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INTERFERENCE EFFECTS OF URBAN RUBBLE ON THE RADIOANALYTICAL ANALYSIS OF STRONTIUM

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ABSTRACT

Most current radioanalytical protocols have been developed for the analysis of air, water, soil and bioassay samples. While these protocols build the foundation of operational environmental monitoring, they are not necessarily suitable for the analysis of samples that will be encountered in the aftermath of a nuclear incident. In such a situation, it will be important to characterize the isotopes of interest present in the affected area to obtain signatures for nuclear forensics and ensure the appropriate response. Specifically, this research is aimed at the determination of strontium-90 and its separation from zirconium-90 in a post-detonation situation.

Strontium-90's relatively long half-life (28.79(6) years) and high fission yield, along with its daughter's high energy beta decay (^{90}Y at 2.281 MeV) make it one of several materials ideally used in radioisotope thermoelectric generators (RTGs) in remote corners of the globe. Unfortunately, many of these RTGs remain in service with little to no security around them. Couple this with ^{90}Sr and ^{90}Y being pure beta emitters requiring relatively little shielding to conceal and ^{90}Sr preferentially depositing in bones, increasing the likelihood of bone or blood cancer, when ingested or inhaled and it is easy to see why these RTGs would be appealing targets for terrorist to obtain material for a so-called "dirty bomb". Following an attack of this nature, it will be important to quantify the total amount of strontium dispersed and to determine if this is equivalent to known missing sources or some fraction thereof, indicating the possibility of multiple attacks with smaller amounts of activity. By separating the ^{90}Sr from its stable grand-daughter ^{90}Zr, it also is possible to age the material originally used in the improvised device and provide insight on where it may have come from or who may have originally manufactured it.

Due to the likelihood of such a device being used in an urban or metropolitan area, it is crucial to have procedures that can be used to rapidly and accurately separate and determine radioactive

materials from matrices found in these environments. Of particular interest for nuclear forensics are methods that can be applied to the analysis of concrete, steel, and glass.

Chromatographic resins have been used for radioanalytical separations for several years now, and a large amount of data has been published on the retention capabilities of many of these resins for a wide variety of elements that can be found in environmental samples. Little can be found, however, on the effect that matrix constituents present in debris samples can have on analyte uptake. This results in potentially very complex pre-concentration methods that slow the throughput of samples. If the effects of matrix constituents could be quantified, ways to streamline or, in some cases, totally eliminate these pre-concentration steps may arise. To this end, the research described here concentrates on characterizing the interference caused by various constituents of urban matrices, as well as alternative acid conditions that could be used for separations based on dissolution procedures likely to be used in a real world scenario.

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CHAPTER 1: INTRODUCTION

1.1 Motivation

Following the terrorist attacks of the last twenty years, the threat of a malicious organization deploying a radiation dispersal device (RDD) has, unfortunately, become a concern.[1] An RDD, or "dirty bomb," is much simpler to build and much more "cost effective" than fabricating a fission device, because it contains materials that are much easier to obtain.[2-4] While it is generally accepted that an RDD would not cause the physical devastation of a fission device, the use of one would likely cause significant public panic and economic disruption, as well as long term loss of property use.[2-3, 5]

Two of the key factors determining the impact of an RDD attack are the quantity and type of radiological material employed. Isotopes important in the discussion of RDDs include the alpha emitters ^{238}Pu, ^{241}Am, and ^{252}Cf, the beta/gamma emitters ^{60}Co, ^{137}Cs, and ^{192}Ir, and the pure beta emitter ^{90}Sr.[3, 6] Taking the possible modes of acquisition a terrorist organization may employ into account, as well as factors such as the breadth of use, security, and sheer number of sources in circulation, most concerned organizations agree that ^{137}Cs, ^{60}Co, ^{192}Ir, and ^{90}Sr pose the most plausible risk to society.[6]

In addition to the factors mentioned above, ^{90}Sr is also considered to have a high radiotoxicity due to the fact that it is chemically similar to calcium, which causes it to be sequestered in bone, and has a fairly long biological half-life (between 14 days and 30 years).[7-9] Strontium-90 and its daughter ^{90}Y are both pure beta emitters, which means that an RDD equipped with ^{90}Sr would require significantly less shielding than a device with a similar amount of one of the other plausible gamma-emitting nuclides mentioned above. While a pure alpha emitter would require even less shielding than a pure beta emitter, those listed also have gamma decay modes associated with them and their daughters, making them significantly easier to detect than ^{90}Sr. Quantification of radioactive strontium dispersed by an RDD would also be much more difficult without first isolating the isotope due to the significant attenuation of beta particles by the debris it would be incorporated into. These factors make ^{90}Sr an isotope of major interest.

Despite this interest, the vast majority of procedures developed for the detection of ^{90}Sr are for environmental samples.[10-37] While these tend to offer excellent detection limits and have been verified to work on their designated matrices, they may not be applicable to the unique compositions of urban environments. This work aims to determine if one of the most popular methods for strontium separation, extraction chromatography, can be applied to urban materials such as steel, cement, and concrete.

1.2 Dissertation Overview

Chapter 1 provides an introduction and background on strontium extraction methods, as well as information on chronometry. Chapter 2 describes the procedures used in the majority of the work carried out as part of this thesis. It describes batch and column studies, as well as the materials and instrumentation used to make measurements. Chapter 3 presents data collected on the characteristics of modern extraction chromatography columns and how the use of vacuum technology can affect elution profiles. The data contained in this chapter has been published as an article in the Journal of Radioanalytical and Nuclear Chemistry.[38] The next portion of this work covers the separation of strontium from urban material matrices using conventional acid systems, with the separation of strontium from steel components being covered in Chapter 4, while the separation from concrete components is found in Chapter 5. At this point, the work shifts to cover digestion methods and alternative matrices for extraction chromatography. Chapter 6 focuses on the retention of strontium by Sr Resin using alternative acid matrices and mixtures of acids. Chapter 7 covers the use of alkaline fusion methods for sample digestion and evaluates their potential improvement. Some broad conclusions and the impact of this work on nuclear forensics are described in Chapter 8, as well as possible directions of future work.

1.3 Project Goals

While an RDD would not achieve the incorporation observed due to the heating associated with an improvised nuclear device, some evidence indicates that the explosive force used to disperse the radioactive material will allow deeper penetration than would necessarily be associated with a contamination event or normal operation at a nuclear power plant.[39-40] This would complicate the use of simple dose rate mapping for the quantification of strontium distributed. The ultimate goal of this research, therefore, is to determine if strontium can be accurately quantified if it is incorporated into urban materials to an extent that precludes simple decontamination efforts. By coupling quantitative data collected via sampling with a dose rate map, a much more accurate estimate of activity dispersed could be achieved. This research is evaluating the impact of urban material constituents on the retention of strontium by commercially available extraction chromatography resin in order to determine if the separations required to make a quantitative measurement can be accomplished. In the same vein, several acid mixtures are being examined to see if lengthy drying/reconstitution steps could be eliminated from established procedures without decreasing the accuracy of these measurements.

1.4 Background

1.4.1 Radiation Dispersal Devices

RDDs are non-fission devices "designed to disseminate radioactive material in order to cause destruction, damage, or injury."[41] Such devices can be separated into two distinct categories, passive and active dispersers. Passive RDDs would spread radioactive material through aerosolization or by simply allowing people to unwittingly spread the contamination via their everyday movements, and also includes placing radioactive material in a location where many people would be exposed without necessarily dispersing it over a large area. Active RDDs, on the other hand, would use conventional explosives to disperse their radioactive payload over an area as well as potentially causing physical damage.[3, 6, 42] In either case, the physical damage caused by an RDD would be minimal, if not nonexistent, but such a device would nonetheless cause significant economic disruption and public fear and could potentially result in the loss of property use for a significant period of time.[2-3, 5] Even an active RDD would likely cause little physical damage, mostly attributed to the explosives used to disperse the material, but the public level of fear associated with anything termed "radioactive" would likely cause widespread panic as damaging to public morale and economic activity as a fission device.[2] For these reasons, an RDD is often referred to not as a weapon of mass destruction, but a weapon of mass disruption.[2]

RDDs are an inherently more plausible terrorism threat than nuclear weapons, because they do not require the significant infrastructure or the sophisticated delivery and detonation systems required of fission devices.[3-4] In addition to their relative simplicity, a much greater variety of acquisition routes are available for the non-weapons grade nuclear material that could be used in an RDD. These include, but are not limited to, finding an orphaned source, stealing it from a legitimate owner/user, or even posing as a legitimate user and attempting to purchase it.[4] Indeed, of the 188 incidences of radioactive materials outside of regulatory control reported in 2015, roughly half involved materials suitable for use in an RDD, with one of these being an individual trying to sell material to ISIS.[43] While theoretically any radioactive material could be used in an RDD, generally only seven to ten nuclides are considered at high-risk of being used in a dirty bomb based on a few key properties used to determine security risk, including energy and mode of decay; half-life; quantity of material; shielding requirements; portability; prevalence of use; and dispersability of the source material.[6, 44] The nuclides generally included based on these parameters are the α-emitters ^{241}Am, ^{252}Cf, ^{238}Pu, ^{210}Po, ^{226}Ra, the γ/β emitters ^{137}Cs, ^{60}Co, ^{192}Ir, and ^{75}Se, and the pure β^- emitter ^{90}Sr.[2, 6, 44]

According to *Ferguson et al.*, who reviewed incidents related to radiological source accidents and illicit trafficking, a subset of the nuclides mentioned above, including ^{60}Co, ^{137}Cs, ^{192}Ir, and ^{90}Sr, warrants heightened focus.[6] This work centers on ^{90}Sr in particular, because it was widely used in large quantities in radioisotope thermoelectric generators (RTGs) during the cold war. Over 1,000 RTGs were manufactured by the Soviet Union alone for use as power sources for remote lighthouses, navigational beacons, and other military facilities, with activities ranging from 1,000 to 10,000 TBq.[1, 4, 6, 45] While RTGs are typically used in hard-to-reach areas, they have also historically had inadequate security measures. As they have been slowly replaced with less dangerous power sources (i.e. solar panels, wind turbines, and batteries), they have frequently been found vandalized or completely missing.[45]

In addition to this lack of security, ^{90}Sr is an attractive target for terrorists due to its relatively long half-life of 28.78 years and its decay via pure beta emission. While ^{90}Sr only has a decay energy of 0.546 MeV, it decays to ^{90}Y, which is also radioactive and has a half-life of 64 hours and a decay energy of 2.281 MeV, before becoming stable ^{90}Zr. The fact that both ^{90}Sr and ^{90}Y are pure beta emitters also means that a dirty bomb utilizing ^{90}Sr would be more difficult to detect than the other candidates. Finally, because it is similar in size and charge to calcium, strontium tends to be sequestered in bone, which leads to a long biological half-life and increases the risk of developing cancer if ingested.[7-9]

1.4.2 Chronometry

Nuclear forensics can be loosely defined as the "analyses of nuclear materials and their near environments for information pertinent to nuclear incident investigations by law enforcement and intelligence agencies."[46] In the post-9/11 world, an entire field of study has arisen and been developed with the objective of making these analyses more accurate and faster. One of the most sought-after pieces of information that can be obtained about nuclear material is its "age," or the time since it was last chemically purified. Knowing a material's age can significantly narrow where it was manufactured and which processes were used in its purification, which can also lead to information on how it might have gotten into the wrong hands to begin with. The science of determining this elapsed time is called chronometry, and is also known as age-dating or ageing.

Chronometry is possible because of the nature of radioactive decay, namely that it is a statistically derived exponential decay with a fixed time constant that results in the ingrowth of a daughter. If this daughter is also radioactive, the Bateman equation can be used to determine the ratios of the various parent and daughter activities after a given decay time, assuming the initial amounts of the daughters present are negligible (or at least well known).[46] This is the case, for instance, after a successful chemical separation. The classical examples of decay chains that can be used for ageing are the 4n, 4n+1, 4n+2, and 4n+3 decay chains, which refer to parent isotopes where dividing the mass number by four results in a remainder of 0, 1, 2, or 3, respectively. Three of these decay chains are present in nature and all four describe the decay of several heavy isotopes important to the nuclear fuel cycle and weapon production (i.e. ^{239}Pu, ^{235}U, ^{233}U, ^{238}Pu, ^{232}Th, ^{241}Am, among others). These decay chains have several different chronometer pairs present in them, making it possible to look at multiple different ratios to confirm the purification date.

Unfortunately, most isotopes used in commercial or medical applications are much lighter than the heavy elements mentioned above, and have significantly shorter decay chains, often consisting of only one or two nuclides. While this does make it easier to “spoof” or alter the resulting age calculation for these sources, it is still possible to calculate an age from a single parent/daughter relationship, which has been demonstrated experimentally.[47] For example, the age of a ^{137}Cs source can be determined by finding the ratio of parent (^{137}Cs) to stable daughter (^{137}Ba), and using equation (1) below. In this case, t is the time since purification, λ is the decay constant of the parent (in inverse time units), and the isotopic ratio refers to the atom ratio of ^{137}Ba and ^{137}Cs in the sample.

$$t = \frac{1}{\lambda} \ln \left[1 + \frac{^{137}Ba}{^{137}Cs} \right] \qquad (1)$$

This example can also be extended to the ratio of ^{90}Sr to its stable grand-daughter ^{90}Zr, which would replace ^{137}Cs and ^{137}Ba, respectively. If the samples are chemically separated prior to measurement in such a way that the ^{90}Y produced as ^{90}Sr’s daughter is contained in the same sample as the ^{90}Zr and it is the 90 isobar that is measured (i.e. by mass spectrometry), no additional information needs to be considered, as all of the ^{90}Y and ^{90}Zr will be read as one signal. On the other hand, if ^{90}Zr is isolated from both ^{90}Y and ^{90}Sr, but only strontium and zirconium are measured, then the equation must take into consideration the decay rate of ^{90}Y to ^{90}Zr. This transforms equation (1) into equation (2), in which the subscripts Sr and Y indicate which decay constants are referred to. This equation also assumes that the source is older than 27 days, and that ^{90}Sr and ^{90}Y will therefore be in secular equilibrium.

$$t = \frac{1}{\lambda_{Sr}} \ln\left[1 + \frac{\lambda_{Sr}}{\lambda_Y} + \frac{^{90}Zr}{^{90}Sr}\right] \qquad (2)$$

Alternatively, the combined activity of ^{90}Sr and ^{90}Y could be determined using a method such as liquid scintillation counting prior to separation and mathematically converted to atoms, after which only the stable ^{90}Zr would need to be measured to use equation (2). This would likely introduce some error from the use of two different instruments, but could provide a way to double check the results obtained by one of the other methods.

1.4.3 Solvent Extraction

Solvent extraction (SX), also known as liquid-liquid extraction, is a separation technique based on the distribution of a solute or solutes between two immiscible phases. Generally, these phases are aqueous and organic liquids, and the partitioning is usually carried out at ambient temperature and pressure. In these systems, the organic phase is usually composed of the organic solvent and an extractant molecule, possibly along with a modifier that improves the physical properties of the system and/or a synergistic agent that improves the effectiveness of the extractant in some way. The aqueous phase is then made up of the solute, or element to be separated, the matrix it is contained in, and acids dissolved in water.[48] Once dissolved in the aqueous phase, cations and anions establish equilibrium between being separate, charged particles and combining to become a neutral complex, as seen in equation (3). When this neutral complex is formed, it is then more miscible in the non-polar organic phase than its polar/charged constituents were and effectively partitions into the organic phase, following Le Châtlier's principle. In many cases, this neutral species is further complexed by the extractant species in the organic phase to aid in extraction, as seen in equation (4), in which the bar denotes the organic phase and E represents the extractant. With the appropriate extractant, it is also possible to extract the individual cations or anions from solution instead. In these cases a neutral complex is formed between the ion in solution and an organic molecule (usually a chelator) at the aqueous/organic interface, which then allows the ion to partition into the organic phase.

$$M^{+2}{}_{(aq)} + 2NO_3^-{}_{(aq)} \rightleftharpoons M(NO_3)_{2(aq)} \tag{3}$$

$$M(NO_s)_{2(aq)} + \bar{E} \leftrightarrow \overline{M(NO_3)_2E} \tag{4}$$

In order to measure the effectiveness of this partition from the aqueous phase to the organic phase, the distribution ratio is used. The distribution ratio is given in equation (5), and is defined as the concentration of the solute in the organic phase divided by its concentration in the aqueous phase.[49]

$$D = \frac{[solute]_{org}}{[solute]_{aq}} \tag{5}$$

While this value is useful in determining which conditions, e.g. acid or ligand concentration, to use in order to extract the solute most effectively, the separation factor is often more useful to real world applications. The separation factor measures the ratio of the distribution ratio of one solute to the distribution ratio of another and is a way to quantify the ability of the process to separate the two. Equation (6) describes the separation factor between two solutes, S1 and S2. The closer to unity the separation factor, the less effective the separation is.

$$SF_{S1/S2} = \frac{D_{S1}}{D_{S2}} \tag{6}$$

Several industrial SX processes are used in the nuclear industry, including the PUREX and FPEX processes. In the Plutonium and Uranium Extraction (PUREX) process, a 30% solution of tributyl phosphate (TBP) in a hydrocarbon diluent such as kerosene or n-dodecane is the organic phase. It is contacted with an aqueous phase consisting of 3M HNO_3 and dissolved nuclear fuel. Under these conditions, metals in the +4 and +6 oxidation states (primarily plutonium and uranium, respectively) are extracted into the organic phase. At this point, the organic phase is contacted with an aqueous solution containing a suitable reductant that converts the Pu (IV) to Pu (III), which causes it to back extract into the aqueous phase. The remaining uranium is then extracted back into the aqueous phase by contacting it with dilute nitric acid.[50]

In contrast to the PUREX process, the Fission Product Extraction (FPEX) process focuses on simultaneously extracting two specific fission products that are prominent heat generators in nuclear waste, ^{137}Cs and ^{90}Sr. In this system, 4,4',(5')-di-(t-butyldicyclohexano)-18-crown-6 (DtBuCH18C6) is used to extract strontium and calix[4]arene-bis-(t-octylbenzo-crown-6) (BOBCalixC6) is used to extract cesium. These are placed in solution with trioctylamine (TOA), and the modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) in an Isopar-L diluent.[51] Upon contact with an acidic aqueous solution containing the fission products, they are extracted into the organic phase. After washing with nitric acid, a dilute nitric acid solution is contacted with the loaded organic phase, stripping the Cs and Sr from the organic phase once again.[52]

1.4.4 Extraction Chromatography

Extraction chromatography (EXC) is essentially the next step in SX technology. It combines the selectivity of SX with the ease of operation and the lesser waste generation of column chromatography. EXC is very similar to SX in that the same extraction mechanisms are seen, but the organic phase of the system has been adsorbed onto an inert framework to make it stationary (also known as a resin), and the aqueous solution containing the solute is passed over the inert framework to affect the partitioning of the solute between the phases. The inert framework is often a porous organic polymer, though inorganic silica-based supports are also somewhat common. A few examples of stationary phase support substrates include Amberchrom CG-71, which is an acrylic ester polymer, Amberlite XAD 4, which is a styrene-divinylbenzene copolymer, and Amberlite XAD 7 HP, which is an aliphatic acrylic polymer. A simplified diagram of the three part system described above can be seen in Figure 1.

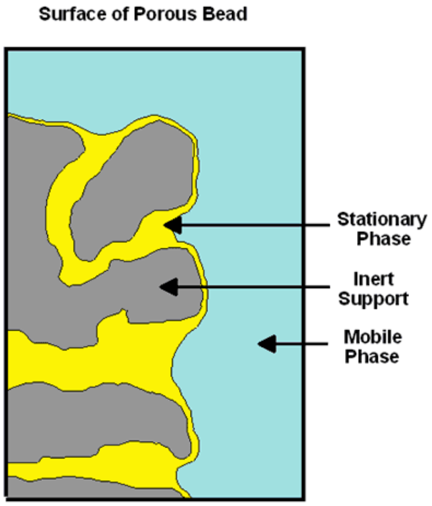

Figure 1: Diagram of an extraction chromatographic resin system[53]

The relationship between SX and EXC continues in that the distribution ratio (D) of a SX process can be directly related to how efficient an EXC process using the same solvent/solute combination will be through equation (7), where k' is the number of free column volumes to peak maximum (also referred to as the chromatographic capacity factor), and v_s and v_m are the volumes of the extractant (stationary phase) and aqueous matrix (mobile phase), respectively.[54]

$$k' = D\frac{v_s}{v_m} \tag{7}$$

Because the concentration of extractant is typically much higher in EXC systems than in conventional SX systems, D and k' values are often not measured directly. Instead the weight distribution ratio (D_w), which is defined as the ratio of metal ion concentration per gram resin to the metal concentration per mL of aqueous phase at equilibrium, is calculated by measuring the concentration of the aqueous solution before and after contact with the resin. Because of the known relationship between concentration and a given isotope's activity, the equation for finding the weight distribution can be converted to equation (8), which contains only easily measureable parameters:

$$D_w = \frac{A_o - A_s}{A_s} \times \frac{V_{aq}}{m_r} \tag{8}$$

where V_{aq} is the volume of aqueous phase, A_o and A_s are the activity of the aqueous solution before and after equilibrium with m_r grams of resin. D_w is also related to the D value of conventional SX processes by equation (9), in which V_o is the volume of organic phase and all other variables are as defined above.

$$\frac{D_w}{D} = \frac{V_o}{m_r} \tag{9}$$

Given that the loading of the resin and the density of extractant at room temperature are constant, the ratio of D_w to D is also constant. If one determines the typical interstitial space of a column packed with a certain resin, it is then possible to directly relate the chromatographic capacity factor to the weight distribution ratio of a column with this resin using a constant via equation (10), in which C is the constant. This is a more useful measure of the efficiency of a column chromatography system and, as such, is primarily how partitioning data is presented when talking about resins and extraction chromatographic systems.

$$k' = D_w C \tag{10}$$

An excellent example of this is Eichrom's strontium specific (Sr-spec) resin. The resin contains 40% w/w of an organic solution, which consists of 1M DtBuCH18C6 in 1-octanol and has a room temperature density of 0.912 g/mL. By using this data along with equation (9), it can be seen that for Sr-spec resin D = $2.28D_w$. It was also determined that the average v_s/v_m ratio for a Sr-spec gravity packed column is 0.2. This results in $k' = 0.456D_w$ or $k' = D_w/2.19$.[49] These calculated k' values can then be used in place of D values in equation (6) to determine the separation factor for a typical column and, by extension, which elements will elute off of the column in what order.

