_3. After ^{90}Y elution with 18.5 mL 0.25M HCl, and adjustment of each volume to 20.0 mL, a small volume of the final purified eluent was taken for ICP-MS assay to determine chemical yield.

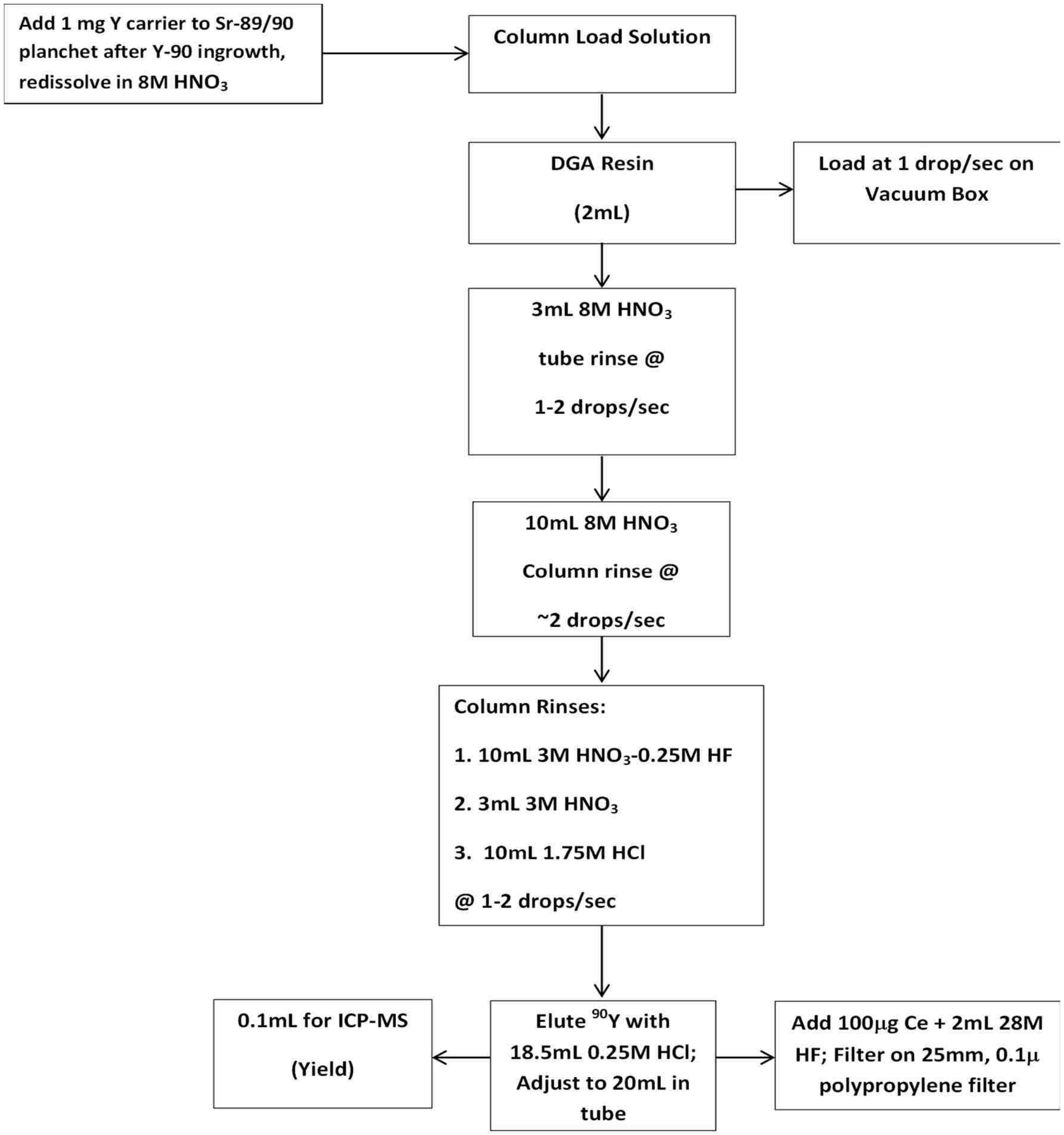


Figure 14: Column Separation for ^{90}Y after Ingrowth on ^{89}Sr +^{90}Sr Planchets

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

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

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

Rapid Method for Y-90 in 10 g Concrete Aliquots Figure 15 shows the sample preparation method for the determination of ^{90}Sr by the direct separation of ^{90}Y from 10 g sample aliquots, eliminating the time for ^{90}Y ingrowth. Stable yttrium carrier (2 mg) was added to each concrete aliquot in 250 mL zirconium crucibles, and the crucibles were dried briefly on a hotplate. After removing crucibles from the hotplate, 40 grams of NaOH pellets were added to each crucible. For a 5 gram aliquot, only 30 g NaOH is needed. The crucibles were covered with a zirconium lid and placed into a furnace at 600˚C for ~30 minutes. The crucibles were removed from the furnace, cooled for about 10 minutes, and transferred to a hot plate. The fusion cakes were transferred to 500 mL tubes as described earlier.

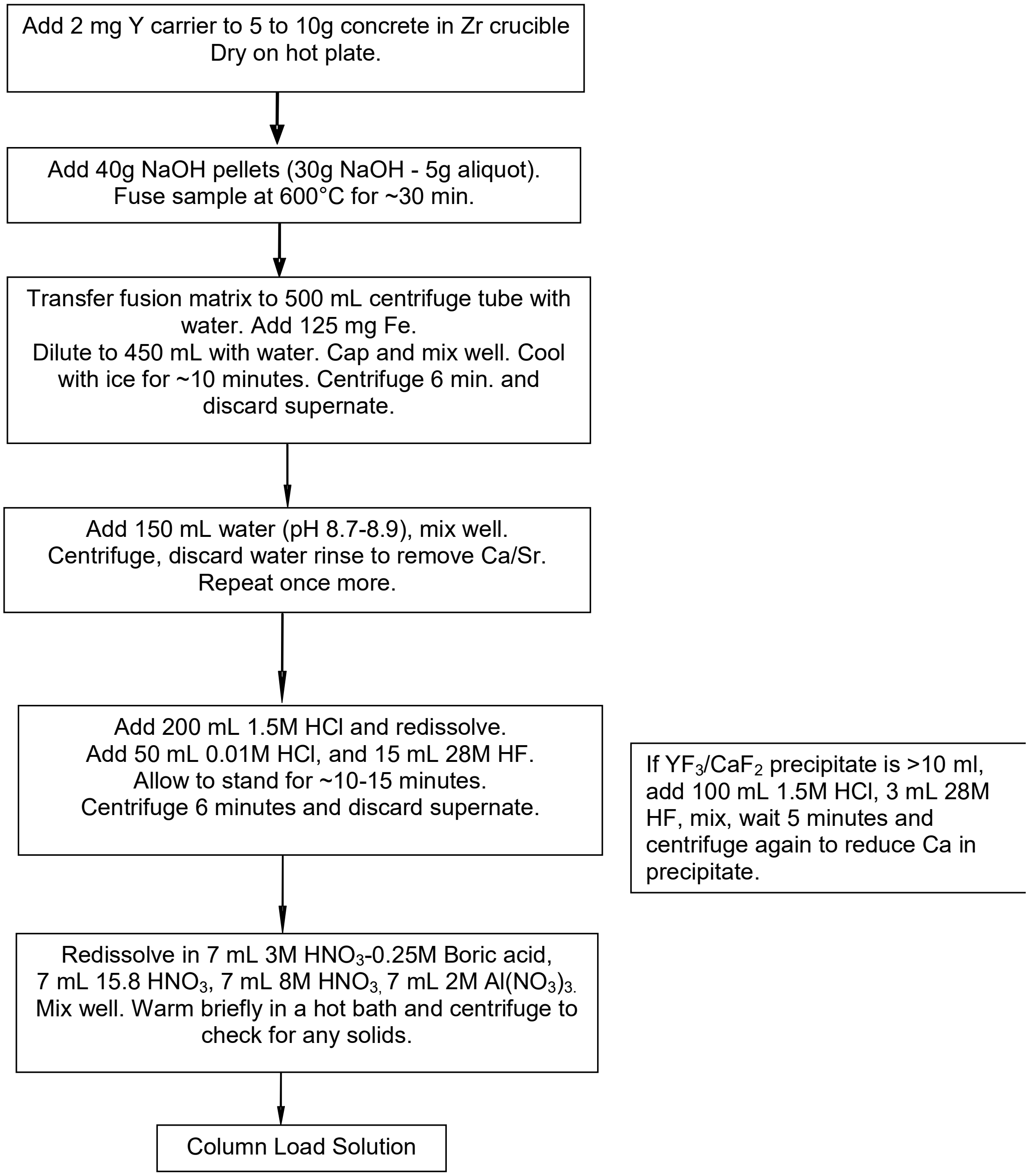


Figure 15: Sample Preparation for Yttrium-90 in 10g Concrete Samples

The preconcentration steps for ^{90}Y in 10 g concrete samples allow for the immediate assay of ^{90}Sr via ^{90}Y (assumed to be in secular equilibrium). The ^{90}Y preconcentration and matrix removal steps are described below. One hundred twenty-five milligrams of Fe (added as Fe (NO_3)$_3$) were added to each 500 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 450 mL with water. The samples were mixed and cooled in an ice bath for ~10 minutes. The tubes were centrifuged at 3500 rpm for ~6 minutes, and the supernate was discarded. The iron hydroxide precipitate was rinsed twice with 150 mL of water (pH of 8.8-8.9).

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

This ^{90}Y preconcentration method is very similar to the ^{89,90}Sr sample preparation method, however, no phosphate was added and additional iron was therefore utilized, since the goal was to remove Ca and Sr. Water rinses of the iron hydroxide precipitate with pH 8.8-8.9 water were performed to ensure effective removal of Ca, as well as the ^{90}Sr parent. The completion of the water rinse of the iron hydroxide precipitate was used as the ^{90}Sr parent separation time to start the ^{90}Y decay calculation for this method. Following the iron hydroxide and yttrium fluoride precipitations, the supernate was discarded and the precipitate containing the YF_3 (plus CaF_2 from a small amount of any residual calcium present) was dissolved in 7 mL of 3M HNO_3-0.25M H_3BO_3 and 7 mL of 15.8M HNO_3, mixed, and transferred to 50 mL tubes. The 500 mL tubes were rinsed with 7 mL of 8M HNO_3 and 7 mL of 2 M $Al(NO_3)_3$, respectively, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed using a vortex stirrer and heated 2 to 5 minutes in a hot block heater at 105°C. The 50 mL tubes containing the load solutions were centrifuged, and any traces of solids were discarded. The column load solutions for Y separation on DGA Resin were prepared in ~8M nitric acid solution to enhance DGA Resin affinity for Y^{+3} and remove Ca^{+2} ions effectively. The volume of YF_3 precipitate is typically <10 mL and dissolves easily. If the YF_3/CaF_2 precipitate is much larger than ~10 mL, a second rinse with 100mL of 1.5M HCl and 3 mL 28M HF may be added to reduce the amount of CaF_2 remaining.

Figure 16 shows the column method used when ^{90}Y was collected directly from the concrete sample for rapid purification. A TRU Resin + DGA Resin separation method is used for ^{90}Y collected immediately from 10 g concrete sample aliquots. TRU Resin was added to provide additional removal of U, Th and Bi isotopes which could bias the ^{90}Y measurement. After collecting ^{90}Y from the concrete samples, the samples were loaded onto stacked TRU Resin + DGA Resin cartridges. Pu, U and Th isotopes are strongly retained on TRU Resin. The stacked resin cartridges were rinsed with 6M HNO_3 and 3M HNO_3, respectively. Twelve milliliters of 4M HCl were added to the stacked TRU Resin + DGA Resin to ensure all Y has been moved to the DGA Resin cartridge. The TRU Resin cartridge was discarded. The DGA Resin was rinsed with 8M HNO_3 to remove Ca and Pb isotopes, and with 0.1M HNO_3 to remove any U isotopes that have bled through from TRU Resin onto DGA Resin. A 25 mL rinse of 3M

HNO_3-0.25M HF was used to remove any residual Th isotopes that may have made it through to TRU Resin. After ^{90}Y elution in 0.25M HCl, a small volume of the final purified eluent was taken for ICP-MS assay to determine chemical yield. The ^{90}Y was then determined by gas flow proportional counting after the CeF_3 microprecipitation source preparation described above. Sample results were corrected for the removal of 0.5% of the Y eluent solution.

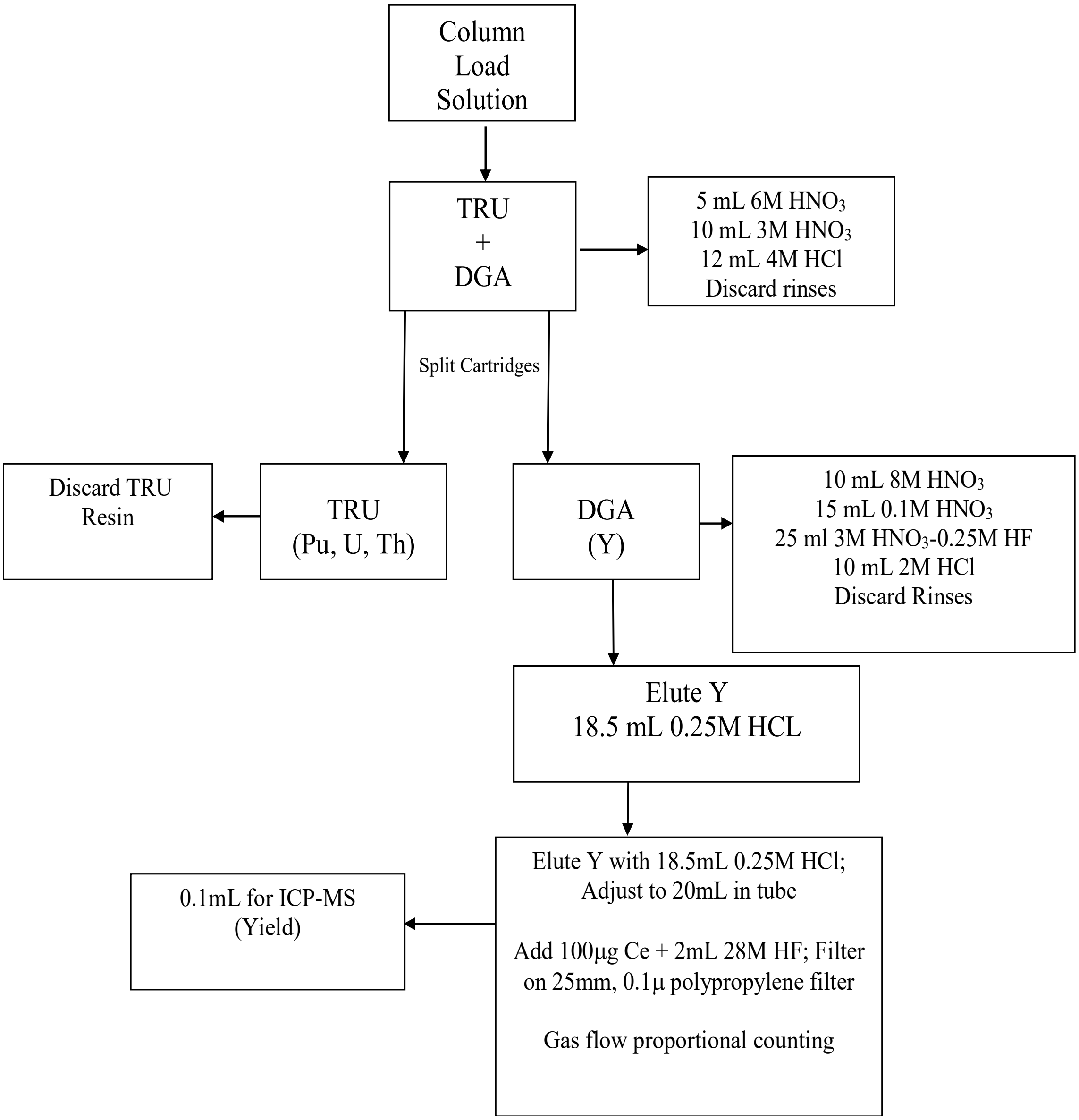


Figure 16: TRU+DGA Resin Y-90 Separation Method for Concrete

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

4.3.3 Apparatus

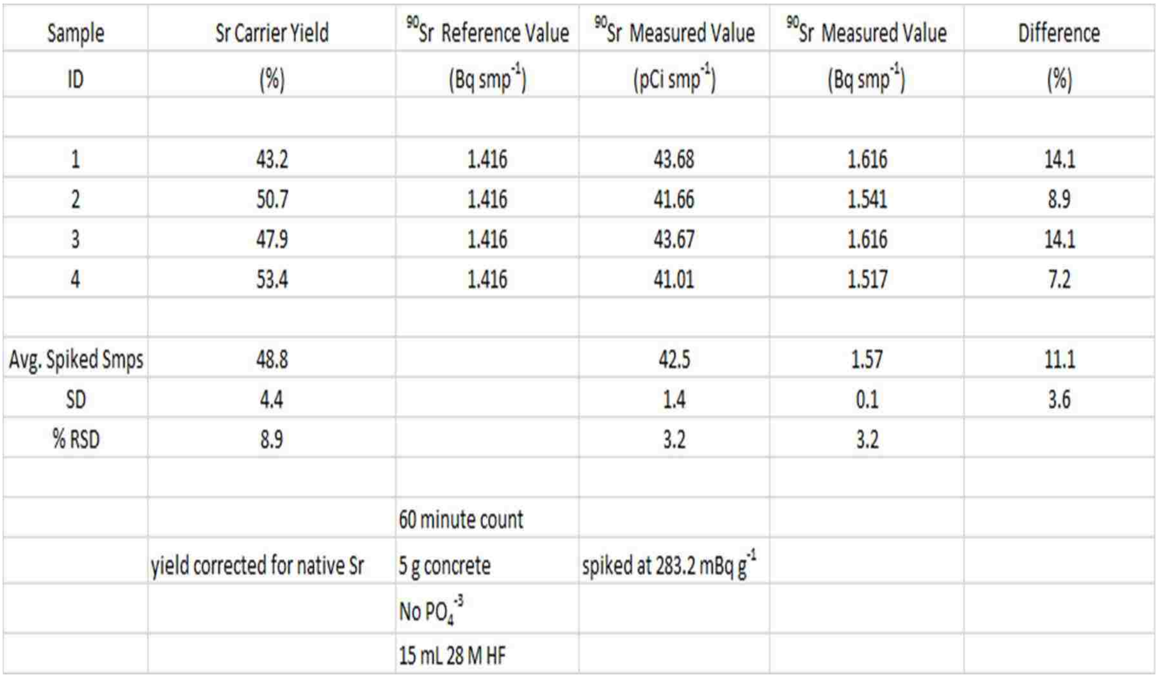
A Tennelec LB 4100 gas flow proportional counter was used to count the ^{90}Sr spiked samples. The detectors were calibrated using NIST Traceable ^{90}Sr/^{90}Y sources matching the sample geometry. Detector backgrounds are determined and subtracted from the sample counts. A mass attenuation correction 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. Annealing the planchets for only 90 minutes at 450˚C was found to provide improved corrosion resistance. Longer, hotter furnace times previously reported, 3.5 hours at 550˚C, apparently oxidizes the planchet surface too much and can lead to iron oxide solids during sample evaporation.

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

4.4 Results and Discussion

Table 13 shows the individual results for the determination of ^{90}Sr in four 5 g concrete samples spiked with ^{90}Sr using the rapid fusion method plus Sr Resin, with gas flow proportional counting to measure ^{90}Sr. In this test, no additional phosphate was added to enhance yields across the iron hydroxide preconcentration step. As expected, the average Sr carrier recovery was only 48.8% ± 4.4% 1SD, standard deviation). The low chemical yields without the addition of phosphate illustrate why phosphate was used in this new method. The average ^{90} Sr result was 1.57 mBq sample^{-1}, with a 11.1% bias and SD (standard deviation) of 0.1Bq sample^{-1}. The bias may be attributed to errors associated with the Sr carrier yield. The ^{90}Sr activity added to each 5 g aliquot was 1.416 Bq (283.2 mBq g^{-1}).

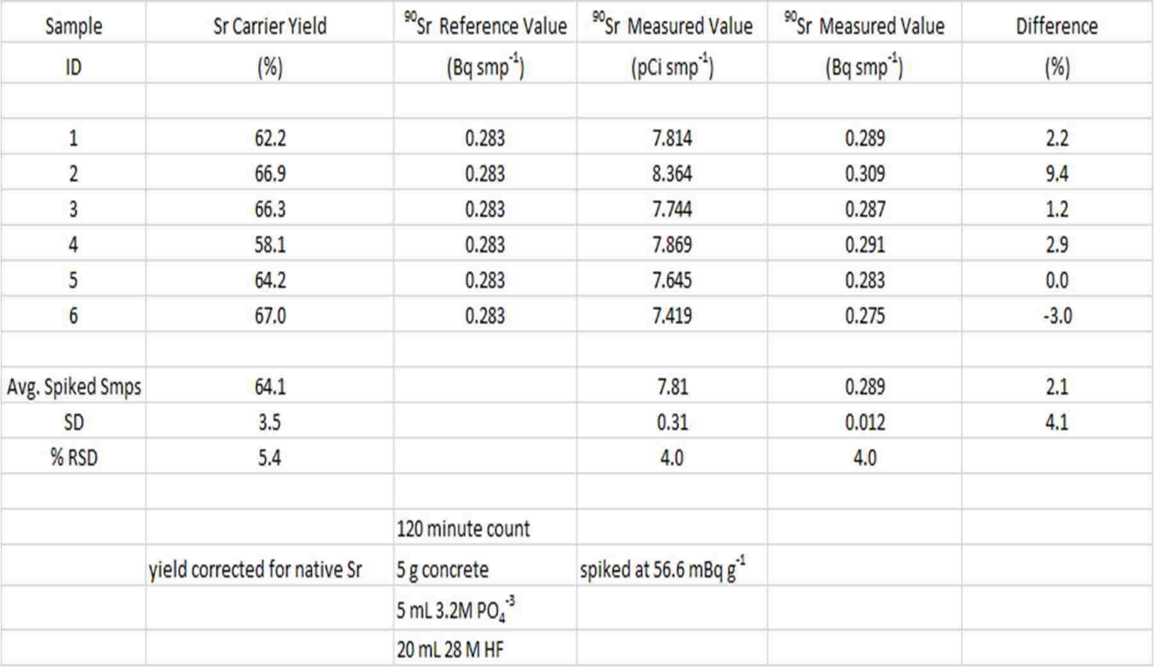
Table 13: Sr-90 in Concrete: 5 g Aliquots using Sr Resin; No PO_4^{-3}



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

Table 14 shows the measured values for six 5 g concrete aliquots spiked with 0.283 Bq ^{90}Sr (56.6 mBq g^{-1}). In this case, 5 mL 3.2 M PO_4^{-3} was added to enhance chemical yields during the initial precipitation with iron hydroxide from the alkaline matrix.. With phosphate added, the average Sr carrier yield increased to 64.1% ± 3.5% (SD), but this average yield was still lower than desired. The average bias for the ^{90}Sr measurements was 2.1%, with an SD of 4.1%. In this case, 20 mL 28M HF was added to facilitate the calcium fluoride precipitation. Since concrete contains high levels of Ca, an additional test was performed to determine whether fluoride might be a limiting reagent in the calcium fluoride step, adversely affecting chemical yield.

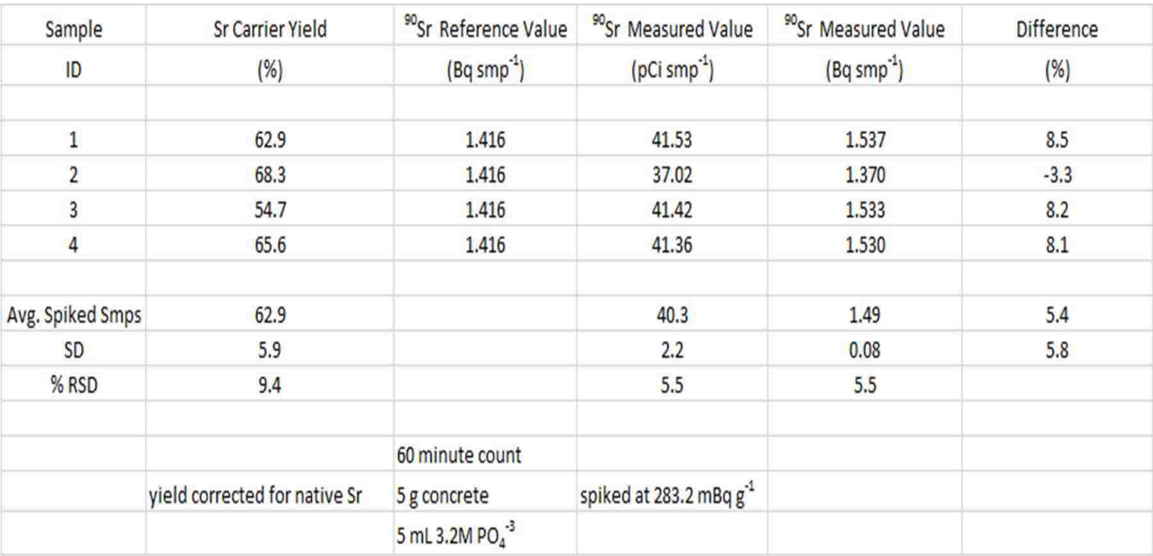
Table 14: Sr-90 in Concrete: 5 g Aliquots using Sr Resin Using PO_4^{-3}



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

Table 15 shows the measured values for four replicates of 5 g concrete spiked with 1.416 Bq ^{90}Sr (283.2 mBq g^{-1}). The same amount of phosphate was used, but additional 28 M HF was added. The Sr carrier chemical yields were still lower than desired, with an average yield of 62.9%± 5.9% (SD). The average ^{90} Sr result, however, was 1.49 Bq $sample^{-1}$, with a 5.4% bias and SD (standard deviation) of 0.1 Bq $sample^{-1}$. The Sr carrier yields indicate that the HF was not a limiting reagent under these test conditions.

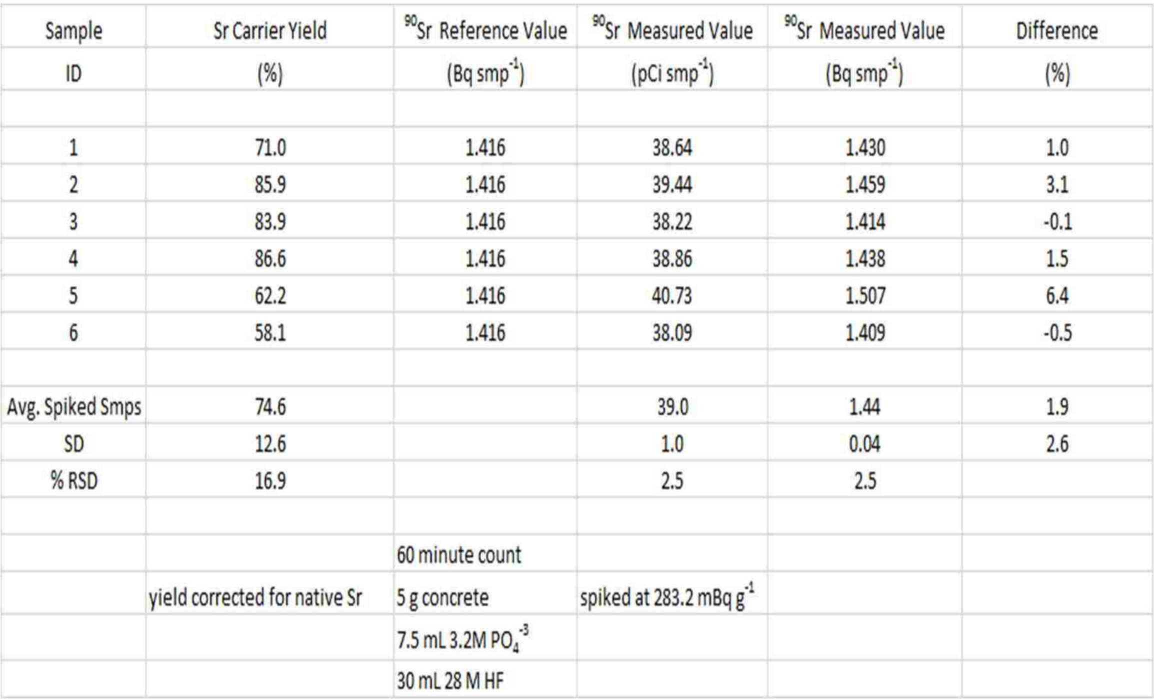
Table 15: Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Increased HF



Sample	Sr Carrier Yield	^{90}Sr Reference Value	^{90}Sr Measured Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp^{-1})	(pCi smp^{-1})	(Bq smp^{-1})	(%)
1	62.9	1.416	41.53	1.537	8.5
2	68.3	1.416	37.02	1.370	-3.3
3	54.7	1.416	41.42	1.533	8.2
4	65.6	1.416	41.36	1.530	8.1
Avg. Spiked Smps	62.9		40.3	1.49	5.4
SD	5.9		2.2	0.08	5.8
% RSD	9.4		5.5	5.5	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq g^{-1}		
		5 mL 3.2M PO_4^{-3}			

Table 16 shows the results for ^{90}Sr in concrete when the phosphate was increased even further. The amount of phosphate added in the initial preconcentration step was increased from 5 mL to 7.5 mL 3.2M PO_4^{-3}. The average Sr carrier yield increased significantly to 74.6%± 12.6% (SD). Several of the individual Sr carrier recoveries were > 80%, indicating the increase in phosphate was beneficial. The average ^{90}Sr result was 1.44 Bq sample^{-1}, with an average bias of 1.9%.