To achieve a meaningful separation, however, band broadening must be kept to a minimum in order to avoid excessive cross-contamination of analytes. Even if the extractant(s) comprising the stationary phase have a very high selectivity for the solute of interest, poor column efficiency, manifested as a tall height equivalent to a theoretical plate, can result in essentially no practical separation. The height equivalent to a theoretical plate (HETP) is a measure of the efficiency of a column. In each hypothetical plate, equilibrium between the aqueous and organic phases occurs and the constituents of the solution are separated to a degree. The more plates a column has, the better the separation becomes. This means that for a column of a given length, the shorter the theoretical plates, the more efficient the separation is.

There is a long list of factors that influence HETP, but it was experimentally determined during the development of EXC that the three most prominent are flow phenomena, diffusion in the stationary phase, and extraction kinetics. Flow phenomena deal primarily with eddy-diffusion, which refers to band broadening caused by atoms of the same element taking a variety of paths, each with a unique length, through the column and eluting at different times. Diffusion in the stationary phase refers to the ability of the solutes to diffuse into the stationary phase, and is dependent primarily on temperature/viscosity, depth of the stationary phase, and the diffusion coefficient of the stationary phase. Lastly, extraction kinetics are dependent on the rate constant for the extraction of the solute ion at the interface from the stationary phase back to the mobile phase.[55]

1.4.4.1 Sr Resin

Crown ethers were first discovered in 1967 when C.J. Pedersen accidentally prepared dibenzo 18-crown-6 while trying to synthesize a bisphenol ether. [56-57] This work also first introduced the idea that crown ethers could be used as complexing agents for alkali metals.[58] Pedersen proposed that the alkali metals are able to fit into the central cavity of the crown ether and form complexes via the ion-dipole interaction with the oxygen atoms present in the ring.[56] Because of the impact of his discovery, Pedersen shared the 1987 Nobel Prize in Chemistry with D. J. Cram and J.-M. Lehn, who both furthered the development of macrocycles and their use as complexants.[59]

In the years since their discovery, a considerable number of crown ethers have been synthesized and investigated with respect to their complexation abilities. Based on these studies, several parameters have been found to govern crown-metal complex stability, including the relative sizes of the cation and the crown ether cavity, the number of donor atoms (oxygen), donor atom arrangement (are they coplanar), donor atom symmetry in the crown, basicity of the donor atoms, crown steric hindrances, and the electrical charge of the complexed cation.[56] By 1990, it had been discovered that dicyclohexano 18-crown-6 and its derivatives complexed strontium relatively well.[60-61] This is unsurprising due to the favorable cavity size of the 18-crown-6 molecules with respect to strontium's ionic diameter (see Table 1 for sizes).

Table 1: Diameters of several crown cavities and the ionic crystal diameter of strontium[56, 58]

Crown Compound/Ion	Cavity/Ionic Diameter (Å)
12-crown-4	1.2 – 1.5
14-crown-4	1.2 – 1.5
15-crown-5	1.7 – 2.2
18-crown-6	2.6 – 3.2
21-crown-7	3.4 – 4.3
Sr^{2+}	2.26

Unfortunately, the complexation was not significant enough to allow its use in the extraction of strontium from aqueous media. It was at this point that *Horwitz et.al.*[62] discovered that the extraction of strontium was not only dependent on the crown, but also the crown diluent, noting that the water content of the organic phase played a large role in extractability.

Based on his work carried out in 1990/91, *Horwitz et.al.* then moved on to develop a new extraction chromatographic resin that could be used to isolate strontium from acidic media with excellent selectivity.[54] The resin is composed of inert acrylic ester polymer beads loaded (40 % w/w) with a 1 M solution of 4,4'(5')-di-t-butylcyclohexano 18-crown-6 (DtBuCH18C6, see Figure 2) in 1-octanol, and is commercially available from Eichrom Technology (Lisle, IL). This resin has been extensively characterized in nitric acid media, and does an exceptional job of extracting strontium at high (> 1 M) nitric acid concentrations, while still having low enough retention to allow for back extraction at low (< 0.1 M) concentrations of nitric acid. During its development, a small study was also performed to examine the performance of the resin in increasing concentrations of several other acids in 3 M HNO_3. No significant reduction was seen in strontium retention at up to 0.5 M of the other acids in 3 M HNO_3.[54] Additional work was published in 2015 by *Filosofov*,[63] which tested the uptake of strontium in HCl, HBr, $HClO_4$, and HPF_6, and found little retention in HCl and HBr systems until high concentrations (10 M) and retention roughly an order of magnitude higher for $HClO_4$ and HPF_6 systems. This was attributed primarily to the differences in anion hydration energy, as well as possible alternative extraction mechanisms.[63]

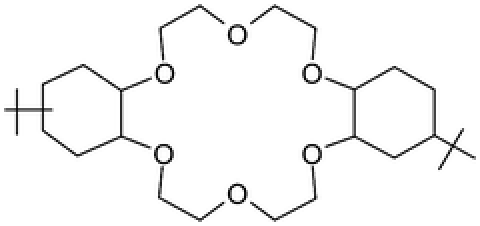

Figure 2: Structural diagram of 4,4'(5')-di-t-butylcyclohexano 18-crown-6[64]

Recently, *Dietz and Jensen*[65] undertook a study of the complexing properties of DtBuCH18C6 using X-ray absorption spectroscopy (XAS) techniques to determine explicitly if the resin behaves as had been assumed since its development, namely that the extraction follows equation (11).

$$Sr^{2+} + 2NO_3^- + \overline{Crown} \rightleftharpoons \overline{Sr(NO_3)_2Crown} \tag{11}$$

Based on the XAS data, it was determined that the reaction indeed followed the proposed mechanism, and that the complex structure is definitively what is shown in Figure 3, though the nitrate groups are not necessarily coplanar. This work also showed that the coordination geometry was consistent for strontium adsorbed on resin loaded with DtBuCH18C6, complexes formed during liquid-liquid extraction from nitric acid into 1-octanol, and solid state complexes, indicating that the mechanism governing partition between aqueous and organic phases is also uniform.[65]

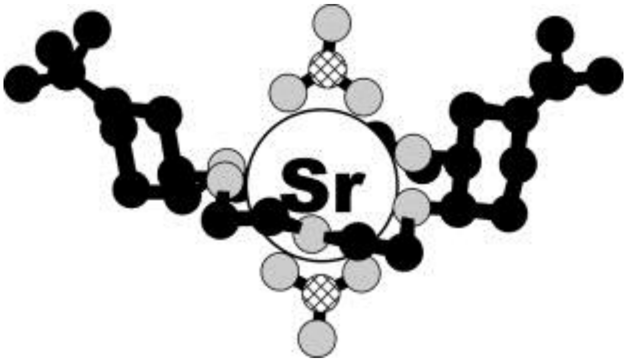

Figure 3: Diagram of the $Sr(NO_3)_2(DtBuCH18C6)$ complex with carbon in black, oxygen in grey, and nitrogen shown with crosshatching[65]

The development of Sr Resin ushered in a new era in radiostrontium analysis, with the vast majority of procedures now using this material. These techniques have largely replaced the traditional precipitation and solvent extraction methods because they produce much less chemical waste and tend to be much faster. Some of the first extraction chromatographic methods developed for the quantification of strontium were produced by *Horwitz et.al.*[22] and *Dietz et.al.*[65] and involved its separation from nuclear waste and urine, respectively. These procedures have served as the basis for many other radiostrontium environmental monitoring methods separating strontium from materials like water,[11, 14, 20, 28, 36] soil,[10, 17, 19, 27, 33, 37] marine sediment,[15, 21, 32] vegetation,[18, 26, 30] animal tissue,[12, 24, 31] and milk.[13, 23, 25, 29, 35]

While these procedures have good detection limits and have been proven to work, they are not necessarily fast enough for emergency situations. The ones that have been developed for rapid analysis[12, 14, 23, 25, 27-31] do not address matrices that contain significant concentrations of components which might interfere with strontium retention during separation. Recently, though, a small number of rapid methods have been developed for the analysis of building materials like concrete, marble, and asphalt.[66-69] Unfortunately, these have been more focused on identifying a robust digestion method that removes components that could potentially interfere with the standard separation than investigating if those components actually cause interference. By identifying the components that could be left in the system prior to extraction chromatographic separation, the developed procedures could potentially be altered to become even faster without loss of accuracy or precision in the strontium measurement. In addition, the rapid methods developed utilize vast amounts of sodium hydroxide to digest the samples. Sodium has been proven to interfere with the resin's uptake of strontium, and must subsequently be removed before analysis, so identifying an alternative digestion method or matrix could also decrease processing time.[54]

CHAPTER 2: EXPERIMENTAL PROCEDURE

2.1 Materials

The resin used in all experiments was composed of Amberchrom CG-71 md inert polymer beads loaded with 40 % w/w of a solution of 1.0 M 4,4’(5’)-di-t-butylcyclohexano 18-crown-6 in 1-octanol, which was obtained from Eichrom Technology (Lisle, IL) in the form of their Sr-Resin products. All batch studies were carried out using their 50 – 100 µm particle size resin, and column studies were carried out using their commercially available dry packed 2 ml cartridges (except where specified) containing the same 50 – 100 µm particle size resin. All resin products were used as received. The radiotracer ^{85}Sr was used as a surrogate for ^{90}Sr to reduce the amount of processing required to make measurements for all of the strontium work accomplished, and was obtained from Eckert & Ziegler Isotope Products in the form of strontium chloride in 0.5 M HCl. All ^{85}Sr used was converted to strontium nitrate by evaporating an aliquot of the stock solution to dryness, reconstituting it twice in concentrated nitric acid, and finally placing it in a nitric acid solution (concentration varied depending on experiment) with a radiostrontium concentration of 600-1200 Bq ml^{-1}. Nickel-63 was used as an additional radiotracer for the studies described in Chapter 4, and it was also obtained from Eckert & Ziegler Isotope Products in the form of nickel (II) chloride in 0.1 M HCl, and prepared in the same manner as ^{85}Sr, resulting in a stock solution concentration of 250 Bq ml^{-1}. All acid solutions were prepared using J.T. Baker analyzed ACS reagent grade nitric and hydrochloric acids obtained from Avantor Performance Materials. The hydrofluoric acid used in chapters 6 and 7 was also ACS reagent grade, obtained from Sigma-Aldrich (St. Louis, MO). Various metal salt solutions were prepared for each study. These are described in their individual chapters. All solutions were prepared with deionized water from a Cascada water purification system from Pall Corporation. Standard reference materials (SRMs) were obtained from the National Institute of Standards and Technology (NIST).

2.2 Methods

For each system examined, two different types of experiments were carried out, batch studies and column studies. Batch studies were carried out to determine the ability of Sr Resin to retain strontium under various conditions. This was followed by column studies intended to ensure the data gathered in static batch studies truly transferred to the dynamic column experiments. This was done more to assess any adverse flow characteristics that could result from the complex concentrated matrices that were being sent through the column than anything else. The procedures used for both the batch studies and column studies are outlined in this section.

2.2.1 Batch Studies

Batch studies are a simple and reliable way to quantify the separation capabilities of resins. By measuring the activity in the solution before and after contact with the resin, the mass of the resin, and the volume of aqueous phase contacted with the resin, the weight distribution value of the resin can be determined. This value can, in turn, be converted to the chromatographic capacity factor (k') using the equations outlined in section 1.4.4 of this document.

For all batch studies carried out in this research, 50 mg of Sr Resin was weighed out into a 2 ml microcentrifuge tube and 0.4 ml of nitric acid was added to precondition the resin. The tube was capped and placed on a shaker table for one hour to allow for the system to equilibrate. Following this, 0.8 ml of the appropriate prepared salt or acid solution was added to the mixture, as well as 0.4 ml of the prepared ^{85}Sr solution. The sample was then placed back on the shaker table and agitated for an additional hour. Once mixing was complete, the aqueous content of the tube was separated from the resin using a 0.45 µm PTFE syringe filter. A 1 ml aliquot of the filtered solution was then taken for radiometric analysis. If stable elements also needed to be assayed, the remaining solution was preserved and eventually diluted in 2% v/v HNO_3 for analysis via inductively coupled plasma-optical emission spectroscopy (ICP-OES). All batch study data points are the average of five replicates.

2.2.2 Batch Study Corrections

In order to simplify these experiments, a subsample of the filtered solution was taken for each analysis, which was then corrected to the original volume added to the resin. To ensure an accurate correction, the density of the acid before and after contact with the resin was verified, which eliminated the possibility of a false correction factor. The density was determined by calibrating a 1 ml pipet by transferring an aliquot of water into a clean, tared vessel. This was repeated 10 times and the average mass was used in conjunction with the density of water at room temperature to determine the volume pipetted. This procedure was then repeated with the acids being tested before and after contact with the resin, using the now known volume to determine the density. There was no appreciable density difference seen in the acid before and after contact with the resin, indicating the volume measured could be directly converted to the volume added in the batch studies.

Although this strategy solved the problem of volume correction, there was still the possibility of the resin selectively retaining nitric acid, which would change the concentration of the acid being analyzed. To determine if this was the case, each concentration of acid was titrated before and after contact with the resin in a batch study without strontium present. Each sample was diluted by a known ratio using deionized water and two drops of 0.1 % phenolphthalein indicator were added. It was then titrated using a 0.1 N NaOH solution. The sodium hydroxide solution was added slowly using a 25 ml buret, while constantly mixing the acid/indicator solution, until a pink endpoint was reached. This procedure was periodically carried out on samples containing strontium to double check that the extraction actively occurring did not result in the loss of nitric acid either. Results of these experiments were employed to ensure the proper concentration of acid was contacted with the resin.

2.2.3 Column Studies

As mentioned above, column studies were carried out to ensure the data collected in the batch studies accurately transferred to real-life use of the resin. Unless otherwise specified, the columns used in these studies were 2 ml vacuum-flow columns dry packed in the factory and used directly out of the packaging. These were used in conjunction with a vacuum box, also obtained from Eichrom. Per manufacturer specifications, each column was pulled to dryness for the collection of each fraction and one FCV was assumed to be 1.4 ml. The columns were preconditioned with 5 ml of either 3 M or 8 M HNO_3, depending on the experiment. Once the column was preconditioned, salt or mixed acid solutions and radiostrontium solutions were added to the column reservoir simultaneously. The resulting mixture was then pulled through the column at a rate of approx. 1 ml min^{-1} (roughly 0.5 in. Hg vacuum pressure) to load the column, collecting the effluent from this step in its own container. The column was then rinsed with 30 FCV of either 3 M or 8 M HNO_3 (specified per project) at 2-4 ml min^{-1} (1 – 3 in. Hg vacuum pressure), collecting five FCV in each fraction. Finally, the column was stripped with 10 FCV of 0.05 M HNO_3 at 1 ml min^{-1}, again collecting five FCV in each fraction. All fractions were collected in 20 ml high-density polyethylene liquid scintillation vials. Each fraction then underwent radiometric analysis, usually by gamma detection using an automated NaI(Tl) counter (described in section 2.3.2). All trials were run in at least duplicate to ensure reproducibility.

The elution strategy using 3 M HNO_3 was established by *Horwitz et al.*[54] in the early 1990's and is considered adequate for the separation of strontium, though subsequent procedures have often called for higher concentrations of nitric acid in the rinse phase to increase the retention of strontium on the resin. For the sake of interference studies, the procedure using 30 FCVs of 3 M HNO_3 in the rinse phase was utilized to ensure a minimum baseline for the retention of strontium. It is assumed that procedures using higher concentrations of nitric acid or smaller rinse phases would have even better/more quantitative results.

2.3 Instrumentation

2.3.1 Liquid Scintillation

Two radionuclides relevant to this research, namely ^{90}Sr and ^{63}Ni, are pure beta emitters. The most straightforward way to quantitatively determine these isotopes in the single nuclide analyses required for this project is in a liquid scintillation counter (LSC). LSCs operate by converting the kinetic energy of charged particles to light, observing these photons, and generating an electronic signal proportional to the initial energy of the radiation, that can be interpreted by the instrument.

In order to convert the energy of the incoming charged particle to light, a scintillation cocktail is used. Once the scintillation cocktail has absorbed the energy of the decay radiation, it promptly emits a photon via fluorescence.[70] The photons emitted during fluorescence are often absorbed by a wave-shifter and emitted at longer wavelengths that are more compatible with the photomultiplier tubes (PMTs) in the instrument and minimize the possibility of self-absorption in the cocktail. Since the light emission is isotropic, it is also possible to reduce false positives by wiring multiple PMTs in coincidence. If the PMTs do not put out a signal at the same time, it cannot have been generated by photons coming from the sample and will not be recorded.[70] One of the drawbacks of liquid scintillation counting is the possibility of sample coloration changing the amount of light detected by the PMT. This known as color quenching, and can be accounted for using quench standards and a quench indicating parameter (QIP) such as the transformed Spectral Index of the External Standard (t-SIE). The QIP can then be used to construct a quench curve that relates the QIP to the count efficiency. A more thorough description of organic scintillators and PMTs can be found in *Knoll* and *RCA.*[70-71]

The LSC used for this work was a Tri-Carb 2800TR (Perkin Elmer, Boston, MA), and is shown in Figure 4. The standard QuantaSmart software included with the instrument was used for data acquisition and analysis. A more detailed description of the instrument is provided by Perkin Elmer.[72] For analysis, aliquots of the samples were pipetted into 15 ml of Ultima Gold AB cocktail (Perkin Elmer, Waltham, MA) contained in a standard 20 ml LSC vial. While Ultima Gold AB was selected for its durability in varying concentrations of mineral acids, quenching was still possible. To counter this, blanks and standards were prepared for each concentration (both acid and salt) analyzed and Quenching Index Parameters (QIPs) were used for corrections. Each sample was counted for 60 min or until the total number of counts in the region of interest reached 40,000 (corresponding to 0.5 % error).

Figure 4: Tri-Carb 2800TR Liquid Scintillation Counter

2.3.2 Gamma Spectroscopy with NaI(Tl)

For this work, the isotope ^{85}Sr was used in place of ^{90}Sr in order to circumvent the ingrowth period required before analysis. In contrast to ^{90}Sr, ^{85}Sr decays primarily by electron capture with an accompanying gamma emission at 514 keV, requiring the use of a gamma spectrometer for detection. While still considered a scintillation detector, NaI(Tl) detectors operate under different principles than LSCs. Where the LSC relies on individual molecules being able to fluoresce to create light, the NaI(Tl) detector relies instead on the energy states determined by the crystal lattice of the detector material.[70] Under normal circumstances in the detector all of the electrons occupy the valence band, but when incident radiation enters the detector and its energy is transferred to the electrons of the crystal, it can give them enough energy to be promoted from the valence band to the conduction band. The electron then de-excites back into the valence band through the emission of light, which is detected by a PMT, converted to a proportional electrical signal, amplified, and processed into a spectrum just like the signal described above in the LSC section. To ensure the crystal is transparent to the emitted light, activator impurities are incorporated into it, allowing the promoted electrons to emit a different energy upon de-excitation. A more thorough description of the fundamentals of inorganic scintillators can be found in *Knoll*.[70]

The gamma-detector used for this work was a 2480 WIZARD^2 automatic gamma counter (PerkinElmer), shown in Figure 5, and outfitted with the standard operating software. The instrument was equipped with a 3 inch well-type NaI(Tl) detector contained in a 75 mm solid lead shield for background reduction. Depending on the volume of the aliquot, samples were counted in either 13 mm diameter culture tubes or 28 mm diameter scintillation vials. All samples were counted for one hour, unless the total number of counts in the counting window reached 40,000 (0.5 % error). A more detailed description of the instrument is provided by Perkin Elmer.[73]

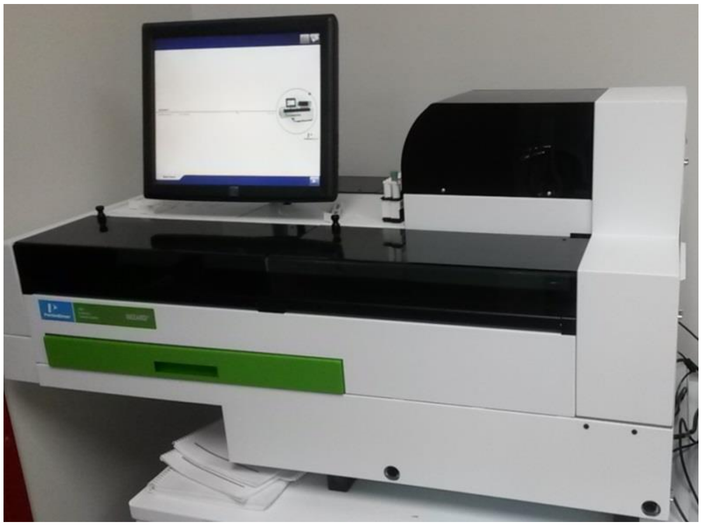

Figure 5: WIZARD^2 2480 automatic gamma counter

2.3.3 Atomic Emission Spectroscopy

Inductively coupled plasma – atomic emission spectroscopy (ICP-AES), also known as optical emission spectroscopy (OES) was used in analyzing the amount of non-radioactive elements present in the eluent (aqueous phase) of the various tests. AES is a commonly used analytical technique in the qualitative and quantitative analysis of samples for stable elements. In most modern AES instruments, the sample is injected through inductively coupled plasma as an aerosol carried by argon. The ICP ionizes the sample and promotes its atoms to a higher electronic state. As the excited atoms relax to lower states, they release ultraviolet and visible light in discrete lines corresponding to the difference in energy between the states. This light then passes through a monochromator, which allows only the selected wavelengths to be seen by the detector. Since each element has characteristic, discrete energy levels, it is then possible to identify the element based on the wavelength of the lines emitted. It is also possible to relate the intensity of the emission to the number of atoms undergoing the relaxation and, by extension, the concentration of the element.[74-75]

The ICP-AES used in this work was an Optima 8000 Spectrometer from Perkin Elmer, Inc. shown in Figure 6. A more detailed description of the instrument is provided by Perkin Elmer.[76] The standard Syngistix software included with the instrument was used for data acquisition and analysis. An aliquot of each sample was transferred to a 15 ml polypropylene centrifuge tube and gently dried, then diluted to 15 ml with 2% v/v HNO_3.

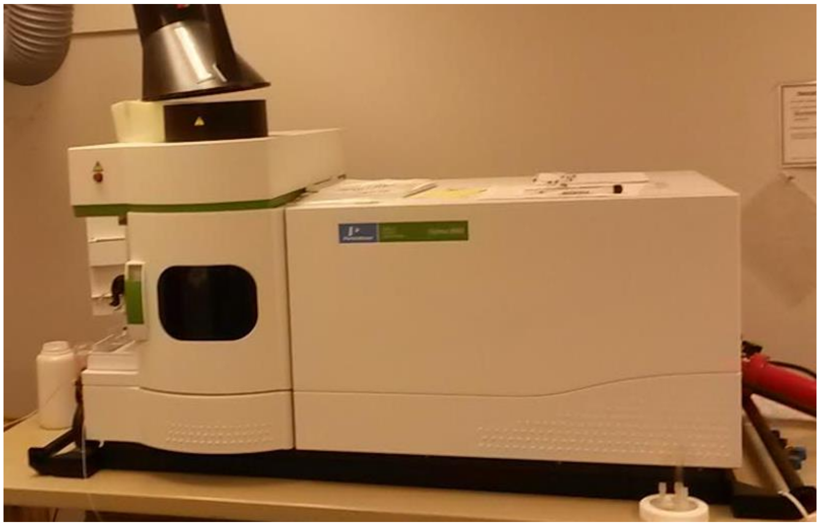

Figure 6: Optima 8000 ICP-AES Spectrometer

2.3.4 Mass Spectrometry

This work also utilized inductively couple plasma – mass spectrometry (ICP-MS) for the quantification of trace levels of analyte or in situations where differentiation between isotopes of the same element was required. As the name suggests, ICP-MS also uses inductively coupled plasma to aerosolize, atomize and excite analytes of interest for analysis. In contrast to OES, however, the ICP in the mass spectrometer excites the analyte to the point of ionization. Once ionized, 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 is tuned such that each analyte is only ionized to the +1 charge, it is then possible to segregate between individual isotopes of elements.

The ICP-MS used at UNLV is a Perkin Elmer ELAN DRC II, shown in Figure 7, which utilizes a quadrupole for mass separation. The quadrupole utilizes four rods arranged in parallel with a radio frequency (RF) voltage and a DC offset voltage applied to opposing rods. The oscillation frequency of the 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.

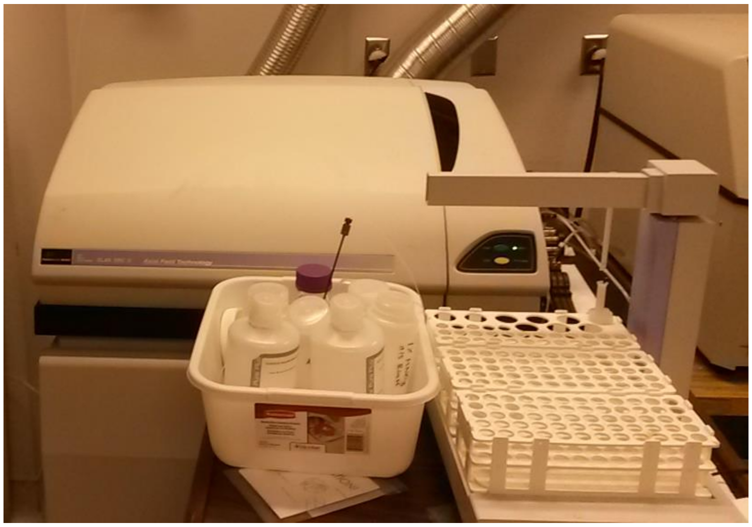

Figure 7: ELAN DRC II mass spectrometer.

CHAPTER 3: A PERFORMANCE COMPARISON OF COMMERCIALLY AVAILABLE STRONTIUM EXTRACTION CHROMATOGRAPHY COLUMNS

This work has been reproduced with the permission of Springer from the Journal of Radioanalytical and Nuclear Chemistry, volume 307, pages 1825-1831 in which it was published with Derek R. McLain as the first author, and Carol J. Mertz and Ralf Sudowe as co-authors.[38]

3.1 Abstract

Extraction chromatographic separations following a nuclear event will require both speed and accuracy. Ideally these separations will be carried out using commercially available products. Because ^{90}Sr is a likely material to be used in a radioactivity dispersal device, commercially available products for the separation of strontium were tested to evaluate differences in their elution profiles that may affect elution procedures. Gravity flow columns show better resolution, but vacuum flow columns are still adequate for purification if multiple aqueous conditions can be employed.

3.2 Introduction

Following the terrorist attacks of the last two decades, a number of previously unconsidered threats have emerged in the minds of government authorities, including radiation dispersal devices.[1] A radiation dispersal device (RDD), or "dirty bomb," could come in many shapes and sizes, but would effectively consist of some conventional explosive combined with radioactive material.[5] Two of the key impact factors of an RDD attack are the quantity and type of radiological material employed. Isotopes important in the discussion of RDDs include the alpha emitters ^{238}Pu, ^{241}Am, and ^{252}Cf, the beta/gamma emitters ^{60}Co, ^{137}Cs, and ^{192}Ir, and the pure beta emitter ^{90}Sr.[3, 6] Taking the possible modes of acquisition a terrorist organization may employ into account as well as factors such as the breadth of use, security, and sheer number of sources in circulation, most concerned organizations agree that ^{137}Cs, ^{60}Co, ^{192}Ir, and ^{90}Sr pose the most plausible risk to society.[6] Strontium-90 and its daughter ^{90}Y are both pure beta emitters, which means that an RDD equipped with ^{90}Sr would require significantly less shielding than a device with a similar amount of one of the other plausible nuclides mentioned above. Quantification of the radioactive material dispersed by the RDD will also be much more difficult because of the low signal available without first isolating the isotope. These factors make ^{90}Sr an isotope of significant interest.

Quantification of ^{90}Sr in a post-RDD-dispersal situation would be an important part of accomplishing several goals, of which the primary two are (1) determination of the age of the radiostrontium source and (2) establishing the total amount of ^{90}Sr used in the attack. There are many procedures that have been developed over the years to isolate strontium from environmental samples and it is likely that a variation of one of these would be used in quantifying the strontium in the area. The majority of the modern methods developed employ extraction chromatography with commercially available Sr Resin, produced by Eichrom Technologies (Lisle, IL), to carry out the actual separation.[77]

While extraction chromatography is a powerful and easy to use technique, it was first developed nearly 50 years ago and employed slow-moving gravity flow columns.[78] Modern techniques tend to employ the same selective resins, but pack them into a ready-to-use cartridge that has solution pulled through it using a vacuum. These cartridges have been in use for several years now with the assumption that they still have the same characteristics as the gravity flow columns. This study investigates whether there are any differences between the vacuum and gravity flow elution characteristics.

3.3 Experimental

3.3.1 Materials

Free resin loaded with 40% w/w of a 1.0 M 4,4’(5’)-di-t-butylcyclohexano 18-crown-6 in 1-octanol solution was obtained from Eichrom Technology in the form of their Sr-Resin. Pre-packed gravity flow columns and cartridges provided by the same vendor for use with Eichrom’s vacuum box technology were also utilized. Cesium-137 was obtained from Eckert & Ziegler Isotope Products in the form of cesium chloride in 0.5 M HCl. All cesium working solutions were prepared by directly taking an aliquot from the stock solution and diluting it in 0.5 M HNO_3. Strontium-85 was obtained from Perkin

Elmer in the form of strontium chloride in 0.5 M HCl. All strontium working solutions were prepared by directly taking an aliquot from the stock solution and diluting it in 0.5 M HNO_3. Nitric acid solutions were prepared from TraceMetal grade nitric acid (Fisher Scientific) and deionized water from a NanoPure ultrapure water system (Barnstead).

3.3.2 Procedure

Column preparation: Three types of columns were analyzed in this work: pre-packed vacuum and gravity cartridges and slurry-packed gravity columns. Vacuum cartridges and pre-packed gravity columns were used as received from the manufacturer. Each slurry packed gravity column was prepared by slurrying a known amount of resin in 0.5 M HNO_3 and quantitatively transferring it to a disposable plastic BioRad PolyPrep column (4 cm H x 0.8 cm ID with 10 mL reservoir). The resin was allowed to settle overnight, then the column was opened to allow the acid to flow through and compact the resin bed. Following this, the bed height was measured and glass wool was added to the top of the column to prevent the bed from being disturbed during the addition of sample. A small additional amount of acid was added to the column to keep the resin wet during storage and the column was sealed with two endcaps until it was used.

Column Characterization: Important column parameters in extraction chromatography are identified in Markl and Schmid, and include the stationary phase volume (resin volume), bed density, bed volume and mobile phase volume (also referred to as interstitial space, void volume, or free column volume).[78] In order to determine these values, the resin density must also be known. In this case it is given by the manufacturer as 1.12 g mL-1.[54]

Because the vacuum cartridges and pre-packaged columns are sealed, the amount of resin in each had to be experimentally determined. For the vacuum columns, this was done by taking the mass of several full cartridges, splitting them open and removing all of the resin, then taking the mass of the empty cartridge. The bed volume was also determined at this time by measuring the length of the column prior to splitting it open, the height of the frit on either end of the column after splitting the column open and subtracting the two to get the bed height, measuring the inner diameter of the cartridge, and geometrically calculating the total bed volume. A similar method was used with the pre-packed gravity columns, except that the resin was also dried in an oven at 90 °C for 18 hours before weighing to determine the mass of resin in each due to the presence of acid in the column. The bed volume of the pre-packed gravity columns was determined by measuring the height of the bed before emptying the column and measuring the inner diameter of the column after.

The amount of resin added to the slurry packed columns was measured prior to packing and the inner dimensions were determined by pipetting 2 mL of water into each column and measuring the height of the water in the column. This was then discarded and the average diameter of the column was calculated. The column was then slurry packed via the method outlined above, and the height of the bed was used in conjunction with the diameter of the column to calculate the total bed volume. For each type of column, the bed volume and mass of resin in the column was then used to determine the bed density. Finally, the free column volume (FCV) of the columns was determined by using the resin density to determine the volume of resin in each column and subtracting this from the total bed volume. Each column was preconditioned with 4 mL of 0.5 M HNO_3, then loaded with 10 µL of cesium working solution (approximately 2,000 CPM µL-1 in 0.5 M HNO_3). The FCV of each column was experimentally determined by measuring the breakthrough volume of ^{137}Cs, which effectively has no affinity for the resin in 0.5 M HNO_3.[54] Fractions were collected in 100 µL increments.

Strontium Elution: After pre-conditioning the columns with 4 mL of 0.5 M HNO_3 the columns were loaded with 0.25 mL of strontium working solution (approximately 340 CPM µL-1 in 0.5 M HNO3) and eluted with 50 FCV of 0.5 M HNO_3, which was collected in roughly 5 FCV increments.

3.3.3 Measurement

Gamma spectroscopy was performed using a WIZARD2 2480 automatic gamma counter from PerkinElmer. The instrument was equipped with a 3 inch well-type NaI(Tl) detector with a 75 mm solid lead shield for background reduction. Samples were counted for five minutes each.

3.4 Results & Discussion

3.4.1 Column Characterization

The characteristics of the slurry packed gravity flow columns are summarized in Table 2. Note that the directly measured free column volume values (found in Table 3) match up well with those calculated from geometric column parameter measurements. The larger amount of variation seen in the measured slurry packed gravity column data is a reflection of the differences in each column which, due to being prepared by hand, have much larger differences in resin packing quality than those prepared in bulk from the distributor. This becomes very evident when the elution profiles are examined. Slurry packed columns numbered one and two have fairly similar profiles, but slurry packed column number three has a much lower, broader peak that also elutes later than the first two, as can be seen in Figure 8. This is likely due to small irregularities in the packing structure caused by allowing the flow of solution to compact the resin bed instead of using compressed gas, as suggested by previous researchers.[55, 78] Regardless of this variation, all of the average parameters still match very well with the previously published bulk and column characterization data.[54]

Table 2: Average measured and calculated column parameters for the three types of columns (error is 1σ)

	Slurry packed	Pre-Packed	Vacuum
Bed Vol. (mL)	1.93(2)	1.71(15)	1.59(1)
Bed Height (cm)	3.68(3)	4.05(5)	2.50(1)
Mass Resin (g)	0.665(2)	0.536(10)	0.577(12)
Bed Density (g mL^{-1})	0.344(3)	0.314(23)	0.363(7)
Stationary Phase Vol. (mL)	0.594(2)	0.600(12)	0.515(10)

Table 3: Average calculated and measured free column volumes for the three types of columns (error is 1σ)

	Slurry packed	Pre-Packed	Vacuum
Calculated FCV (mL)	1.34(2)	1.11(14)	1.08(1)
Calculated Column %	69.3(3)	64.8(25)	67.9(7)
Breakthrough Volume (mL)	1.42(10)	1.25(5)	0.52(1)
Column % Breakthrough	73.3(50)	73.3(78)	32.7(5)

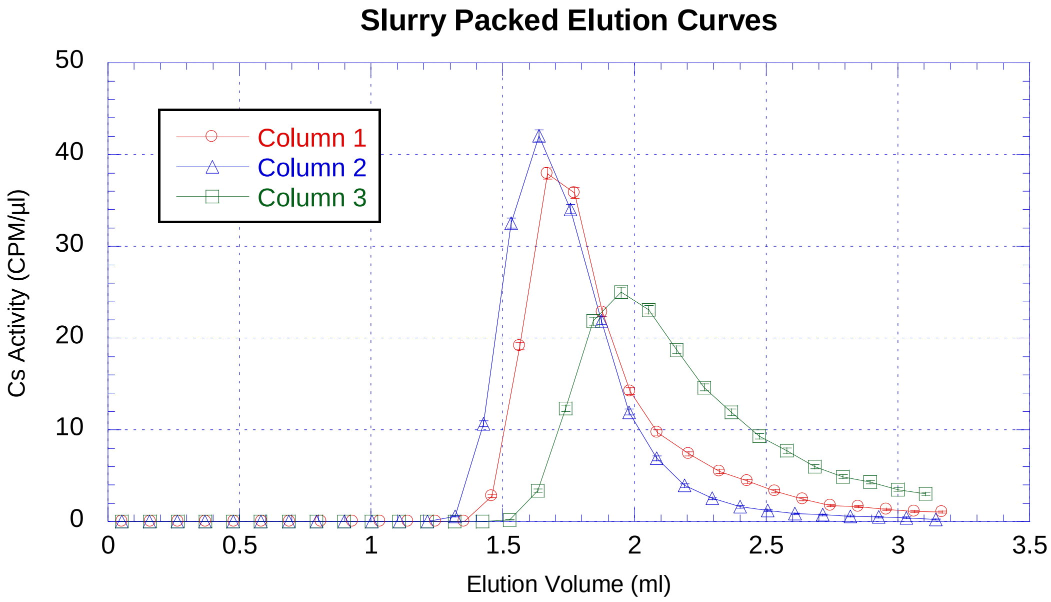

Figure 8: Elution profiles of cesium using slurry packed gravity columns

The pre-packed gravity columns show equally good agreement with the previously published data.[54] Their parameters can also be found in Table 2, and FCV data in Table **3**. It should be noted that the calculated free column volume of the pre-packed columns are somewhat low. This is likely caused by the larger deviation in measured resin contained in the pre-packed columns. Despite this, the elution profiles are much more reproducible than the slurry packed columns, which can be seen by comparing the profiles from the slurry packed columns in Figure 8 with those of the pre-packed columns in Figure 9. The pre-packed columns are also slightly longer than the slurry packed columns, giving them a larger number of theoretical plates, indicating better separations would be possible given the same acid matrices.

The vacuum column cartridges, in contrast to the two gravity-type columns, show significant differences between the measured parameters determined for the columns and the previously published data.[54] The average column parameters are summarized in Table 2, with the average FCV data found in Table 3. While the amount of resin contained by the vacuum cartridges corresponds to a calculated FCV similar to that of the slurry packed gravity flow columns (approx. 70%), the FCV measured experimentally via breakthrough volume is much lower (approx. 30%). In all likelihood, the answer to why this occurs can be found in the mechanism by which these columns are operated.

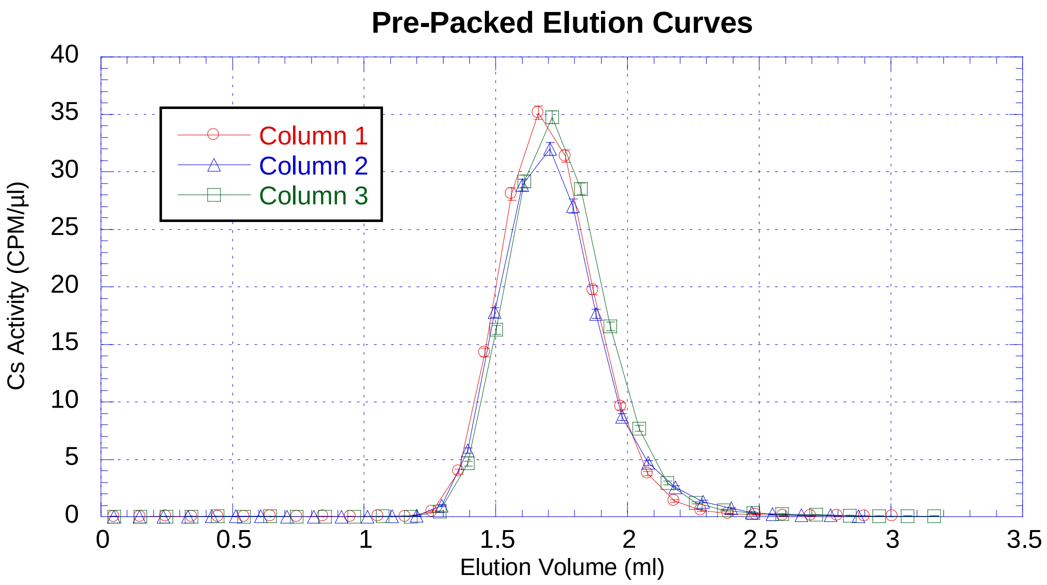

Figure 9: Elution profiles of cesium using pre-packed gravity columns

The conventional use of vacuum cartridges calls for the column being dried each time a fraction is pulled through. Since the elution band is not an infinitely thin line, there will be portions of the band farther down the column that are still in solution while portions farther up the column are already dried, making band broadening in the direction of flow much more pronounced than in traditional columns that are kept wet the duration of the elution. If an analyte is eluted that is negligibly retained by the resin (such as cesium[54]), there will therefore be significant band broadening and the breakthrough volume will actually be less than one full free column volume. However, the peak of the elution profile should still correspond to the most concentrated part of the elution band. This means that if the "un-retained" analyte could be added in a sufficiently small volume, the peak of the elution profile should correspond roughly to the FCV, regardless of the band broadening caused in the forward direction. Because the cesium was added in very small (10 µL) load fractions in this study and the elution profiles seen in Figure 10 are very reproducible, the peak locations were compiled in Table 4 and compared to the calculated average FCV from Table **3**. It can be seen from this that the average peak location differs from the predicted FCV by much less than the breakthrough volume (7.9 % and 51.8 % differences, respectively), indicating a much better prediction. Furthermore, this argument is strengthened by the fact that the previously published retention values agree with the elution profiles generated in this study when the peak of the cesium elution is used as the FCV instead of the breakthrough for the vacuum columns.[54]

Table 4: Peak locations for each of the five vacuum columns. Average peak location is less than 8 % different from calculated free column volume (Table **3**)

Column	1	2	3	4	5	Average	Deviation (1σ)
Peak Location (mL)	0.970	1.061	1.068	0.947	0.931	0.995	0.065
Column Percentage (%)	60.97	66.71	67.15	59.55	58.54	62.58	4.07

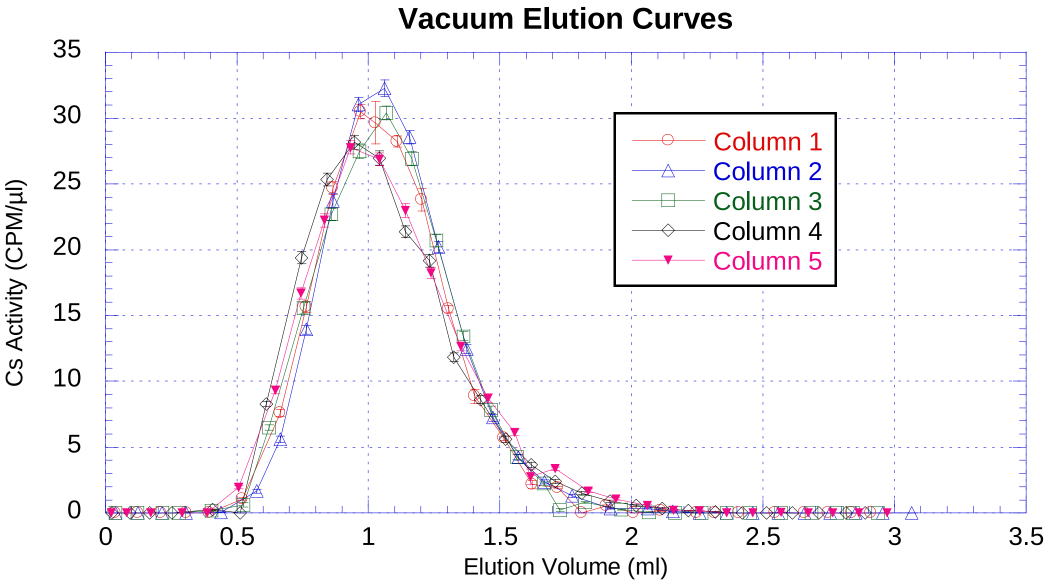

Figure 10: Elution profiles of cesium using vacuum cartridge columns

3.4.2 Strontium Elution

According to work previously carried out by the authors as well as data published by the developers of strontium resin, the number of FCVs to the elution peak maximum (k') of strontium in 0.5 M HNO_3 should be in the range of 12-15 free column volumes.[54] As seen in Figure 11, both types of gravity columns and the vacuum columns show elution peaks occurring at approximately 15-18 FCV. Given that the data points are plotted at the middle of the collection volume, the size of the fractions collected (roughly 6 mL), and the error associated with the preparation of the acid, this is in excellent agreement with the published values.[54] Both the vacuum and slurry packed columns also have effectively quantitative elution of strontium, with 95 % or more being recovered from each of the columns and an average recovery of 97.9 %. The pre-packed columns have slightly lower recovery, but still average 93.5 %. Despite these similarities, there are also significant differences in the elution profiles of the three types of columns, which can be seen in Figure 11.