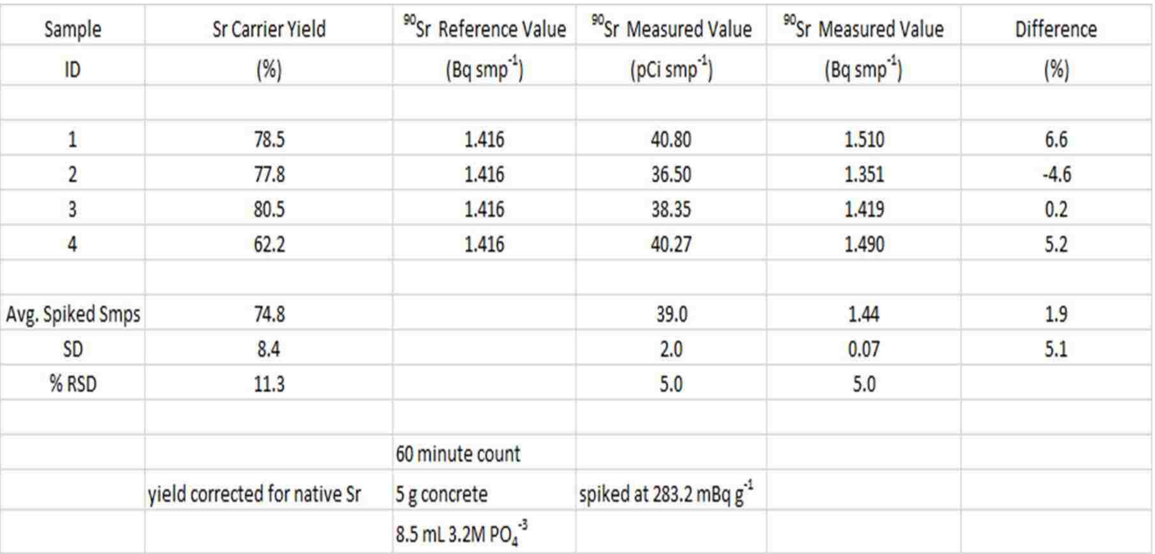
Table 16: Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Increased PO_4^{-3}



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

Table 17 shows the results for ^{90}Sr in 5 g concrete samples when the phosphate added in the initial preconcentration step was increased to an even higher level, from 7.5 mL to 8.5mL 3.2M PO_4^{-3}. The average Sr carrier yield was 74.8%± 8.4% (SD). These results indicate that the additional increase in phosphate was neither beneficial nor harmful. The average ^{90}Sr result was 1.44 Bq sample^{-1}, with an average bias of 1.9%. Despite variations in chemical yield with the different conditions employed, the ^{90}Sr results were typically very good.

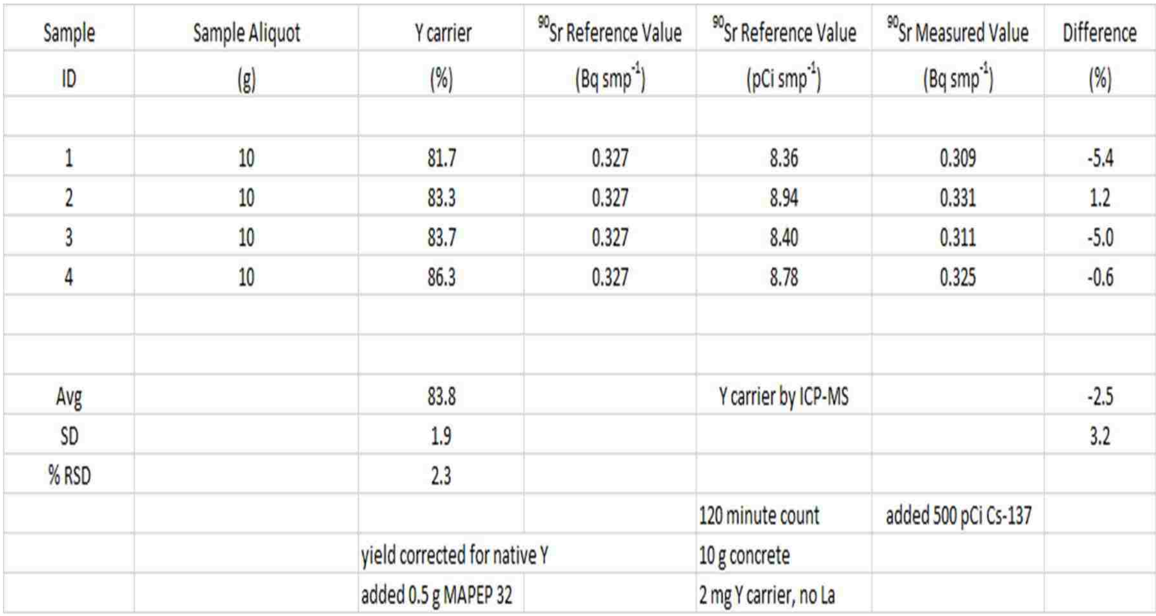
Table 17: Sr-90 in Concrete: 5 g Aliquots using Sr Resin with Even Higher PO_4^{-3}



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

Table 18 shows results for the ^{90}Sr method that measures ^{90}Y in the sample with no waiting for ^{90}Y ingrowth. This method employed the ^{90}Y sample preparation steps shown in Figure 15, coupled with ^{90}Y purification using the TRU Resin + DGA Resin column method shown in Figure 16. In this test, 0.5 g MAPEP 32 soil was added to 10 g concrete aliquots. MAPEP 32 soil contains ^{90}Sr and potentially interfering radionuclides. To test the ruggedness of the method even further, a relatively high level of ^{137}Cs (18.5 Bq) was added to each sample aliquot to test for the removal of this potential interference. Due to its relatively long half –life ($T_{1/2}$=30.17 yrs), it would not be surprising to encounter ^{137}Cs fission product activity in decommissioning samples. Y carrier (2 mg) was used to determine the Y chemical yield. Four 10 g aliquots were analyzed, with an average Y chemical yield of 83.9% %± 1.9% (SD). The average ^{90}Sr result was -2.5%, with SD ±3.2%, showing excellent results. The high, consistent Y yields indicate that the sample preparation method is very rugged. The effective removal of MAPEP 32 soil radionuclides, despite the presence of 18.5 Bq ^{137}Cs and other interferences indicate that the method removes other beta-emitting interferences very well.

Table 18: Sr-90 in Concrete: 10 g Aliquots using TRU+DGA Resin (Y-90)



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

Stable yttrium carrier was added to enhance ^{90}Y precipitation during the sample preconcentration steps and to determine chemical yield. Initial testing with 1 mg stable Y was successful, but the stable Y amount was increased to 2 mg to reduce potential errors in the Y chemical yield associated with native Y in the concrete. A correction of approximately 7% was made in the chemical yield for the native Y, which was measured to be ~150 ug in the 10 g concrete aliquot. Up to 4 mg Y carrier was tested to further minimize any contribution from native Y, but with this much Y added the amount of YF_3 solids on the final sample test source was larger than desired. Initially La was added as a carrier to enhance Y recovery, as was reported for ^{90}Sr in seawater [74], but it was found that La was not required to enhance chemical yields. The $Fe(OH)_3$ precipitation appears to be highly effective for preconcentration of Y and the combination of a small amount of Y and Ca appears to work very well to collect Y as a fluoride precipitate, without the addition of La. Y^{+3} ions are retained much more strongly than La^{+3} on DGA Resin, however La is still retained. [61] Eliminating La reduced the risk of Y loss on DGA Resin, and allowed for an increase in the amount of Y carrier to at least 2 mg Y. Native Y levels in concrete may be determined by digestion and analysis of an aliquot by ICP-MS. An alternate approach, perhaps less disruptive to the laboratory, is to process a representative number of the concrete samples through the method without the addition of Y carrier to determine the native content in that way. Employing a native Y correction gives the best possible ^{90}Y results. It may also be possible, however, to minimize the impact of native Y in the samples and not make a native Y correction. By analyzing slightly smaller aliquots of concrete, and increasing the Y carrier to 3-4 mg, for example, the impact would likely be < 5%.

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

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

The MDA (Minimum Detectable Activity) for ^{90}Sr and ^{89}Sr using this method with gas flow proportional counting was calculated according to equations prescribed by Currie shown in equation (7): [75]

$$MDA = [2.71+4.65\sqrt{B}]/(CT*R*V*Eff*0.060) \qquad (7)$$

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

CT = sample count time (min)

R = Chemical Recovery

V = Sample aliquot (L)

EFF = Detector Efficiency

0.060 = conversion from dpm to mBq

Figure 17 shows the MDA for these methods plotted vs. count time for 5 g and 10 g aliquots using ~54% efficiency gas flow proportional detectors, assuming ~80% chemical yield and 1.35 cpm (counts per minute) average background count rate. The MDA (minimum detectable activity) for the method can be adjusted as needed, depending on the sample aliquot and count time.

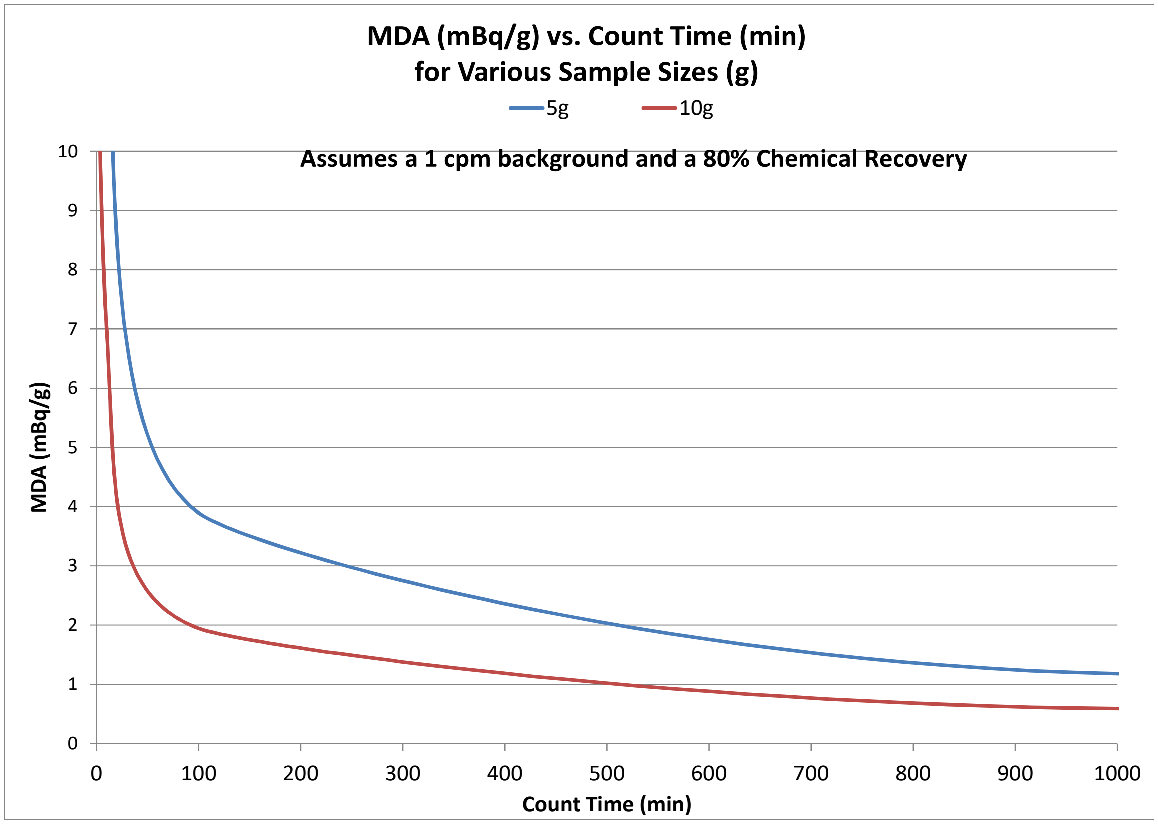


Figure 17: MDA for 5g and 10 g Aliquots vs. Count Time

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

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

4.5 Conclusions

A new rapid fusion method to determine ^{89}Sr and ^{90}Sr in 5 g -10 g concrete samples has been developed that allows the separation of Sr isotopes with high chemical yields and effective removal of interferences. Several analytical options were presented that offer significant method flexibility, depending on which Sr isotopes are required. One method collects, purifies and measures ^{89,90}Sr in 5 g concrete aliquots. Another approach allows the immediate determination of ^{90}Sr in 10 g concrete aliquots with no waiting for ^{90}Y ingrowth. The total digestion and separation method is not only rapid (< 6 hrs), but it provides ruggedness that can help maintain the public trust regarding the quality of the measurements. Count times may be adjusted depending on the MDA and uncertainty requirements, and detection limits below 1 mBqg^{-1} can be achieved to meet new, lower regulatory limits.

4.6 Acknowledgment

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CHAPTER 5: RAPID METHOD TO DETERMINE PLUTONIUM, NEPTUNIUM, AMERICIUM AND CURIUM IN GRANITE SAMPLES

5.1 Abstract

A novel rapid method for the determination of plutonium, neptunium, americium and curium isotopes in granite has been developed at the Savannah River Environmental Laboratory (SREL). Granite samples are pulverized and fused with sodium hydroxide to achieve complete dissolution. Rapid precipitation steps are utilized to preconcentrate the actinide isotopes and remove sample matrix interferences. Plutonium, neptunium, and americium/curium are separated using extraction chromatography and measured by alpha spectrometry. This approach results in sample preparation time of less than four hours for granite samples.

5.2 Introduction

Granite is a construction material for many important buildings in the United States, including the U.S. Treasury Building and the Vietnam Memorial in Washington, DC. It has also been employed as an important building material for skyscrapers and monuments throughout the world. If a radiological event such as a radiological dispersive device (RDD), an improvised nuclear device (IND) or a nuclear incident such as the accident occurs, then there will be hundreds of thousands of environmental and bioassay samples to analyze over a recovery period of approximately 12 months. Rose et al. note that if an IND detonation occurs that as part of a disaster response timeline laboratory sample analysis needs to occur in the first 6-24 hours. [6] It is critical therefore that rapid methods be completed in just a few hours. Inn et al. have compiled lists of radionuclides for which rapid analytical capability is needed, including plutonium isotopes, uranium isotopes, americium and curium isotopes, ^{90}Sr, and ^{226}Ra. [7] Solid matrices offer significant challenges, and the analytical methods employed must be able to overcomes these difficulties.

Radiological events have the capacity to trigger great anxiety and fear, creating widespread panic. [2] If the event occurred in a metropolitan area, the ability to analyze urban building materials very quickly to support dose mitigation and environmental clean-up is very important. SREL continuously develops and improves rapid methods for use in emergency situations. Recently published methods included applications for soil, concrete and brick, asphalt and steel. [15, 16, 43, 84]

Granite is a hard, granular, crystalline, igneous rock consisting mainly of quartz, mica, and feldspar. Often used as a building stone, granite is much more resistant to digestion with acids than carbonate materials such as marble and limestone. [24] Therefore, fusion methods are often required for effective dissolution.

In methods development, the goal of SREL is to provide the rapid, reliable measurement of radionuclides, while maintaining method ruggedness and accuracy, in order to provide defensible results that maintain the public trust. Complete sample dissolution, is required to ensure accurate analyses and to adequately deal with refractory particles that may be present in samples. [19] This is supported by recent inter-laboratory proficiency tests, where laboratories employing acid leach procedures, including hydrofluoric acid digestion, reported $^{234/238}$U analyses 60% lower than soil reference values. [44] These procedures were found to be inadequate for recovery of analytes from certain high fired refractory materials. Laboratories employing fusion techniques reported values much closer to true reference value.

Gascoyne et al. [32] report a lithium metaborate fusion technique for analysis of granite rock samples for the determination of uranium and thorium isotope abundances using alpha spectrometry. Uranium and thorium were both extracted with 10% tributylphosphate (TBP) in amyl acetate using $Al(NO_3)_3$ as the salting agent, and then back-extracted into 1 M H_2SO_4. Uranium was separated from thorium using anion exchange resin. The sample preparation in this work took about 8 hours, however, overall chemical yields were only 20 to 60%. In addition, mixed solvent waste was generated and relatively large anion resin columns were utilized, generating significant volumes of acidic aqueous waste. Mixed waste issues with solvents are one reason that radiochemical laboratories over the course of the last 20 years have moved toward extraction chromatography (EXC). [85] The use of small EXC resin columns or cartridges yields reduction in acid waste as well as in labor costs. Additionally, stackable EXC resin cartridges allow for the efficient sequential separation of multiple metal ions from a single sample using highly selective extractant coated resins.

In an example of more modern sample preparation methods, Varga et al. [33] reported two improved techniques for the determination of americium and plutonium from environmental samples by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and alpha spectrometry. Both procedures involved a rapid CaF_2 co-precipitation step for pre-concentration and matrix removal followed by extraction chromatographic separations. The average recovery after sample preparation was greater than 85 % for americium and plutonium. The methods developed could be performed within 6 hours for one batch of samples. The selectivity of LaF_3/CaF_2 precipitations to remove soil matrix components including Fe and Si has been well-documented. [15, 16, 43]

Jurečič et al. [34] reviewed several soil decomposition techniques and found that alkaline fusion resulted in a complete digestion of uranium in the soils studied. Other analytical digestion techniques, such as conventional wet dissolution with mixtures of HNO_3, $HClO_4$ and HF acids, or microwave dissolution using HNO_3 and HF were less effective, with significant uranium losses. Two reference materials, including NIST-4353a Rocky Flats Soil, and six soil samples taken near a former uranium mine were investigated. Relatively long digestion and evaporation times (up to 2 days) were cited in this work. A rapid sodium hydroxide fusion, in direct contrast, can be completed in < 30 minutes, with subsequent preconcentration steps typically taking < 2 hours. No evaporation steps are needed, and uranium chemical recoveries are nearly quantitative, even when refractory material is present in the environmental sample.

The use of such rapid sodium hydroxide fusion methods has been reported by this laboratory for many different sample matrices, including soil, concrete, brick, asphalt limestone and marble. The ruggedness of these techniques has been validated by analyzing soil containing refractory Pu or U. Application of the sodium hydroxide fusion to granite, and optimization of the subsequent matrix removal and separation steps has led to a new method to determine actinides in granite materials. The method, developed in the Savannah River Environmental Laboratory, effectively digests refractory actinide isotopes and allows the preparation of batches of 12 granite samples in less than four hours. Several samples are fused simultaneously at 600˚C in relatively inexpensive, reusable zirconium crucibles in muffle furnaces. It should be noted that flux materials such as sodium carbonate require much higher temperatures and are typically performed one at a time over a propane burner. [45] The alkaline fusion method used can be performed in about 15 minutes at relatively low temperature (600°C) due to its lower melting point, without a burner, and multiple samples can be processed simultaneously in furnaces. Lithium metaborate fusion may be used for solid samples, however, it has a relatively high melting point and requires either more expensive platinum crucibles, or graphite crucibles, and often is performed one sample at a time over a burner. The ability to process multiple samples simultaneously is key following a radiological emergency.

Once the sample is digested and the actinides are effectively preconcentrated, there are many different stacked cartridge options, depending on which analytes are desired. [56, 81] In this work, plutonium and neptunium are separated quickly and efficiently using TEVA Resin cartridges. Am/Cm can be sequentially separated using TEVA plus DGA Resin cartridges. The use of vacuum boxes and stacked resin makes the sample preparation steps more rapid, with enhanced flow rates and effective removal of matrix interferences. The combination of rapid rugged sample digestion and efficient column separation techniques is a key component in developing robust radiochemical method for urban matrices for use during a radiological emergency or for routine laboratory assays. In addition to ruggedness, the fusion of soil samples used in this method is much faster than hot plate or microwave digestion where acid digest volumes must be evaporated.

5.3 Experimental

5.3.1 Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336) and DGA Resin, Normal (N,N,N’,N’-tetraoctyldiglycolamide available from Eichrom Technologies, LLC, (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acid solutions 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 and ^{243}Am were obtained from Eckert Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1} to enable yield corrections. The standards ^{237}Np and ^{244}Cm were obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1}. Single element standards (10 mg/L) of yttrium, scandium, and the rare earth elements were obtained from High Purity Standards (North Charleston, SC). The radiotracers ^{241}Am, ^{147}Pm, ^{152}Eu, and ^{244}Cm, used in determination of column capacity factors (k') were obtained from Eckert and Ziegler Isotope Products (Valencia, CA) and used as received. MAPEP soil samples were provided by the Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA.

5.3.2 Procedures

Column preparation. TEVA and DGA Resins (2 mL cartridges) and a 24 position vacuum extraction system were obtained from Eichrom Technologies, LLC. Flow rates of ~1-2 mL min^{-1} were typically used for this work, slower during sample loading onto the column and final elution steps, faster for the column rinses used to remove sample matrix interferences.

Sample Preparation. Figure 18 shows the sample preparation flowchart for actinides in granite samples. This method was adapted from those used for concrete and brick [16] and limestone and marble [81], adjusting parameters to optimize for the particular challenges of the granite matrix, including high silica and alumina content and relatively low calcium content. Granite samples were pulverized, homogenized and passed through a 50 mesh sieve prior to sampling so that representative samples could be taken. It is very important to pulverize the granite sample to a very fine particle size as the radionuclides may not be distributed homogeneously in the samples. Although uranium was not included in this study, non-homogeneity has been experienced in particular for this element in granite. One gram aliquots of granite were analyzed for the respective actinides. MAPEP 24 soil aliquots (~0.25 g), containing refractory ^{239}Pu, were also placed into 250 mL low form zirconium crucibles along with the granite sample aliquots. Reference activities were calculated based on the activity added per mass of granite analyzed, excluding the mass of the MAPEP soil added. MAPEP 32 soil standard was also added to some granite samples to provide additional test results at different analyte levels.

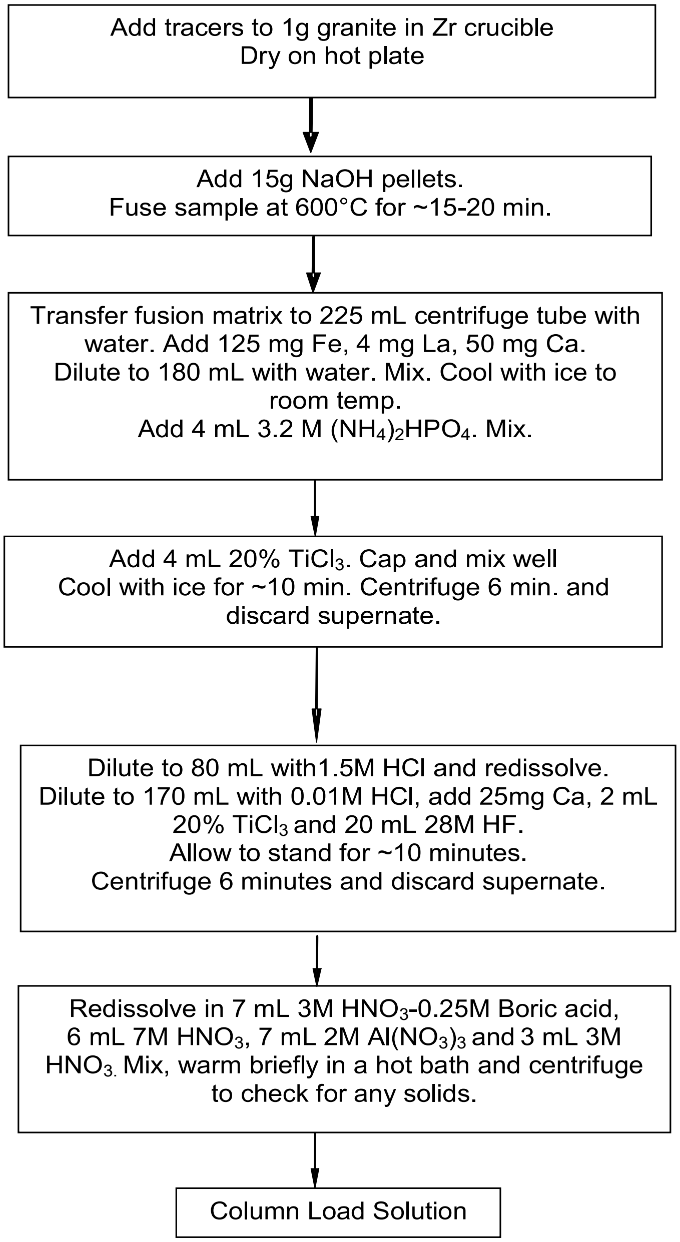


Figure 18: Rapid Sample Preparation for Actinides in Granite

Samples and chemical yield tracers were added to Zr crucibles. Residual moisture was removed by heating on a hotplate. NaOH pellets (15 g) were added, and the crucibles covered with zirconium lids. The samples were fused at 600˚C for ~ 15-20 minutes in a muffle furnace. The crucibles were cooled for 10 minutes. Water was added to dissolve the samples, heating as necessary. Dissolved samples were transferred to 225 mL centrifuge tubes. Residual solids were removed from the crucibles with additional rinsing. Addition of 10 mL 3M HNO_3 to each crucible and heating on the hot plate completed removal of residual actinides. The HNO_3 rinse was then carefully added to the alkaline matrix in the 225 mL centrifuge tube.

Preconcentration of Actinides. The dissolved samples were valence adjusted with $TiCl_3$ (ensures Np(IV)) and ammonium hydroged phosphate added to form a Ca/Fe phosphate precipitation. The precipitation concentrates the actinides and removes the large amount of NaOH from the fusion. Addition of 50 mg of Ca fortifies the calcium present in the sample and ensures efficient recovery of the actinides during the phosphate precipitation.

Following removal of the supernate, the precipitate was dissolved in dilute HCl. Additional $TiCl_3$ was added, along with HF to initiate a LaF_3 precipitation. The LaF_3 precipitate further concentrates the actinides and effectively removes iron and silicates which can adversely impact the chromatographic separation steps. A large excess of HF is used to ensure solubility and efficient removal of silicates and alumina material.

The supernate was discarded, and the precipitate containing the actinides was dissolved in 7 mL of 3M HNO_3-0.25M H_3BO_3. Boric acid complexes the fluoride and facilitates dissolution of the precipitate. The sample was transferred to 50 mL tubes, and the 225 mL tubes were rinsed with

HNO_3 and 2 M $Al(NO_3)_3$, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed heated and in hot block heater at 105°C. Samples were centrifuged to remove solid particulates, and clear solutions submitted to final valence adjustment prior to chromatographic separation of actinides.

Column separation for Pu, Np, Am and Cm. Column separation techniques previously reported were used to separate and purify actinide isotopes. [15,16, 43, 56, 81] Depending on the desired actinide isotopes to be measured, several separation schemes can be employed. Pu and Np isotopes were rapidly separated using a 2 mL TEVA Resin cartridge. Figure 19 illustrates the use of TEVA+DGA Resin as stacked cartridges to rapidly separate Pu, Np and Am, Cm with this method. Am and Cm are separated from interferences using TEVA in tandem with DGA Resin.

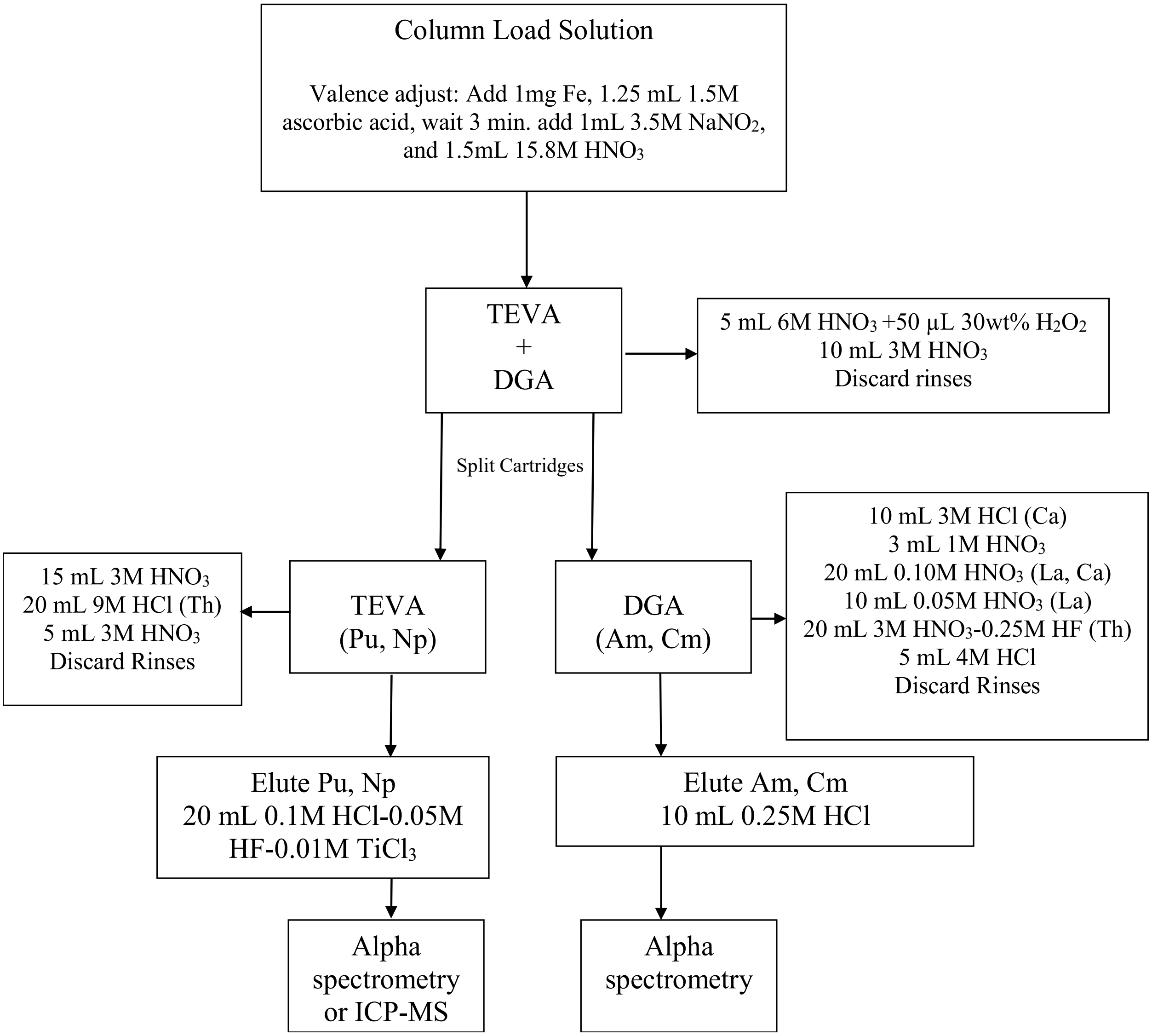


Figure 19: Rapid Column Separation for Pu, Np, Am and Cm isotopes in Granite

Following chromatographic separation, actinide samples were prepared for alpha spectrometry measurements via cerium fluoride microprecipitation. [56] The microprecipitation was facilitated by addition of 40-50 µg of Ce (as cerium nitrate), 0.5 mL 30 wt% H_2O_2 and 1 mL 28 M HF to each sample eluent. After 15 minutes, the solution was filtered through 25 mm polypropylene filters (0.1 µm pore size disposable Resolve™ filter funnel). Filters were rinsed with 5 mL deionized water, and 3 mL ethanol to facilitate drying. The filters were heated briefly under a heat lamp to ensure dryness, and minimize fluoride volatility that might damage silicon alpha spectrometry detectors. Adding hydrogen peroxide to the Pu and Am/Cm precipitation steps provides additional decontamination from uranium isotopes, as U(VI) does not carry on the CeF_3 precipitate.