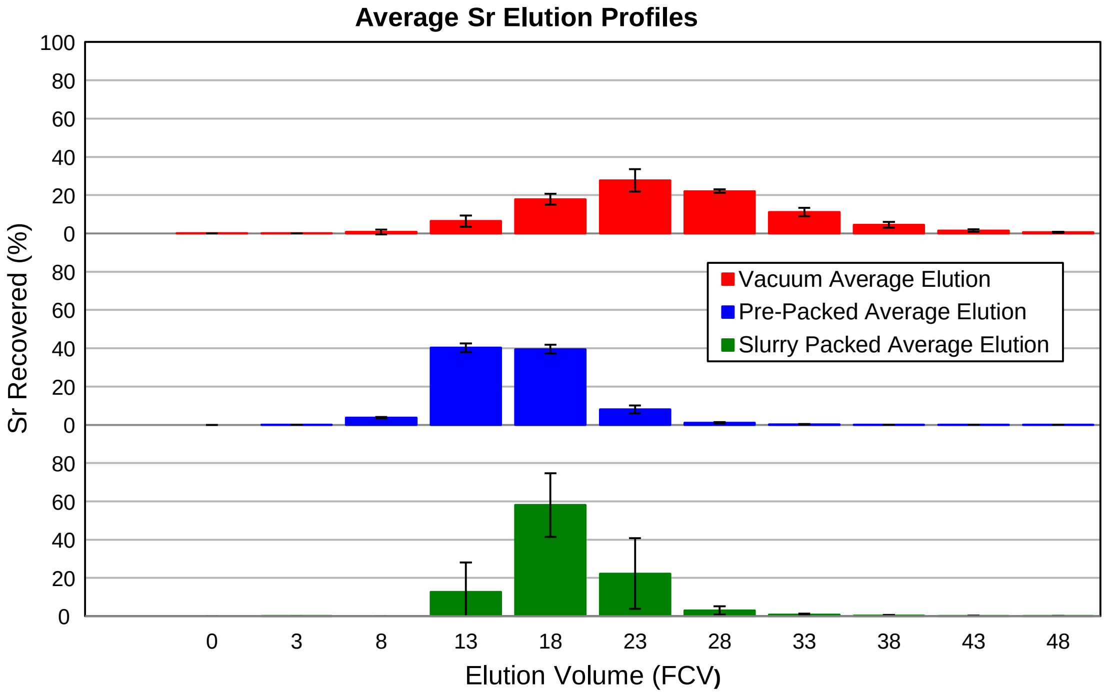

Figure 11: Comparison of the average strontium elution data from each column. Elution volumes shown are averaged across column type, but are still within ± 1 FCV

The most obvious difference in the elution profiles is the band broadening. The vacuum flow columns show significant amount of band broadening and tailing in comparison to both types of gravity columns. While it was hypothesized that this could be explained by the much higher flow rate of the vacuum columns (approx. 1 mL min^{-1} compared to approx. 0.2 mL min^{-1}), results from examining this variable were mixed. Initially, a second vacuum column elution was performed at roughly 4 mL min^{-1} that showed that the faster flow rate resulted in a much broader elution profile, as seen in Figure 12. An additional set of vacuum columns was also run at 4 mL min^{-1} at a different facility, however, and resulted in an elution profile similar to that obtained at 1 mL min^{-1} the first time. This can be seen in Figure 13, where ANL denotes work done at Argonne National Laboratory and UNLV denotes work done at the University of Nevada, Las Vegas. While the data presented in Figure 12 indicates that flow rate does play an important role in band broadening, the data presented in Figure 13 shows that there are clearly also effects based on the lot of resin used in packing the cartridges. Because of this, it is difficult to draw any sound conclusions other than that, for a given lot of cartridges, higher flow rates will result in more band broadening.

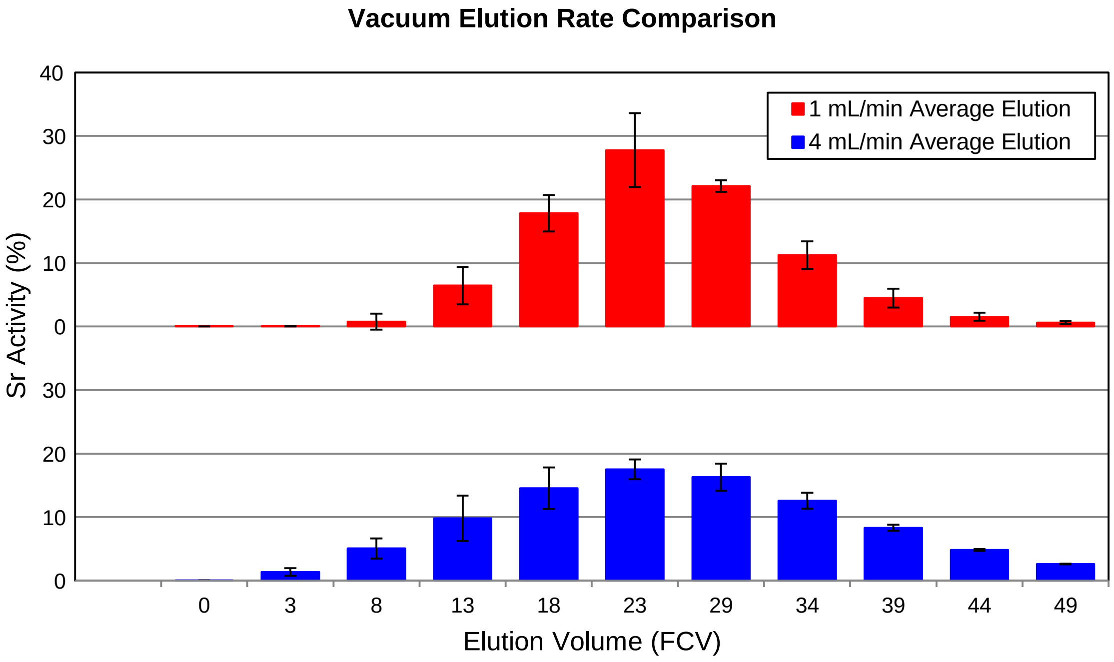

Figure 12: Comparison of two different flow rates on the same set of vacuum columns

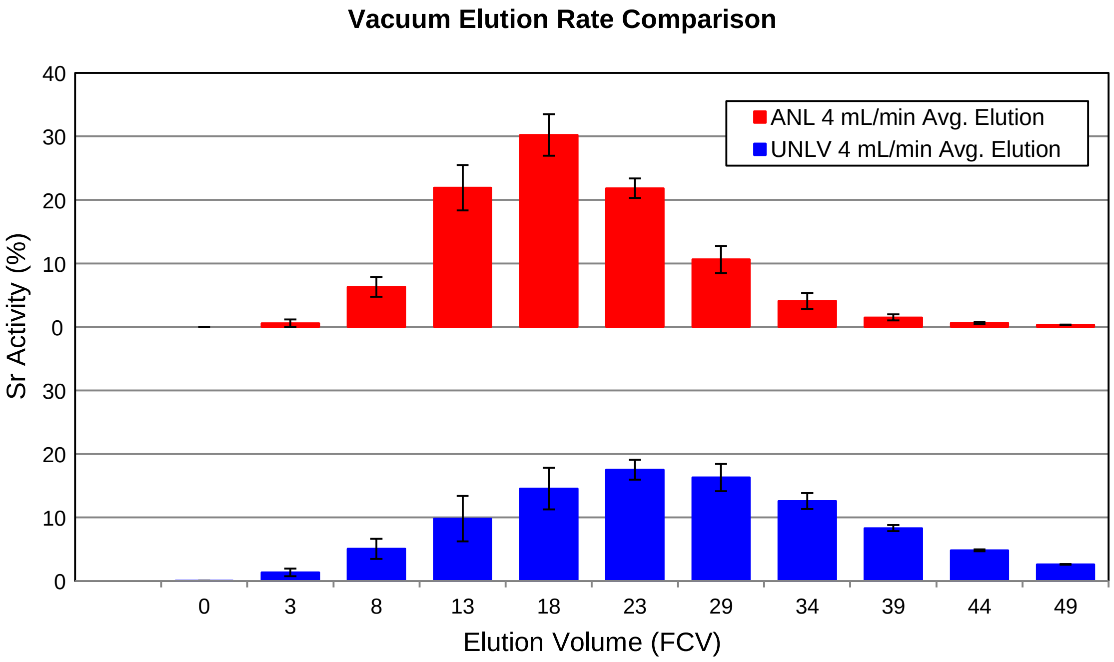

Figure 13: Comparison of two different sets of vacuum columns at the same flow rate

The pre-packed gravity columns and the vacuum columns are much more reproducible than the slurry packed gravity columns, as evidenced by the substantially smaller error bars (representing 1σ variation) associated with these in comparison to the slurry packed columns in Figure 11. The resolution of both the slurry packed and pre-packed columns are much better than the vacuum columns (and could likely be better with smaller fraction sizes), with more than 80% of their activity being concentrated in two fractions instead of up to six, as is the case with the vacuum columns.

One interesting trend that becomes apparent from this study is that, while the geometric and experimentally measured free column volumes correspond to approximately 70 % of the total bed volume for each of the different columns, the manufactured columns are smaller than the 2 mL advertised volume. This is especially true of the vacuum columns, which are a full 0.4 mL short. Subsequent experimentation in this study, however, shows that in practice the published retention values are accurate when the free column volume is assumed to be 1.4 mL instead of the experimentally determined FCV. This is evidenced by elution profiles consistently have peaks in the 15-23 FCV range when using the measured FCV instead of the factory specified value. If the listed FCV is applied, these peaks all shift down by approximately three FCVs, making the range 12-20, slightly more in line with the published values of 12-15 FCV.[54]

3.5 Conclusion

While both types of gravity flow columns appear to have better resolution than the vacuum flow columns, the massive difference in speed and the ability to measure out fractions before eluting them makes vacuum columns still the more desirable separation method for processing purposes. The vacuum columns also do not require constant attention, can be handled without having to worry about disturbing the bed, and the resolution can (likely) be improved by using elution strategies that utilize high retention load and rinse fractions followed by extremely low retention stripping fractions. If a situation requires a chromatographic separation without changing the elution matrix, however, it would be a better choice to use some form of gravity flow column.

CHAPTER 4: SEPARATION FROM STEEL

Steel is commonly encountered in urban environments. Though it may not always be found in plain sight, it is present in most every concrete structure in the form of reinforcing bars. It is also commonly used in highway overpasses, signs and traffic signals, cars, trains, power generators, tools, decoration/finishing on the outside of buildings, and myriad other uses, each of which has its own set of physical requirements. Because steel is used in such a variety of ways, each having its own physical demands, there are more than 3,500 different grades of steel each with a distinct chemical composition.[79] Fortunately, these can be loosely divided into three categories by composition: carbon steel, alloy steel, and stainless steel. Carbon steel is by far the most common type of steel, and is limited to less than 1 % carbon, 0.6 % copper, 1.65 % manganese, 0.4 % phosphorous, 0.6 % silicon, and 0.05 % sulfur.[79-80] Stainless steels are also common, and contain significant amounts of chromium (10 – 20 %) alloyed with smaller amounts of nickel (trace – 8 %) and trace levels of other elements, such as aluminum, titanium, or molybdenum.[79] Alloy steels fit between these two, exceeding the specifications for carbon steel and often containing other elements, but having a chromium content lower than stainless steels.[80]

Despite the abundance of steel in construction (including objects like nuclear reactors), very little information is available on the effects it may have on strontium uptake. The only data found is in the paper originally describing the resin for use in nuclear waste streams.[54] This study indicates that aluminum, chromium, manganese, nickel, and copper are entirely eluted in the first five free column volumes, but no detailed study of their impact on strontium retention was ever carried out. The study also kept each of the constituents it analyzed (34 in total) to less than 10 % of the capacity of the column. In the case of an RDD detonation, the concentrations of various steel components could potentially be much higher than that. This research tests the uptake of strontium in the presence of high concentrations (up to 1 M) of several steel components to ensure that the separations will still be possible in a post-detonation scenario. Based on the compositional information outlined above, as well as the compositions of several NIST standard reference materials and the likelihood of extraction by the resin based on ionic radius, six elements were chosen for analysis using batch studies and column studies outlined in Chapter 2.2.1 and 2.2.3.[81-86]

4.1 Materials

Because of the complexity and variation found in steels used in different applications, the number of elements analyzed in this work was pared down using two criteria: ionic radius[86] and abundance in various steel types.[79-85] These parameters were used because the resin extracts the neutral strontium nitrate species by coordinating the metal in the cavity of the ring, meaning ions likely to be retained by the resin would be closer in size to strontium. In addition, if an ion is abundant enough in steel and is concentrated enough in the dissolved analyte, even a relatively small effect could overwhelm the resin. Based on these two criteria, the +2 metals nickel, copper, and manganese, and the +3 metals chromium, iron, and aluminum were selected for analysis.

The resin, strontium and nickel isotopes, acids, and preparation methods used in this set of experiments were all described in chapter 2.1. Metal salt solutions were made from $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, Puratronic 99.9985% metals basis), $Cu(NO_3)_2 \cdot 2.5H_2O$ (Alfa Aesar, 98%), $MnCl_2$ (Alfa Aesar, ACS, 98-101%), $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich, 99%), $Fe(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar, 98+% metals basis), and $Al(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt Chemicals, J.T.Baker 98-100%). All salts were diluted to desired concentration using 3 M HNO_3 in individual volumetric flasks. The SRM samples were prepared by dissolving 1 g of NIST SRM 361 or SRM 14f in a mixture of concentrated nitric and hydrochloric acids (3:1 and 10:1 HNO_3:HCl v/v, respectively) before being evaporated to dryness and reconstituted in 3 M HNO_3 for use. SRM 361 is AISI 4340 alloy steel and SRM 14f is AISI 1078 carbon steel, both in the form of 0.5 – 1.18 mm chips.[81, 83] The compositions of the two materials are shown in Table 5.

Table 5: Compositions of SRM 361 and SRM 14f, as obtained from NIST.[81, 83] For the sake of brevity, elements of < 0.01 % abundance were omitted from this table. (--) indicates the element was not listed as a component in the certificate of analysis

Constituent	SRM 361 (% Mass)		SRM 14f (% Mass)	
Aluminum	0.021	± 0.005	--	
Arsenic	0.017	± 0.001	--	
Carbon	0.383	± 0.001	0.753	± 0.007
Chromium	0.694	± 0.005	0.070	± 0.004
Cobalt	0.032	± 0.001	--	
Copper	0.042	± 0.001	0.072	± 0.002
Manganese	0.66	± 0.01	0.410	± 0.003
Molybdenum	0.19	± 0.01	0.013	± 0.001
Nickel	2.00	± 0.01	0.053	± 0.003
Niobium	0.022	± 0.001	--	
Phosphorus	0.014	± 0.001	0.009	± 0.001
Silicon	0.222	± 0.001	0.172	± 0.003
Sulfur	0.0143	± 0.0003	0.039	± 0.002
Tantalum	0.020	± 0.001	--	
Tin	0.010	± 0.001	--	
Titanium	0.020	± 0.001	--	
Tungsten	0.017	± 0.001	--	
Vanadium	0.011	± 0.001	0.002	± 0.001
Iron	95.61	± 0.02	98.41	± 0.01

4.2 Procedure & Measurement

Batch studies and column studies were carried out following the procedure outlined in chapters 2.2.1 and 2.2.3, respectively. All batch studies and column preconditioning, loading, and rinsing were carried out using 3 M HNO_3. Radiometric analysis of ^{85}Sr was carried out using the gamma detector described in chapter 2.3.2, while analysis of ^{63}Ni was performed on the LSC described in chapter 2.3.1 using Ultima Gold AB LSC Cocktail. All radiometric measurements were taken on 1 ml aliquots. Stable constituents were analyzed using the ICP-OES system and dilution scheme described in chapter 2.3.3.

4.3 Results & Discussion

4.3.1 Batch Studies

After an initial characterization of the resin, it was determined that the gain in retention at concentrations higher than 3 M was minimal and all batch studies and column loading in this research therefore utilized 3 M nitric acid. The baseline chromatographic capacity factor for the resin under these conditions was 59.1 ± 1.1. Each metal salt was investigated at concentrations of 1.0, 0.5, 0.25, 0.1, 0.05, 0.01, 0.005, and 0.001 M in order to cover a vast range of possible concentrations that could be seen after the dissolution of steel.

Upon analysis, synergistic trends were observed with the increase of the salt concentration. Figure 14 and Figure 15 show how the k' value for strontium changes when varying the concentration of the associated +2 and +3 metal salts, respectively.

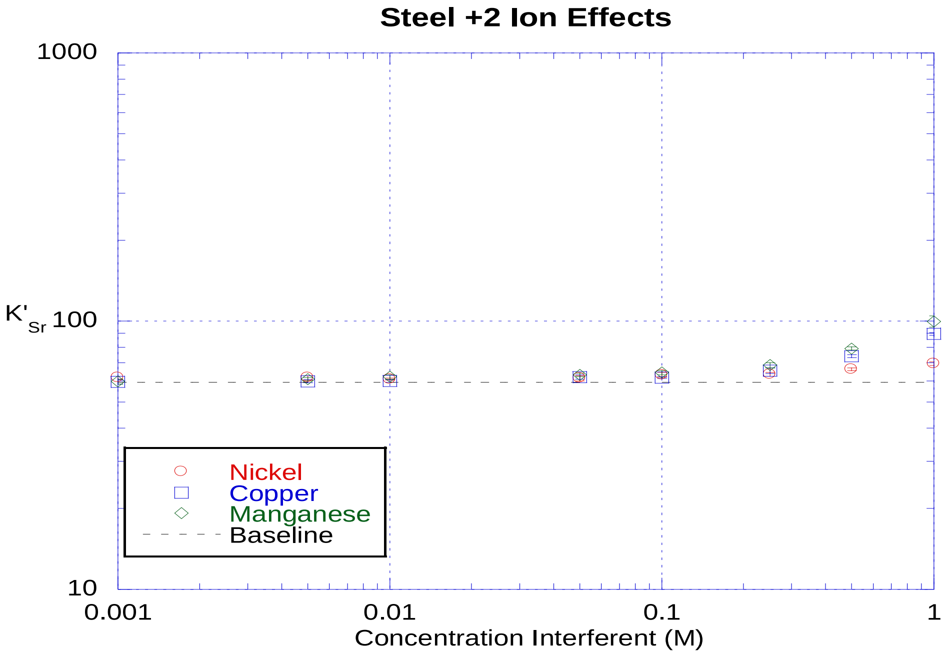

Figure 14: Batch study results of the +2 ions nickel, copper, and manganese on the Sr chromatographic capacity factor with Sr resin in 3 M HNO_3. The baseline k' value under these conditions is 59.1 ± 1.1. Error bars are 1σ

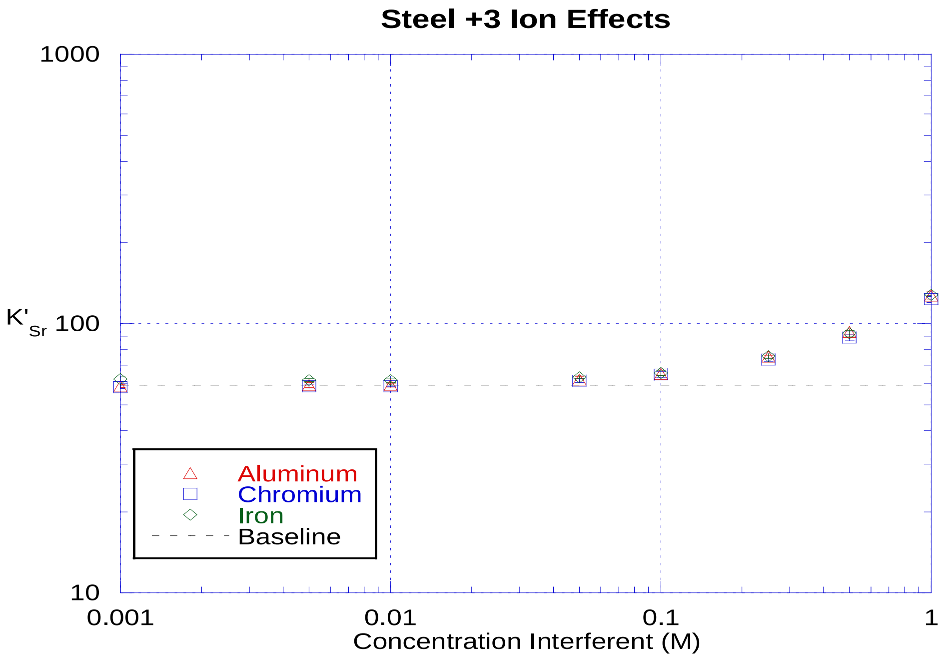

Figure 15: Batch study results of the +3 ions aluminum, chromium, and iron on the Sr chromatographic capacity factor with Sr resin in 3 M HNO_3. The baseline k' value under these conditions is 59.1 ± 1.1. Error bars are 1σ

This trend is most likely due to a phenomenon known as "salting out," which is described in detail in *Braun and Ghersini.*[87] Salting out occurs when charged ions sequester water molecules in their solvation sphere. This effectively increases the concentrations of the remaining analytes and the likelihood that they will be able to recombine with (in this case) a nitrate anion in solution to make the neutral species. Indeed, it is often suggested to add $Al(NO_3)_3$ to load (and occasionally rinse) solutions to increase the retention of strontium on the column for this reason. Because salting out is dependent on the analytical activity of the solution, which tracks with ionic strength, all of the data points in Figure 14and Figure 15 were plotted against ionic strength, shown in Figure 16. This plot also includes the retention data when increasing the ionic strength of the solution by just adding nitric acid. When mapped in this way, all of the ions analyzed appear to follow approximately the same trend with the exception of nickel. Also notable, the increase seen when only the nitric acid concentration is increased is significantly less than what is seen with the addition of the majority of salts. This means that the increase in retention seen as a result of increasing salt concentrations cannot be explained by the increase in nitrate anion present in solution alone and strengthens the argument for salting out. It also appears to indicate that nickel is the only constituent analyzed that does not cause a salting out phenomenon. Based on these measurements, it actually appears as though nickel could cause a slight decrease in strontium retention at high concentrations (with respect to the increased extraction caused by the increase in nitrate anions from the salt).

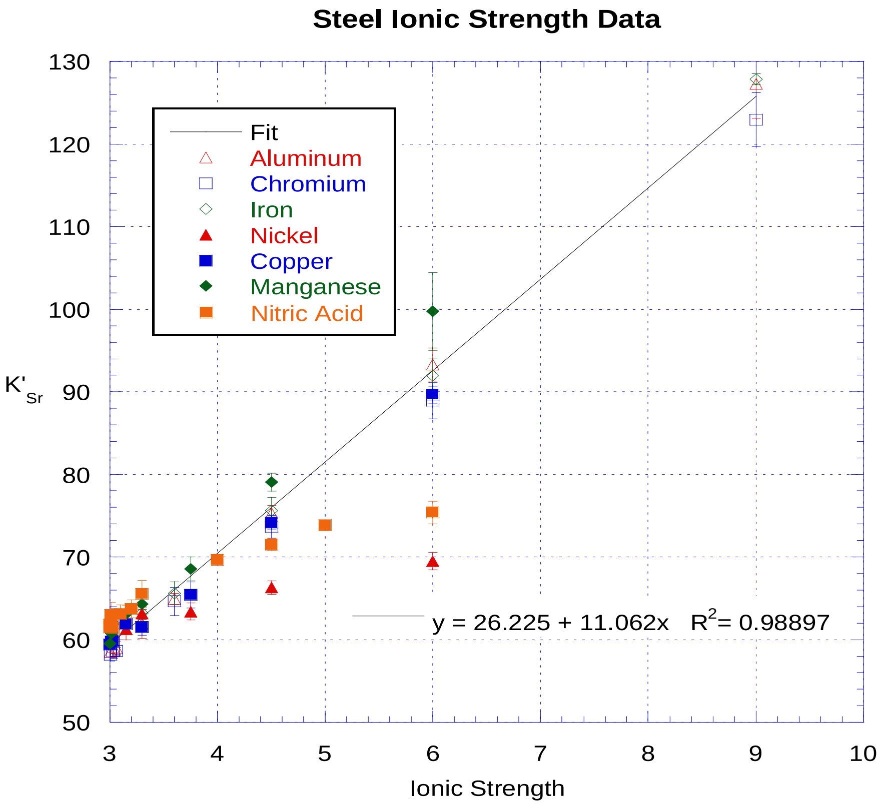

Figure 16: Plot of strontium uptake against ionic strength of the aqueous phase due to the addition of various metal salts. The trend line excludes the nickel data, but indicates a good fit for the rest of the ions

Despite the slight possibility of nickel interference, analysis of the various samples via ICP-OES indicated no observable uptake of any of the steel components at the concentrations examined (Figure 17), which is to be expected if salting out is occurring.

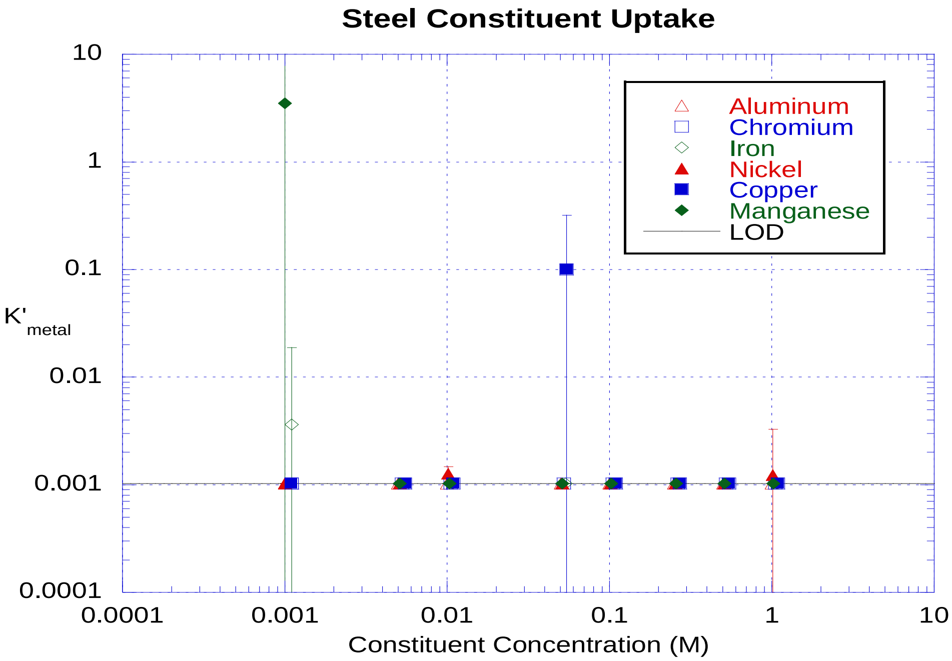

Figure 17: Steel constituent uptake on Sr Resin in the presence of strontium in 3 M HNO_3. All points are within measurement error of the LOD for K'

Because nickel behaved differently than the rest of the components, it was also analyzed individually for uptake with a ^{63}Ni tracer. This study also indicated no appreciable uptake of nickel, even down to concentrations as low as 10^{-10} M (18 Bq ml^{-1}). The data from this batch study is shown in Figure 18. Batch studies were also carried out using dissolved SRMs. SRM 14f was carbon steel, and SRM 361 is a low alloy steel containing chromium, nickel, and molybdenum. Each was dissolved using a mixture of nitric and hydrochloric acid. The resulting solutions were then filtered, evaporated to dryness, and re-dissolved in concentrated nitric acid twice to ensure conversion of all remaining salts. These solutions were again evaporated to dryness and the remaining salts were dissolved using 3 M HNO_3. The batch studies of each of these materials show synergistic effects matching those seen for the individual constituents (Figure 19).

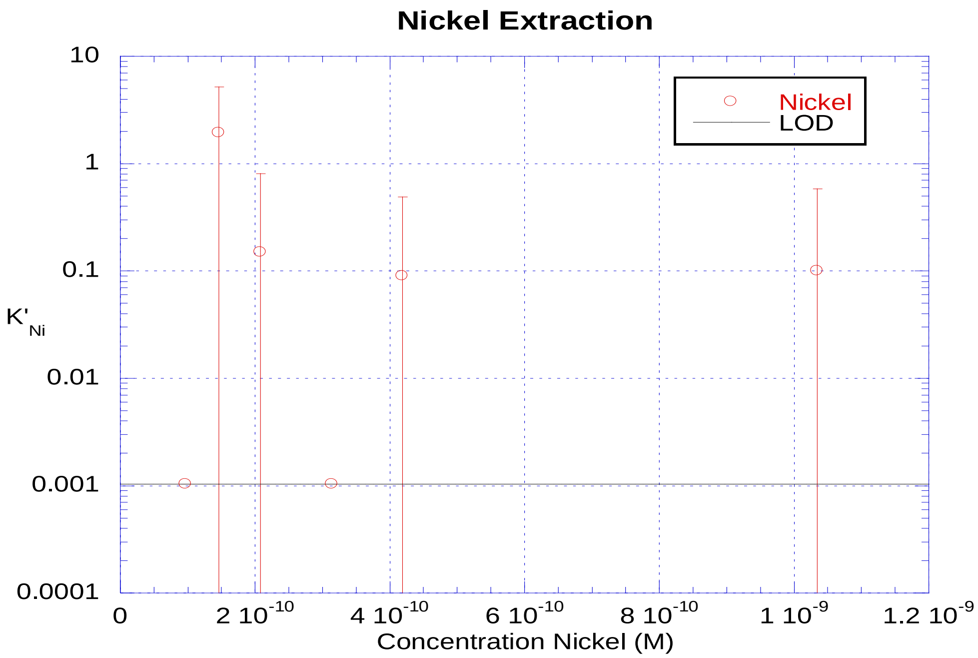

Figure 18: Nickel uptake on Sr Resin at low concentrations of Ni in 3 M HNO_3. 10^{-10} M ^{63}Ni equates to approx. 18 Bq ml^{-1}. All points are within measurement error of the K' LOD

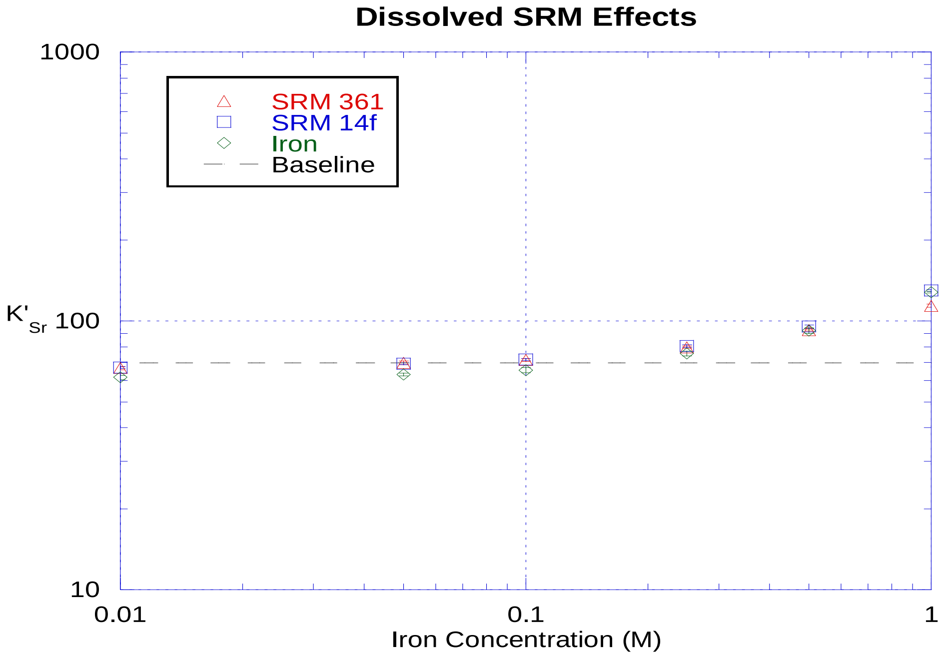

Figure 19: Batch study results of the dissolved SRMs and iron (included for reference) on the Sr chromatographic capacity factor with Sr resin in 3 M HNO_3. The baseline k' value under these conditions is 59.1 ± 1.1. Error bars are 1σ

4.3.2 Column Studies

Because each of the steel components, excluding nickel, behaved similarly to iron and because iron constitutes greater than 90% of most steels, it was deemed satisfactory to only analyze iron and nickel individually in column studies. In addition to these constituent studies, columns were eluted using the same dissolved SRMs spiked with Sr-85 described above. In all of the column studies, the interference was studied with 1 M concentrations of individual constituents in the load fraction. In the case of the SRMs, the solutions were diluted such that the most abundant element (iron) was at 1 M. The results of all of these column studies are shown in Figure 20 and indicate that neither the individual constituents nor the dissolved SRMs cause significant premature breakthrough of the strontium while the recovery in the elution fractions remains high. This data can be found below, in Table 6.

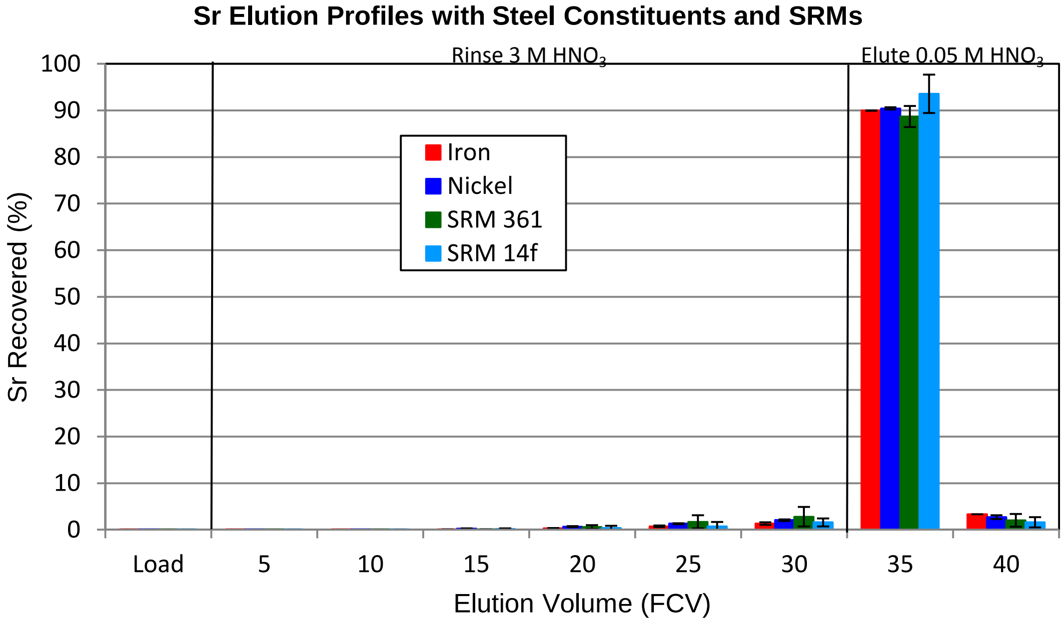

Figure 20: Column elution profiles for strontium with steel matrix constituents or dissolved SRMs. Constituents were present in the load solution at 1 M. SRM load solutions were dilute such that iron was at 1 M. Error bars are 1σ.

Table 6: Comparison of strontium recovered in the rinse elution fractions for the various column studies

Constituent/SRM	Rinse Fraction Recovery (% Sr)	Elution Fraction Recovery (% Sr)
Iron	2.5 ± 0.3	93.33 ± 0.03
Nickel	4.3 ± 0.2	93.2 ± 0.5
SRM 361	5 ± 3	91 ± 3
SRM 14f	3 ± 1	95 ± 4

4.4 Conclusions & Future Work

This work shows that strontium can be effectively analyzed in the presence of some common steel components using extraction chromatography. It also demonstrates that such a separation can be done without removing any of the steel constituents prior and that the most common steel components will actually cause an increase in the extraction capabilities of Sr resin, most likely due to a salting out effect. One common constituent of steel (nickel) did not act similarly to the others in the systems investigated. This work was able to show that the different behavior of nickel did not arise from it being retained by the resin, though a definite reason for the differences was not discovered and will require further experimentation.

While this work shows the possibility of separation from steel components in principle, the practical application will require additional studies. Other relatively common steels and alloys use significantly different compositions to achieve their desired physical properties. Special consideration should be given to molybdenum. While it was not examined in this study because of its low concentrations in the steels considered for this work, it is a common low level constituent of steel that could cause problems due to its penchant for forming oxy-cations in solution similar to uranium (which is retained at high acid concentrations).[54] Silicon is another common low level impurity in steels. While it is unlikely that Si would cause actual interference in strontium uptake, it is possible that silicon’s complex chemistry could result in clogging the column or other physical manifestations that would need to be taken care of. Additional studies looking at these components and the behavior of strontium during dissolution would be insightful, and likely necessary for the complete development of a separation of radiostrontium from steel.

CHAPTER 5: SEPARATION FROM CONCRETE

Cement and concrete are also of interest when considering urban building materials that are likely to become contaminated in the aftermath of an RDD strike. Unfortunately, the aggregate used in creating concrete is extremely variable, as the aggregate is generally locally sourced and can be sand, gravel, crushed stone, blast furnace slag, crushed recycled concrete, or some combination thereof. It is often more of an inexpensive filler than a component providing physical properties.[88-89] In order to make this a manageable project, two of the most common aggregate materials were chosen for testing as "representative" of aggregates as a whole. The aggregates tested in this work were limestone and dolomitic limestone, with representative compositions obtained from the National Institute of Standards and Technology, NIST (SRMs 1D and 88B, respectively).[90-91] The two most common types of cement used in construction are hydraulic cement and Portland cement, both of which have similar chemical requirements (outlined by the American Society for Testing and Materials, ASTM) in the United States.[92-93] Because of these similarities, the compositions analyzed were taken only from NIST Portland cement SRMs (SRM 634, 635, and 637).[94-96]

While little previous work had been done on the effects of individual primary components of steel, a much clearer picture is presented concerning the primary components of most cements and concretes. This is due to the fact that the primary constituents of cement and concrete tend to be other alkali earth metals and alkali metals, which are similar in both charge and size to strontium. Indeed, fairly detailed retention curves have been generated for Cs, Na, Rb, K, Ca, Ra, and Ba, and interference curves have been generated for Ca, Na, NH_4, and K.[54] This work aims at confirming the retention trends of strontium in the presence of previously investigated cement and concrete constituents (Na, K, and Ca). It also looks at other common components of cement and concrete (Mg and Zn) that could potentially interfere. All of these interferences are analyzed using both batch studies and column studies, as outlined in Chapter 2.2.1 and 2.2.3.

5.1 Materials

Based on the compositions of several NIST cement and aggregate SRMs, sodium, potassium, calcium, magnesium, and zinc were chosen as potentially interfering elements for this study. The resin, strontium isotopes, acids, and preparation methods used in this set of experiments were described in chapter 2.1. Metal salt solutions were made from $NaNO_3$ (ACS Reagent), KNO_3 (99+% ACS Reagent), $Ca(NO_3)_2{\cdot}4H_2O$ (99%+), $Mg(NO_3)_2{\cdot}6H_2O$ (≥98%), and $Zn(NO_3)_2{\cdot}6H_2O$ (Reagent Grade 98%), all obtained from Sigma-Aldrich (St. Louis, MO). All salts were diluted to desired concentration using 3 M HNO_3 in individual volumetric flasks. The SRM samples were prepared by combining the listed metal salts in ratios corresponding to the compositions NIST of SRM 634 and SRM 88B, listed in Table 7. SRM 634 is Portland Cement and SRM 88B is Dolomitic Limestone, commonly used as an aggregate in concrete. The salt combinations generated for batch studies were also then diluted to the appropriate concentrations in volumetric flasks using 3 M HNO_3.

Table 7: Composition of an SRM aggregate (88B) and an SRM cement (634). (--) indicates the constituent was not listed as a component in the certificate of analysis. *Measured as Mn_2O_3 in SRM 634 and converted.