Measurement of column capacity factors (k'). Column capacity factors (k') for selected elements on DGA Resin, Normal were measured as previously described. [61] Aqueous solutions (0.5-10 mL) containing the desired acid concentration and 5-100 mg/L of the desired stable metal ions or 10,000-50,000 cpm of radiotracer were equilibrated with a known mass of resin (0.10-0.25 grams) for 1-2 hours at 21(1)°C on an orbital plate shaker or tumbling mixer. After equilibration, the aqueous phase was filtered through 0.45mm polypropylene syringe filters to remove resin particles. Stock solutions of the metal ion and solutions that had been equilibrated with resin were then measured using microwave plasma atomic emission spectrometry (MP-AES) for stable elements or radiometric counting techniques for radioactive tracers.

5.3.3 Apparatus

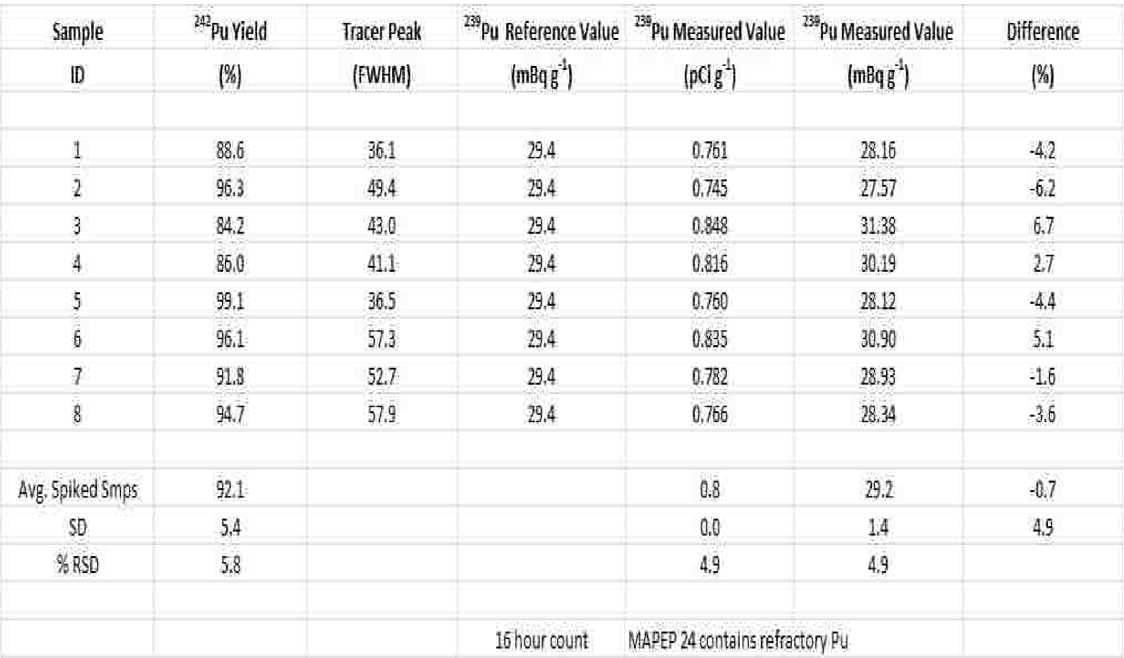
Plutonium, neptunium, americium and curium isotopic measurements were performed using alpha spectrometry on a Canberra Alpha Analyst Integrated Alpha Spectrometer. The alpha system utilized Passivated Implanted Planar Silicon (PIPS) detectors (450 mm^2 active surface) with counting efficiency 28-30% and 3 mm distance between the sample test source and the detector surface.

Stable elements were measured on an Agilent 4200 microwave plasma atomic emission spectrometer (MP-AES). Gamma emitting radioisotopes (^{241}Am and ^{152}Eu) were measured using a Packard Cobra Autogamma Na(Tl)I detector. All other radiotracers were measured using a Packard Tri Carb 2550 TR/AB liquid scintillation counter using 7mL glass vials with 5mL of Ultima Gold LLT scintillation cocktail.

5.4 Results and Discussion

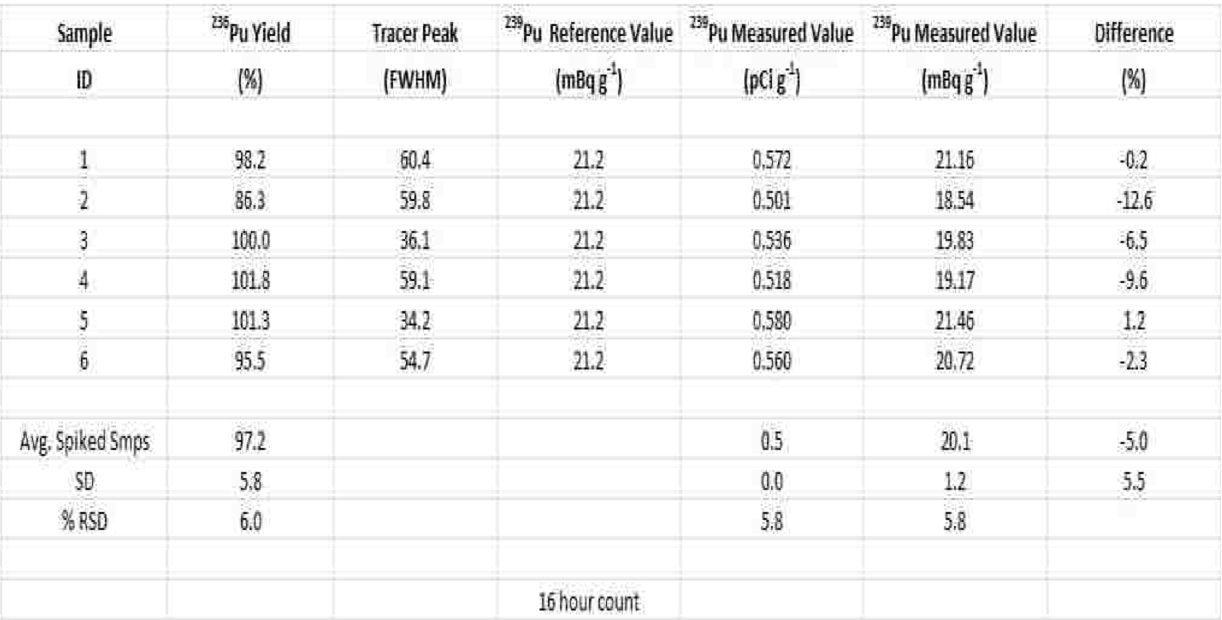
Tables 19-26 show the individual results for the determination of actinides in 1 g granite samples. When Pu was analyzed without Np, ^{242}Pu was used as a tracer yield monitor.

Table 19: Pu-239/240 Results for Granite Spiked with MAPEP 24 Soil



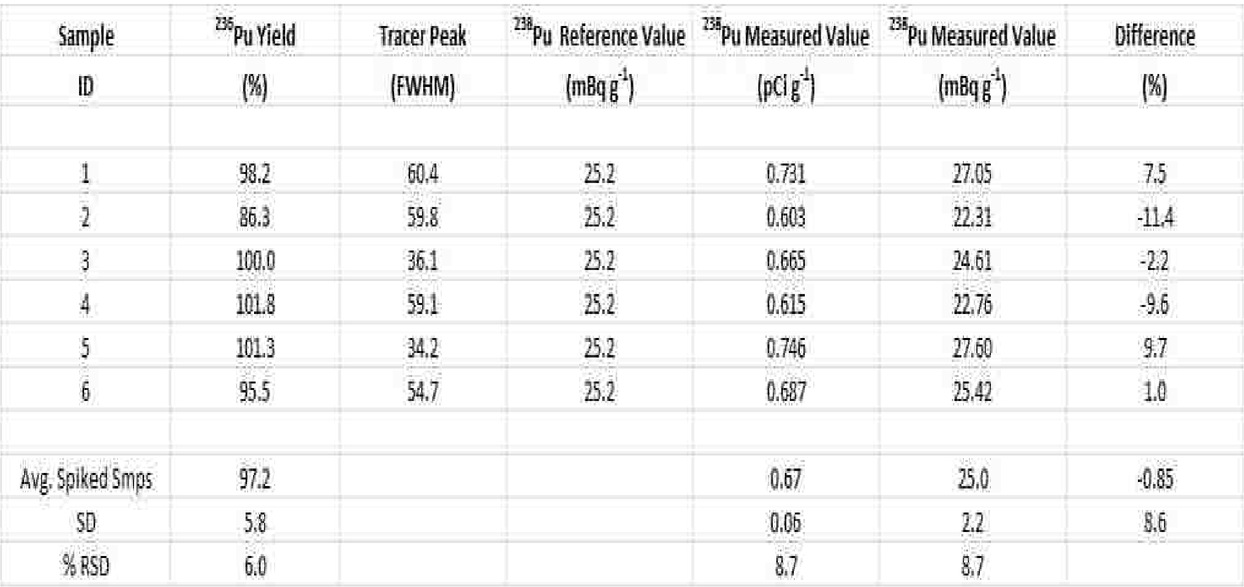
Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	88.6	36.1	29.4	0.761	28.16	-4.2
2	96.3	49.4	29.4	0.745	27.57	-6.2
3	84.2	43.0	29.4	0.848	31.38	6.7
4	86.0	41.1	29.4	0.816	30.19	2.7
5	99.1	36.5	29.4	0.760	28.12	-4.4
6	96.1	57.3	29.4	0.835	30.90	5.1
7	91.8	52.7	29.4	0.782	28.93	-1.6
8	94.7	57.9	29.4	0.766	28.34	-3.6
Avg. Spiked Smps	92.1			0.8	29.2	-0.7
SD	5.4			0.0	1.4	4.9
% RSD	5.8			4.9	4.9	
			16 hour count	MAPEP 24 contains refractory Pu		

Table 20: Pu-239/240 Results for Granite Spiked with MAPEP 32 Soil



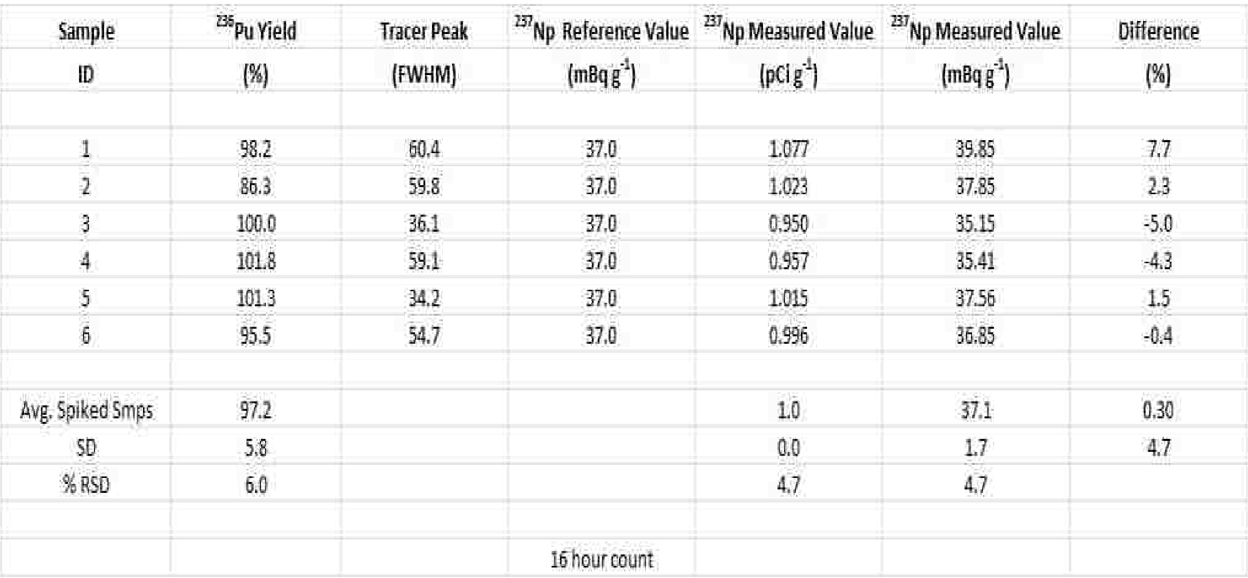
Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	98.2	60.4	21.2	0.572	21.16	-0.2
2	86.3	59.8	21.2	0.501	18.54	-12.6
3	100.0	36.1	21.2	0.536	19.83	-6.5
4	101.8	59.1	21.2	0.518	19.17	-9.6
5	101.3	34.2	21.2	0.580	21.46	1.2
6	95.5	54.7	21.2	0.560	20.72	-2.3
Avg. Spiked Smps	97.2			0.5	20.1	-5.0
SD	5.8			0.0	1.2	5.5
% RSD	6.0			5.8	5.8	
			16 hour count			

Table 21: Pu-238 Results for Granite Spiked with MAPEP 32 Soil



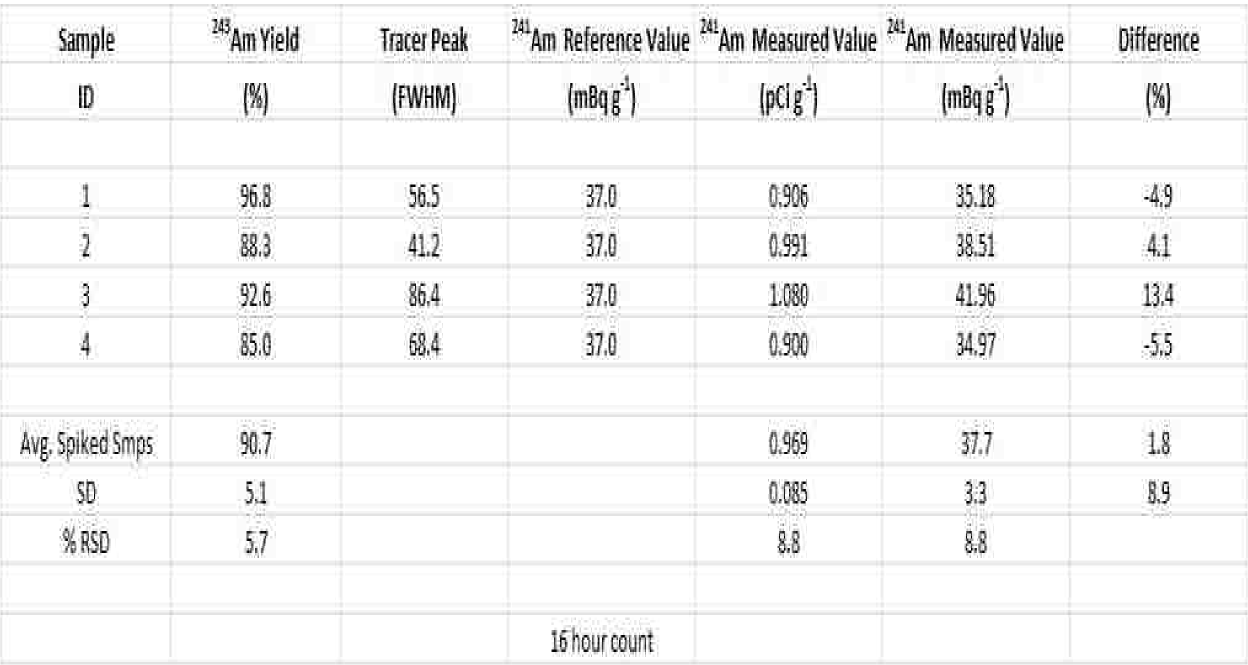
Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq g^{-1})	^{238}Pu Measured Value (pCi g^{-1})	^{238}Pu Measured Value (mBq g^{-1})	Difference (%)
1	98.2	60.4	25.2	0.731	27.05	7.5
2	86.3	59.8	25.2	0.603	22.31	-11.4
3	100.0	36.1	25.2	0.665	24.61	-2.2
4	101.8	59.1	25.2	0.615	22.76	-9.6
5	101.3	34.2	25.2	0.746	27.60	9.7
6	95.5	54.7	25.2	0.687	25.42	1.0
Avg. Spiked Smps	97.2			0.67	25.0	-0.85
SD	5.8			0.06	2.2	8.6
% RSD	6.0			8.7	8.7	

Table 22: Np-237 Results for Granite Spiked with MAPEP 32 Soil



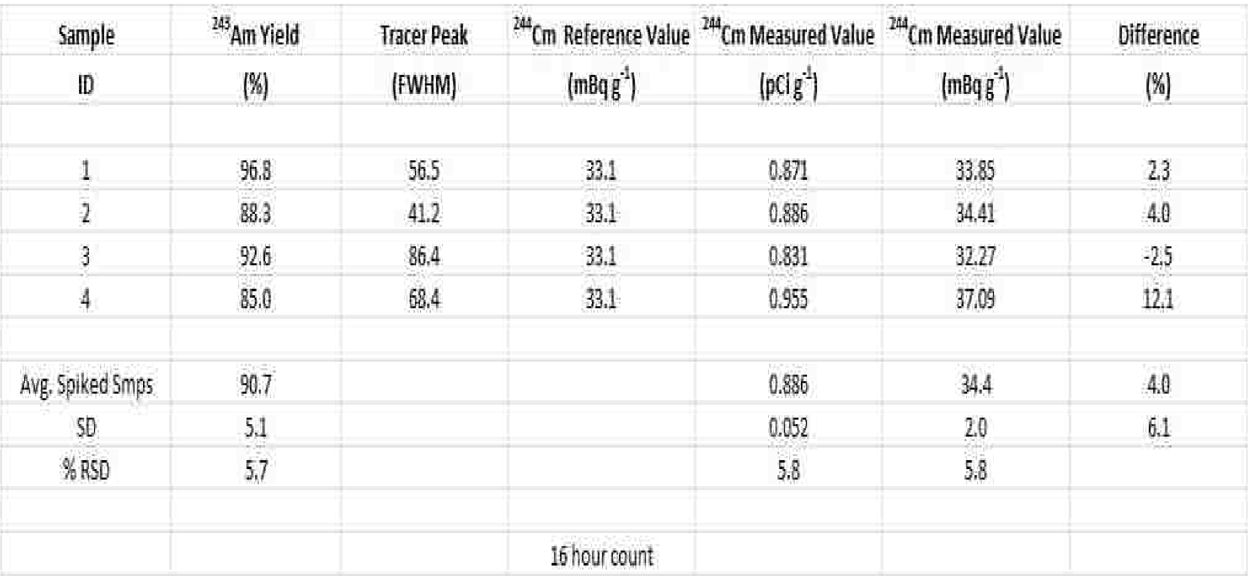
Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{237}Np Reference Value (mBq g^{-1})	^{237}Np Measured Value (pCi g^{-1})	^{237}Np Measured Value (mBq g^{-1})	Difference (%)
1	98.2	60.4	37.0	1.077	39.85	7.7
2	86.3	59.8	37.0	1.023	37.85	2.3
3	100.0	36.1	37.0	0.950	35.15	-5.0
4	101.8	59.1	37.0	0.957	35.41	-4.3
5	101.3	34.2	37.0	1.015	37.56	1.5
6	95.5	54.7	37.0	0.996	36.85	-0.4
Avg. Spiked Smps	97.2			1.0	37.1	0.30
SD	5.8			0.0	1.7	4.7
% RSD	6.0			4.7	4.7	
			16 hour count			

Table 23: Am-241 Results for Spiked Granite Samples (Extra Purification)



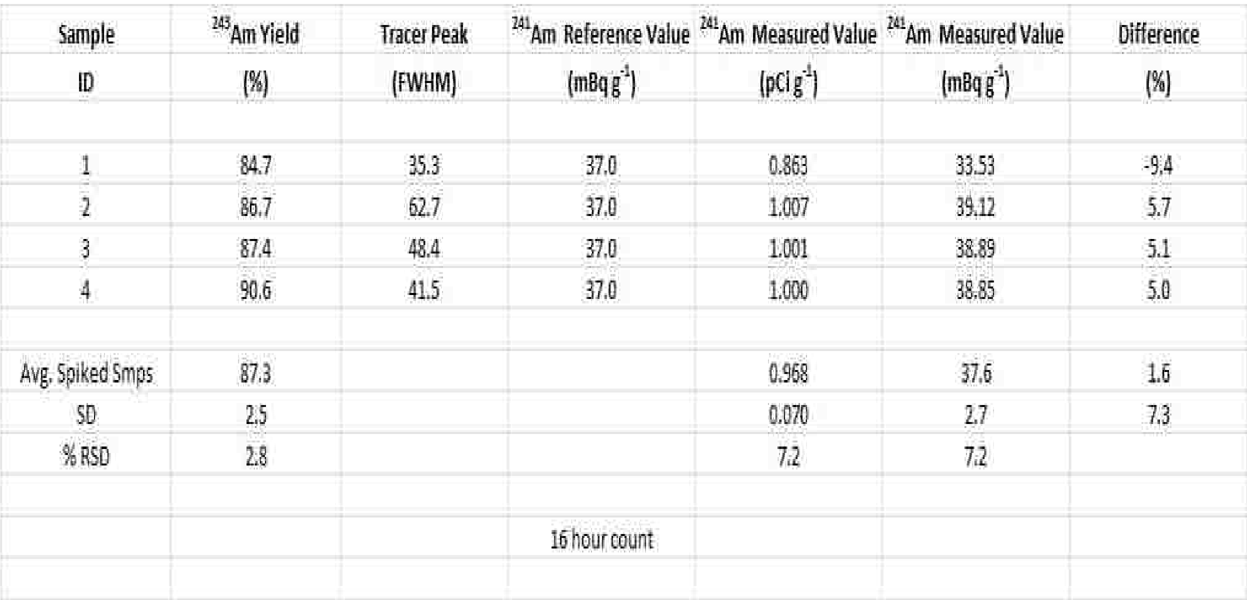
Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{241}Am Reference Value (mBq g^{-1})	^{241}Am Measured Value (pCi g^{-1})	^{241}Am Measured Value (mBq g^{-1})	Difference (%)
1	96.8	56.5	37.0	0.906	35.18	-4.9
2	88.3	41.2	37.0	0.991	38.51	4.1
3	92.6	86.4	37.0	1.080	41.96	13.4
4	85.0	68.4	37.0	0.900	34.97	-5.5
Avg. Spiked Smps	90.7			0.969	37.7	1.8
SD	5.1			0.085	3.3	8.9
% RSD	5.7			8.8	8.8	
			16 hour count			

Table 24: Cm-244 Results for Spiked Granite Samples (Extra Purification)



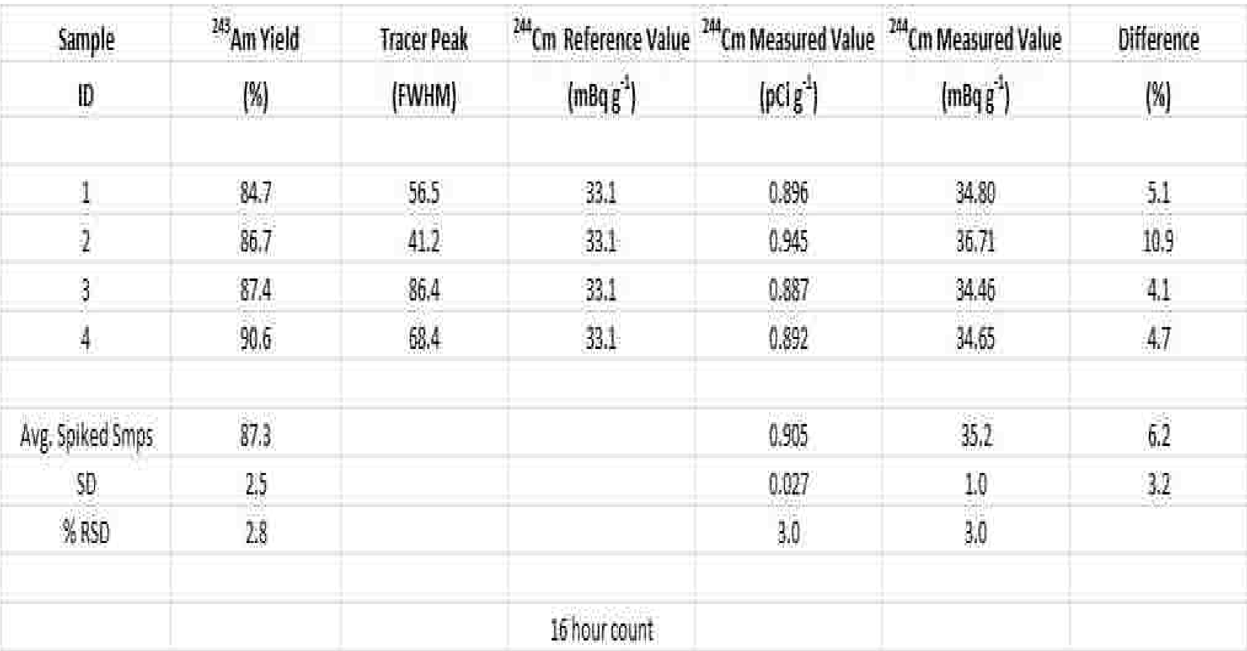
Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{244}Cm Reference Value (mBq g^{-1})	^{244}Cm Measured Value (pCi g^{-1})	^{244}Cm Measured Value (mBq g^{-1})	Difference (%)
1	96.8	56.5	33.1	0.871	33.85	2.3
2	88.3	41.2	33.1	0.886	34.41	4.0
3	92.6	86.4	33.1	0.831	32.27	-2.5
4	85.0	68.4	33.1	0.955	37.09	12.1
Avg. Spiked Smps	90.7			0.886	34.4	4.0
SD	5.1			0.052	2.0	6.1
% RSD	5.7			5.8	5.8	
			16 hour count			

Table 25: Am-241 Results for Spiked Granite Samples



Sample	^{243}Am Yield	Tracer Peak	^{241}Am Reference Value	^{241}Am Measured Value	^{241}Am Measured Value	Difference
ID	(%)	(FWHM)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
1	84.7	35.3	37.0	0.863	33.53	-9.4
2	86.7	62.7	37.0	1.007	39.12	5.7
3	87.4	48.4	37.0	1.001	38.89	5.1
4	90.6	41.5	37.0	1.000	38.85	5.0
Avg. Spiked Smps	87.3			0.968	37.6	1.6
SD	2.5			0.070	2.7	7.3
% RSD	2.8			7.2	7.2	
			16 hour count			

Table 26: Cm-244 Results for Spiked Granite Samples



Sample	^{243}Am Yield	Tracer Peak	^{244}Cm Reference Value	^{244}Cm Measured Value	^{244}Cm Measured Value	Difference
ID	(%)	(FWHM)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
1	84.7	56.5	33.1	0.896	34.80	5.1
2	86.7	41.2	33.1	0.945	36.71	10.9
3	87.4	86.4	33.1	0.887	34.46	4.1
4	90.6	68.4	33.1	0.892	34.65	4.7
Avg. Spiked Smps	87.3			0.905	35.2	6.2
SD	2.5			0.027	1.0	3.2
% RSD	2.8			3.0	3.0	
			16 hour count			

When ^{237}Np analysis is required, ^{236}Pu was used as a yield tracer due to the overlapping alpha energies of ^{242}Pu and ^{237}Np. (Figure 20). For Am/Cm analysis, ^{243}Am was used a yield monitor. Tracer recoveries were typically >87% for Am and >92% for Pu.

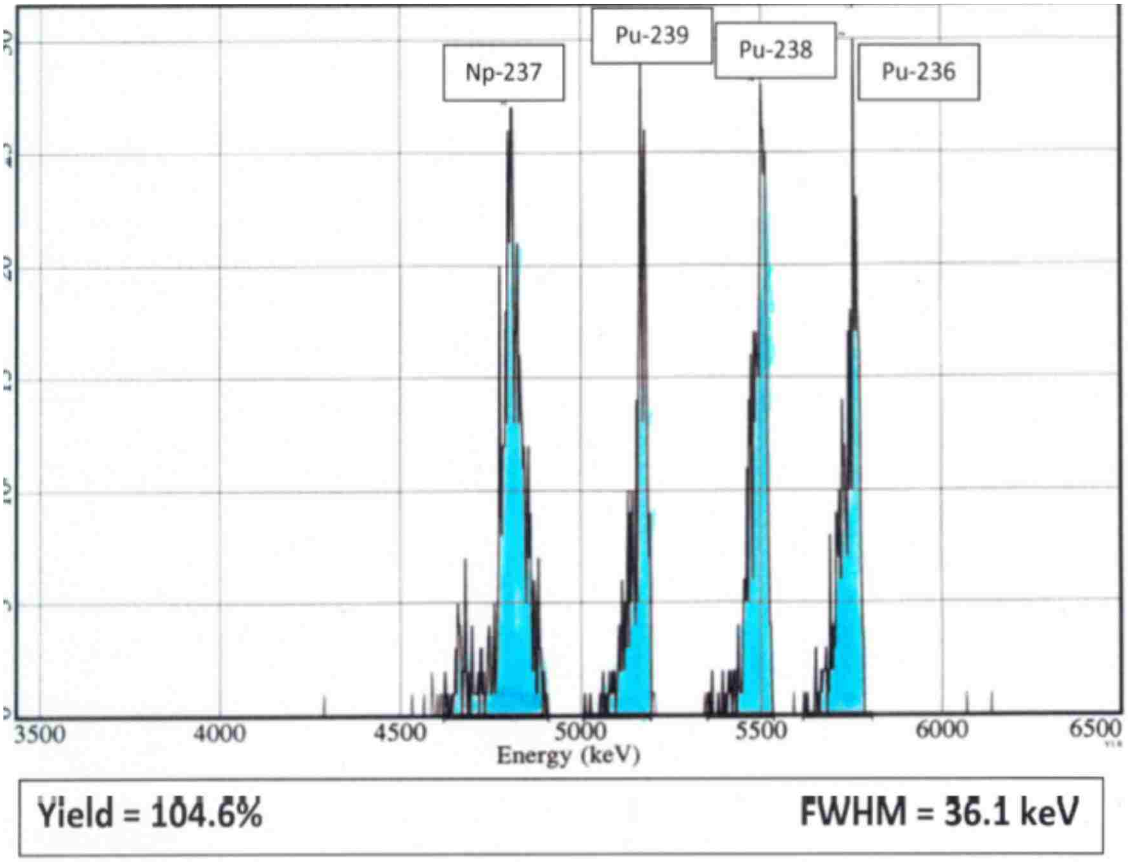


Figure 20: Alpha Spectra Showing Plutonium and Neptunium Peaks

Analysis of the granite samples by ICP-MS showed relatively large amounts of rare earth elements, including Ce and Nd. La is removed effectively during the chromatographic separation on DGA, but higher mass rare earth elements such as Ce, Nd, Sm, co-elute with the Am/Cm (Figure 21). The native rare earth elements can degrade the alpha spectra (Figure 22). Further purification of the Am/Cm via TEVA Resin separation from thiocyanate removed rare earth elements [56] yielding alpha spectra with much improved peak resolution (Figure 23). The Full Width Half Max (FWHM) resolution for the Am peaks was reduced from >500 keV to ~40 keV.