	SRM 88 B		SRM 634	
Constituent	(% Mass)		(% Mass)	
Al_2O	0.336	± 0.013	5.21	± 0.05
CaO	29.95	± 0.05	62.58	± 0.05
CO_2	46.37	± 0.12	--	
Fe_2O_3	0.277	± 0.002	2.84	± 0.01
K_2O	0.1030	± 0.0024	0.42	± 0.01
MnO*	0.0160	± 0.0012	0.13	±0.01
MgO	21.03	± 0.07	3.30	± 0.05
Na_2O	0.0290	± 0.0007	0.15	± 0.01
SiO_2	1.13	± 0.02	20.73	± 0.05
SrO	0.0076	± 0.0003	0.12	± 0.01
SO_2	--		2.21	± 0.05
TiO_2	--		0.29	± 0.01

5.2 Procedure & Measurement

Batch studies and column studies were carried out following the procedure outlined in chapters 2.2.1 and 2.2.3, respectively. All batch studies and column preconditioning, loading, and rinsing were carried out using 3 M HNO_3.

Radiometric analysis of ^{85}Sr was carried out using the gamma detector described in chapter 2.3.2. All radiometric measurements were taken on 1 ml aliquots.

5.3 Results & Discussion

5.3.1 Batch Studies

Based on the previous steel work, it was determined that the gain in retention at concentrations higher than 3 M was minimal and all batch studies and column loading in this research therefore utilized 3 M nitric acid. The baseline chromatographic capacity factor for Sr under these conditions was roughly 59.1 ± 1.1. Each salt was investigated at concentrations of 1.0, 0.5, 0.25, 0.1, 0.05, 0.01, 0.005, and 0.001 M in order to cover a vast range of possible concentrations that could be encountered after the dissolution of concrete.

Prior to this work, it had been shown that the alkali and alkali earth metals tend to interfere with the uptake of strontium.[49, 54] It is not surprising, therefore, that this trend was seen in the batch study results shown for sodium, potassium, and calcium in Figure 21. These results match those obtained by *Horwitz et.al*[54] and *Chiarizia et.al*[49] in 1992 when the resin was first developed. Interestingly, magnesium does not show the same trend, despite also being an alkali earth metal. This is likely due to its much smaller ionic radius prohibiting the effective complexation by the crown extractant. Zinc, unsurprisingly, follows this same trend, since its ionic radius is much closer to that of magnesium than that of sodium, potassium, and calcium. Given that cement and concrete are composed primarily of calcium, it is possible that an early breakthrough of radiostrontium could be seen. The concentration at which a premature breakthrough would occur would depend on the elution strategy employed. If the strategy from this work were used, it is likely that premature breakthrough would begin at potassium concentrations between 0.01 and 0.05 M, or calcium or sodium concentrations between 0.5 and 1 M. While the k' values indicate the elution peak maximums would still be in the strip phase of the elution strategy at these concentrations, the peaks are not infinitely thin, and will likely become broader as more eluent passes through the column. These estimates would also, therefore, depend on flow rate and column characteristics with faster flowing, shorter columns having more significant breakthrough than longer, slower flowing columns.

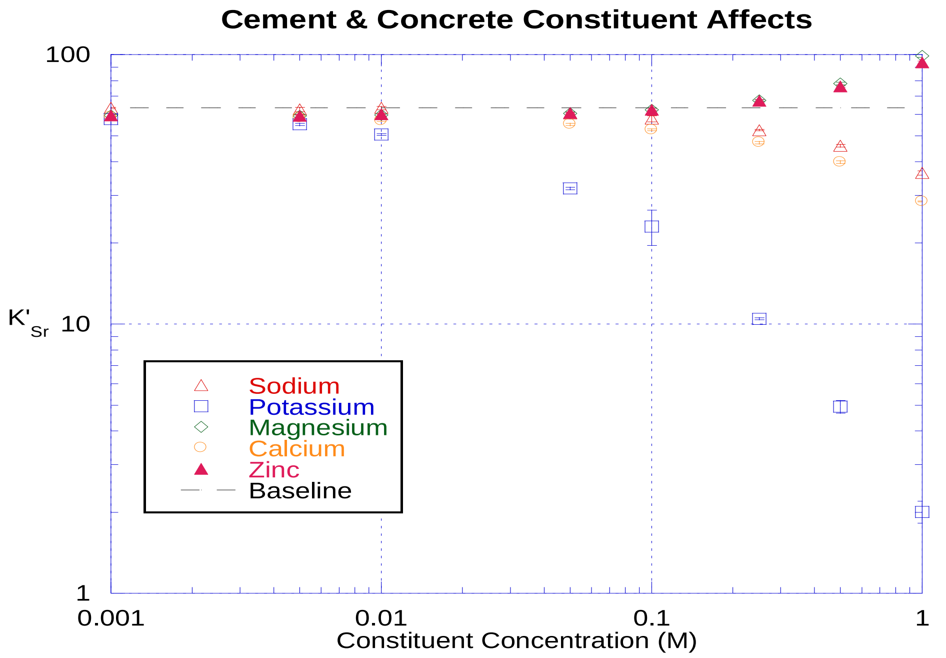

Figure 21: Batch study results of the primary constituents of cement and concrete on the Sr chromatographic capacity factor with Sr resin in 3 M HNO_3. The baseline k' under these conditions is shown as a dashed line. Error bars are 1σ.

As with the steel constituents analyzed in the previous chapter, synergistic affects are seen when the constituents are not adsorbed by the resin. To demonstrate the similarities to the steel trials, this data set was also plotted as a function of ionic strength. This is seen in Figure 22, which shows the trend line associated with magnesium and zinc. This is very similar to that of the +2 and + 3 ions in the steel work, with slopes and intercepts varying slightly. While not exactly the same, it is still larger than the increase seen from nitric acid, which would indicate salting out is also occurring in these systems. In contrast to this, strontium retention in the calcium and sodium systems declines fairly linearly with increasing ionic strength, and in the potassium system decreases with a somewhat exponential trend.

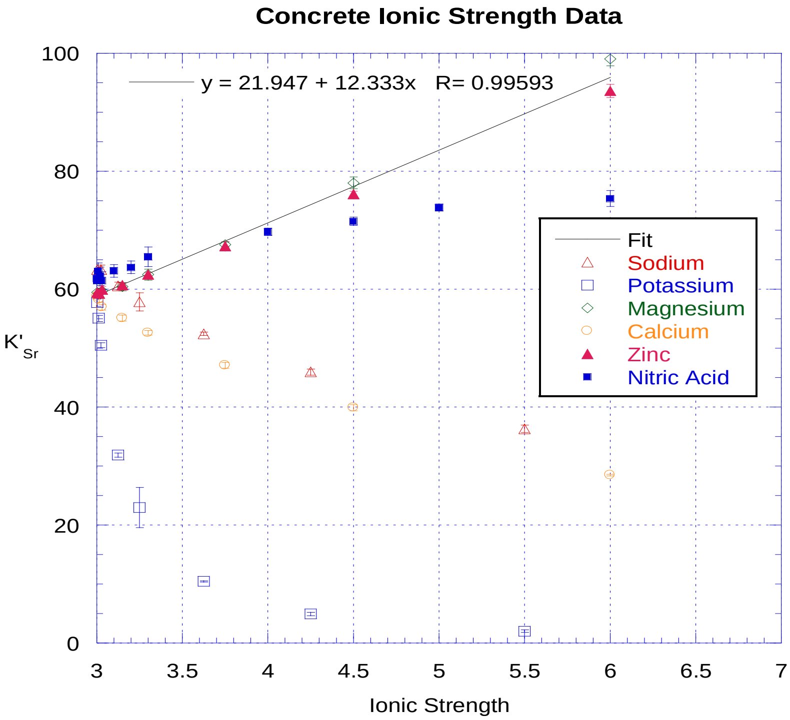

Figure 22: Plot of strontium uptake against ionic strength of the aqueous phase due to the addition of various metal salts. The trend line includes only magnesium and zinc data.

5.3.2 Column Studies

The column studies carried out with individual constituents at 1 M concentrations indicated that only potassium gave rise to a k' low enough to result in significant breakthrough during the loading phase of the column elution. While none of the other constituents caused as drastic a breakthrough as potassium, strontium did have significant breakthrough (>5%) in the first 30 FCVs for each of the remaining constituents, as seen in Figure 23. This resulted in poor recoveries of 65 – 72% in the strip fractions of the elution profile (FCVs 35 and 40). Although these results indicate that inferior recoveries would be likely when working with dissolved cement and concrete, it is possible that samples with representatively proportioned compositions would not result in such significant breakthrough.

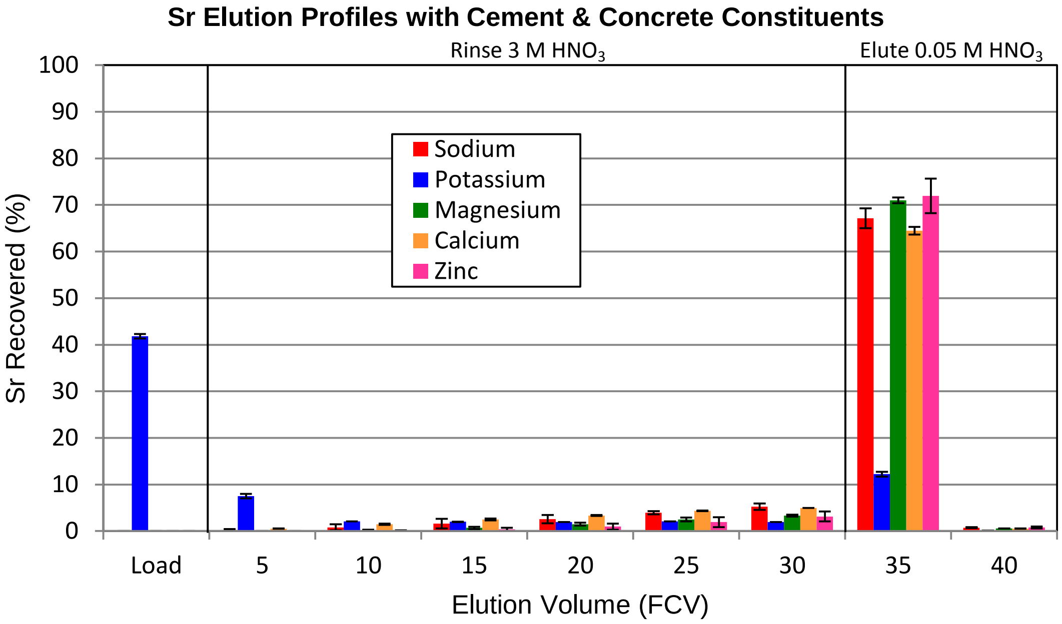

Figure 23: Column elution profiles for strontium with cement and concrete aggregate matrix constituents. Constituent were all present in the load solution at a concentration of 1 M. Error bars are 1σ.

To test whether this is the case, simulated solutions were prepared based on the compositions of Portland cement and dolomite (Dolomitic Limestone) SRMs obtained from NIST (SRM 634 and 88B, respectively). While it would have been preferable to directly dissolve the SRMs and perform these tests, digestion is not straight forward due to the significant amounts of silica in each. Further work involving cement and concrete digestion is found in Chapter 6. Table 8 shows the final molar concentrations of each constituent for the two simulated solutions.

Table 8: Molar concentrations of various constituents in simulated solutions of dissolved cement (SRM 634) and dolomite (SRM 88B)

Element	SRM 634 (M)	SRM 88B (M)
Ca	1.694	0.221
Mg	0.733	1.564
K	0.0806	0.00677
Na	0.0452	0.00287
Zn	0.0276	N/A

The results of the vacuum column studies are shown in Figure 24, and indicate that cement on its own will cause significant premature breakthrough of strontium (approx. 27.5%). The breakthrough associated with the simulated dolomite is significantly lower than that seen for cement, but still high (approx. 9.5%). This makes sense, as the dolomite has a much higher concentration of magnesium, which was shown to increase the retention of strontium. However, it also contains less calcium, which could have caused the decrease in breakthrough as well.

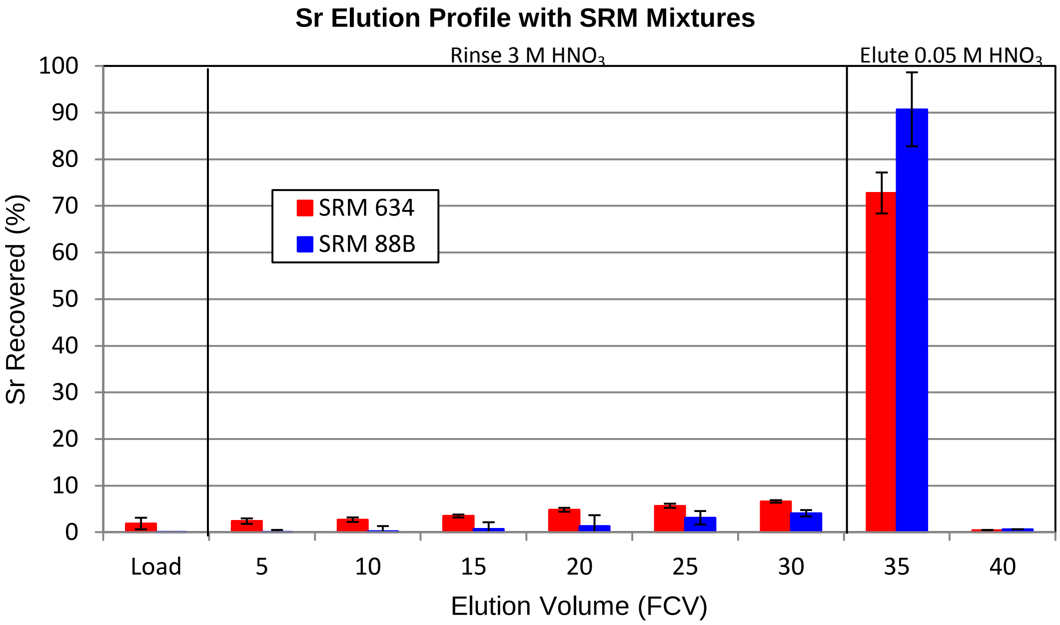

Figure 24: Column elution profiles for strontium with cement and concrete aggregate simulated solutions (Concentrations listed in Table 5). Error bars are 1σ.

5.4 Conclusions & Future Work

Although recoveries of better than 85% in the appropriate fractions was achieved with the dolomite simulated solution, premature breakthrough was significant in both mixture trials and all of the individual constituent trials. This is likely due to the difference in either calcium or magnesium concentration in the two simulated solutions, though an additional set of experiments where one element concentration is held constant while varying the other would be required to definitively say which. It must be acknowledged that dolomitic limestone is not the only aggregate used in concrete, and that the ratio of aggregate to cement will also vary from application to application. Because of this, it is difficult to say just how much of an impact dissolved cement or concrete would have on strontium retention without some form of pre-processing to standardize the solution.

While the overall composition of many cements is fairly constant, the aggregates can vary widely depending on local geology and ease of access. One could expect significant differences in aggregate mined from a quarry compared to aggregate gathered from river or lake beds, and even more significant differences between those and steel furnace slag, which is also common. A more thorough investigation of other aggregate types would be useful in determining any additional effects that might be seen.

CHAPTER 6: USING SR RESIN WITH ACID MIXTURES

While there are many proven dissolution procedures for steel and alloys, the chemicals used in the dissolution reflect both the analysis method and the composition of the steel. The majority of methods developed do appear to use some mixture of nitric and hydrochloric acid as the primary dissolution reagent.[45, 97] Unfortunately, the only published retention data found for Sr Resin is in pure mineral acid systems.[54, 63] Given that the most common methods of steel dissolution involve mixtures of nitric and hydrochloric acids, it would be desirable to know if it is possible to perform strontium extractions directly from such mixed acid solutions. To that end, varying blends of concentrated nitric acid and hydrochloric acid were tested to see if a separation could be carried out without taking steps to convert the matrix to purely nitric acid.

In addition to studying mixtures of nitric and hydrochloric acid, mixtures of nitric, hydrochloric, and hydrofluoric acid with two different compositions were analyzed. This was undertaken because combinations of the three are often required for the digestion of soil samples, which could potentially be implemented for the digestion of urban materials with higher concentrations of silica, such as cement and concrete. The ratios of hydrochloric to nitric to hydrofluoric acid that were examined were chosen based on digestion work being performed at multiple national laboratories.[98-99] It is likely that these mixtures will require some processing (i.e. addition of $Al(NO_3)_3$ and/or boric acid) to ensure strontium does not precipitate out as SrF_2, which is relatively insoluble and could potentially clog the column.[100]

6.1 Materials

The resin, strontium isotopes, acids, and preparation methods used in this set of experiments were described in chapter 2.1. Acid mixtures were prepared by mixing the volumetric ratio of acids listed, then diluting that mixture with deionized water to achieve different total acid concentrations. Strontium solutions were prepared with the undiluted mixed solutions, except for the acid mixtures containing HF. For those solutions containing HF, the various total acid concentration solutions were prepared and separate strontium tracer solutions were made using a portion of each. These tracer solutions ranged from 17 – 32 Bq ml^{-1}.

6.2 Procedure & Measurement

Batch studies and column studies were carried out following the procedure outlined in chapters 2.2.1 and 2.2.3, respectively. Preconditioning of the batch study resins and the loading of the columns utilized the acid solutions specified. All column preconditioning and rinsing was carried out using 8 M HNO_3. The higher acid concentration was used because the results of the batch studies. These indicated favorable retention at total acid concentrations higher than 3 M and it seemed logical to utilize a similar concentration of nitric acid for rinsing the column.

Radiometric analysis of ^{85}Sr was carried out using the gamma detector described in chapter 2.3.2. All radiometric measurements were taken on 1 ml aliquots.

6.3 Results & Discussion

6.3.1 Batch Studies

The results of batch studies using different ratios of nitric acid to hydrochloric acid are shown below in Figure 25. It should be noted that all total acid concentrations listed in this work were derived from calculations based on the concentration of the initial acids mixed in solution. Because the mixture of nitric and hydrochloric acids causes the decomposition of the two acids into several volatile gaseous products (including NOCl, Cl_2, NO, NO_2, and O_2), over time this estimated total acid concentration decreases and will no longer be accurate. It has been previously stated that increasing the hydrochloric acid concentration does not decrease the effectiveness of the resin until a concentration of 0.5 M HCl is reached.[54] The data from this work indicates that the effectiveness at high total acid concentration (>5 M combined concentration) does not appreciably decrease as long as the solution contains at least 25 % v/v nitric acid. The usable ratio may be even lower than this, but a more thorough examination of mixing ratios would be required. The lower limit for k' in this study was 0.001. Any results (notably many of the HCl concentrations) that were lower than this have been plotted at this value.

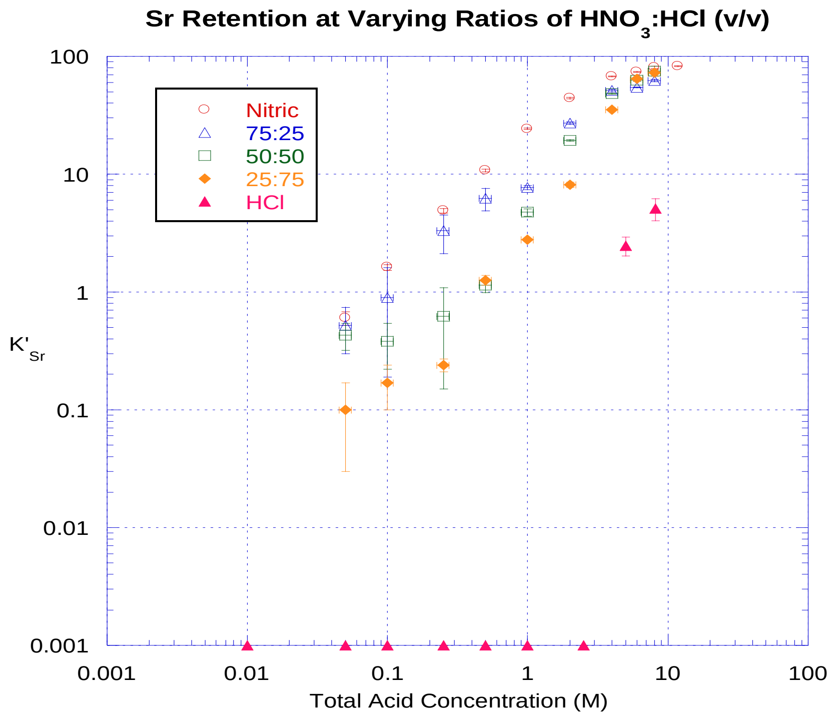

Figure 25: Batch study results for different ratios of HNO_3:HCl, which were then diluted to various total acid concentrations. Vertical error bars are 1σ, horizontal error bars are 10% (due to inaccurate pipetting from gas formation).

The results of the batch studies on mixtures including hydrofluoric acid, shown in Figure 26, are also promising. At high total acid concentrations, it is seen that the extraction of strontium is still quite high, if not higher than that seen in purely nitric acid matrices with similar concentrations. It is possible this has something to do with the high charge density associated with the F^- ion, resulting in a salting out phenomenon. If this was the only factor, however, it would also be expected to appear to a smaller degree in the nitric/hydrochloric samples, which is not seen. Finally, although SrF_2 is significantly less soluble than $SrCl_2$ or $Sr(NO_3)_2$, the batch study was carried out in such a way that formation of this species should not have had any influence on the k' values recorded. Individual ^{85}Sr tracer solutions were prepared for each of the mixtures, which allowed any precipitation to happen prior to being added to the resin. Even with this precaution being taken, minimal differences in activity were seen between the various tracer solutions from which these values were calculated.

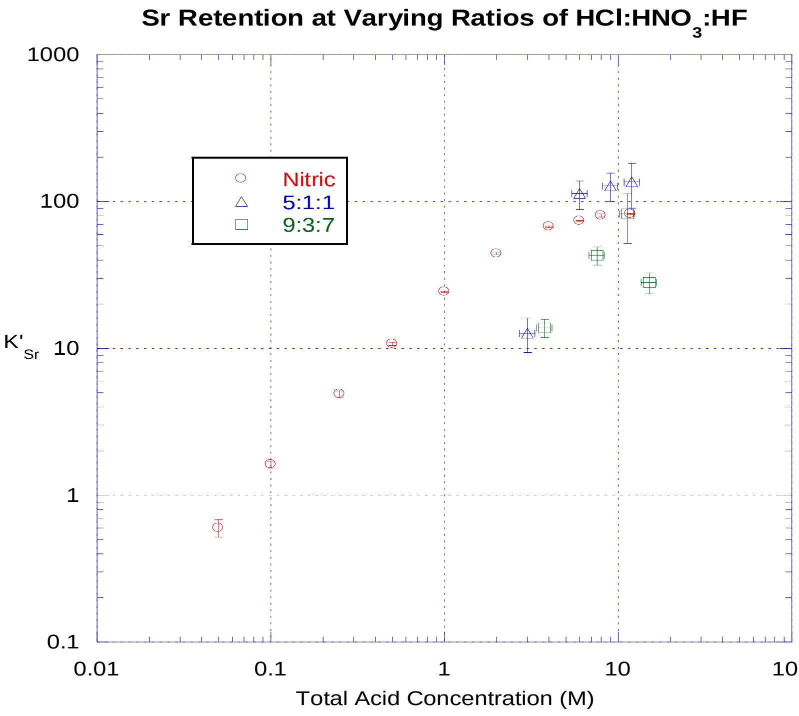

Figure 26: Batch study results for different ratios of HNO_3:HCl:HF, which were then diluted to various total acid concentrations. Vertical error bars are 1σ, horizontal error bars are 10% (due to inaccurate pipetting from gas formation).

6.3.2 Column Studies

Although the batch studies indicate that it is possible to accomplish this separation at several different ratios of HNO_3:HCl, they do not take into account the geometry of the column and how the generation of gas bubbles, which is common in these mixtures, might affect the width of the elution band or the ability of the column to retain the strontium. To this end, column studies were also carried out with the same mixture ratios. Figure 27 displays the elution profiles generated using the different loading solutions. Notably, even though the strontium showed minimal retention on the resin in HCl batch studies, the vast majority of the strontium was recovered in the elution phase of the column study shown above. This is because the loading of these columns used very small volumes of acid, making it possible to carry out the separation. When the volume of the loading phase for this the elution strategy was increased to represent something potentially seen in the real world (14 ml, or 10 FCV), there was significant breakthrough of the strontium in HCl, as can be seen in Figure 28. While there is some breakthrough prior to the elution phase of the procedure (FCVs 31 – 40) for the other acid mixtures, none of them have greater than 3 % of the strontium eluted in the wrong fractions.

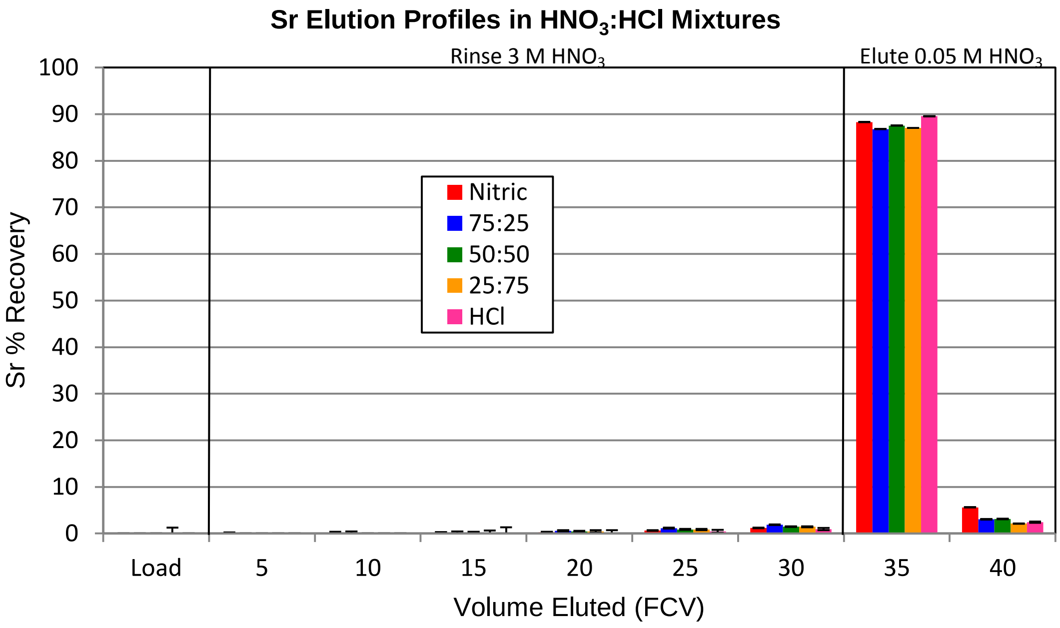

Figure 27: Elution profiles generated using various mixtures of nitric and hydrochloric acid for the loading solution. Small load volumes were used for these trials (0.25 ml). The load solution always had a calculated total acid concentration of 8.

When mixtures of nitric acid, hydrochloric acid, and hydrofluoric acid were tested in column studies, similar results were obtained. Vacuum column studies carried out with 14 ml load solutions showed less than 5 % breakthrough prior to the elution fractions with the 5:1:1 mixture, and just over 12 % breakthrough prior to the elution fractions for the 9:3:7 mixture (Figure 29). While this amount of breakthrough is significant in many cases, recovery in the elution phase was still 94.25 and 84.70 %, respectively, indicating that a separation could likely be done with the 5:1:1 mixture, and could possibly be performed with the 9:3:7 mixture, if a smaller rinse volume were used.

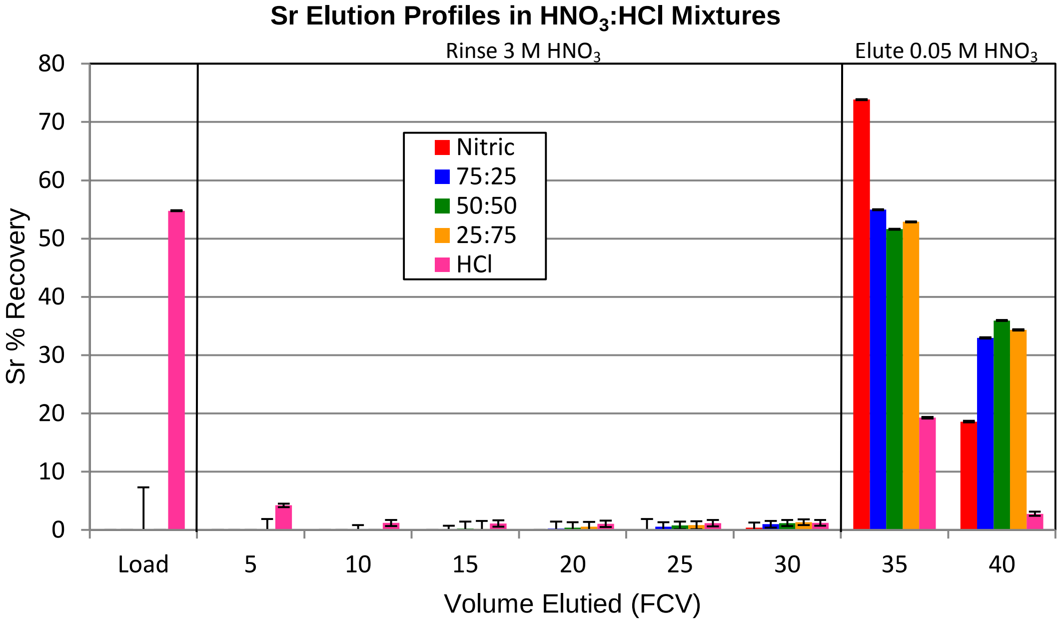

Figure 28: Elution profiles generated using various mixtures of nitric and hydrochloric acid for the loading solution. Realistic load volumes were used for these trials (14 ml). The load solution always had a calculated total acid concentration of 8.

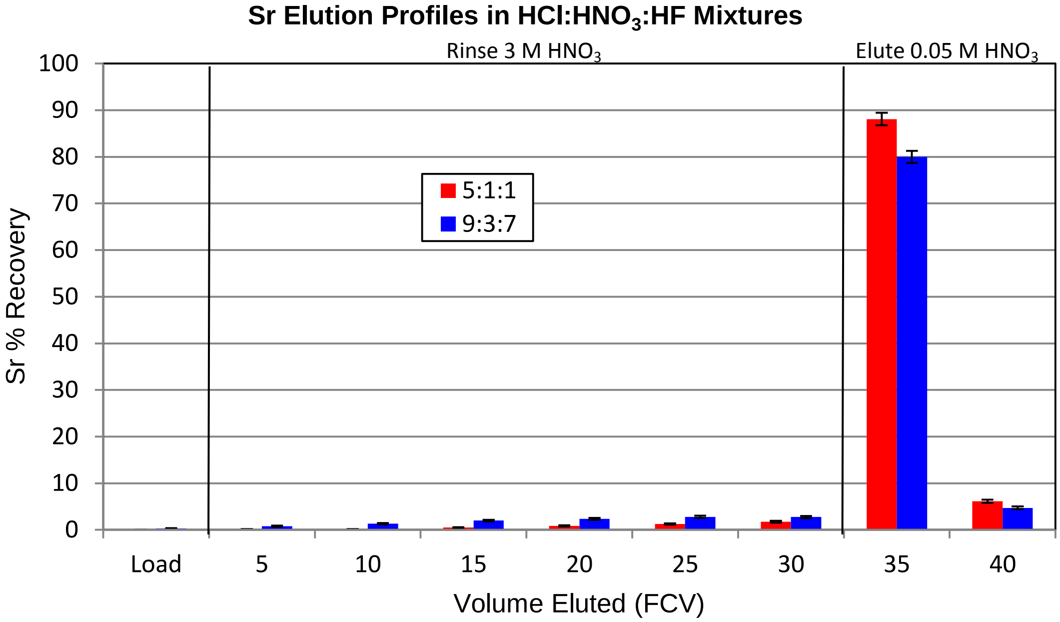

Figure 29: Elution profiles generated using two different mixtures of hydrochloric acid, nitric acid, and hydrofluoric acid. Load solutions were 14 ml of 80 % strength dilutions of the concentrated acids.

6.4 Conclusions & Future Work

The batch and column studies carried out indicate that separations performed directly from mixed nitric and hydrochloric acid matrices are possible. The primary requirement for these separations appears to be high total acid concentration. However, given the very low k' values obtained in even very high concentration hydrochloric acid, it seems clear that a certain amount of nitric acid is also required to be in solution. While these results indicate that there must be a minimum concentration of nitric acid below which the extraction will not take place even in high total acid concentration solutions, this limit was not discovered during the course of this work. It can be speculated that enough nitric acid has to be present for all of the strontium to form neutral nitrate salts for extraction, but this will need to be investigated further for confirmation.

Batch and column studies carried out using hydrochloric acid, nitric acid, and hydrofluoric acid mixtures gave similar results, though only two different mixtures were tested. While this is promising for the use of these acid mixtures directly after sample digestion, more work needs to be done to examine how the acids may affect the columns and how constituents other than strontium may interact with the mixtures. Many elements are either insoluble or sparingly soluble in hydrofluoric acid, and could cause significant flow problems if precipitated during the loading of the column, and previous work has shown significant degradation of the capacity of these columns after repeated use.[101] Since the acid mixtures examined in this work are often even more aggressive than concentrated pure acids, this could also be a concern.

CHAPTER 7: SEPARATION AFTER FUSION TECHNIQUES

Recently, a significant number of rapid methods have been published for the analysis of actinides and strontium in solids.[27, 30-31, 67-69, 102-105] These methods apply to a variety of solid material types, ranging from vegetation and food items to asphalt and limestone. The vast majority of these methods involve the use of a sodium hydroxide fusion for sample digestion, which has proven to be a surprisingly robust technique. Alkali metal hydroxide fusions have been used for opening-out materials since as early as 1790[106] and are attractive because of the relatively low melting points of the salts used as flux, which allows for them to be carried out in most standard muffle furnaces, and rapid incorporation of samples. Indeed, the procedures cited above are carried out in zirconium crucibles at 600°C and the primary digestion step is complete after only 15 – 20 minutes.

In addition to using easily accessible equipment, these digestion procedures also eliminate the need for extensive use of hydrofluoric or perchloric acids to solubilize complex matrices. Neither of these acids is desirable to use in procedures because of toxicity and incompatibility with organic compounds/formation of explosive compounds upon drying, respectively. These fusion procedures have even been adopted by the Environmental Protection Agency (EPA) for the digestion of concrete and brick prior to actinide, strontium, and radium analyses following radiological incidents.[66] The full procedure, which is outlined in Chapter 6.2, is effective and reliable, or it would not have been selected for use in emergency situations. It is notable, however, that previous work done by *Horwitz et al.*[54] and the experiments described in Chapter 4 of this work indicate that sodium causes significant interference with the uptake of strontium. Since large amounts of sodium are employed in the NaOH fusion technique, this research explores if better yields or retention of strontium is possible with the use of one of the other alkali hydroxides as a flux material. Because potassium causes even worse interference effects than sodium, LiOH was chosen as the most likely alternative to NaOH.

7.1 Materials

The resin, strontium isotopes, acids, and preparation methods used in this set of experiments were described in Chapter 2.1. Lithium solutions used in batch studies were prepared using ReagentPlus grade $LiNO_3$ from Sigma-Aldrich. The NaOH and $LiOH\cdot H_2O$ used in the fusion procedure were both ACS reagent grade, and came from Anachemia and J.T. Baker, respectively. The fusion procedure also required solutions made with boric acid (ACS Reagent, Anachemia), $Al(NO_3)_3\cdot 9H_2O$ (ACS Reagent, Mallinckrodt Baker Inc), $Fe(NO_3)_3\cdot 9H_2O$ (ACS Reagent, J.T. Baker), $Ca(NO_3)_2\cdot 4H_2O$ (ACS Reagent, Fisher), and Na_2CO_3 (Anhydrous Powder, EM Science). All solutions were prepared with deionized water from a Cascada water purification system from Pall Corporation. The SRMs used in this work were NIST SRM 634, SRM 635, SRM 637, SRM 88B, and SRM 1D, which are three different samples of Portland cement, dolomitic limestone, and argillaceous limestone, respectively. These SRMs were used without any prior treatment.

7.2 Procedure & Measurement

Batch studies were carried out following the procedures outlined in Chapter 2.2.1. All batch studies were carried out using 3 M HNO_3.

Radiometric analysis of ^{85}Sr was carried out using the gamma detector described in Chapter 2.3.2. All radiometric measurements were taken on 1 ml aliquots. Lithium uptake was analyzed using the ICP-OES system and dilution scheme described in Chapter 2.3.3.

7.2.1 Fusion Procedure

The fusion procedure used for digestion is briefly described here. A complete copy of the procedure can be obtained from the EPA.[66] The procedure calls for adding 1 g of cement/concrete sample and 15 g of NaOH to a zirconium crucible, and placing the mixture in a furnace at 600°C for 15 minutes. After removing the crucible and allowing it to cool for a few minutes, 25-50 ml of water is used to quantitatively transfer the salt cake to a 250 ml centrifuge tube. This is then diluted to approx. 150

ml with water and acidified with concentrated hydrochloric acid. At this point calcium and iron carriers are added, followed by Na_2CO_3 to co-precipitate calcium and strontium carbonate. The precipitate is centrifuged and decanted, then re-dissolved in 50 ml 1.5 M HCl, diluted to 170 ml with 0.01 M HCl, and concentrated HF is added for a second co-precipitation of calcium and strontium, this time as fluorides. This new precipitate is again centrifuged and decanted, then re-dissolved with a combination of nitric acid, boric acid, and $Al(NO_3)_3$. This final solution is then ready to be run through a Sr Resin column. For this work, batch studies were carried out on solutions from the end of this procedure and from the step directly prior to the HF co-precipitation. For pre-HF samples, the solution was diluted by half (i.e. 10 ml to 15 ml) with concentrated HNO_3 to facilitate extraction.

7.3 Results & Discussion

7.3.1 Lithium Studies

Lithium uptake by strontium resin was never studied in the initial characterization of the resin, but because of its vast size difference, it was not expected to be retained by the resin. This, coupled with the lower solubility of Li_2CO_3, made lithium an obvious choice when debating which salts might increase yields. Batch studies were carried out to see if lithium caused any reduction in strontium retention and if lithium itself was retained by Sr Resin. The batch studies carried out on lithium alone indicated it was not retained by the resin in measureable amounts, as shown in Figure 30. The batch studies looking at strontium retention in the presence of lithium indicated no adverse effects, and a slight synergistic trend was seen at higher concentrations, possibly due to salting out (Figure 31). This combination of no uptake and somewhat synergistic effects with respect to strontium uptake indicate that the use of LiOH as an alternative flux to NaOH could result in better retention of strontium in the final solution. A column study was also carried out, and similar results to those seen in previous studies were found, with less than 10% of the strontium being prematurely eluted, and a recovery in the elution fractions of approximately 72%.

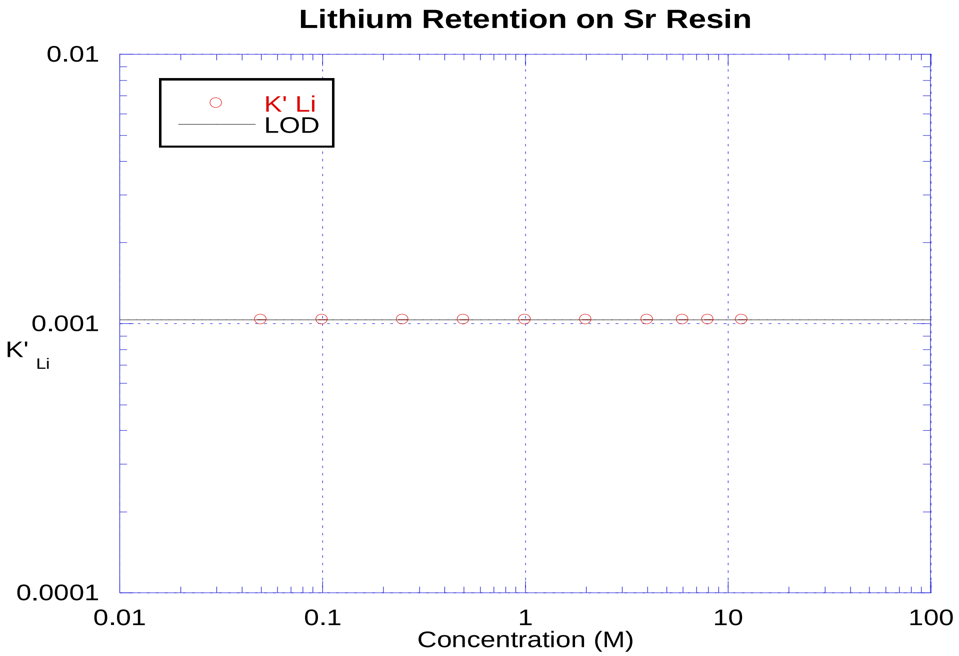

Figure 30: Batch study results indicating negligible lithium uptake by strontium resin regardless of nitric acid concentration

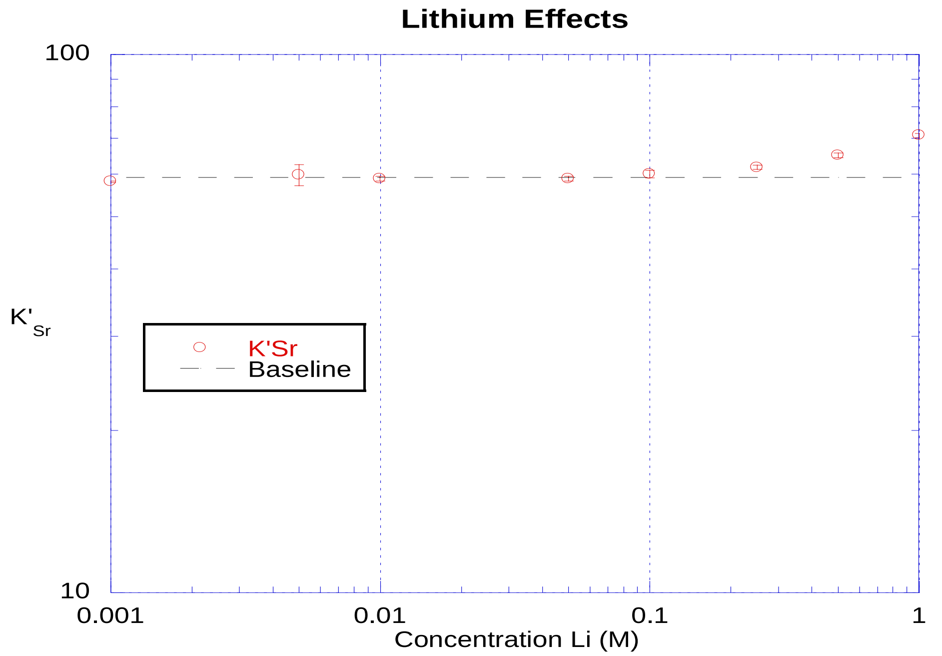

Figure 31: Lithium batch study results. The baseline k' under these conditions is shown as the dashed line. Error bars are 1σ.

7.3.2 Digestion Batch Studies

Following the evidence that lithium would not cause significant interference in the uptake of strontium, batch studies were carried out using solutions of several different standard reference materials that had been taken through the fusion process with either NaOH or LiOH as flux material. The standard reference materials used were SRMs 88B (dolomitic limestone), 1D (limestone), 634, 635, and 637 (different Portland cement standards). Dolomite and limestone were chosen as representative of common aggregate materials, because they are some of the most common to be used in the U.S., though it must be acknowledged that aggregate material will vary from location to location based on local geology and what is readily available.