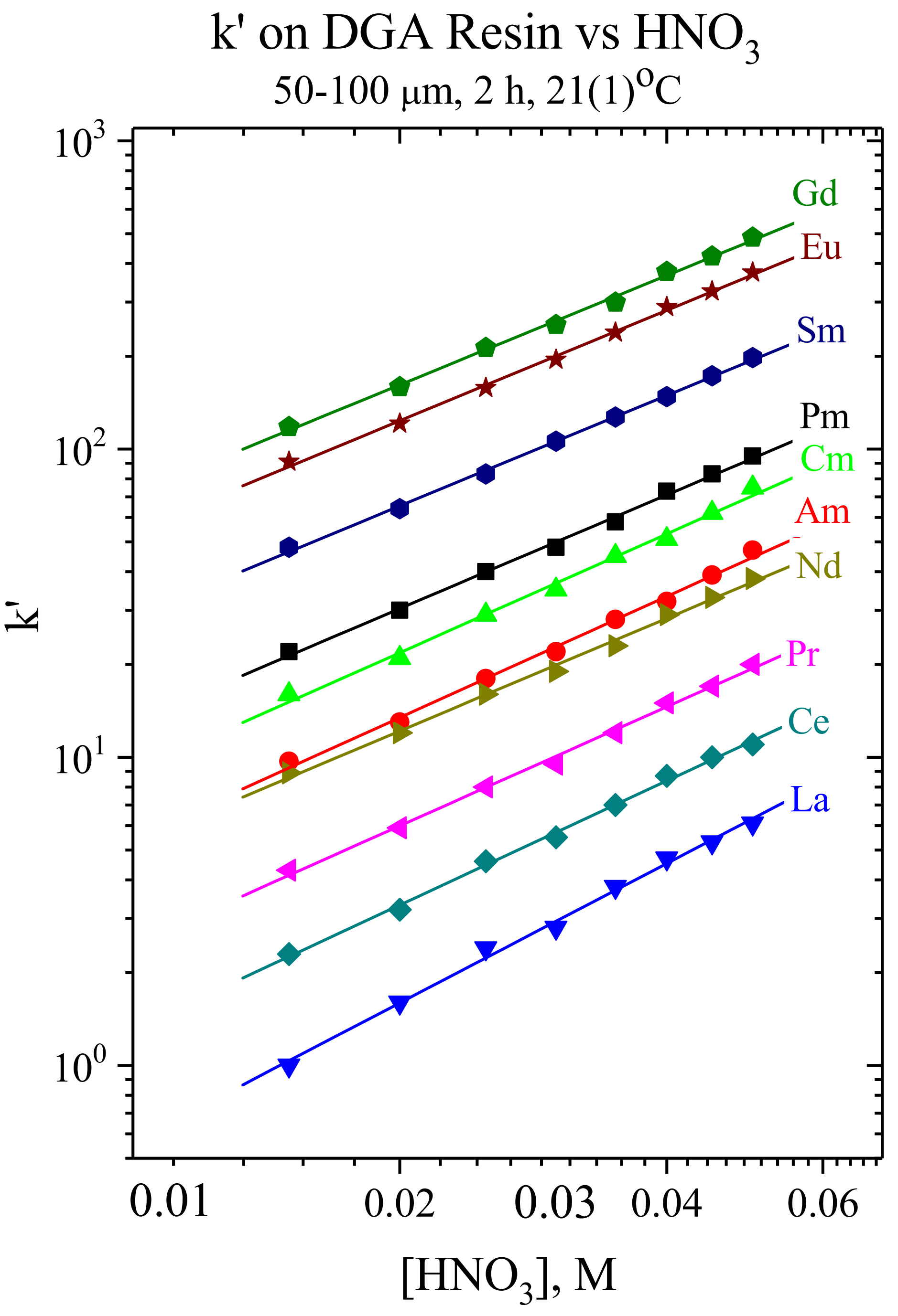
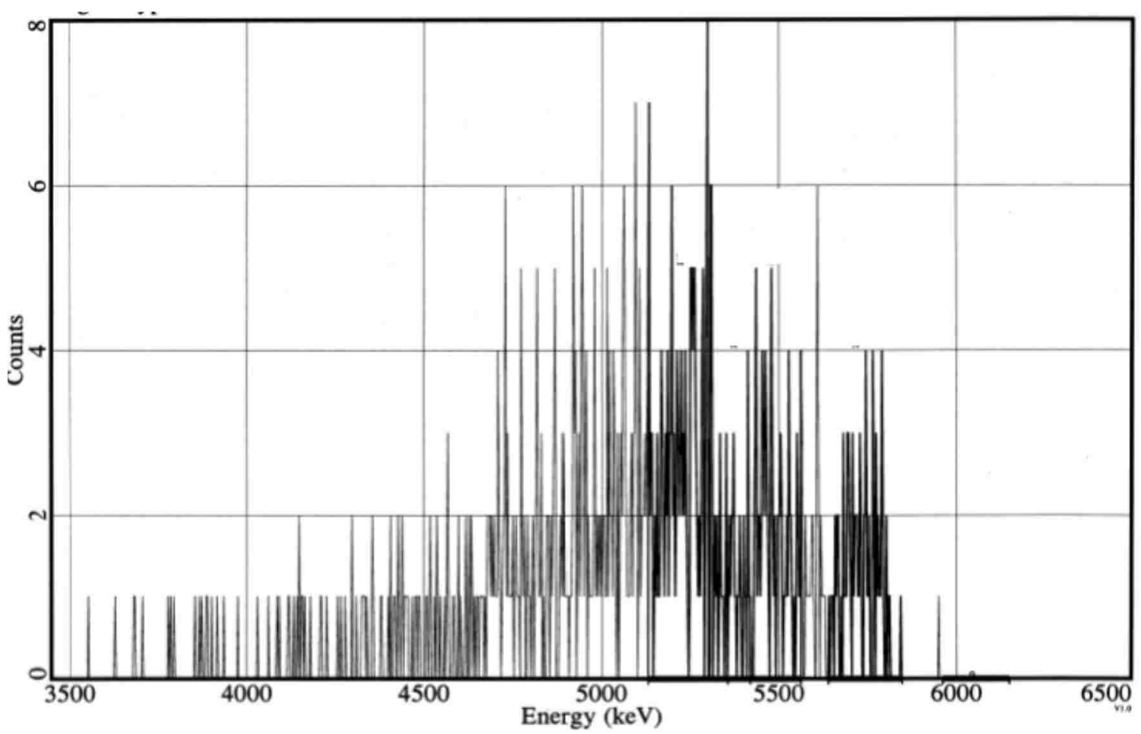


Figure 21: Affinity of Rare Earth Elements for DGA Resin in Dilute Nitric Acid



Yield = (16.7%)	**FWHM = (194.2 keV)**

Figure 22: Alpha Spectra Showing Rare Earth Interference Without Additional Purification

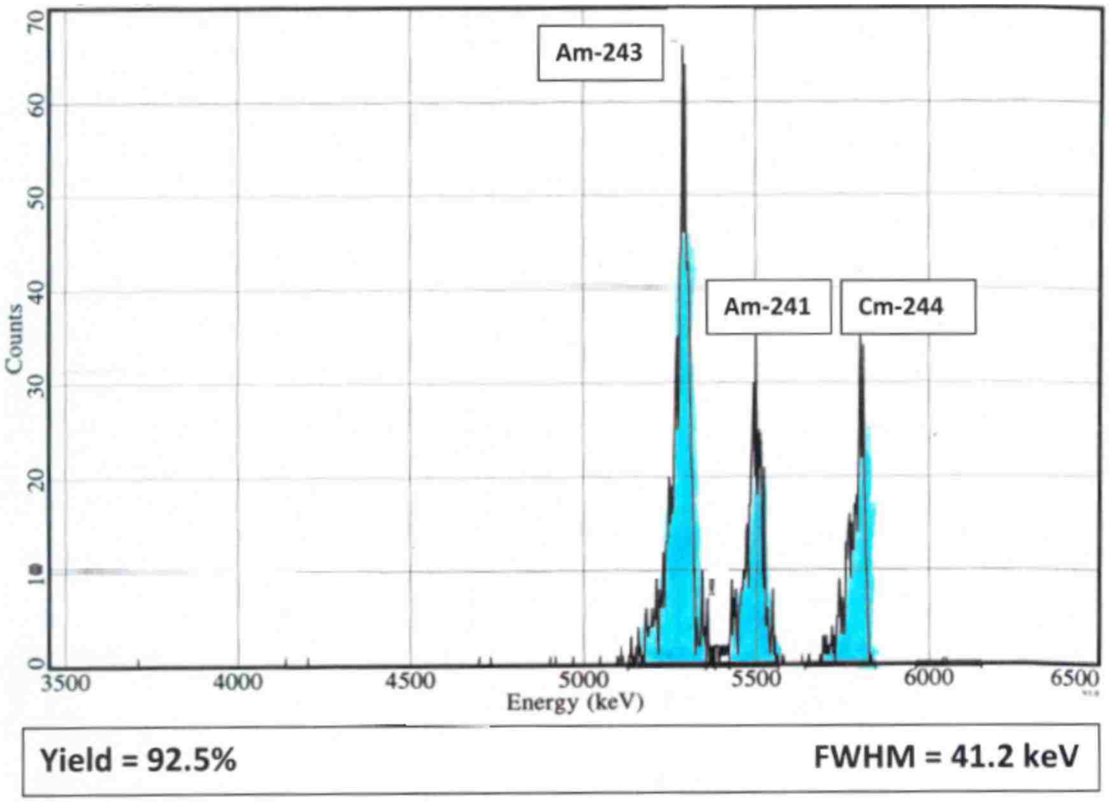


Figure 23: Alpha Spectra Showing Americium and Curium Peaks

The Minimum Detectable Activities (MDA) for each nuclide measured were calculated as previously described in equation 8: [75]

$$MDA = [2.71+4.65\sqrt{B}]/ (CT*R*V*Eff*\mathbf{A}*0.060) \quad (8)$$

where B = total background counts; 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. For a 1g granite 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}. Sample size and count time can be adjusted to meet the required MDA.

5.5 Conclusions

A novel rapid method for the determination of actinide isotopes in 1 g granite samples has been developed that allows the separation and measurement of these isotopes with high chemical yields and effective removal of matrix interferences. By adding MAPEP 24 soil standards containing refractory ^{239}Pu isotope to granite samples, the method protocol has been validated rigorously The sodium hydroxide fusion technique used to digest the granite samples is fast and robust. The extraction chromatography method utilized in this work offers many options, depending on the actinide isotopes needed. The data presented indicates this method can be used successfully for granite samples following a radiological event.

CHAPTER 6: RAPID METHOD TO DETERMINE PLUTONIUM ISOTOPES IN STEEL SAMPLES

This work has been reproduced with the permission of Springer from the Journal of Radioanalytical and Nuclear Chemistry, volume 314, pages 1103-1111 in which it was published with Sherrod L. Maxwell as the first author, and Brian Culligan, Dan McAlister and Ralf Sudowe as co-authors.

6.1 Abstract

The rapid measurement of plutonium isotopes in steel samples is very important in the event of a radiological emergency as well as for the characterization of nuclear decommissioning samples. A new method for the determination of plutonium isotopes in steel samples has been developed at the Savannah River Environmental Laboratory. The new method employs a rugged acid digestion method that includes hydrofluoric acid, followed by a single preconcentration step to rapidly preconcentrate the plutonium isotopes and remove most of the dissolved steel sample matrix. A fusion option improves ruggedness when soil or concrete is present and can be implemented after the steel dissolution. The Pu isotopes are separated using an extraction chromatographic resin and measured by alpha spectrometry. The method can also be adapted for measurement by inductively-coupled plasma mass spectrometry. This approach has a sample preparation time of 6-8 hours for steel samples.

6.2 Introduction

During a national radiological emergency, the laboratories providing analytical support will be faced with an overwhelming number of environmental and bioassay samples. Many of the environmental samples will likely consist of urban matrices, containing building materials such as concrete, brick or asphalt. If a radiological event involving either a Radiological Dispersive device (RDD), an Improvised Nuclear Device (IND) or a nuclear incident such as the accident at the Fukushima Nuclear Power Plant in March of 2011 occurs, then the use of rapid methods will be essential to quickly assess the scope and impact of the event. In case of such an emergency there will be an urgent need for rapid radiochemical analyses to support dose mitigation and environmental clean-up. [16,86, 87, 30] In addition to other environmental samples, steel samples from building debris or remaining structures must to be analyzed quickly to ascertain the radioactive content. It is very important to couple rapid, effective sample digestion and preconcentration techniques with fast, innovative column purification methods so that building material samples can be quickly analyzed for radioactive contaminants. The use of high flow rates due to vacuum assistance and stacked cartridges containing highly selective extractant-coated chromatographic resins allows for the rapid sequential separation of multiple analytes in an emergency. This includes recently published methods for soil, concrete, limestone and marble. [16, 81] These radiochemical methods are both fast and reliable, therefore offering highly defensible quality.

There is also an emerging need for rapid, reliable cost-effective methods to support decommissioning of older nuclear facilities, especially in Europe. A significant reduction in very high decommissioning costs can be achieved through the development and implementation of vastly improved measurement techniques. [77] The application of new, streamlined radiochemical techniques to nuclear decommissioning samples or other routine environmental samples can reduce labor costs and facilitate improved analytical 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. [44, 34, 31] Consistent with this need, a fusion method for 10-20 g soil and concrete samples was recently published by this laboratory. [56] While sodium hydroxide fusion has been used with great success for soil, concrete, asphalt, vegetation and other solid samples, steel samples cannot adequately dissolved with a sodium hydroxide fusion technique alone. However, once the steel sample is effectively digested with acid initially, then a fusion technique can be applied to digest residual soil, concrete or refractory residues remaining. A rigorous acid digestion method for steel was investigated, with and without hydrofluoric acid, along with a secondary fusion of the acid digested residue for enhanced ruggedness.

A review by Hou et al. surveyed a wide range of analytical separation methods for Pu in waters and environmental solid samples [36]. These methods included various combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40-85%. Improvements in chemical yield should help to reduce detection limits and improve overall method ruggedness.

Tavčar et al. [14] reported a method to determine actinides in up to 10g soil and sediment samples by leaching samples with strong nitric acid, subsequent filtration, followed by evaporation. The residue was redissolved in 1M HNO_3, and following valence adjustment, the acid concentration was increased to 8M HNO_3. Samples were loaded onto Dowex 1X8 anion resin, and Pu was eluted using 9M HCl in the presence of iodide ion as a reductant. Np was eluted with 4M

HCl. The chemical yields for Pu and Np were ~60% and ~40%, respectively. The acid leach used in this method would not effectively digest refractory particles that might be present in the sample.

A new method has been developed at the Savannah River Environmental Laboratory to measure Pu isotopes in steel samples. The method employs a preconcentration technique that effectively manages the high iron content resulting from the dissolution of the steel sample, while simultaneously keeping the sample preparation volumes small so that rapid column separation can be achieved.

6.3 Experimental

6.3.1 Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336), TRU-Resin® (octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) in tri-n-butylphosphate (TBP) available from Eichrom Technologies, LLC, (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acid solutions 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 standards of ^{242}Pu and ^{238}Pu were obtained from Eckert Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1} for this work.

6.3.2 Apparatus

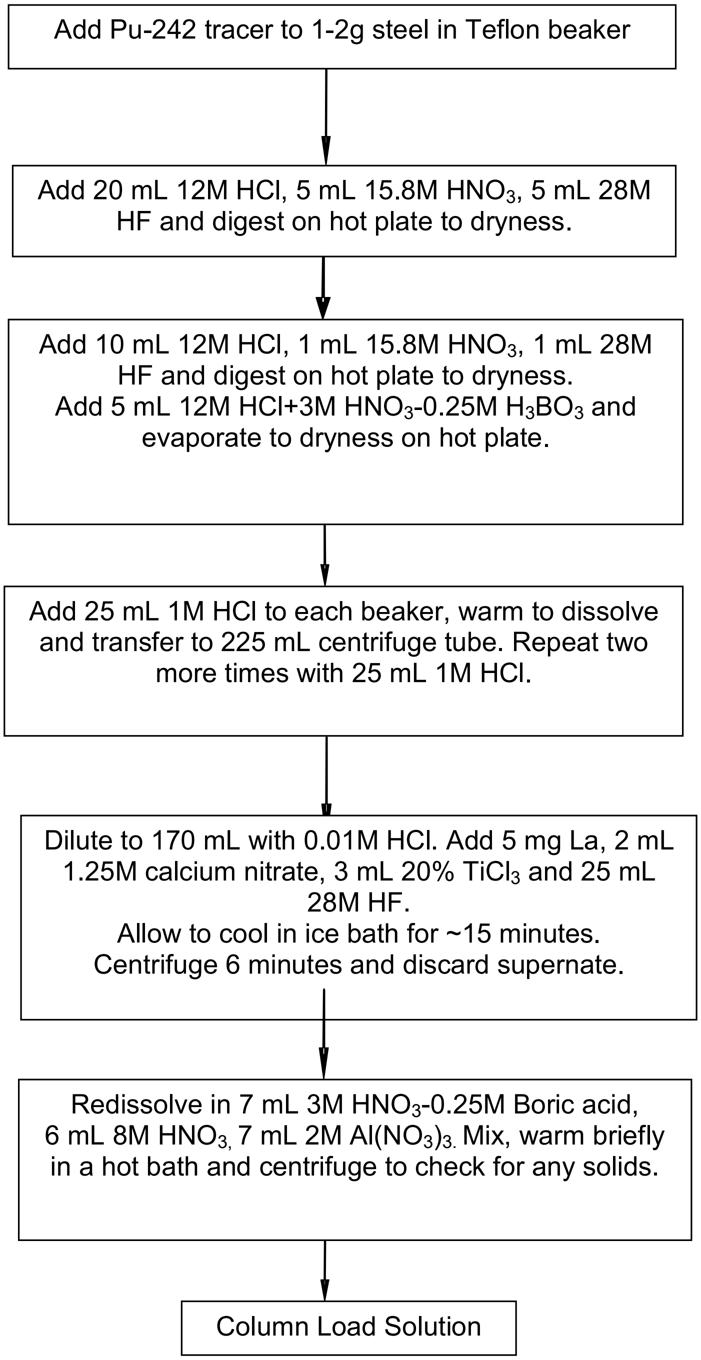
Plutonium isotopic measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors in a Canberra Alpha Analyst alpha spectrometry system. The PIPS detectors had an active surface of 450 mm^2. The nominal counting efficiency for these detectors was 28-30%. The distance between the sample and detector surface was ~3 mm.

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

6.3.3 Procedures

Column preparation. TEVA Resin was obtained as 2 mL cartridges. Small particle size (50-100 μm) resin was employed, along with a vacuum extraction system. The small particle size coated support, with enhanced surface area, improves column separation efficiencies. Flow rates of ~1-2 drops sec^{-1} were typically used for this work, slower during 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 the final elution of plutonium isotopes.

Sample Preparation. Figure 24 shows the sample preparation flowchart for Pu isotopes in steel samples. Samples of 304 stainless steel disks (17.5-20% chromium, 8-11% nickel, <0.08% carbon, <2% manganese, <1% silicon, <0.045% phosphorus, <0.03% sulfur, balance iron), weighing approximately 1g, were used for this study. Most of the tests were performed using 1 or 2 g of steel, but one test was carried out using 5 g of 304 stainless steel. Pu isotopes were added to each steel sample to test the method performance. To examine the ruggedness of the steel digestion for refractory particles, aliquots of MAPEP 24 soil (~0.25 g) were also added to the steel samples for some of the tests. 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. Successful analysis would indicate analytical method ruggedness and applicability when refractory particles are present.



Add Pu-242 tracer to 1-2g steel in Teflon beaker

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3, 5 mL 28M HF and digest on hot plate to dryness.

Add 10 mL 12M HCl, 1 mL 15.8M HNO_3, 1 mL 28M HF and digest on hot plate to dryness.
Add 5 mL 12M HCl+3M HNO_3-0.25M H_3BO_3 and evaporate to dryness on hot plate.

Add 25 mL 1M HCl to each beaker, warm to dissolve and transfer to 225 mL centrifuge tube. Repeat two more times with 25 mL 1M HCl.

Dilute to 170 mL with 0.01M HCl. Add 5 mg La, 2 mL 1.25M calcium nitrate, 3 mL 20% $TiCl_3$ and 25 mL 28M HF.
Allow to cool in ice bath for ~15 minutes.
Centrifuge 6 minutes and discard supernate.

Redissolve in 7 mL 3M HNO_3-0.25M Boric acid, 6 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

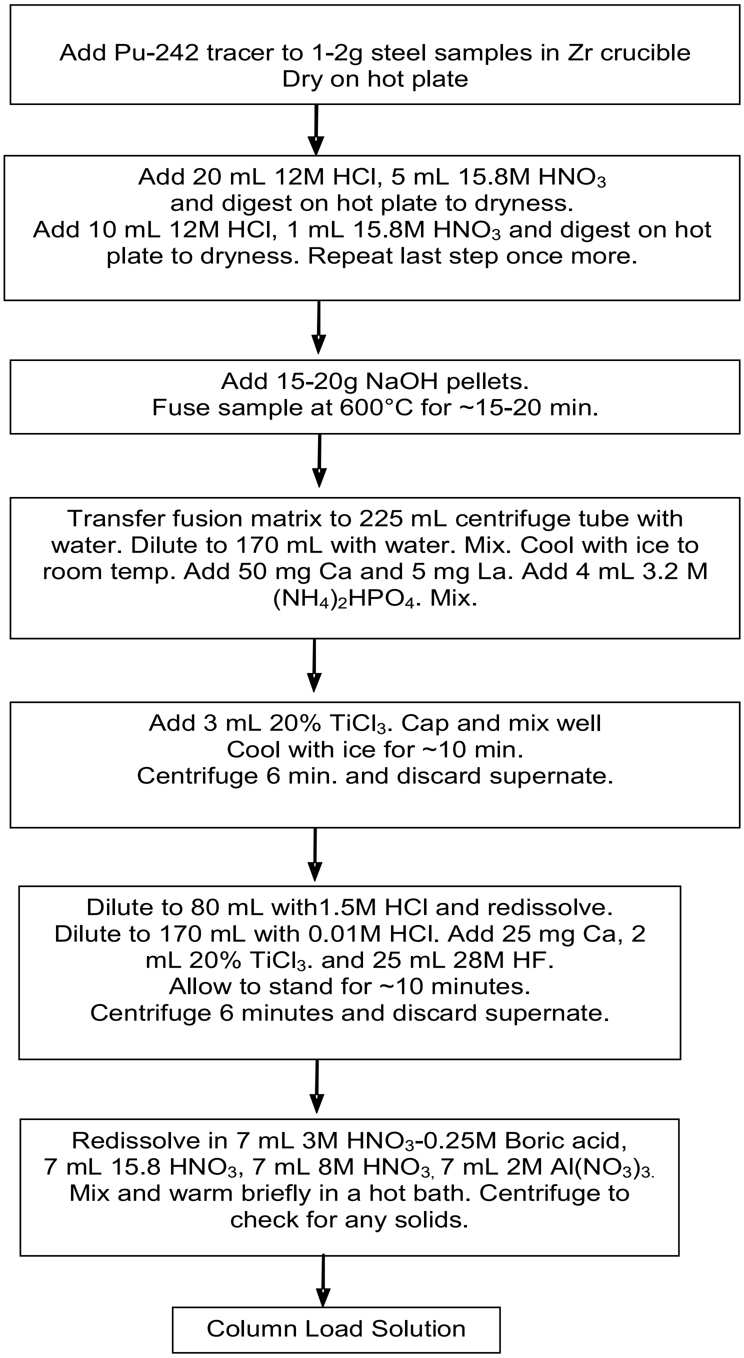
Figure 24: Steel Dissolution with Pu Isotopes Sample Preparation Method

Each sample was placed in a 250 mL Teflon beaker and spiked with a ^{242}Pu tracer. If the simultaneous collection and purification of plutonium and ^{237}Np is desired, a ^{236}Pu tracer must be used to overcome alpha energy overlap between ^{237}Np and ^{242}Pu. [88] Twenty milliliters of 12 M HCl, 5 mL 15.8 M HNO_3, and 5 mL 28 M 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 12 M HCl, 1 mL 15.8 M HNO_3, and 1 mL 28 M HF were added to each beaker and the samples were again evaporated to dryness on a hot plate. Finally, 5 mL 12 M HCl and 5 mL 3 M HNO_3-0.25 M H_3BO_3 were added to each beaker to remove fluoride. This step was found to facilitate complete removal of the sample residue from the beaker. The contents of each beaker were evaporated to dryness on a hot plate.

To dissolve the sample residue, 25 mL 1 M HCl was 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 1 M HCl was repeated two more times, warming each beaker as needed. Each sample was diluted to 170 mL with 0.01 M HCl in the 225 mL tube and mixed well. To precipitate the Pu from the dissolved steel sample, 5 mg lanthanum (as 1 mg La/mL stock solution of $La(NO_3)_3$ in 5% HNO_3), 2 mL 1.25 M calcium nitrate and 2 mL 20% $TiCl_3$ were added to each 225 mL tube. After mixing each sample tube well, the tubes were cooled in ice bath for ~15-20 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 7 mL 3 M HNO_3-0.25 M boric acid and transferred to a 50 mL centrifuge tube. To rinse the 225 mL tube, 7 mL 3 M HNO_3 and 7 mL 2 M $Al(NO_3)_3$ were added and the rinses were transferred to each

50 mL 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 residual solids.

Figure 25 shows the flow sheet for a fusion option that can be used for additional digestion rigor when either a steel sample mixed with soil or concrete or refractory particles may be present. Samples were placed into 250 mL low form zirconium crucibles. Twenty milliliters of 12 M HCl and 5 mL 15.8 M HNO_3 were added to each crucible and the samples were digested to dryness on a hot plate on medium heat. HF was omitted in this option, because it will attack the zirconium crucibles. After the samples were taken to dryness, 10 mL 12 M HCl and 1 mL 15.8 M HNO_3 were added to each beaker and evaporated to dryness on a hot plate. Sodium hydroxide pellets were added and the sample was fused and processed similar to the fusion technique described previously [81], except that no additional Fe was added. In this fusion option, an initial precipitation was performed using iron and titanium hydroxide enhanced with calcium phosphate to remove the high levels of hydroxide. Following the initial precipitation, the samples were then dissolved in dilute HCl and a calcium fluoride precipitation was performed to remove the Fe, Ti and silicates.



Add Pu-242 tracer to 1-2g steel samples in Zr crucible
Dry on hot plate

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3
and digest on hot plate to dryness.
Add 10 mL 12M HCl, 1 mL 15.8M HNO_3 and digest on hot plate to dryness. Repeat last step once more.

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

Transfer fusion matrix to 225 mL centrifuge tube with water. Dilute to 170 mL with water. Mix. Cool with ice to room temp. Add 50 mg Ca and 5 mg La. Add 4 mL 3.2 M $(NH_4)_2HPO_4$. Mix.

Add 3 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 25 mg Ca, 2 mL 20% $TiCl_3$. and 25 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 and warm briefly in a hot bath. Centrifuge to check for any solids.

Column Load Solution

Figure 25: Steel Dissolution with Pu Isotopes Fusion Option

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. No problems are anticipated since iron, the key matrix component in steel, is effectively removed during the final precipitation step, and chromium, nickel, carbon and the other constituents do not interfere with the TEVA Resin separation methods. [52]

Column separation for Plutonium. Plutonium is separated using a 2 mL TEVA Resin cartridge, utilizing the vacuum box to achieve higher flow rates. The TEVA Resin method used is similar to a procedure previously published for the determination of actinides in limestone and marble samples. [81] After cooling the samples to room temperature, a valence adjustment was performed on the load solution by adding 1.25 mL 1.5 M ascorbic acid. Typically, 1 mg of Fe is added along with ascorbic acid to facilitate Pu reduction, but since a small amount of residual Fe was already present in the load solution from the steel sample, no additional Fe was added. Following a three minute wait to ensure reduction of plutonium to Pu(III), 1 mL 3.5 M $NaNO_2$ was added to oxidize plutonium to Pu(IV). After waiting 10 minutes, the sample load solutions were loaded onto a 2 mL TEVA Resin column at a flow rate of approximately 1 drop per second. Sample tubes were rinsed with 5 mL 3 M HNO_3, which was transferred to the TEVA Resin column and allowed to pass through the resin at ~1-2 drops per second.

It has been found that U (VI) can be partially reduced to U (IV) during the valence adjustment steps, with Fe(II) and ascorbic acid present. As a result, a fraction of the uranium present may be retained on TEVA Resin despite the addition of nitrite ions to oxidize Pu(III) to Pu(IV). While Pu(III) oxidation to Pu(IV) with nitrite in nitric acid is nearly instantaneous, waiting 10 minutes or longer after adding the sodium nitrite facilitates re-oxidation of U(IV) to

U(VI). Adding a small amount (50 µL) of 30% hydrogen peroxide to the 3M HNO_3 tube rinse also helps ensure than any uranium that may have been reduced to U(IV) (possibly also due to traces of Ti(III) remaining from the precipitation step) is re-oxidized to U(VI), and not retained on the TEVA Resin. While additional uranium decontamination will be achieved during cerium microprecipitation source preparation, uranium contamination could be a problem if electrodeposition is used. It is also desirable to remove U very effectively if inductively-coupled plasma mass spectrometry (ICP-MS) will be used to measure ^{239}Pu, since formation of a ^{238}U hydride can lead to isobaric interference in the ^{239}Pu assay.

Each TEVA Resin column was rinsed with 15 mL of 3 M HNO_3 at ~2 drops per second, followed by Th elution with 20 mL of 9 M HCl at 1-1.5 drops per second. After the elution of Th from TEVA Resin, a column rinse of 5 mL 3 M HNO_3 at ~2 drops per second was carried out to reduce any extractant bleed-off. Pu was eluted at ~1 drop per second with 20 mL of 0.1 M HCl-0.05 M HF-0.01 M $TiCl_3$ for measurement by alpha spectrometry. The presence of the Ti (III) reductant helps to remove Pu from TEVA Resin as Pu(III). When electrodeposition of the purified eluents will be employed, sodium formaldehyde sulfoxylate (rongalite) reductant or hydroxylamine hydrochloride should be used instead of $TiCl_3$.

Cerium fluoride microprecipitation was used to prepare the purified samples for measurement by alpha spectrometry. Fifty micrograms of Ce (as 1 mg Ce/mL Ce(III) nitrate standard), 0.5 mL 30wt% H_2O_2 and 1 mL 28 M HF were added to each Pu eluent. The hydrogen peroxide ensures additional removal of any uranium present, by enabling oxidation of U(IV) to U(VI). After waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable Eichrom Resolve™ filter funnel). Each sample tube was rinsed with ~5 mL deionized water, adding the rinse to the filter. After the entire sample was filtered, ~3 mL of ethanol was added to each filter to facilitate drying. The filters were heated briefly under a heat lamp to guarantee complete dryness. Samples were counted for 16 hours to ensure sufficient counts were obtained and reduce counting uncertainty to effectively evaluate performance on the spiked samples. In an emergency, shorter count times may be used, with appropriate adjustments to tracer activity levels.

While alpha spectrometry was used in this work to demonstrate the effectiveness of the new method, the method can be successfully adapted for ICP-MS, based on past experience in this laboratory. The sample can be counted for ^{238}Pu by alpha spectrometry and then redissolved from the sample test source filter using warm 3 M HNO_3-0.25 M boric acid. The dissolved Pu isotopes can be processed quickly through TEVA Resin, eluted and measured by ICP-MS to determine the ^{239}Pu/^{240}Pu ratio. This "hybrid" approach allows ^{238}Pu ,^{239}Pu and ^{240}Pu to be determined, if needed.

The CeF_3 microprecipitation step with hydrogen peroxide present can remove an additional 1000 x ^{238}U, so this approach, in combination with another TEVA Resin separation, can result in extremely high ^{238}U decontamination factors. If the redissolved sample is reprocessed through TEVA Resin, a Pu eluent solution of 0.05 M HCl-0.025 M HF-0.02 M hydroxylamine hydrochloride may be used to allow ICP-MS assay.

For improved ^{238}U removal that will facilitate the measurement of ^{239}Pu and ^{240}Pu by ICP-MS, Pu can be eluted directly from TEVA Resin as Pu^{+3} (with 15-20 mL $_{3M}$ HNO_3-0.1M ascorbic acid-0.02 M Fe^{+2}) through a coupled UTEVA Resin cartridge (1mL) onto a stacked DGA Resin cartridge to achieve very high uranium decontamination factors (~1x10^7). This eliminates eluting and reloading Pu to TEVA Resin multiple times. After a single elution and rapid clean-up on DGA Resin, Pu isotopes can be eluted from DGA Resin with a 5 mL volume of 0.02 M HCl-0.005 M HF (or also with -0.01 M hydroxylamine hydrochloride) and assayed by ICP-MS. [89]

6.4 Results and Discussion

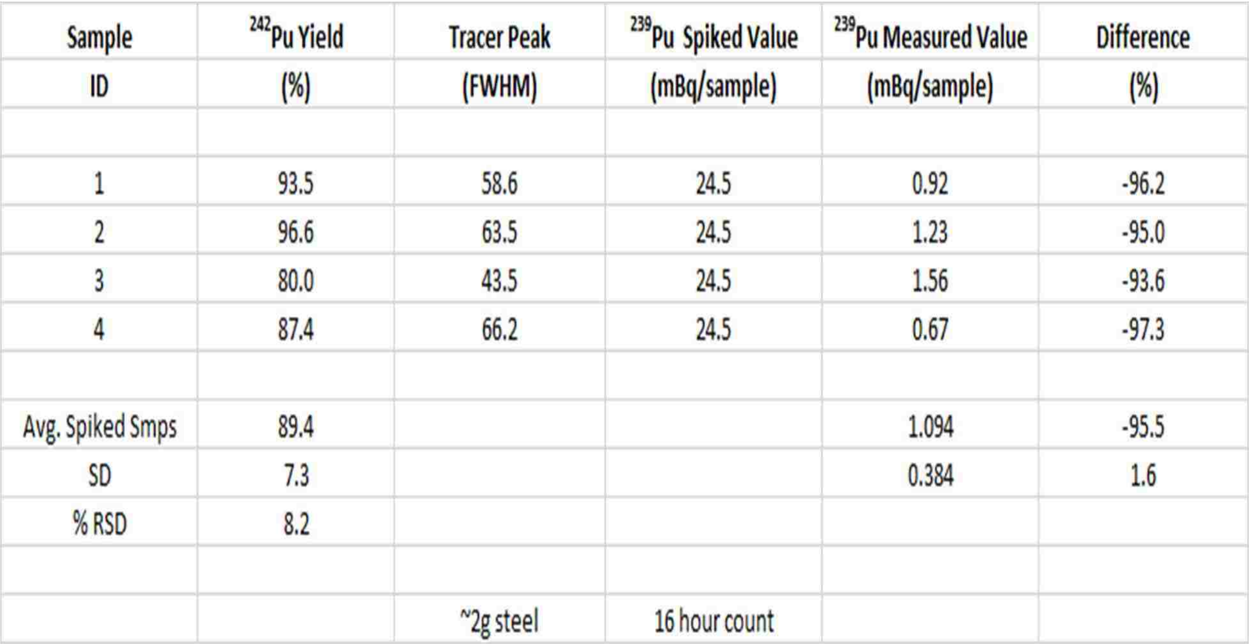
Table 27 shows the individual results for the determination of Pu isotopes in five 2 g steel samples spiked with ^{238}Pu obtained with this rapid method, the TEVA Resin separation and alpha spectrometry. The average ^{238}Pu result was 37.7 mBq per sample, with a 1.9% bias and SD (standard deviation) of 1.6 mBq per sample. The average tracer recovery for ^{242}Pu was 89.3% ± 2.3% (SD). The high ^{242}Pu tracer recoveries and excellent results for ^{238}Pu versus known values indicate the robust nature of the sample preparation and measurement steps. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual ^{238}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 27: Pu-238 Results for Spiked Steel Samples

Sample	^{242}Pu Yield	Tracer Peak	^{238}Pu Spiked Value	^{238}Pu Measured Value	Difference
ID	(%)	(FWHM)	(mBq/sample)	(mBq/sample)	(%)
1	90.8	37.1	37.0	36.56	-1.2
2	85.4	49.8	37.0	35.83	-3.2
3	89.6	43.0	37.0	37.53	1.4
4	90.7	42.4	37.0	39.19	5.9
5	90.2	46.9	37.0	39.37	6.4
Avg. Spiked Smps	89.3			37.7	1.9
SD	2.3			1.6	4.2
% RSD	2.5			4.2	
		~2 g stainless steel	16 hour count		

Table 28 shows the individual results for the determination of Pu isotopes in four 2 g steel samples spiked with 0.25 g MAPEP 24 soil containing refractory $^{239/240}$Pu using this rapid method with hydrofluoric acid not included. The Pu was separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 1.094 mBq per sample, with a -95.5% bias and SD (standard deviation) of 0.38 mBq per sample. The average tracer recovery for ^{242}Pu was 89.4% ± 7.3% (SD). The very low $^{239/240}$Pu results show the importance of using HF in the steel digestion step when refractory Pu is present.

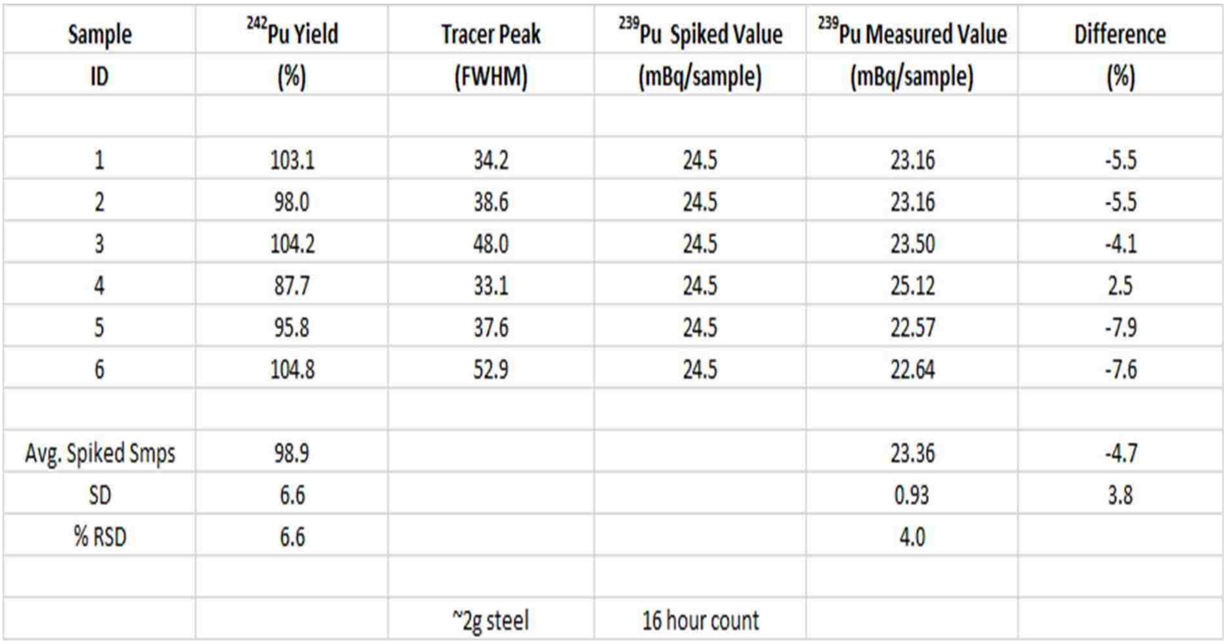
Table 28: Pu-239/240 Results for Steel Spiked with Refractory Pu MAPEP 24 Soil (no HF)



Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Spiked Value (mBq/sample)	^{239}Pu Measured Value (mBq/sample)	Difference (%)
1	93.5	58.6	24.5	0.92	-96.2
2	96.6	63.5	24.5	1.23	-95.0
3	80.0	43.5	24.5	1.56	-93.6
4	87.4	66.2	24.5	0.67	-97.3
Avg. Spiked Smps	89.4			1.094	-95.5
SD	7.3			0.384	1.6
% RSD	8.2				
		~2g steel	16 hour count		

Table 29 shows the individual results for the determination of Pu isotopes in six 2 g steel samples spiked with 0.25 g MAPEP 24 soil containing refractory $^{239/240}$Pu using this rapid method with hydrofluoric acid included. The Pu was separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 23.36 mBq per sample, with a -4.7% bias and SD (standard deviation) of 0.93 mBq per sample. The average tracer recovery for ^{242}Pu was 98.9% ± 6.6% (SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of this rapid method with HF included in the acid digestion. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 29: Pu-239/240 Results for Steel Spiked with Refractory Pu MAPEP 24 Soil (with HF)



Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Spiked Value (mBq/sample)	^{239}Pu Measured Value (mBq/sample)	Difference (%)
1	103.1	34.2	24.5	23.16	-5.5
2	98.0	38.6	24.5	23.16	-5.5
3	104.2	48.0	24.5	23.50	-4.1
4	87.7	33.1	24.5	25.12	2.5
5	95.8	37.6	24.5	22.57	-7.9
6	104.8	52.9	24.5	22.64	-7.6
Avg. Spiked Smps	98.9			23.36	-4.7
SD	6.6			0.93	3.8
% RSD	6.6			4.0	
		~2g steel	16 hour count		

Table 30 shows the individual results for the determination of Pu isotopes in five 1 g steel samples plus 0.5 g concrete. The samples were spiked with 0.25 g MAPEP 24 soil containing refractory $^{239/240}$Pu and analyzed using this rapid method using the sodium hydroxide fusion option. The Pu isotopes were separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 24.4 mBq per sample, with a -0.2% bias and SD (standard deviation) of 1.6 mBq per sample. The average tracer recovery for ^{242}Pu was 98.9% ± 6.6% (SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of this rapid method using the fusion option. The Full Width Half

Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 30: Plutonium Results for Steel Samples + Concrete and Refractory Pu Samples (Fusion)

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Spiked Value (mBq/sample)	^{239}Pu Measured Value (mBq/sample)	Difference (%)
1	99.2	50.5	24.5	25.35	3.4
2	98.2	32.3	24.5	22.94	-6.4
3	92.0	36.2	24.5	26.42	7.8
4	93.8	37.3	24.5	24.90	1.6
5	99.3	36.6	24.5	22.61	-7.7
Avg. Spiked Smps	96.5			24.4	-0.2
SD	3.4			1.6	6.6
% RSD	3.5			6.6	
		~1 g stainless steel	16 hour count		
		+0.5 concrete			

Table 31 shows the individual results for the determination of Pu isotopes in four 5 g steel samples spiked with ^{238}Pu. The acid digestion method was scaled up with increased acid volumes, and 500 mL centrifuge tubes were used to accommodate the larger volumes. After digestion and preconcentration, the TEVA Resin separation was used along with alpha spectrometry to measure the Pu isotopes. The average ^{238}Pu result was 38.3 mBq sample, with a 3.4% bias and SD (standard deviation) of 1.0 mBq per sample. The average tracer recovery for ^{242}Pu was 92.1% ± 14.3% (SD). The average ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of method, even with a 5 g steel aliquot. The variations in the tracer recover likely result from the more difficult sample matrix with 5 g of steel digested. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 31: Pu-238 Results for Spiked Steel Samples (5g steel)

Sample	^{242}Pu Yield	Tracer Peak	^{238}Pu Spiked Value	^{238}Pu Measured Value	Difference
ID	(%)	(FWHM)	(mBq/sample)	(mBq/sample)	(%)
1	108.0	34.8	37.0	37.37	1.0
2	100.1	30.8	37.0	38.22	3.3
3	77.7	52.4	37.0	37.85	2.3
4	82.7	44.0	37.0	39.63	7.1
Avg. Spiked Smps	92.1			38.3	3.4
SD	14.3			1.0	2.6
% RSD	15.5			2.5	
		~5 g stainless steel	16 hour count		

Figure 26 shows an example of the spectra of Pu isotopes in a 2 g steel sample. The ^{242}Pu tracer recovery was 91.9% and the Full Width Half Maximum (FWHM) was 33 keV, showing acceptable alpha peak resolution and good tracer recovery. The ^{239}Pu peak labeled on the spectra represents ^{239}Pu plus ^{240}Pu, since these isotopes have overlapping alpha energies.

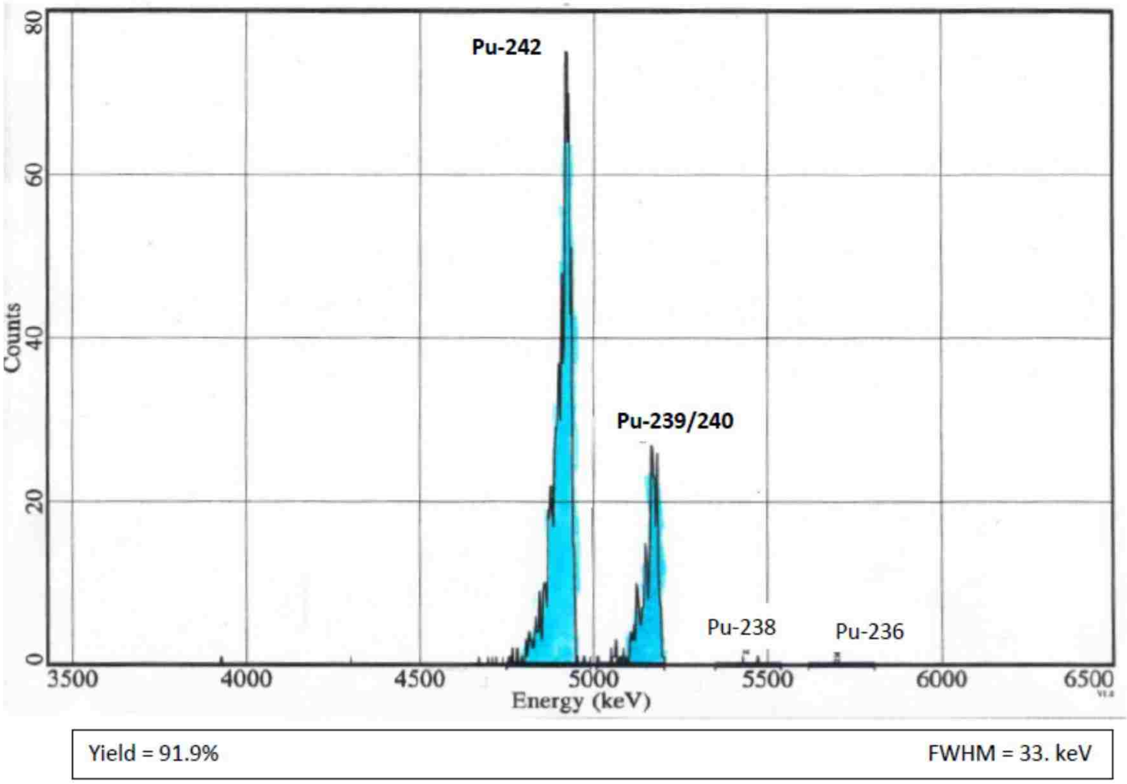


Figure 26: Alpha Spectra for Pu Isotopes in Steel

The MDA (Minimum Detectable Activity) for Pu isotopes using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie shown in equation (9): [75]

$$MDA = [2.71+4.65\sqrt{B}]/\ (CT*R*V*Eff*\mathbf{A}*0.060) \tag{9}$$

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 2g steel aliquot, the method MDA for the plutonium isotopes with a 16 hour count time is ~250 uBq/g, which is sufficient to meet current analytical action levels for plutonium in environmental remediation samples (~70 mBq/g) [90]

While the fusion option provides additional ruggedness for this method, it does add processing time. In an emergency, the aqua regia plus HF acid digestion method would likely be acceptable, unless very high fired Pu was present. In the MAPEP 24 soil preparation, the Pu was taken up to ~900°C to form refractory Pu by the Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. For high fired material such as ^{238}Pu oxide used as radioisotope thermoelectric generator, the fusion option should be utilized. [91] This study does illustrate why a simple nitric acid leach of the steel surface alone and processing of the leachate for Pu without HF attack may give highly unreliable results, if refractory Pu is present. It should be noted that it would be very easy to include other actinides in this steel method using the sequential separation techniques described previously. [44, 81]

6.5 Conclusions

A new rapid method to determine plutonium isotopes in steel samples has been developed that effectively digests steel samples (or steel plus concrete) for samples received in a radiological emergency or from routine nuclear decommissioning samples. The new method features a rapid preconcentration and separation of Pu isotopes with high chemical yields and effective removal of interferences. The method digests the samples with ruggedness and is very flexible, allowing several different measurement options.

6.6 Acknowledgment

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CHAPTER 7: RAPID METHOD TO DETERMINE $^{89/90}$SR IN STEEL SAMPLES

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7.1 Abstract

The rapid measurement of $^{89/90}$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 1-2 gram 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}Sr + ^{90}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}Sr + ^{90}Sr, ^{90}Sr, and discrimination between ^{89}Sr and ^{90}Sr are discussed. This approach has a sample preparation time of 6-8 hours for steel samples.

7.2 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), an Improvised Nuclear Device (IND) or a nuclear incident such as the accident at the Fukushima Nuclear Power Plant in March of 2011. [16, 30, 86, 87] In addition to other environmental matrices, steel samples from debris or remaining structures may need to be analyzed quickly to ascertain the radioactive content. It has been the approach of the Savannah River Environmental Laboratory (SREL) to combine rapid, rugged sample digestion with fast, innovative column purification methods to analyze samples of different building materials for radioactive contaminants quickly. The use of high flow rates through vacuum assistance and stacked cartridges containing highly selective extractant-coated chromatographic resins allows for the rapid sequential separation of multiple analytes in an emergency. Recently published methods developed at SREL include analyses for soil, concrete, limestone and marble. [44, 81] All these rapid methods share two key components: 1) swift and complete sample dissolution and matrix removal techniques coupled with 2) rapid innovative, sequential purification techniques. These radiochemical methods are both fast and reliable, therefore 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 can be achieved through the development and implementation of more efficient analytical methods. [77] The application of state-of-the-art 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. [19] Consistent with this need, a sodium hydroxide fusion method for complete dissolution of 10g concrete samples was recently published by this laboratory. [92] Similar sodium hydroxide fusion methods have been used with great success for soil, concrete, vegetation and other solid samples. Steel samples cannot be adequately dissolved with a sodium hydroxide fusion technique. However, 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.

A comprehensive description of sample preparation methods for ^{89,90}Sr for a wide range of sample matrices is provided by Vajda and Kim. [79] Many techniques published 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. [12] reported a method for actinides and ^{89,90}Sr in soil and vegetation samples in which 10g samples were digested and analyzed. An 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}Sr measurements reported were within ±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 the 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 in combination with Cerenkov counting to determine ^{90}Sr via the assay of ^{90}Y in vegetation samples. [93] 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. [61] For this reason, DGA Resin has been used in the determination of ^{90}Sr in seawater and concrete in our laboratory as well. [44, 62] 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 analysis techniques has also led some laboratories to pursue inductively-coupled plasma mass spectrometry (ICP-MS) to measure ^{90}Sr. [82] While ICP-MS offers a simplicity that may be appealing, it suffers from poor detection limits when compared with beta emission measurement methods [92] 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. [94] investigated 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 an O_2 reaction cell technique was employed 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 samples containing high levels of ^{90}Sr, but is not currently feasible for decommissioning or low level environmental analyses.

A new procedure has been developed in the Savannah River Environmental Laboratory to measure ^{89,90} Sr in steel samples. The method employs preconcentration techniques that effectively manage the high iron content resulting from the dissolution of the steel sample, while simultaneously keeping the sample preparation volumes small so that rapid column separation can be achieved. Two options were investigated in this study. In the first approach, ^{89}Sr and ^{90}Sr were purified and counted together to determine total radiostrontium, 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}Sr+^{90}Sr count. The second option utilizes the collection of ^{90}Y directly from the sample with no waiting for ingrowth to determine the amount of ^{90}Sr in the steel sample.

7.3 Experimental

7.3.1 Reagents

The extraction chromatography resins employed in this work are DGA Resin, Normal (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 acid solutions 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. Sr-90 was obtained from Eckert Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2.96 Bq mL^{-1}. Sr-89 was obtained from Eckert Ziegler 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).

7.3.2 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}Sr/^{90}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}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.

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 Efficiency^2/Background) allowing for a reduction in the calculated MDA.

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.

Stable Yttrium recoveries were measured with a Perkin Elmer model DRC-e inductively coupled plasma-mass spectrometer operated with 1400W RF power, 5.5 mm torch depth, 15L/min plasma gas, 1L/min carrier gas, 0.98L/min nebulizer gas, 6.25V E1 lens voltage, 0.0165 E1 lens slope, 4.413 E1 lens intercept, -12 CPV cell path votage, -17V cell rod offset, and -4V Q-pole rod offset.

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.

7.3.3 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. [61] Aqueous solutions (5-10 mL) 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)ºC on an orbital plate shaker or tumbling mixer. After equilibration, the aqueous phase was filtered through 0.45 μm polypropylene syringe filters to remove resin particles. Stock solutions of the metal ion and solutions that have been equilibrated with resin were 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, Inc.). The small particle size coated support, with enhanced surface area, improves column separation efficiencies. Flow rates of ~1-2 drops sec^{-1} were typically used for this work, slower during 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 27 shows the sample preparation flowchart for ^{89}Sr and ^{90}Sr in steel samples. Samples of 304 stainless steel disks (Engineering and Information Systems, Aiken, SC, ~18% chromium, ~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 (6 mg) was added to each sample when the Sr Resin separation was employed. When ^{90}Y was collected directly for separations using DGA Resin, 2 mg of yttrium was added to determine chemical yield. Yttrium carrier (2 mg) 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. Preliminary 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 digesting refractory particles more rigorously. This was confirmed in parallel testing undertaken at this laboratory where a small amount of soil containing refractory plutonium was added to the steel sample, with and without HF. [95]

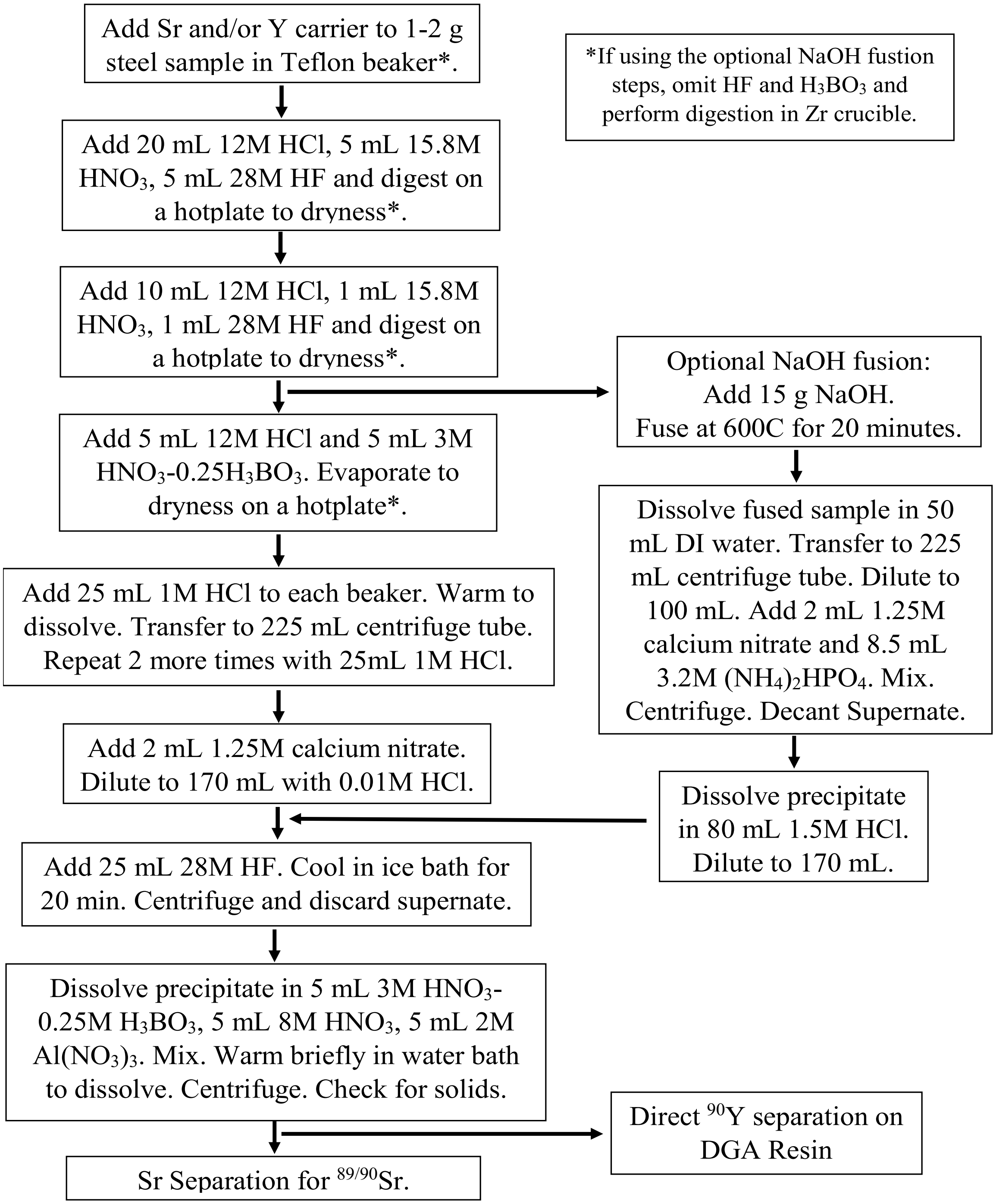

Figure 27: Steel Dissolution with ^{89}Sr, $^{90}Sr/^{90}Y$ Preconcentration and Separation Method

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 HNO_3, 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 HNO_3, and 1 mL 28M HF were added to each beaker and the samples were evaporated to dryness again on a hot plate. Finally, 5 mL 12M HCl and 5 mL 3M HNO_3-0.25M H_3BO_3 were added to each beaker, and samples were evaporated to dryness to remove fluoride. It was found that this step assisted in facilitating 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 was 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 each sample, 2 mL 1.25M calcium nitrate was added as a carrier for Sr/Y. Twenty-five milliliters of 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 then added to the 225 mL tube to coprecipitate Sr or Y on CaF_2 or CaF_2/YF_3. The high HF concentration is required to effectively precipitate CaF_2 and SrF_2 (K_{sp} = 3.45E-11 and 4.33E-9, respectively). [96] After mixing each sample tube well, the tubes were cooled in an 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 HNO_3-0.25M Boric acid, 5 mL 15.8 HNO_3, and transferred to a 50 mL centrifuge tube. To rinse the 225 mL tube, 5 mL 8M HNO_3, and 5 mL 2M $Al(NO_3)_3$ 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 HNO_3 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 [81], except that no additional Fe was added. In this fusion option, an initial precipitation was performed using iron hydroxide enhanced with calcium phosphate to remove the high levels of hydroxide. Following the initial precipitation, the samples were then 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 28 and 29 show that there is minimal affinity for these ions in nitric acid on Sr Resin or DGA Resin.

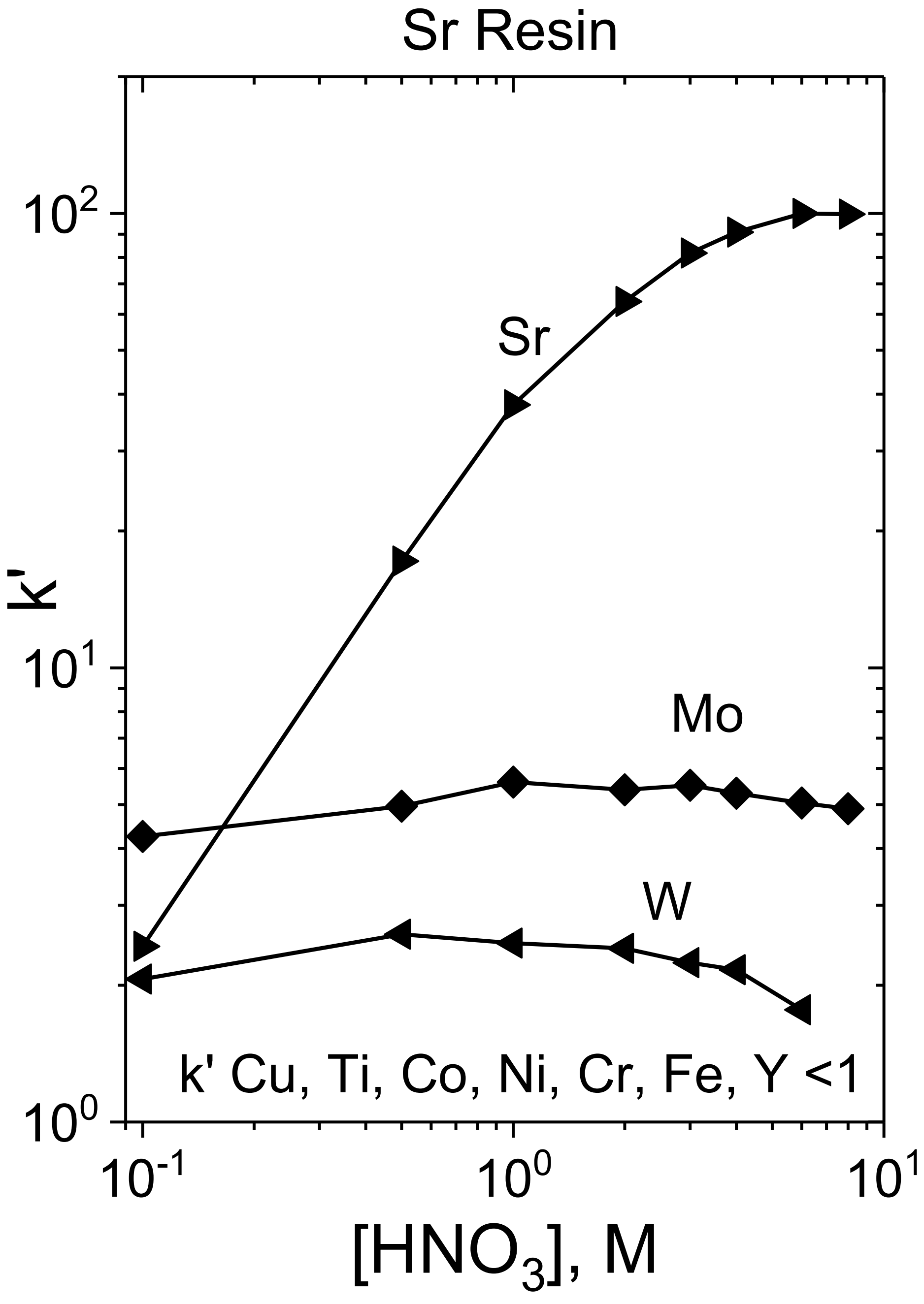

Figure 28: k’ Steel Components, Sr, and Y on Sr Resin from Nitric Acid

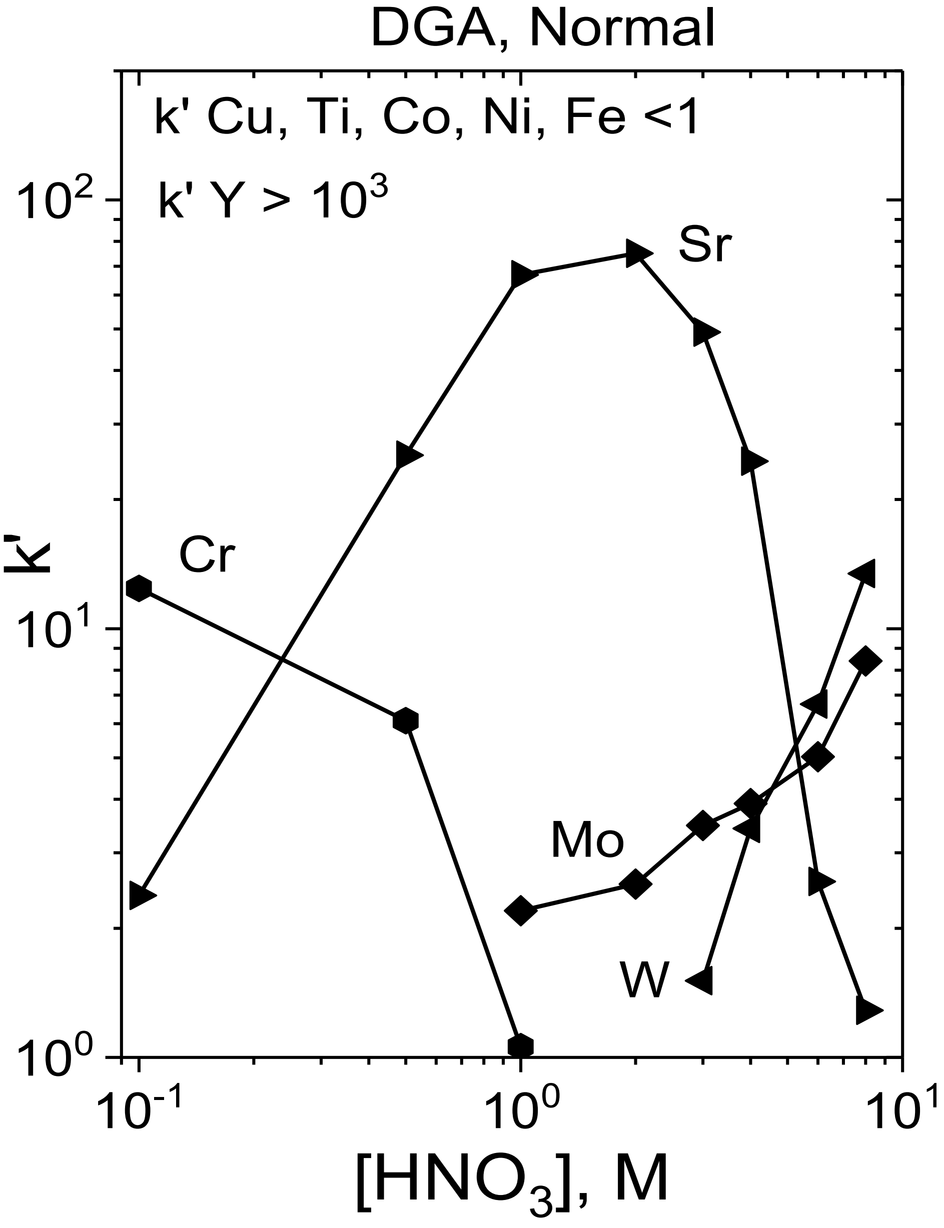

Figure 29: k' Steel Components, Sr, and Y on DGA Resin from Nitric Acid

Column separation for Strontium-89,90. Sr was separated using Sr Resin (3 mL Sr Resin, by means of stacked 2 mL+1 mL resin cartridges) utilizing a method similar to that previously published for the determination of ^{89}Sr and ^{90}Sr in limestone and marble samples. [81] 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 the stacked cartridges (3 mL Sr Resin) with 15 mL 0.05M HNO_3 at ~1 drop per second. This eluent was then transferred to pre-weighed planchets and evaporated on a hot plate with medium heat to dryness. Two milliliters of 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 for an additional ~10-15 minutes on the hot plate. The dried planchets were allowed to cool and weighed to determine gravimetric carrier recovery. The planchets were then counted by simultaneous gas flow proportional counting for 60 minutes to determine $^{89/90}Sr$. 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 the actual samples.

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 amount of ^{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, such as would be 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 consequently 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 $^{89/90}$Sr and after a suitable ingrowth period, can offer a much more reliable assay of ^{90}Sr. (Figure 30) 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. In this method, 2 mg yttrium carrier was added to the planchet containing the purified ^{89}Sr/ ^{90}Sr after 2-3 days (or longer) ^{90}Y ingrowth period. The residues from the planchets were dissolved in 8M HNO_3, warmed on a hot plate, and the planchet was rinsed 3 times with ~5 mL 8M HNO_3. All aliquots were transferred to a 50 mL tube, and the 20mL 8M HNO_3 solution was loaded onto DGA Resin column to rapidly purify ^{90}Y. The ^{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 chemical yield for yttrium. The ^{90}Y separation time used is the midpoint of the time required for the sample loading step.

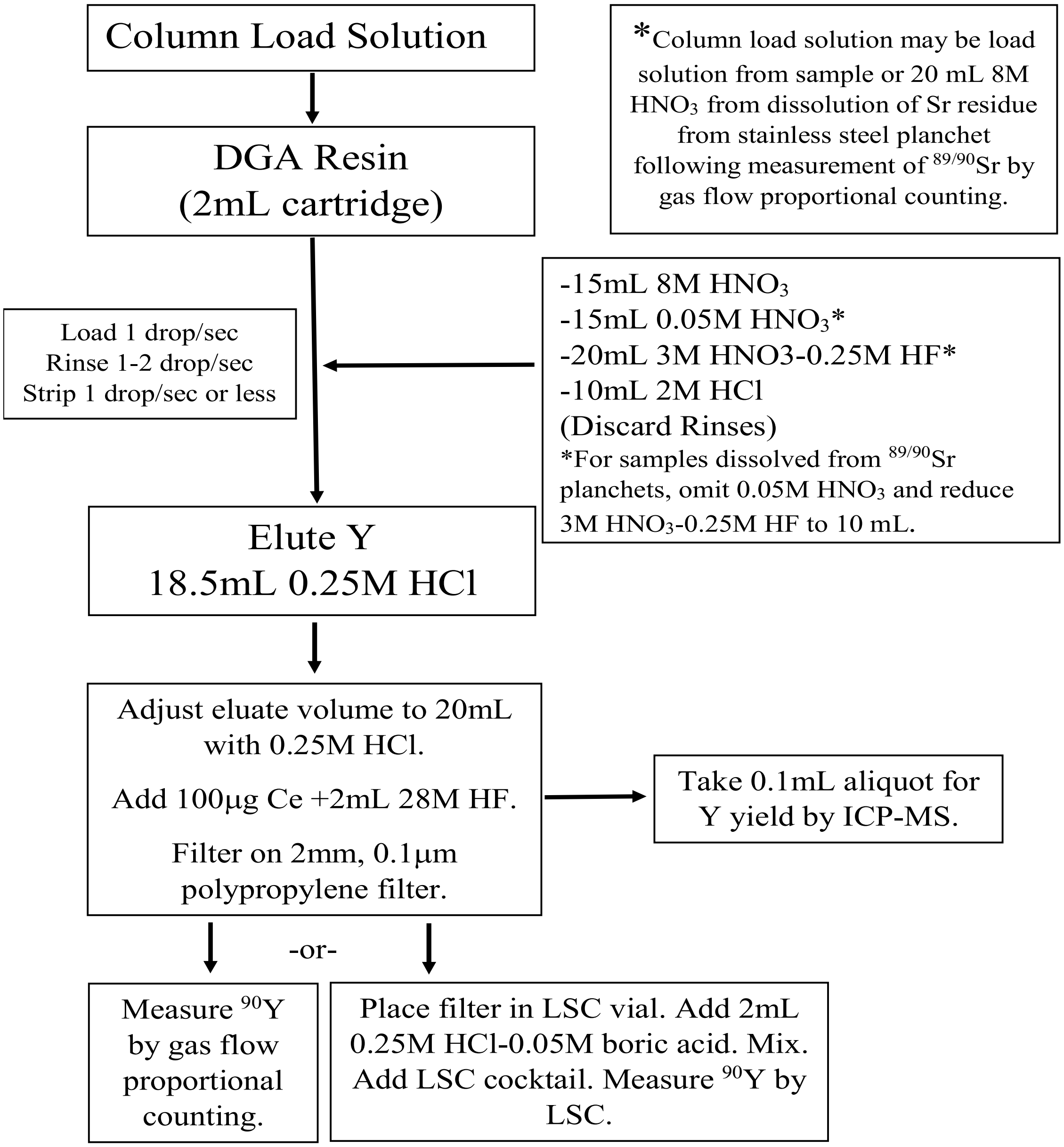

Figure 30: DGA separation for ^{90}Sr in steel

Column separation for Strontium-90 (using ^{90}Y). Figure 30 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 dissolution of the steel samples (Figure 28), the yttrium was loaded onto DGA Resin cartridges. The DGA Resin was rinsed with 8M HNO_3 to remove Ca, Sr 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. For gas flow proportional counting, 25 mm polypropylene filters were 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 20 mL 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 of 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 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 both 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. Additionally, LSC is a destructive analysis and does not allow secondary separation of ^{90}Y from the $^{89/90}Sr$ sample to discriminate the ^{89}Sr and ^{90}Sr activities. If LSC is used then the only $^{89/90}Sr$ discrimination technique available would be a 2-count method, where the sample is counted at two different times and the $^{89/90}Sr$ activities are calculated by using a series of equations [79].

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. [12, 97, 98] 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. [98] 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 the counting efficiency for ^{90}Y 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.

7.4 Results and Discussion

Table 32 shows the individual results for the determination of ^{90}Sr in ten 2 gram 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% ± 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 ± 3-4% (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 32: Steel Sample Results: Sr Resin Method for ^{90}Sr (Gas Proportional Counting)

Sample	Sr Carrier Yield	^{90}Sr Known Value	^{90}Sr Measured Value	Difference
ID	(%)	(Bq smp^{-1})	(Bq smp^{-1})	(%)
1	87.5	1.415	1.432	1.2
2	88.5	1.415	1.464	3.5
3	87.5	1.415	1.441	1.8
4	91.6	1.415	1.397	-1.3
5	87.5	1.415	1.440	1.7
6	88.5	1.415	1.390	-1.8
7	91.6	1.415	1.408	-0.5
8	91.6	1.415	1.338	-5.4
9	92.6	1.415	1.409	-0.4
10	93.6	1.415	1.377	-2.7
Avg. Spiked Smps	90.1		1.41	-0.39
SD	2.4		0.04	2.6
% RSD	2.6		2.6	
1.415 Bq/sample = 38.2 pCi/sample				
		60 minute count		

Table 33 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 Bq ^{90}Sr and 4 steel samples were spiked with 2.83 Bq ^{90}Sr. The average bias versus the known values was -2%. The average Y carrier recovery was 96.9% ± 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 ± 3-4% (1 SD), with a 60 minute count time.

Table 33: Steel Sample Results: DGA Resin Method for ^{90}Sr (^{90}Y) (Gas Proportional Counting)

Sample ID	Y carrier Yield (%)	^{90}Sr Known Value (Bq smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	96.5	1.415	1.396	-1.3
2	98.5	1.415	1.383	-2.3
3	95.6	1.415	1.393	-1.6
4	89.4	1.415	1.343	-5.1
5	100.0	2.830	2.822	-0.3
6	101.9	2.830	2.748	-2.9
7	96.6	2.830	2.904	2.6
8	97.1	2.830	2.675	-5.5
Avg. Spiked Smps	96.9			-2.0
SD	3.7			2.6
% RSD	3.8			
1.415 Bq/sample = 38.2 pCi/sample, 2.830 Bq/sample = 76.5 pCi/Sample				
		60 minute count		

Table 34 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% ± 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 ± 3-4% (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 34: Steel Sample Results: DGA Resin Method for ^{90}Sr (^{90}Y) (Liquid Scintillation Counting)

Sample ID	Y carrier Yield (%)	^{90}Sr Known Value (Bq smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	94.8	1.447	1.374	-5.0
2	92.1	1.447	1.444	-0.2
3	91.6	1.447	1.447	0.0
4	93.6	1.447	1.420	-1.8
5	93.8	1.447	1.429	-1.2
6	96.1	1.447	1.411	-2.5
Avg. Spiked Smps	93.7		1.42	-1.8
SD	1.7		0.03	1.8
% RSD	1.8			
1.447 Bq/Sample = 39.1 pCi/Sample				
		60 minute count		

Table 35 shows the individual results for the determination of ^{89}Sr + ^{90}Sr in eight 1 g steel samples spiked with ^{89}Sr and ^{90}Sr. Sr Resin was used to retain the $^{89/90}$Sr. Purified $^{89/90}$Sr was measured by gas flow proportional counting. The results were corrected for stable Sr carrier yield. The average of total ^{89}Sr+ ^{90}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% ± 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 ± 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 35: Steel Sample Results: Sr Resin Method for ^{89}Sr +^{90}Sr (Gas Proportional Counting)

Sample	Sr Carrier Yield	^{89}Sr+^{90}Sr Known Value	^{89}Sr+^{90}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 Smps	94.1		3.97	4.1
SD	2.8		0.09	
% RSD	2.9			
3.816 Bq/Sample = 103 pCi/Sample				
		60 minute count		

Table 36 shows the individual results for the determination of ^{90}Sr via ^{90}Y in eight 1 g steel samples. After the initial count to determine ^{89}Sr+ ^{90}Sr in (Table 4), the strontium residue was dissolved in 8M HNO_3, and ^{90}Y was separated using DGA resin (Figure 30). Following the DGA Resin separation, the ^{90}Y was precipitated as YF_3 and 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% ± 2.9% (SD). The uncertainties for the individual ^{90}Sr results were typically ± 3-4% (1 SD), with a 60 minute count time.

Table 36: Steel Sample Results: ^{90}Sr via ^{90}Y Assay after 5 days ingrowth and ^{90}Y separation from samples

Sample ID	Y Carrier Yield (%)	^{90}Sr Known Value (Bq smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
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			
0.556 Bq/Sample = 15.0 pCi/Sample				
		60 minute count		

Table 37 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}Sr+ ^{90}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.

Table 37: Steel Sample Results: ^{89}Sr Calculated by Difference After ^{90}Sr Assay

Sample ID	Sr Carrier Yield (%)	^{89}Sr Reference Value (Bq smp^{-1})	^{89}Sr Measured Value (Bq smp^{-1})	Difference (%)
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 Smps	94.1		3.425	4.7
SD	2.8		0.099	
% RSD	2.9			
3.270 Bq/Sample = 88.4 pCi/Sample				

In a similar test, ^{89}Sr + ^{90}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 35 and 36 were obtained. For the initial Sr Resin separation assay of total ^{89}Sr+ ^{90}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% ± 2.7% (SD).

The MDA (Minimum Detectable Activity) for the radiostrontium beta particle emission using this method with measurement was calculated according to equations prescribed by Currie, as shown in equation (10): [75]

$$MDA = [2.71+4.65\sqrt{B}\ ]/\ (CT*R*V*Eff*A*0.060) \qquad (10)$$

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 gas flow proportional count 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 estimated to be ~ 25 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 ~12 mBq g^{-1}. The MDA represented for each instrument reflects its ability to detect beta particles resulting from total ^{89}Sr +^{90}Sr or ^{90}Y decay. If ^{90}Sr is present in the sample, this may impact the ability of the method to detect ^{89}Sr, depending on the amount of ^{90}Sr present (if any), but that is beyond the scope of this work.

For ^{89}Sr or ^{90}Sr in steel samples using liquid scintillation counting, the MDA is ~ 60-80 mBq g^{-1} for a 1 g sample aliquot, 60 minute count time, 90% chemical recovery, ~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 and E^2/B), allowing for a slight reduction in the calculated MDA. Regarding detection limits of LSC counting, Ultra low level LSC counters such as the Quantalus Ultra Low Level LSC (Perking 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. [99] 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.

7.5 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.

7.6 Acknowledgment

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CHAPTER 8: RAPID METHOD TO DETERMINE ^{226}RA IN STEEL SAMPLES

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8.1 Abstract

The rapid measurement of ^{226}Ra in steel samples is very important in the event of a radiological emergency. ^{226}Ra ($T_{1/2}$ = 1600 y) is a natural radionuclide present in the environment and a highly toxic alpha-emitter. Due to its long life and tendency to concentrate in bones, ^{226}Ra ingestion or inhalation can lead to significant committed dose to individuals. A new method for the determination of ^{226}Ra in steel samples has been developed at the Savannah River Environmental Laboratory. The new method employs a rugged acid digestion method that includes hydrofluoric acid, followed by a single precipitation step to rapidly preconcentrate the radium and remove most of the dissolved steel sample matrix. Radium is then separated using a combination of cation exchange and extraction chromatography, and ^{226}Ra is measured by alpha spectrometry. This approach has a sample preparation time of ~8 hours for steel samples, has a very high tracer yield (>88%), and removes interferences effectively. A ^{133}Ba yield tracer is used so that samples can be counted immediately following the separation method, avoiding lengthy ingrowth times that are required in other methods.

8.2 Introduction

^{226}Ra ($T_{1/2}$ = 1600 y) is one of the most toxic of the long-lived alpha-emitters present in the environment. Due to its long half-life and tendency to concentrate in bones, ingestion or inhalation of ^{226}Ra can lead to a significant committed dose to individuals. Rapid methods are needed to measure ^{226}Ra in various matrices in the event of a national radiological emergency. [15,86, 100, 101] The recent theft of nuclear material in Mexico highlights the need for nuclear safeguards and raises concerns about a radiological dispersive device (RDD) or “dirty bomb”. [102] The ^{226}Ra isotope has been identified by the International Atomic Energy Agency as a radionuclide that can harm human health if used in a terrorist attack using a RDD. [103]

According to Steinhäusler et al., natural radionuclides can pose a significant risk for radiological terrorism, as ^{226}Ra has been trafficked repeatedly through different countries. Furthermore, ^{210}Po has been used in a criminal act, [8] with former Russian intelligence officer Alexander Litvinenko dying in a London hospital on November 23, 2006, after he was deliberately poisoned with^{210}Po. Police discovered that those involved in this crime had spread ^{210}Po over many locations in London. [9] Because ^{226}Ra has a high specific activity relative to Uranium and many other naturally occurring radionuclides, the potential is higher for a radiological event leading to a significant committed dose from ^{226}Ra.

During a national radiological emergency, the laboratories providing analytical support will be faced with a tremendous number of samples to be analyzed very quickly. Many of the environmental samples will consist of urban matrices, building materials such as concrete, brick or asphalt. The availability of proven rapid methods will be essential to allow incident commanders to assess the scope and impact of the event. If such an emergency occurs, there will be an urgent need for rapid radiochemical analyses for building materials, including steel from building debris, to support dose mitigation and environmental clean-up. The defensibility of results is very important to maintain public trust. [84]

The application of rapid, streamlined radiochemical techniques to environmental and decommissioning samples can reduce labor costs and facilitate improved analytical efficiencies. Furthermore, reliable, high quality analyses are essential, not only following a radiological emergency, but also for routine laboratory analyses. The International Atomic Energy Agency (IAEA) AMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network administered proficiency testing for the rapid analysis of ^{226}Ra in water and phosphogypsum in 2008. The ALMERA network, established by the IAEA in 1995, is a technical collaboration of existing institutions and makes available to member states a worldwide network of analytical laboratories capable of providing reliable and timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity. Forty-nine labs from 39 member states participated in this study. Most of the laboratories used gamma spectrometry to measure ^{226}Ra by measuring the gamma ray emission of its ^{214}Bi or ^{214}Pb progeny, requiring at least a 21 day ingrowth period. This time delay would not be acceptable during a radiological emergency. For the two water samples that contained ^{226}Ra, 43% and 31% of the lab results, respectively, were unacceptable versus IAEA test criteria. For the phosphogypsum sample, 19% of the ^{226}Ra results were unacceptable. Recommendations in this study to improve measurement quality addressed gamma calibration geometry issues, gamma emission interferences and, of particular importance the loss of the decay chain progeny ^{222}Rn due to leakage in the sample counting containers. [104]

In an emergency, where time is of the essence, long ingrowth times and poor quality results are unacceptable. A new method has been developed at the Savannah River Environmental Laboratory to measure ^{226}Ra isotopes in steel samples using alpha spectrometry. The method employs preconcentration technology that effectively manages the high iron content resulting from the dissolution of the steel sample. Rapid sample digestion and preconcentration prepare samples for column purification. The use of a ^{133}Ba yield tracer allows the direct measurement of ^{226}Ra by alpha spectrometry without waiting for progeny ingrowth, facilitating rapid analysis of samples, which will be very important in a radiological emergency. While rapid, the new method is robust, and the ^{226}Ra measurements can be performed quickly with high reliability.

8.3 Experimental

8.3.1 Reagents

The resins employed in this work are strong acid cation exchange resin (50W-X8, H^+ form, 200-400 mesh) and DGA Resin, Normal (N,N,N',N'-tetraoctyldiglycolamide), (available from Eichrom Technologies, Inc., Lisle, Illinois, USA, and Triskem, Bruz, France). Nitric 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 reagent grade. Radiochemical isotopes ^{226}Ra and ^{133}Ba were obtained from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq mL^{-1} and 37 Bq mL^{-1} respectively.

8.3.2 Apparatus

The ^{226}Ra 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.

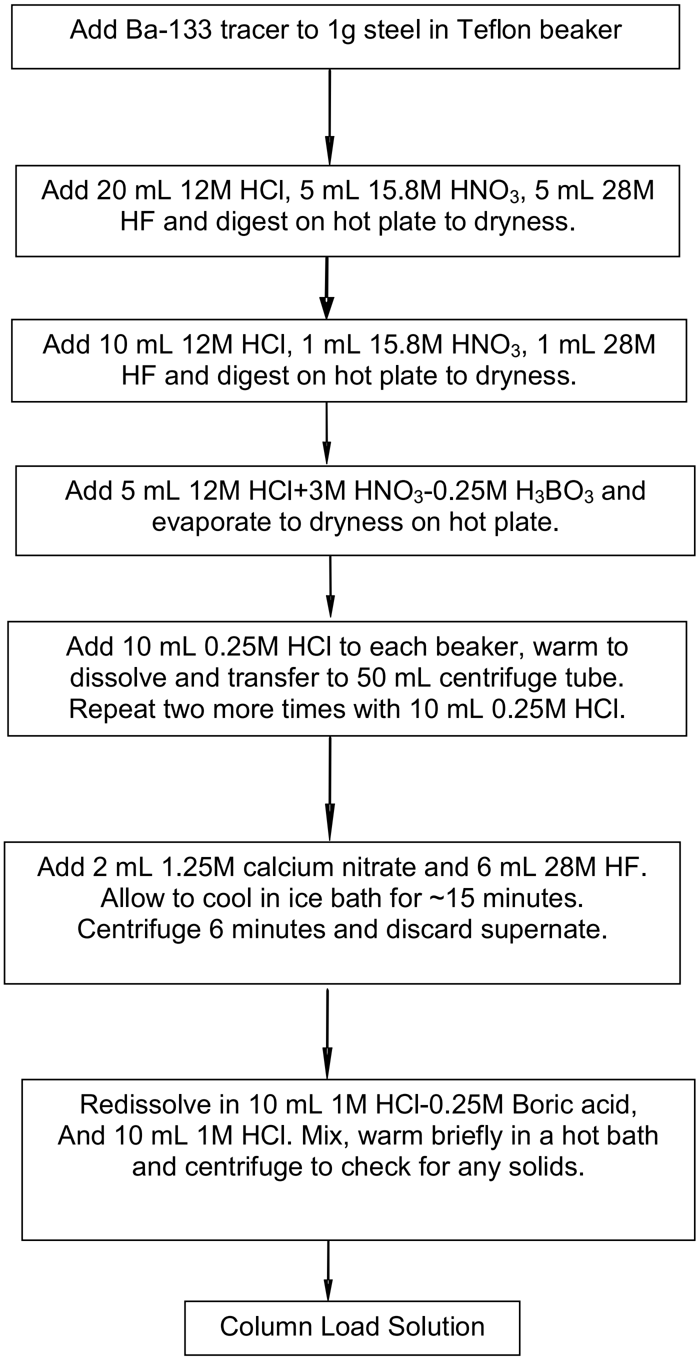
A Canberra (Meriden, CT, USA) high purity germanium detector (Model GC4019), with a relative efficiency of 40% at 1332 keV was used to measure the ^{133}Ba tracer yield for each sample. The gamma spectrometry count time was 20 minutes per sample. Canberra Genie 2000 Gamma software (version 1.3) was used to process the sample results.

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.

8.3.3 Procedures

Column preparation. Cation exchange resin (Eichrom 50WX8, 200-400 mesh) was obtained as bulk resin and columns were prepared by weighing out the resin amounts in large ion exchange columns with reservoirs (Environmental Express, Mount Pleasant, SC, USA). DGA Resin cartridges containing 2 mL of resin were obtained from Eichrom Technologies, Inc. (Lisle, IL). Small particle size (50-100 μm) resin was employed, along with a vacuum extraction system (Eichrom Technologies) that will handle 24 samples at a time. Flow rates of ~1-2 mL min^{-1} were typically used. For the cation exchange resin (200-400 mesh), optimum flow rates were achieved (in most cases) using gravity flow.

Sample Preparation. Figure 31 shows the flowsheet for the sample preparation for ^{226}Ra in 1 gram samples of 304 stainless steel disks ((Engineering and Information Systems, Aiken, SC, ~18% chromium, ~8% nickel). Each sample was placed in a 250 mL Teflon beaker and spiked with a ^{133}Ba tracer (~33 Bq). Twenty milliliters of 12M HCl, 5 mL 15.8M HNO_3, 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 HNO_3, 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 5 mL 3M HNO_3-0.25M H_3BO_3 were added to each beaker to remove fluoride. This step was found to facilitate complete removal of the sample residue from the beaker. The contents of each beaker were evaporated to dryness on a hot plate.



Add Ba-133 tracer to 1g steel in Teflon beaker

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3, 5 mL 28M HF and digest on hot plate to dryness.

Add 10 mL 12M HCl, 1 mL 15.8M HNO_3, 1 mL 28M HF and digest on hot plate to dryness.

Add 5 mL 12M HCl+3M HNO_3-0.25M H_3BO_3 and evaporate to dryness on hot plate.

Add 10 mL 0.25M HCl to each beaker, warm to dissolve and transfer to 50 mL centrifuge tube. Repeat two more times with 10 mL 0.25M HCl.

Add 2 mL 1.25M calcium nitrate and 6 mL 28M HF. Allow to cool in ice bath for ~15 minutes. Centrifuge 6 minutes and discard supernate.

Redissolve in 10 mL 1M HCl-0.25M Boric acid, And 10 mL 1M HCl. Mix, warm briefly in a hot bath and centrifuge to check for any solids.

Column Load Solution

Figure 31: Steel Dissolution with ^{226}Ra Sample Preparation Method

To dissolve the sample residue, 10 mL 0.25M HCl was added to each beaker. Each sample was warmed on a hot plate to dissolve the residue, and the dissolved sample was transferred to a 50 mL centrifuge tube. The dissolution and transfer with 10 mL 0.25M HCl were repeated two more times, warming each beaker as needed. To precipitate the Ra from the dissolved steel sample, 2 mL 1.25M calcium nitrate and 6 mL 28M HF were added to each 50 mL tube. After mixing each sample tube well, the tubes were cooled in ice bath for ~15 minutes to facilitate the complete co-precipitation of ^{133}Ba and ^{226}Ra on CaF_2. The HCl concentration was kept low (0.25M HCl) and large excess of HF was used to facilitate co precipitation of barium and radium fluoride with calcium fluoride, since BaF_2 (K_{sp} $1x10^{-6}$) has a relatively high solubility product constant compared to CaF_2 (K_{sp} $5.3x10^{-9}$). Each sample was centrifuged at 3500 rpm for 6 minutes and the supernate was discarded. Each sample precipitate was redissolved in 10 mL 1 M HCl-0.25M boric acid and 10 mL 1 M HCl. 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 residual solids.

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 removed during the final precipitation step, while trace amounts of chromium, nickel, carbon and the other constituents of steel remaining following precipitation do not interfere with the cation exchange and DGA Resin separation methods.

Column separation for Radium-226. Figure 32 shows the column separation for radium which employs cation exchange resin for the initial sample load and rinse steps, followed by elution of ^{226}Ra through DGA Resin to remove alpha emitting interferences. The cation exchange resin column contained 5 grams of resin (200-400 mesh), although slightly more resin can be used for larger sample aliquots or for samples containing large amounts of Ca, such as steel with residual soil or concrete. The cation exchange resin columns were set-up on a vacuum box with a large inner liner to collect rinses. However, vacuum is normally only needed to get the flow started, and gravity flow can then be used for the bulk of sample elution prior to the addition of the DGA Resin cartridges.

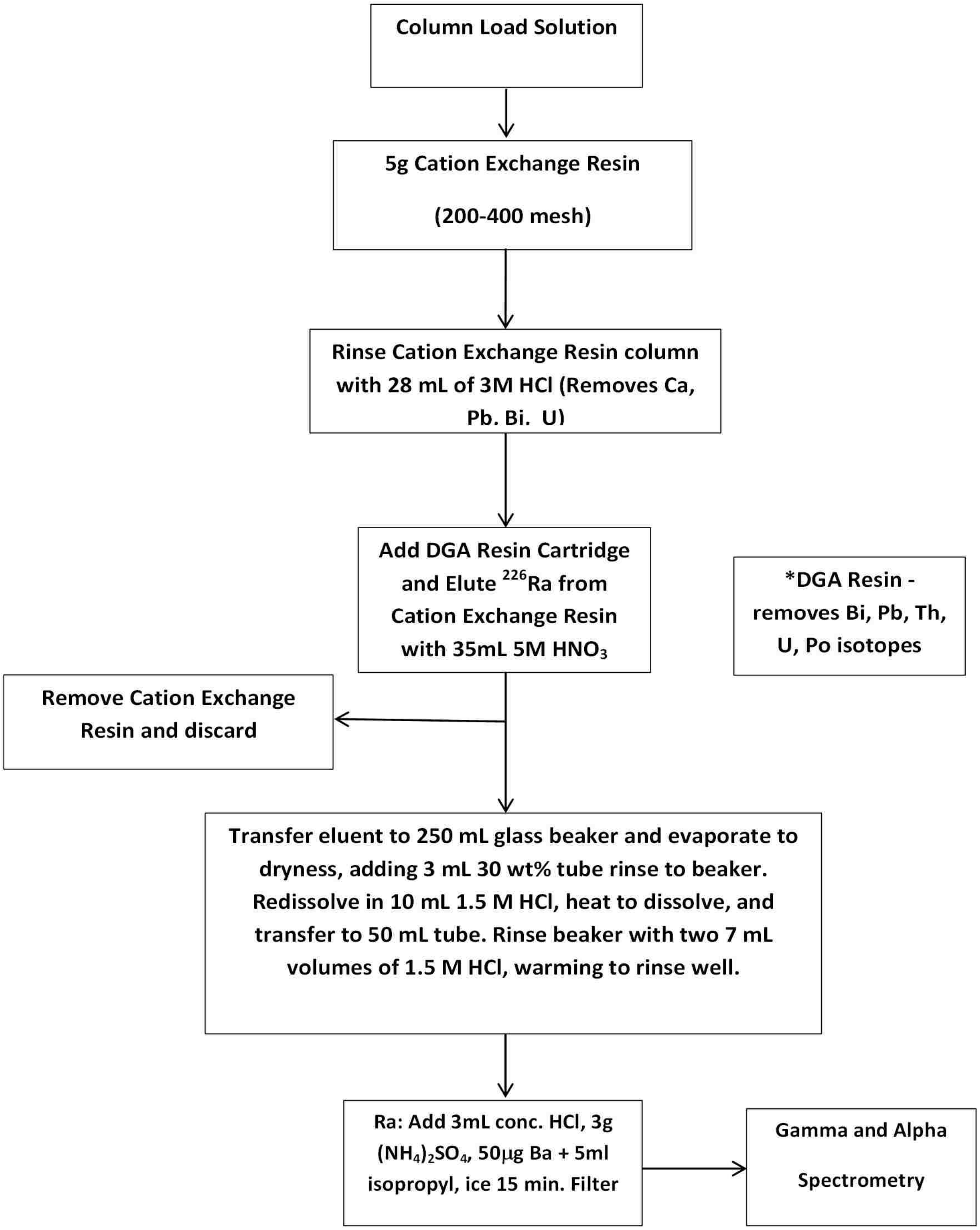


Figure 32: Rapid Column Separation Method for ^{226}Ra in Steel

Prior to loading the sample, the cation resin was cleaned as follows, using gravity flow rates of 3-4 drops per second, to ensure very low blanks: 20mL deionized water, 20 mL 6M HCl, 10mL deionized water, and 10 mL 0.5M HCl. To each sample load solution, 3 mL 1.5M ascorbic acid was added to reduce Fe (III) to Fe (II) to minimize retention on the cation resin of any residual iron present. The samples were loaded at ~1 drop per second. After sample loading, the column was rinsed at ~1-2 drops/second with 25 mL 3M HCl to remove Ca^{2+}, Pb^{2+}, Bi^{3+} and UO_2^{2+} ions that may be present in the sample.

After the 3M HCl rinse, a 2 mL DGA cartridge was placed onto the bottom of each cation exchange column, and a clean labeled tube was added below each column to collect the purified eluent. To elute Ba/Ra from each cation column, 35 mL 5M HNO_3 was added to each column and eluted at ~1 drop per second. The eluents were transferred to 250 mL glass beakers, and sample tubes were rinse with 3 mL 30wt% H_2O_2. The tube rinses added to each sample beaker, and samples were quickly taken to dryness on a hotplate. The sample residues were redissolved in 10 mL 1.5M HCl with heating on a hot plate, transferred to clean 50 mL tubes. The beakers were rinsed with two 7 mL volumes of 1.5M HCl to complete transfer to the 50mL tubes, yielding purified radium fraction volumes of ~20 mL 1.5M HCl total. The purified samples are now suitable for final microprecipitation of ^{226}Ra with $BaSO_4$.

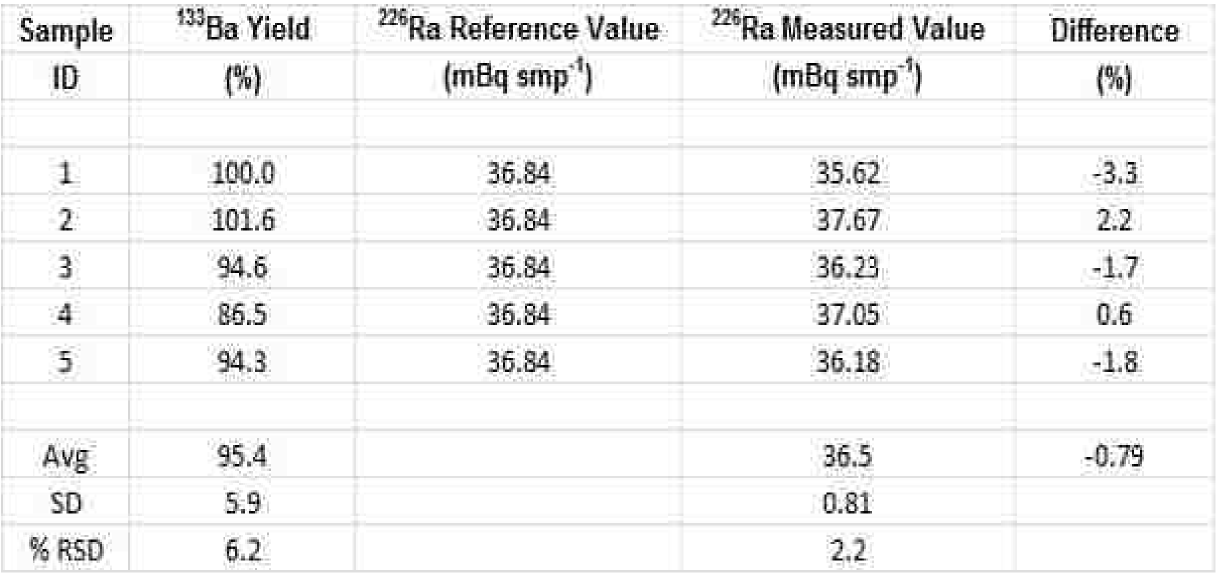
Three grams of ammonium sulfate were added to each sample, and tubes were mixed well to complete dissolution. Fifty micrograms of barium, from a 1 mg mL^{-1} Ba stock solution, was added to each sample, and the tubes were mixed well. Five milliliters isopropanol were added to each sample to reduce barium sulfate solubility, and tubes were mixed again. The tubes were iced for 15 minutes and periodically vortexed (beginning, middle and on removal from ice).

The samples were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve- Filter-Eichrom Technologies) to collect the microprecipitate, and filters were rinsed with 3-5 mL of 20% isopropanol. The filters were dried under a heat lamp, counted by gamma spectrometry to determine ^{133}Ba yield and alpha spectrometry to measure ^{226}Ra. It should be noted that sulfuric acid may be used instead of ammonium sulfate, if desired. The disposable Resolve Filters funnel units were used on vacuum boxes with a liner to save time.

8.4 Results and Discussion

Table 38 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 36.4 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 36.5 mBq, with a -0.8% bias and SD (standard deviation) of 0.8 mBq. The average tracer recovery for ^{133}Ba was 95.4% ± 5.9% (SD). The high ^{133}Ba tracer recoveries and excellent results for ^{226}Ra versus known values indicate the effectiveness of the sample preparation and measurement steps. The use of calcium fluoride to coprecipitate barium fluoride and radium fluoride was successful despite the greater solubility of the Ba/Ra fluorides. The ^{226}Ra peaks for all samples show good alpha peak resolution (typically ~45keV, Figure 33). The uncertainties for the individual ^{226}Ra results in all sample sets were typically ± 7-8% (1 SD), with a 16 hour count time. Shorter alpha spectrometry measurement times may be used in a radiological emergency.

Table 38: Ra-226 Results for Spiked Steel Samples



Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	100.0	36.84	35.62	-3.3
2	101.6	36.84	37.67	2.2
3	94.6	36.84	36.23	-1.7
4	86.5	36.84	37.05	0.6
5	94.3	36.84	36.18	-1.8
Avg	95.4		36.5	-0.79
SD	5.9		0.81	
% RSD	6.2		2.2	

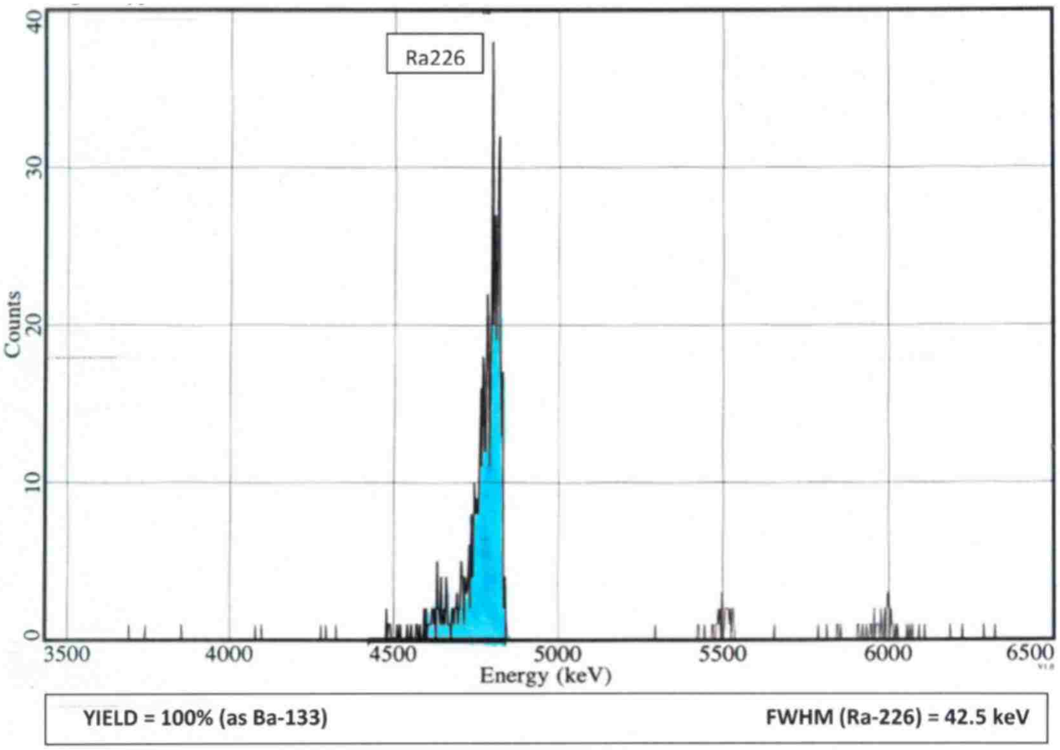
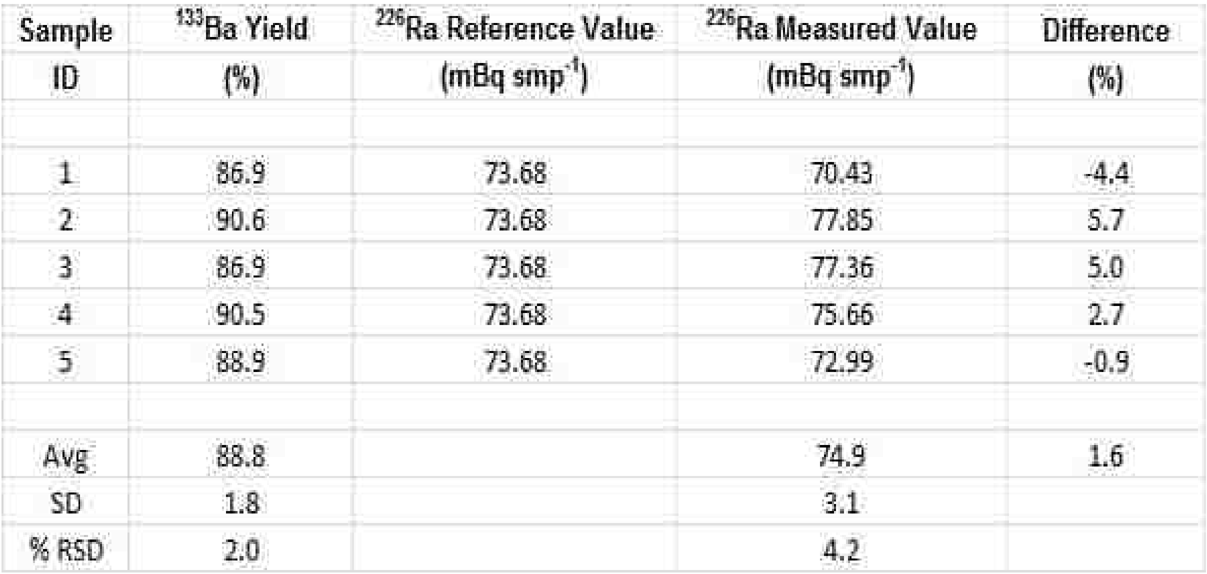


Figure 33: Alpha Spectra for ^{226}Ra in Steel

Table 39 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 73.68 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 74.9 mBq, with a 1.6% bias and SD of 3.1 mBq smp^{-1}. The average tracer recovery for ^{133}Ba was 88.8% ± 1.8% (SD).

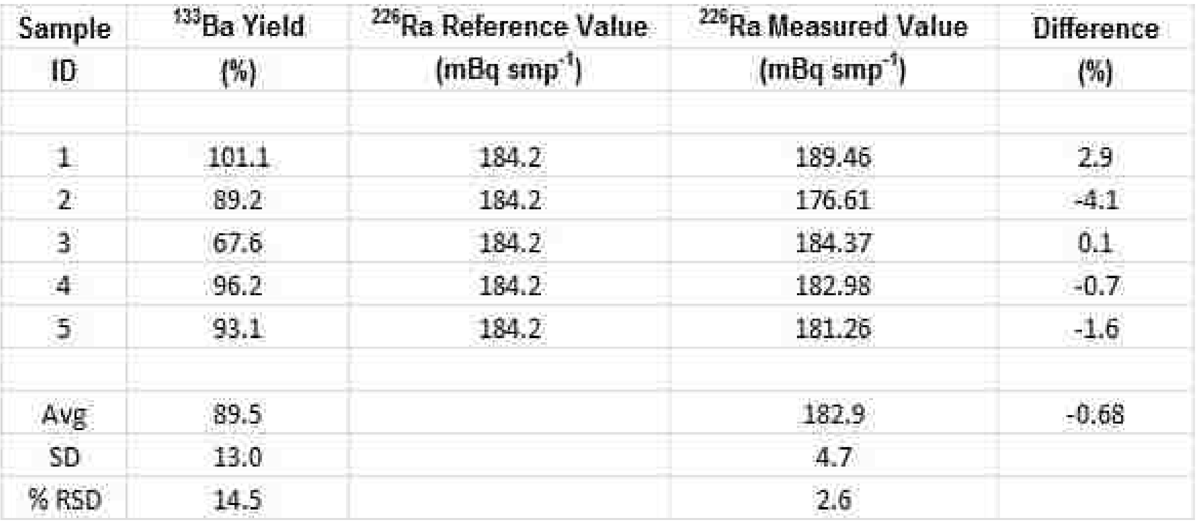
Table 39: Ra-226 Results for Spiked Steel Samples



Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	86.9	73.68	70.43	-4.4
2	90.6	73.68	77.85	5.7
3	86.9	73.68	77.36	5.0
4	90.5	73.68	75.66	2.7
5	88.9	73.68	72.99	-0.9
Avg	88.8		74.9	1.6
SD	1.8		3.1	
% RSD	2.0		4.2	

Table 40 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 182.3 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 182.9 mBq, with a -0.7% bias and SD of 4.7 mBq. The average tracer recovery for ^{133}Ba was 89.5% ± 1.8% (SD). It is not known why sample aliquot #3 has a lower ^{133}Ba yield, however it is interesting to note that without this sample aliquot the average ^{133}Ba yield is 94.5%.

Table 40: Ra-226 Results for Spiked Steel Samples



Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	101.1	184.2	189.46	2.9
2	89.2	184.2	176.61	-4.1
3	67.6	184.2	184.37	0.1
4	96.2	184.2	182.98	-0.7
5	93.1	184.2	181.26	-1.6
Avg	89.5		182.9	-0.68
SD	13.0		4.7	
% RSD	14.5		2.6	

The MDA (Minimum Detectable Activity) for ^{226}Ra using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie, as shown in equation (11): [75]

$$MDA = [2.71+4.65\sqrt{B}]/ (CT*R*V*Eff*\mathbf{A}*0.060) \qquad (11)$$

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 steel aliquot, the method MDA for ^{226}Ra with a 16 hour count time is ~500 uBq g^{-1}. Shorter count times may be used in an emergency.

It should be noted this steel digestion method could be coupled with ICP-MS, however, the minimum detectable concentration is about 1 Bq g^{-1} for a 1 g steel sample, much higher than alpha spectrometry. [105] In addition, the isobaric interference of ^{88}Sr (82.58% natural isotopic abundance) + ^{138}Ba (71.7% natural isotopic abundance), on ^{226}Ra by ICP-MS must be addressed. Both Sr and Ba can be removed using an extraction chromatographic resin containing an 18-crown-6 derivative (Sr Resin, Eichrom Technologies). [100]

8.5 Conclusions

A new rapid method to determine ^{226}Ra in emergency steel samples has been developed that effectively digests steel samples, such as those that may be received in a radiological emergency or from routine nuclear decommissioning. The new method features a rapid preconcentration and separation of ^{226}Ra with high chemical yields and effective removal of matrix and alpha emitting interferences. The method is rugged and very flexible, allowing several different measurement options.

8.6 Acknowledgment

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CHAPTER 9: CONCLUSIONS

The primary focus of this dissertation was to determine if new, highly reliable rapid methods could be developed for urban building materials such as limestone, marble, concrete, granite and steel. The various challenges of each matrix type were discussed and challenges with each type of matrix were addressed, including total dissolution of refractory particles that may be present from an IND, RDD or nuclear accident. The chemical yields for each method were optimized for each sample matrix, and sample matrix interferences were successfully removed using the swift purification methods employed. These methods can be utilized in the immediate and recovery phases following a radiological event to provide rapid, reliable measurements for the sample matrices tested.

9.1 Limestone and Marble Study

A new rapid fusion method to determine actinide isotopes, ^{89}Sr and ^{90}Sr in limestone and marble samples was successfully developed that allows the fast separation of these isotopes with high chemical yields and effective removal of interferences. It has been validated by adding MAPEP 24 soil standard containing refractory ^{239}Pu to the limestone and marble test samples. The sodium hydroxide fusion technique is swift and robust, and the preconcentration steps are designed to reduce calcium interference for the high levels present in limestone and marble. Strong acid was added to the sodium hydroxide fusion matrix to reduce the matrix alkalinity as well as to reduce high levels of carbonate This step reduced Ca precipitation during the iron/titanium hydroxide precipitation and helped optimize the rapid method performance. Additional phosphate was optimized to effectively precipitate the relatively high levels of calcium present and coprecipitate the analytes of interest. The use of DGA Resin for Am/Cm separations was utilized with steps tailored to remove calcium in that separation as well. The adverse impact of Ca on Am/Cm retention on DGA Resin was minimized by utilizing nitric acid level that is relatively high during the column loading step. In this case the total nitrate was 8M or higher, reducing Ca retention. The stacked extraction chromatographic cartridge approach provided rapid sequential purification of the analytes. The high chemical yields were an strong indicator the challenges were overcome and that the method is rugged. The use of Sr Resin to measure total ^{89}Sr +^{90}Sr, followed by a short ingrowth time, and the subsequent collection and purification of ^{90}Y using DGA Resin to determine ^{90}Sr was observed to be very effective. This is particularly important when there are high ^{89}Sr/^{90}Sr activity ratios that one would expect following an IND detonation.

9.2 Concrete Study

A new rapid fusion method to determine ^{89}Sr and ^{90}Sr in 5g to 10 g concrete samples was developed that allows the separation of Sr isotopes with high chemical recoveries and effective elimination of sample matrix interferences. The larger amount of calcium and silicates were successfully overcome with novel preconcentration steps to remove these sample matrix interferences. This was carried out by scaling up the amount of sodium hydroxide, phosphate levels, acid volumes used to effectively accommodate the 5 to 10g of concrete sample aliquots, which contained high levels of Ca and silicates. Several analytical options were presented that offer significant method flexibility, depending on which Sr isotopes are required. One method collects, purifies and measures ^{89,90}Sr in 5 g concrete aliquots. Another approach allows the immediate determination of ^{90}Sr in 10 g concrete aliquots with no waiting for ^{90}Y ingrowth. The total digestion and separation method was rapid (< 6 hrs), Count times may be adjusted depending on the detection limit and uncertainty requirements. It was shown in this study that detection limits below 1 mBq g^{-1} can be achieved to meet new, lower regulatory limits for nuclear facility decommissioning. The new method to rapidly collect and purify ^{90}Y from 10 g concrete samples so that ^{90}Sr can be measured without waiting on ^{90}Y ingrowth worked well, and significantly advances the capabilities needed to measure ^{90}Sr at very low levels to meet regulatory disposal limits.

9.3 Granite Study

A method for the determination of actinide isotopes in granite samples employing a rapid fusion approach has been developed that allows the separation of these isotopes with high chemical yields and effective removal of chemical and radiological interferences. It has been validated by adding MAPEP 24 soil standard containing refractory ^{239}Pu isotope to the granite samples. One of the challenges with granite samples is the hardness of these rock samples. The sodium hydroxide fusion technique employed is rapid and very effective, and was found to facilitate total digestion of the granite samples. The stacked extraction chromatographic cartridge approach utilized offers many separation options, depending on the actinide isotopes required. Sequential separation capability was shown to be effective. Problems with high rare earth levels in the granite were overcome for Am/Cm purification and assay by utilizing an additional TEVA Resin separation that employed thiocyanate complexing. The rare earths were removed sufficiently to enable good alpha peak resolution, important for reliable quantification of Am and Cm isotopes. The method was shown to fast and robust for 1 gram granite samples.

9.4 Steel Study

9.4.1 Plutonium Isotopes Method for Steel Samples

A new rapid method to determine plutonium isotopes in steel samples was developed that effectively digests steel samples (or alternately steel plus concrete) for samples received in a radiological emergency or from routine nuclear decommissioning samples. The new method features a rapid preconcentration and separation of Pu isotopes with high chemical yields and effective removal of sample matrix interferences. One of the challenges with processing steel samples is the very high iron content. The LaF_3 precipitation effectively removed the iron, which stayed in the HF supernate. This was a very important step in the chemical processing to allow the successful analysis of steel samples. While the enhanced digestion of the steel by adding HF to aqua regia was found to successfully dissolve the refractory Pu added, an acid digestion coupled with a sodium hydroxide fusion was also presented as an option to add even more ruggedness if that approach were deemed necessary.

9.4.2 ^{89}Sr and ^{90}Sr Isotopes Method for Steel Samples

A new method to determine ^{89}Sr and ^{90}Sr isotopes in steel samples was developed that effectively digests steel samples (or steel plus concrete). The new method offers rapid separation of these Sr isotopes with high chemical yields and effective removal of sample matrix interferences such as ^{137}Cs. Cesium-137, a fission product that may be present in samples, has a half-life of 30.08 years. 94.7 percent of ^{137}Cs decays by beta emission to the metastable nuclear isomer of barium: ^{137m}Ba. [106, 107] The remainder directly populates the ground state of ^{137}Ba, which is stable. Ba-137m has a half-life of 153.1 seconds, and decays to ground state by emission of gamma rays having energy 661.7 keV. Since ^{137}Cs can interfere with beta emission measurements of Sr isotopes, it must be effectively removed. The preconcentration step using

CaF_2 removes most of the iron present as well as ^{137}Cs that may be in the sample. 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. It was shown that Sr Resin could be used to determine ^{89}Sr and ^{90}Sr, while ^{90}Sr could be measured using DGA Resin to collect and purify ^{90}Y. The chemical yields for all the Sr methods developed for steel had chemical yields above 90%, indicating method ruggedness.

9.4.3 ^{226}Ra Method for Steel Samples

A new rapid method to determine ^{226}Ra in emergency steel samples has been developed that effectively digests steel samples, such as those that may be received in a radiological emergency or from routine nuclear decommissioning. The new method features a rapid preconcentration and separation of ^{226}Ra with high chemical yields and quick removal of the steel matrix and alpha emitting interferences. The collection of Ra along with CaF_2 was achieved by keeping the sample solution acidity very low to facilitate effective coprecipitation, since RaF_2 typically has a higher solubility than CaF_2.This approach has a sample preparation time of ~8 hours for steel samples, has a very high tracer yield (>88%), and removed interferences effectively. A ^{133}Ba yield tracer was used so that samples can be counted immediately following the separation method, avoiding lengthy ingrowth times that are required in other methods, such as utilizing ^{225}Ra. The blend of more traditional cation exchange with extraction chromatography was shown to be a very good strategic approach. It offered reliable removal of Ca and very good removal of alpha-emitting interferences.

9.5 Future Work

These rapid methods develop share certain common characteristics, such as fast, effective sample digestion and novel preconcentration steps, swift extraction chromatographic separation, and reliable, rapid quantification. There may be opportunities to further this work. Expanding the study of steel samples to include additional actinide isotopes is perhaps an option. In addition, application of ICP-MS measurements for plutonium isotopes measurements instead of employing only alpha spectrometry would also be of interest. Removal of ^{238}U to eliminate mass interference on ^{239}Pu will be critical in this work to allow measurement of ^{240}Pu/^{239}Pu ratios by ICP-MS. Future work regarding other urban building material matrices such as stucco or clay pipe roof, or slate roof material may be of interest for continued studies, in readiness for an emergency response radiological event. In addition, quick methods for the analysis of foods such as ^{89,90} Sr in cheese, and ^{226}Ra in fish and beef samples will likely be of great interest. There may be value in new methods for ^{210}Po in solid samples such as soil and air filter samples, using rapid separation and microprecipitation of sample test source instead of using the older auto-deposition method on spinning disks. Autodeposition can suffer from alpha spectrum peak degradation issues when difficult samples are encountered. Po-210 volatilization that may occur on heating, must be taken into account. [108, 109]

APPENDIX A: ADDITIONAL DETAILS ON SEPARATION METHODS UTILIZED

This section provides a summary of the sample preparation and extraction chromatographic techniques employed in this study, including methods for actinide separations, strontium and radium.

A.1 Extraction Chromatography Method for Plutonium, Neptunium and Uranium

Plutonium and neptunium isotopes were separated on TEVA Resin, while uranium isotopes were separated using TRU Resin. TEVA Resin enables one to selectively retain all tetravalent actinide ions (as their nitrato complexes) over a wide range of nitric acid concentrations. The retention of Pu (IV) and Np(IV) is at a maximum around 3M HNO_3, much lower than a strong-base anion exchange resin such as Dowex 1X8 which requires approximately 8M HNO_3 to achieve the maximum uptake. The stationary phase in TRU resin consists of a mixture of carbamoylmethylphosphine oxide derivative (CMPO) and tri-n-butyl phosphate (TBP). The CMPO-TBP combination increases significantly the retention of trivalent actinides, e.g. Am(III), as well as tetra and hexavalent actinides [46].

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

A valence adjustment was performed on the column load solution by adding 1mg Fe (as iron nitrate) and 1.25 mL 1.5M ascorbic acid (AA) with a three minute wait step to reduce plutonium to Pu(III) (and Np to Np(IV). It is convenient to allow the Fe added to be reduced to Fe(II) by ascorbic acid in the load solution, rather than adding Fe(II) ions directly, since these solutions have short shelf lives (~1 week) due to air oxidation. Following the reduction step, 1 mL 3.5M $NaNO_2$ was added to oxidize plutonium to Pu(IV). This ensures that Pu present is retained on TEVA Resin as Pu(IV). The ascorbic acid/ Fe (II) combination, however, offers effective plutonium valence reduction of Pu isotopes to Pu(III) and thus enable effective adjustment of plutonium to Pu(IV) upon the addition of $NaNO_2$.

Figure 11 shows the column separation method used. TEVA Resin cartridges and TRU Resin cartridges were stacked and placed on the vacuum box (TEVA Resin on top) and 50 mL centrifuge tubes were used to collect rinse or final purified fractions.

After the valence adjustment as described above, the sample solution was loaded onto the stacked TEVA and TRU Resin cartridges at ~1 drop per second. After the sample was loaded, a tube rinse of ~ 5 mL 6M HNO_3 + 50 µL 30wt% H_2O_2 was transferred to the TEVA and TRU resin cartridges and allowed to pass through the resin at ~1-2 drops per second. Hydrogen peroxide ensures than uranium that may have been reduced to U(IV) (possibly due to traces of Ti(III) remaining from the precipitation steps) is reoxidized to U(VI) and not retained as (U(IV) on TEVA Resin. Tracer yields for U increased when hydrogen peroxide was added, indicating a reduction in U(IV) loss on TEVA Resin.

The column reservoir was replaced to ensure maximum removal of matrix interferences and the cartridges were rinsed with 10 mL of 3M HNO_3 at ~2 drops per second. The TEVA Resin and TRU Resin cartridges were separated and processed separately on two different vacuum boxes simultaneously to minimize the sample preparation processing time.

Each TEVA Resin column was rinsed with 10 mL of 3M HNO_3 at ~2 drops per second, followed by Th elution into to new labeled 50 mL tubes with 15 mL 9M HCl at 1-1.5 drops per second. After the elution of Th from TEVA Resin, column rinses of 5 mL 9M HCl at 1-2 drops per second followed by 5mL 3M HNO_3 at ~2 drops per second were used to remove any traces of Th and reduce any extractant bleed-off. Pu is eluted at ~1 drop per second with 20 mL of 0.1M HCl-0.05M HF-0.01M $TiCl_3$ for measurement by alpha spectrometry. A reductant is needed to reduce Pu (IV) to Pu(III) to facilitate complete elution of Pu from TEVA Resin.

The TRU Resin cartridge was rinsed with 5 mL 8M HNO_3 at ~1-2 drops per second. Twenty milliliters of 4M HCl-0.2M HF-0.002M $TiCl_3$ was added at 1-2 drops per second to TRU Resin to remove any Th, Am, Cm, Pu, Np, and Po present, followed by 10 mL 8M HNO_3 to ensure complete polonium (Po) removal. Po-210 has an overlapping alpha energy with the ^{232}U tracer used and thus removal of ^{210}Po is very important to achieve reliable tracer yield measurements for uranium. For example, a 20% positive error in the ^{232}U tracer measurement will result in a 20% negative bias in the uranium results. After changing the column reservoirs and connector tips, U was eluted effectively with 15 mL of 0.1M ammonium bioxalate at ~1 drop per second, with breaks the analyte-extractant complex.

Once the purified actinide isotopes are eluted, they must be prepared in a sample test source geometry for counting. Cerium fluoride microprecipitation was used to prepare the purified samples for alpha spectrometry counting. For uranium samples, 100 µg Ce, 0.3-0.5 mL 20% $TiCl_3$ and 1 mL 28 M HF were added. Slightly higher mass of cerium was used for uranium than for Pu, Np, Am and Cm isotopes, since the mass of ^{238}U is typically higher dues due its lower specific activity. After mixing well by vortex mixing and waiting 15-20 minutes, the solution was filtered using a 25mm polypropylene filter (0.1 µm pore size disposable Resolve™ filter funnel, Eichrom Technologies, LLC). Each sample tube was rinsed with ~5 mL deionized water and added to the filters. The filters were then rinsed with 2-3 mL of ethanol to facilitate drying and affixed to adhesive disks (Environmental Express, Mount Pleasant, SC, USA). The filters were heated briefly under a heat lamp to ensure dryness, and minimize fluoride volatility that might damage silicon alpha spectrometry detectors.

A.2 Extraction Chromatography Method for Plutonium, Neptunium and Americium, Curium Separations

TEVA + DGA Resin as stacked cartridges are employed to rapidly separate Pu, Np and Am, Cm with this method (TEVA on top as in Figure 19). Am and Cm are separated from interferences using TEVA Resin in tandem with DGA Resin. DGA Normal resin utilizes N,N,N’,N’-tetra-n-octyldiglycolamide as an extractant, with straight chain C8 groups.

Am (III) and Cm (III) have very strong retention on DGA Resin in 3M HNO_3 nitric acid (k’ ~50,000) much higher than on TRU Resin (k’~100). [61] This has made achieving high yields for Am and Cm from very difficult sample matrices possible. TEVA and DGA Resins were obtained as 2 mL cartridges. As described above, small particle size (50-100 micron) resin was employed, along with the 24 position vacuum extraction system. The valence adjusted sample solution (Pu (IV) and Np (IV)) was loaded onto the TEVA + DGA Resin stacked cartridges at ~1 drop per second. Plutonium and neptunium are retained on TEVA Resin, and americium (and curium) are retained on DGA Resin. The DGA Resin separation for Am and Cm is described below.

After the sample was loaded onto the column, a tube rinse of ~ 5 mL 6M HNO_3 + 50 µL 30wt% H_2O_2 was transferred to the TEVA Resin + DGA Resin column and allowed to pass through the resin at ~1-2 drops per second. A rinse of 10 mL 3M HNO_3 was added to each stacked column at ~2 drops per second. The TEVA Resin and DGA Resin cartridges were separated and processed individually on two different vacuum boxes at the same time to collect the purified Pu and Am/Cm fractions for assay.

Fifteen milliliters of 3M HNO_3 were added to each TEVA Resin column at ~2 drops per second, followed by Th removal with 20 mL 9M HCl rinse at 1-2 drops per second. It should be noted that enhanced Th removal can be achieved by increasing the 9M HCl rinse on TEVA Resin as needed. Plutonium and neptunium are recovered from TEVA resin with 20 mL of 0.1M HCl-0.05M HF-0.01M $TiCl_3$.

The DGA Resin was rinsed with 10 mL of 3M HCl at ~2 drops per second to ensure complete Ca removal. Lanthanum and uranium were removed with rinses of 3 mL 1M HNO_3 and 20 mL 0.1M HNO_3 at ~1-2 drops per second. Removal of any thorium that may have bled through TEVA Resin, was achieved with 20 mL of 3M HNO_3-0.25M HF, taking advantage of the strong affinity of fluoride ions for Th(IV). Five milliliters of 4M HCl rinse removes any residual fluoride ions, and Am isotopes were eluted with 10 mL 0.25M HCl at ~ 1 drop per second. If rare earth removal was not required, Am and Cm were precipitated directly from the 0.25M HCl eluent solution using cerium fluoride microprecipitation.

If additional separation of Am/Cm from rare earth elements was required, the Am eluent solutions were transferred to 100 mL glass beakers using ~3 mL of concentrated nitric acid with 0.05mL of 1.8M sulfuric acid. The Am eluent solutions were evaporated to dryness on a hotplate and wet-ashed with 2 mL concentrated nitric acid and 2 mL 30 wt% hydrogen peroxide to destroy any residual extractant that may have bled off the resin. The samples were redissolved in 5 mL of 4M ammonium thiocyanate-0.1M formic acid, warming gently as needed. These solutions were loaded onto a TEVA Resin cartridge to remove any native rare earths present in the soil sample which can degrade alpha spectrometry peak resolution. The TEVA Resin cartridges were rinsed with 10 mL of 1.5M ammonium thiocyanate-0.1M formic acid. The original load solution beaker was rinsed with 5 mL of warm 1M HCl to ensure all the americium was removed from this beaker. The beaker rinse solution, followed by an additional 15 mL of 1M HCl also used to rinse the beaker, was passed through the TEVA Resin to recover the americium.

As noted above, cerium fluoride microprecipitation was used to prepare the purified eluents for alpha spectrometry counting. After adding 50 µg of Ce (as cerium nitrate), 0.5 mL 30 wt% H_2O_2 and 1 mL 28 M HF to each Pu eluent solution and waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable filter funnel). Each tube was rinsed with ~5 mL deionized water, followed by ethanol to facilitate drying. A similar approach was used for the Am/ Cm eluents. For Am/Cm, 40 µg of Ce (as cerium nitrate), 0.2 mL 30 wt% H_2O_2 and 1 mL 28 M HF were added. The use of less Ce, 40 µg Ce instead of 50 µg Ce, improves the peak resolution by depositing less mass on the filter, enhancing the resolution between ^{243}Am and ^{241}Am peaks in the alpha spectrum. This is important due to the close proximity of ^{243}Am and ^{241}Am alpha peaks. Table 1 shows the most abundant alpha energies for ^{243}Am and ^{241}Am. [107]

Nuclide	Half-Life (Years)	λ (s^{-1})	Abundance	α Energy (MeV)
^{241}Am	432.6	5.077×10^{-11}	0.848	5.486
			0.131	5.443
			0.0166	5.388
^{243}Am	7.37×10^{3}	2.98×10^{-12}	0.871	5.275
			0.112	5.233
			0.0136	5.181

Adding hydrogen peroxide to the Pu and Am/Cm precipitation steps provides additional decontamination from uranium isotopes by ensuring the U is present as U(VI), which does not carry on the CeF_3 precipitate.

A.2.1 ICP-MS Measurement Option for Plutonium

While alpha spectrometry was used in this work to demonstrate the effectiveness of the new methods, the Pu method can also be adapted so that Pu isotopes can be measured by ICP-MS. In this case ^{238}Pu, which has a high specific activity and very low mass, can be measured initially by alpha spectrometry, while ^{239}Pu, ^{240}Pu can be assayed subsequently by ICP-MS. The sample can be counted for ^{238}Pu by alpha spectrometry and then redissolved from the sample test source filter using warm 3M HNO_3-0.25M boric acid. The dissolved Pu isotopes can be processed quickly through TEVA Resin, eluted and measured by ICP-MS to determine the ^{239}Pu / ^{240}Pu ratio. The CeF_3 microprecipitation step with hydrogen peroxide present used to prepare the intial sample test source typically remove an additional 1000 x ^{238}U, so this approach, in combination with another TEVA Resin separation, can result in extremely high ^{238}U decontamination factors. If the redissolved sample is reprocessed through TEVA Resin, a Pu eluent solution of 0.05M HCl-0.025M HF-0.02M hydroxlyamine hydrochloride may be used to allow ICP-MS assay. [56, 110, 111, 112]

For enhanced ^{238}U removal to facilitate the measurement of ^{239}Pu and ^{240}Pu by ICP-MS, Pu can be eluted directly from TEVA Resin as Pu^{+3} (with 3M HNO3-0.1M ascorbic acid-0.02M Fe^{+2}) through a coupled UTEVA Resin cartridge (1mL) onto a stacked DGA Resin cartridge to achieve very high uranium decontamination factors (~$1x10^7$). This eliminates eluting and reloading Pu to TEVA Resin multiple times. After a single elution and rapid clean-up on DGA Resin, Pu isotopes can be eluted from DGA Resin with a 5 mL volume of 0.02M HCl-0.005M HF (or also with -0.01M hydroxylamine hydrochloride) and assayed by ICP-MS.

A.3 Extraction Chromatography Method for Sr-89,90 in Urban Matrices

Sr-89,90 was separated using Sr Resin (3 mL Sr Resin, by means of stacked 2 mL+1 mL resin cartridges) utilizing a method similar to that previously published for the determination of ^{89}Sr and ^{90}Sr in vegetation samples. [113] Figure 34 shows the Sr Resin separation employed.

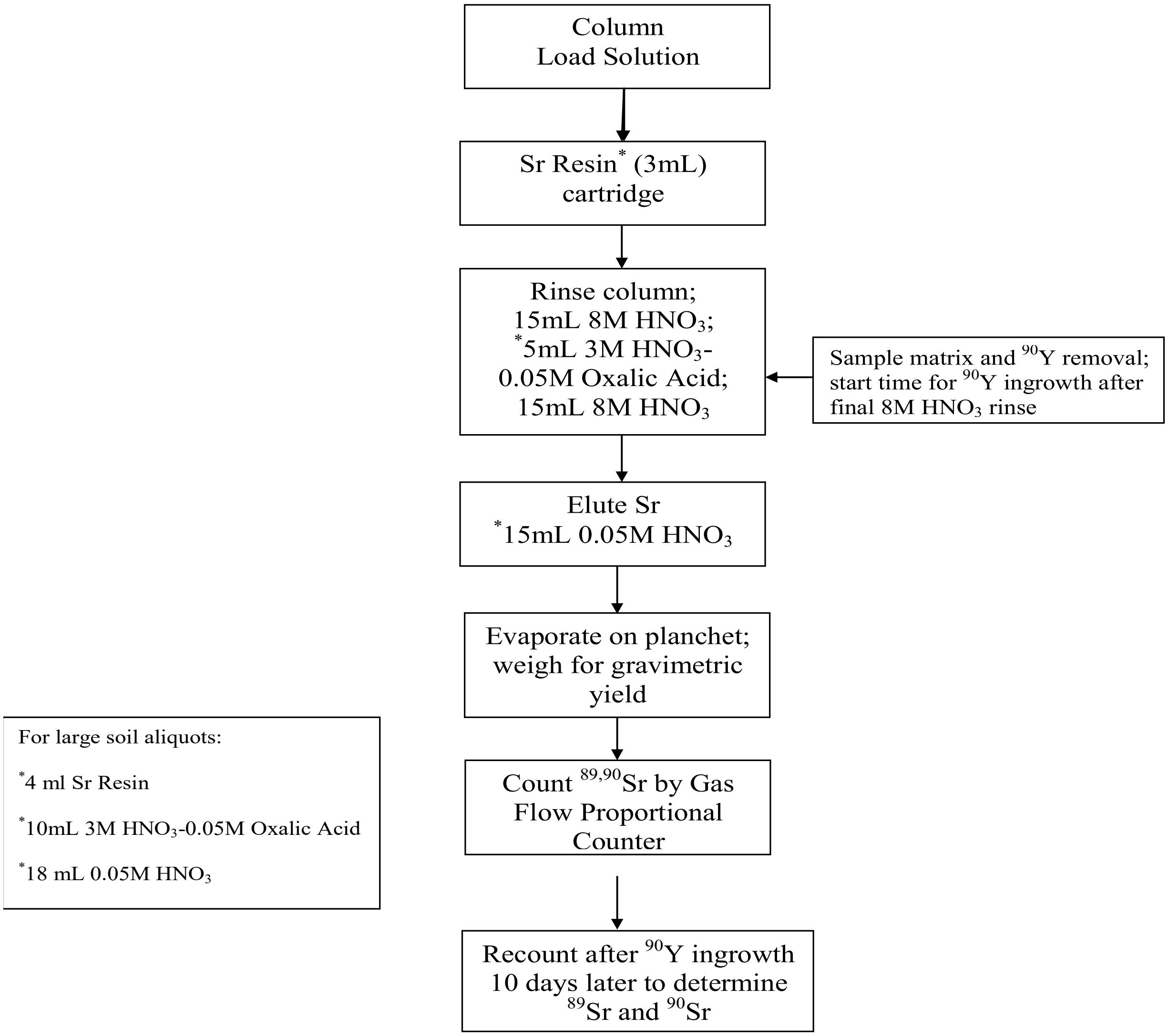

Figure 34: Rapid Column Separation for Sr-89/90 in Urban Matrices

The selectivity of Sr Resin for Sr^{+2} ions is based on the principle of ionic recognition, Retention is due to the favorable cavity size of the 18-crown-6 molecules with respect to strontium's ionic diameter [63]. The stationary phase consists of a dicyclohexano-18 crown-6 derivative dissolved in an aliphatic alcohol, 1-octanol.

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 the stacked cartridges (3 mL Sr Resin) with 15 mL 0.05M HNO_3 at ~1 drop per second. This eluent was then transferred to pre-weighed planchets and evaporated on a hot plate with medium heat to dryness. Two milliliters of 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 for an additional ~10-15 minutes on the hot plate. The dried planchets were allowed to cool and weighed to determine gravimetric carrier recovery. The planchets were then counted by simultaneous gas flow proportional counting for 60 minutes to determine $^{89/90}$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 the actual samples.

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. [81] 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 14 shows a DGA Resin separation method that may be used for urban matrices to collect and purify ^{90}Y following ^{89}Sr,^{90}Sr purification and a short ingrowth period. 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. 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. DGA Resin can be used to collect and purify ^{90}Y so that ^{90}Sr can be determined.

Figure 35 shows the DGA Resin method employed when ^{90}Y was collected directly from the 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 dissolution of the samples the yttrium was loaded onto DGA Resin cartridges. The DGA Resin was rinsed with 8M HNO_3 to remove Ca, Sr 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 the yttrium chemical yield. Sample results were corrected for the removal of 0.5% of the ^{90}Y eluent solution.

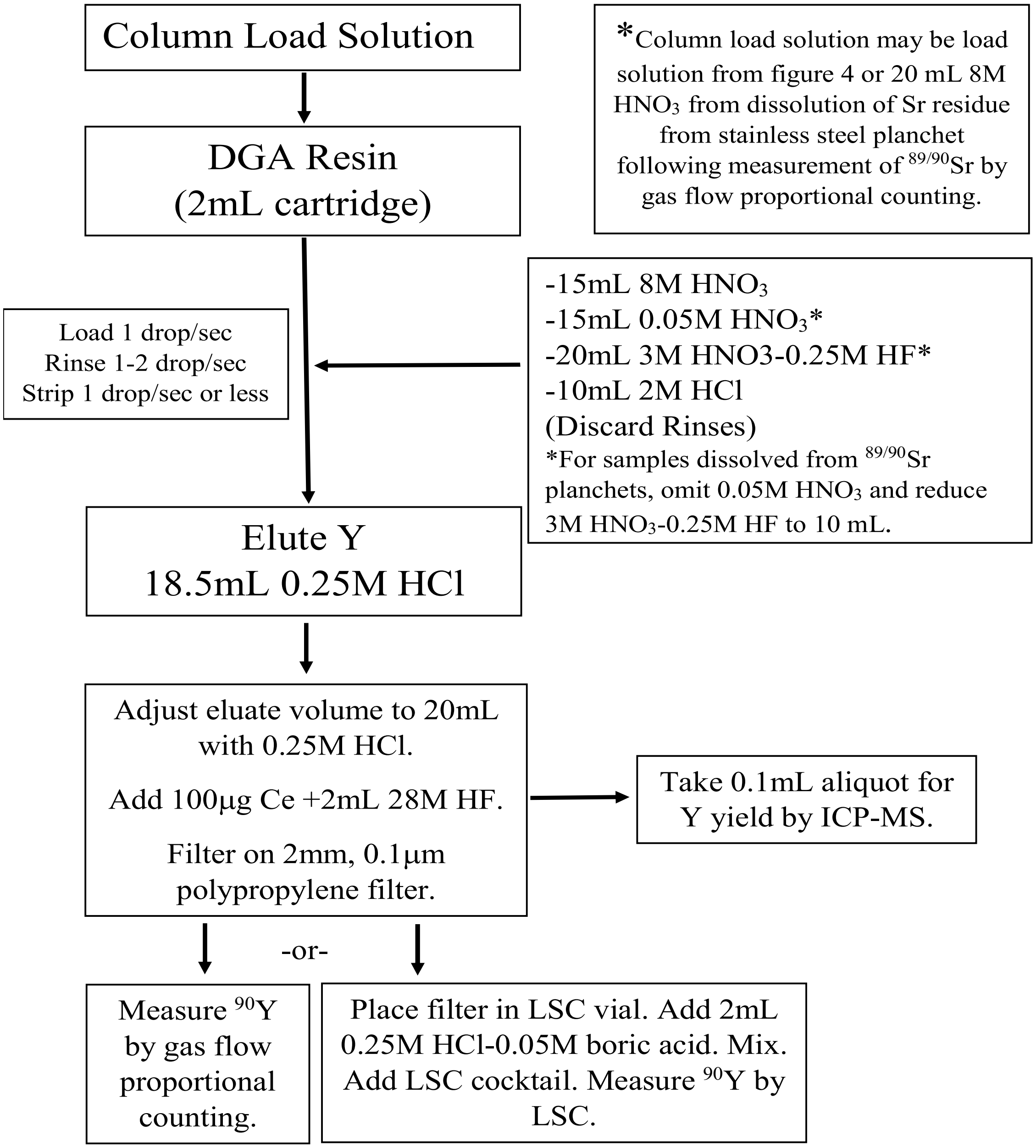

Figure 35. DGA separation for ^{90}Y to determine ^{90}Sr in Urban Matrices

A.4 Sr-89,90 Counting Methods Used in this Study on Urban Matrices

Two different measurement techniques were tested in this study, 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. For gas flow proportional counting, 25 mm polypropylene filters were used to collect the filtered YF_3 microprecipitate aand 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 20 mL 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 of Ecolite (MP Bioamedicals, Santa Ana, Ca) 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 scintillation cocktail. It was found 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 both 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. Additionally, LSC is a destructive analysis and does not allow secondary separation of ^{90}Y from the $^{89/90}$Sr sample to discriminate the ^{89}Sr and ^{90}Sr activities. If LSC is used then the only $^{89/90}$Sr discrimination technique available would be a 2-count method, where the sample is counted at two different times and the $^{89/90}$Sr activities are calculated by using a series of equations [81].

A.5 Cation Exchange -Extraction Chromatography Method for ^{226}Ra

Ra-226 was separated using a cation exchange-DGA Resin separation method. The resins employed in this work are strong acid cation exchange resin (50W-X8, H^+ form, 200-400 mesh) and DGA Resin. Figure 32 shows the column separation for radium which employs cation exchange resin for the initial sample load and rinse steps, followed by elution of ^{226}Ra through DGA Resin to remove alpha emitting interferences. The cation exchange resin column contained 5 grams of resin (200-400 mesh), although slightly more resin can be used for larger sample aliquots or for samples containing large amounts of Ca, such as steel with residual soil or concrete. The cation exchange resin columns were set-up on a vacuum box with a large inner liner to collect rinses. However, vacuum is normally only needed to get the flow started, and gravity flow can then be used for the bulk of sample elution prior to the addition of the DGA Resin cartridges.

Prior to loading the sample, the cation resin was cleaned as follows, using gravity flow rates of 3-4 drops per second, to ensure very low blanks: 20 mL deionized water, 20 mL 6M HCl, 10 mL deionized water, and 10 mL 0.5M HCl. To each sample load solution, 3 mL 1.5M ascorbic acid was added to reduce Fe (III) to Fe (II) to minimize retention on the cation resin of any residual iron present. The samples were loaded at ~1 drop per second. After sample loading, the column was rinsed at ~1-2 drops/second with 25 mL 3M HCl to remove Ca^{2+}, Pb^{2+}, Bi^{3+} and UO_2^{2+} ions that may be present in the sample.

After the 3M HCl rinse, a 2 mL DGA cartridge was placed onto the bottom of each cation exchange column, and a clean labeled tube was added below each column to collect the purified eluent. To elute Ba/Ra from each cation resin column, 35 mL 5M HNO_3 was added to each column and eluted at ~1 drop per second. The eluents were transferred to 250 mL glass beakers, and sample tubes were rinse with 3 mL 30 wt% H_2O_2. The tube rinses added to each sample beaker, and samples were quickly taken to dryness on a hotplate. The sample residues were redissolved in 10 mL 1.5M HCl with heating on a hot plate, transferred to clean 50 mL tubes. The beakers were rinsed with two 7 mL volumes of 1.5M HCl to complete transfer to the 50 mL tubes, yielding purified radium fraction volumes of ~20 mL 1.5M HCl total. The purified samples are now suitable for final microprecipitation of ^{226}Ra with $BaSO_4$.

Three grams of ammonium sulfate were added to each sample, and tubes were mixed well to complete dissolution. Fifty micrograms of barium, from a 1 mg/mL stock solution, were added to each sample, and the tubes were mixed well. Five milliliters isopropanol were added to each sample to reduce barium sulfate solubility, and tubes were mixed again. The tubes were iced for 15 minutes and periodically vortexed (beginning, middle and on removal from ice). The samples were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve- Filter-Eichrom Technologies) to collect the microprecipitate, and filters were rinsed with 3-5 mL of 20% isopropanol. The filters were dried under a heat lamp, counted by gamma spectrometry to determine ^{133}Ba yield and alpha spectrometry to measure ^{226}Ra. The disposable Resolve Filters funnel units were used on vacuum boxes with a liner to save time.

The rapid extraction techniques described above were highly effective at rapidly purifying the isotope of interest and removing interferences. While the extraction chromatographic resins employed are often different, the separation principles are very similar. Rapid flow rates and small particles sizes were employed to minimize analysis times, critical following a radiological emergency where results are needed almost immediately.

APPENDIX B: SPECIAL PERMISSIONS

Figure 2: reproduced from The Chemistry of the Actinide and Transactinide Elements (3rd ed., Volumes 1-5) Editors: Morss, L.R.; Edelstein, N.; Fuger, J.; Katz, J.J., (Eds.) page 1168 with the permission of Springer

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The goal of this research is to develop new, rapid techniques that can be used with a variety of urban matrices and that utilize rapid digestion and preconcentration methods, coupled with fast extraction chromatography techniques. These new methods will need to overcome challenges associated with each sample type. Rugged digestion of refractory particles, that may be present resulting from the intense heat and pressure of a detonation, was tested for a wide range of urban matrices. This research focuses on the rapid measurement of actinides, ^{89}Sr, ^{90}Sr and ^{226}Ra isotopes in limestone, marble, concrete and steel samples.

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Patents

Patent Actinides in Large Soil Samples	SRS-06-006
Patent Actinide Recovery Method	SRS-97-034

Savannah River Site

Aiken, SC
(January 2003 -Present)

Senior Fellow Scientist
Made significant improvements resulting in laboratory cost savings
Pioneered the development of many new radioanalytical methods for environmental, bioassay and food samples, providing technical assistance to EPA, DOE, DOD, CDC, FDA, Joint Research Centre (Ispra, Italy)
In-depth knowledge of extraction chromatographic resins with experience and knowledge of actinide chemistry
Extensive knowledge of sample preparation techniques for a wide range of sample types

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Methods development and technical support for SRS Canyon, HB Line Operations and high-level waste tank analyses, mixed oxide campaigns

Environmental Management Support

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Consultant on rapid methods technology and method validation to assist EPA with solid urban matrices following radiological event and hydraulic fracturing wastewater methods

Recent Publications

Maxwell, S.; Culligan, B.; Noyes, G.; Jones, V.; Nichols, S.T.; Bernard, M., Rapid determination of ^{237}Np and Pu isotopes in large soil samples by inductively-coupled plasma mass spectrometry, *Anal Chim Acta*., **2010,** 682 (1-2):130-6

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Men, W.; Zheng, J.; Wang, H.; Ni, Y.; Aono, T.; Maxwell, S. L.; Tagami, K.; Uchida, S.; Yamada, M., Establishing rapid analysis of Pu isotopes in seawater to study the impact of Fukushima nuclear accident in the Northwest Pacific*, Scientific Reports*, **2018**, 8,1892 | DOI:10.1038/s41598-018-20151-4 1.

Presentations

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