The results of these batch studies are shown below, in Figure 32. For this work, SRM 88B is designated “dolomite,” SRM 1D is “limestone,” SRM 634 is “blue,” SRM 635 is “gold,” and SRM 637 is “pink.” The colors simply refer to the colors of the caps used to differentiate the samples. As mentioned in the procedure section of this chapter, batch studies were carried out on solutions from both before and after the HF co-precipitation step. This was done to see if the second co-precipitation was truly required, or if it could be taken out to decrease the overall processing time. Whether the batch study was performed on samples from before the HF step or at the end of the procedure is denoted by the “Pre-HF” or “Post-HF” in the legend.

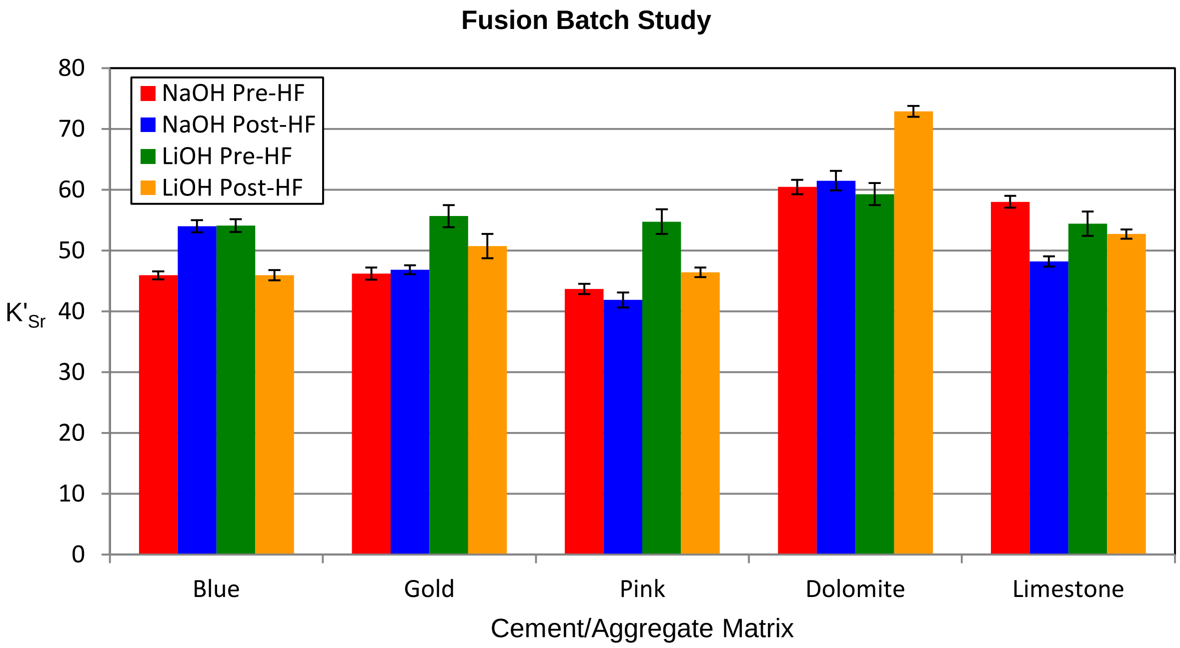

Figure 32: Batch study results of the fusion matrices cement and concrete. Error bars are 1σ.

As seen in Figure 32, strontium retention at the various stages of the fusion processing procedure is quite similar, with the LiOH flux showing a slight advantage in some of the reference materials. More notable is that there appears to be no significant difference in retention whether the sample has undergone the second precipitation with HF or not. During these trials, however, it was noted that it took significantly longer to remove the LiOH salt cake from the crucible than it did to detach the NaOH salt cake. This is likely a product of lithium hydroxide's significantly lower solubility.[100] The extra time required to remove the lithium salt cake effectively negated any advantage that could be gained by potentially higher chemical yields from the carbonate precipitation step of the procedure, so a study was undertaken in which the temperature of the crucible was varied and the time required to remove the salt cake was monitored. The longest it took to remove a sodium salt cake was slightly less than 60 minutes at room temperature, so it was determined that the lithium salt cake needed to be entirely removed in less than an hour to be deemed worthy of further investigation.

Table 9: Temperature dependence data for the removal of salt cakes after fusion using either NaOH or LiOH as flux material.

Temperature (°C)	NaOH Removal Time (min:sec)	LiOH Removal Time (min:sec)
100	38:30	> 60:00
150	22:00	> 60:00
200	12:25	> 60:00
250	8:40	> 60:00
300	6:59	59:30

The data in Table 9 indicates that LiOH will not be able to be removed from the crucible in a timely manner with just water. While it was possible to get the removal time down below an hour while keeping the hotplate set at 300°C, the temperature was such that spattering occurred upon addition of the water. In addition to this, the water held a rolling boil while in the crucible, which would lend itself to additional spatter. With inactive samples this is not necessarily a problem but, since this procedure is intended to be used with radioactive materials, it would likely result in significant contamination in this case. Some spatter also occurs upon the first addition of water when the hotplate is held at 250°C, so even this temperature may be too high. Additional trials were carried out using concentrated and dilute nitric and hydrochloric acids to assist in the removal of the LiOH salt cake. Although there was some improvement in the rate of removal, the recovery of strontium also suffered, dropping as low as 66% in some cases.

7.4 Conclusions & Future Work

This study determined that it does not appear as though the HF co-precipitation step results in the removal of anything that would cause interference with the uptake of strontium on the resin. Unfortunately, the silica that is removed from the system during that step could still be a problem for the separation, as it would likely polymerize to some degree and block the column. Unfortunately, since the amount of silica is dependent on the sample composition, it would be difficult, if not impossible, to determine a procedure that would take the silica blockage into account without HF treatment. Use of a pre-filter before the column may be able to remove the silica from solution, but would also be subject to blockage depending on its concentration. In addition, while lithium showed no detriment with respect to strontium uptake, there was potential for an increase in strontium retention on the column based on the replacement of NaOH with LiOH. Unfortunately, due to the removal of the resulting salt cake taking an exorbitant amount of time, LiOH turned out not to be a good replacement. Because of these results, the best course of action, at least currently, is likely to continue using the procedure without modification.

If it were possible to remove the LiOH salt cake from the crucible in a timely manner, it is likely that the procedure would result in higher yields and better retention of strontium on the column with minimal other modification. Although a drop in recovery was seen when acid was added to the salt cake removal step, it is unclear why this happened, as the amount of acid was kept at or below what was supposed to be added in the initial acidification step anyway. The significant drop in recovery may be able to be countered by increasing the carbonate added in the first co-precipitation step, or by adding additional calcium carrier to the system prior to the co-precipitation. Until it is determined why the drop was seen, it will be difficult to find a course of action to counter it. To this end, future studies looking at ways to increase the overall yield of the procedure and/or ways to fix the problems that arise when using LiOH as a flux material would be of significant interest.

CHAPTER 8: CONCLUSIONS AND IMPLICATIONS

The primary objective of this research was to determine if strontium could accurately be quantified via the use of extraction chromatography and radiometric measurement when incorporated into urban materials. Batch and column studies were carried out on two extremely common types of materials used in urban environments, namely steel and concrete. Both individual constituents and full matrices of these materials were studied. Additionally, since a myriad of ways exist to digest these urban materials but Sr Resin has only been characterized in one acid, several alternative acid matrices were also investigated. Finally, though rapid digestion methods have been recently developed, there was evidence that they possibly could be improved upon with only slight changes to the procedures. These were therefore also investigated.

This chapter will summarize the conclusions laid out in the previous chapters, and suggest future work that could be undertaken to further develop the knowledge gained here.

8.1 Column Characterization

While vacuum-flow extraction chromatography columns have been shown to be effective in separating analytes over the last several years, the question has often been asked if these new columns really behave the same as the gravity-flow columns of old. The primary reason for this skepticism is the violation of one of the principle rules of column chromatography when they are used, namely that the columns are pulled to dryness during the collection of each fraction. The work carried out indicates that the commercially available gravity-flow and vacuum flow columns give extremely reproducible results, but that these results are indeed different. Even the characterization of the two different types of columns showed significant differences.

The gravity columns characterized follow the trends established in the original characterization of the resin. The calculated and measured free column volumes agree and are around 70 % of the total bed volume, while the vacuum columns had vast differences in the calculated and measured free column volumes when using the same techniques. In the end, it was determined that the experimental method being used to find the free column volume of the vacuum-flow columns needed to be modified to achieve accurate results. When characterizing the vacuum columns with a negligibly retained analyte, it was necessary to use the peak volume instead of the breakthrough volume to establish the free column volume. This was supported by subsequent elutions of an analyte that was retained by the resin.

Comparing elution profiles of slurry packed gravity columns, commercially purchased gravity columns, and commercially purchased vacuum columns also indicated differences. Both types of gravity flow columns had better resolution than the vacuum flow columns, though the vacuum columns were able to be eluted much more quickly and did not require constant monitoring. The characteristics observed support that the vacuum columns are best used for cases in which elution strategies can be utilized to retain the analyte(s) of interest well while rinsing contaminants off the column before changing matrices to elute it. Gravity columns are still necessary, however, if a sequential elution of analytes without changing the elution matrix or a well characterized elution profile is required.

8.2 Steel Study

The batch studies carried out on the steel constituents iron, aluminum, chromium, copper, manganese, and nickel indicate that none of these major components of steel will cause interference with the uptake of strontium by the resin. In fact, this research points toward an increase in the retention of strontium in the presence of these transition metals. When the reason behind this was investigated, the results hinted at a salting out phenomenon caused by the sequestration of additional water molecules by the highly charge-dense cations added to the system. This sequestration causes the effective concentration of nitrate anions to increase, which in turn makes them more available to the strontium cations to complex with for extraction. The only constituent that did not follow the trend indicating the uptake was a product of salting out was nickel. Further tests were undertaken to see if perhaps the nickel was being retained by the resin while also sequestering water, which could potentially have accounted for the mild increase in strontium extraction as nickel concentration increased. Unfortunately, the uptake of nickel was insignificant, even down to the minute concentrations achieved by using the radiotracer Ni-63.

When two different standard reference materials were dissolved and tested via batch and column studies, similar trends were seen. Further analysis indicated that the increase was similar in nature to that seen for the +3 ions analyzed in the individual constituent studies. This is likely due to the steels that were tested being composed of > 95 % w/w iron. In any event, the batch studies indicate that the complex mixtures of ions still did not cause any detriment to the uptake of strontium by the resin. Column studies with these materials also indicate that an effective separation could be run without the removal of any constituents.

8.3 Concrete Study

The batch studies performed on the cement and concrete constituents sodium, potassium, magnesium, calcium, and zinc behaved approximately as expected. Previous work had shown that potassium, sodium, and calcium would cause interference with the uptake of strontium.[54] This interference was also seen in this work. Interestingly, although zinc and magnesium are also +2 ions in solution, they did not cause a decrease in strontium uptake. This is likely due to their much smaller ionic radii (88 and 86 pm, respectively, with strontium being 113).[86] In fact, the uptake data shows an increase in retention similar to that seen in the steel study.

Column studies on the individual constituents performed approximately as expected, with zinc and magnesium having the smallest premature strontium breakthroughs. Unfortunately, the strontium recovery was low in all cases, never reaching more than 75 % in the elution fractions, and never more than 82 % over all of the fractions collected. The reason for this significantly lower yield is unclear, though the columns themselves were not preserved to see if the remainder of the activity was still on them or if an error occurred in the spiking of the load solutions. When column studies were carried out with simulated solutions based on SRM compositions, it was found that the solution simulating cement (SRM 634, see Table 8) caused significant breakthrough of strontium, with roughly 27.5 % being eluted prior to the elution phase of the procedure. The solution simulating dolomitic limestone (SRM 88B, see Table 8) showed significantly less premature breakthrough, though still approx. 9.5 %. As a result, the recovery of strontium in the elution fractions was low (72 %) for the simulated cement and acceptable (90 %) for the simulated aggregate. Interestingly, for these two mixtures, the total strontium recovered is 99.5 %. This indicates that the recovery discrepancy seen in the individual constituent trials was caused by some error in the analysis or method, rather than the rest of the activity still being on the column (see data in Table 23and Table 24).

It must also be noted that, while the constituents chosen to be analyzed and the simulated solutions used are representative of a large portion of the cements and concrete aggregates used in the United States, one can expect significant differences in aggregate composition based on local practices. Aggregate tends to be regulated primarily based on size distribution, which allows for large variation in chemical composition. Aggregates are often composed of some form of limestone mined from local quarries with small differences based on local geology, but can also be taken from river or lake beds, or even steel furnaces (slag).

8.4 Mixed Acids

While Sr Resin was only characterized in nitric acid when it was developed, a diverse range of acids and acid mixtures are often employed in sample digestion procedures. Commonly, mixtures of nitric and hydrochloric acid are used, often with some amount of hydrofluoric acid present to ensure the solubilization of silicon species. This, unfortunately, adds a step to most analysis protocols to dry down the digested solution so it can be converted to a purely nitric acid system. This work examined if that conversion step was entirely necessary, or if the extraction could take place in systems other than just nitric acid.

Initial batch studies on nitric acid were in agreement with the trends published during the original characterization of Sr Resin.[54] A study in hydrochloric acid followed, and no uptake of strontium was observed until high concentrations (≥ 5 M). Even then, the maximum chromatographic capacity factor achieved was roughly 5 (at 8 M HCl). Despite this, significant extraction was seen in all of the nitric acid/hydrochloric acid mixtures observed. The mixtures tend to follow the trend established by nitric acid, with slightly lower levels of extraction at low total acid concentration. At total acid concentrations greater than 4 M, the chromatographic capacity factor is seen to be equal to or higher than that of nitric acid at the interpolated 3 M concentration, which was the concentration originally recommended to stay at or above.[54] While these results indicate that there must be some amount of nitric acid and that at some point even high total acid concentration systems (i.e. concentrated HCl) will not work, this point was not identified. It is likely that enough nitric acid is required to complex all of the strontium for extraction by the crown, as the chloride anion is much harder to desolvate, but this will need to be investigated further for confirmation. The results from these batch studies were supported by the column studies as well. Little premature breakthrough was seen in any of the mixed acid matrices, though the hydrochloric acid matrix used had significant breakthrough during the loading of the column.

When two systems including hydrofluoric acid were analyzed, different trends were seen. The two systems analyzed were composed of hydrochloric acid, nitric acid, and hydrofluoric acid in the ratios 5:1:1 and 9:3:7 ($HCl:HNO_3:HF$, by volume). To test different total acid concentrations of the two systems, the concentrated acids were combined in their respective ratios and then diluted to 80 %, 60 %, 40 %, and 20 % by volume using deionized water. The total acid concentrations of the resulting solutions were then calculated using the original molarities of the acids. In the 5:1:1 system, excellent uptake of strontium was seen at total acid concentrations higher than three. The batch study results indicate the retention was better even than the pure nitric acid matrix (see Figure 26). The 9:3:7 system had mediocre retention (k' ≈ 14) at the lowest total acid concentration tested (3.78), which increased to a usable k' of roughly 83 at a total acid concentration of 11.33 before falling back down to approximately 28 at a total acid concentration of 15.11. When these acid mixtures were tested on columns containing the resin, the results were promising. The 5:1:1 mixture performed quite well, with nearly 95 % recovery in the elution fractions. The 9:3:7 mixture, on the other hand, had more than 12 % of the strontium collected during the load and rinse fractions, and less than 85 % recovery in the elution fractions. While the results of the 9:3:7 mixture indicate a less than adequate separation would take place, this could be remedied by a smaller rinse volume or (potentially) by dilution with nitric acid instead of water after digestion.

8.5 Fusion Techniques

Several digestion and preparation methods have recently been developed utilizing sodium hydroxide fusion techniques. Most of these also contain an early calcium carbonate co-precipitation step. Since sodium has been shown to have an adverse effect on strontium uptake by Sr Resin and lithium carbonate is less soluble than sodium carbonate (and could therefore increase the yield of the co-precipitation step), an alternative flux of LiOH was investigated. The procedures developed for strontium pre-concentration before separation also include an HF co-precipitation step. Because of the precautions required when working with concentrated HF, it was also investigated if this step could be taken out without detriment to the results of the procedure.

Batch studies were used to evaluate the effects lithium would have on the uptake of strontium, and found that if anything the uptake of strontium increases with increasing lithium concentration. Batch studies on standard reference materials that had been digested by either NaOH or LiOH fusion, followed by pre-concentration processing to either just before the HF co-precipitation step or to the end of the procedure. The results indicate that similar chromatographic capacity factors are achieved without the fluoride co-precipitation. Unfortunately, this study also showed that the removal of the LiOH salt cake from the crucible for further processing takes significantly longer than the NaOH salt cake. The difference in processing time is so large that anything gained in yield or retention would be cancelled.

8.6 Impact on Forensics

The experiments carried out in this research suggest that existing separations can be carried out on urban debris if large portions of it are steel. It also indicates that cement and concrete are less than ideal matrices. It is likely that these high-calcium matrices could still be used, but it would be necessary to increase the size of the column used in the separation (or stack two Sr Resin columns together) to achieve little breakthrough. As mentioned earlier in this work, these experiments also set a baseline for interference by using 3 M HNO_3 as the rinse medium. Better retention (and thereby less premature breakthrough) would be likely with a higher concentration of nitric acid for the rinse. In either case, the accurate quantification of strontium has been shown to be possible, with recoveries in the 90 – 95 % range being common.

These experiments also showed that separation from mixed acid matrices is not only possible, but in some cases performs as well as, or better than, a purely nitric acid system. This means that, barring any un-dissolvable solids, samples that are digested in $HCl:HNO_3$ mixtures do not need to be converted to a purely nitric acid matrix prior to separation, and that it is also likely that this is possible with a mixed $HCl:HNO_3:HF$ system, assuming there are no insoluble fluorides present. The possibility of performing separations in a system with some fluoride present is important not only because it indicates further processing may not be necessary for some soil/debris samples, but also because strontium's stable grand-daughter, zirconium, often requires fluoride to stay in solution without forming polymeric species, especially at high concentrations.[107] It should be noted that *Steeb et al.*[108] did develop an ageing procedure that did not require the use of HF during the separation, but if HF is used in the digestion already, being able to do the separation without conversion could remove one source of error.

Finally, it must be acknowledged that Sr Resin may not be the best suited resin for strontium age dating in all cases. The primary reason behind this is that, while it retains strontium very well, it does not retain either yttrium or zirconium (^{90}Sr's daughter and grand-daughter, respectively). Because of this, the daughter and grand-daughter must either be separated prior to measurement using a different method, the total ^{90}Zr and ^{90}Y must be measured on a mass spectrometer that can have radioactive material in it, or the ^{90}Y must be allowed to decay away prior to measurement (≥ 26.67 days). Waiting nearly four weeks before measurement is likely to be an unacceptable option in an emergency situation, and measuring radioactive materials on a mass spectrometer severely decreases the number of places a sample like this could be measured. Because of these inadequacies, some work has been done using an alternative extraction chromatography system that would selectively elute first zirconium, then strontium, while leaving yttrium on the column.[109-110] Some additional research was carried out on this system, and can be found in Appendix A.

8.7 Future Outlook

The fusion work presented in this dissertation did not result in any improvements being made to the standard NaOH procedure. That being said, it was found that lithium had no adverse effect on strontium uptake and, theoretically, the presence of Li_2CO_3 should aid in the co-precipitation of $SrCO_3$ and $CaCO_3$ in post-digestion processing. Further investigation into using dilute acids to remove the LiOH salt cake from its crucible after fusion could prove worthwhile. Such a line of experimentation would also need to find the optimal co-precipitation conditions with the different flux material.

Experiments carried out which examined the effects of urban material constituents on strontium uptake showed mixed results. With respect to concrete and cement, it appears that some post-digestion processing will be required. Barring that, larger (or stacked) columns could be used to handle the large calcium loads generally found in concrete and cement. In contrast to this, steel constituents appear to cause no problems with strontium separation. In fact, just the opposite was observed in that strontium retention increased in the presence of all steel constituents tested. This would suggest that samples taken from steel in the aftermath of a dispersal device attack would behave favorably with respect to cements and concretes. Unfortunately, due to time constraints, two very common urban materials, glass and asphalt, were not examined. Future studies looking at the components of these two materials would definitely be worthwhile. Glass would present many of the same constituents as concrete, though would likely present more of a hurdle with respect to digestion, given its much larger silicon percentage. Asphalt would also likely pose some unique issues due to its high organic content.

The acid mixture experiments carried out in this dissertation indicate the direct separation of strontium from urban materials after dissolution in a variety of acids is at least plausible, if not likely. More research needs to be undertaken before these techniques can be used confidently, though. The biggest concerns stem from the insoluble species that could be present in materials causing column flow problems. This is true both with HF processing (causing the precipitation of fluoride salts like CaF_2) and without HF processing (creating insoluble or polymerized silica). A continuation of this research examining urban matrices and their constituents' impacts on strontium extraction in mixed acid systems would be an excellent next step, and could result in faster analysis times and streamlined digestion and analysis procedures for strontium in emergency situations. Additional work examining the robustness of the resin would also be useful, as the acids proposed are quite aggressive and could cause column bleed. Analyzing this would also lend itself to determining the capabilities of this resin over many uses. These columns are designed for single use and disposal, but in an emergency situation it would be much more convenient if the columns could be regenerated and reused. This would also lend itself to automation, which would be another advantage in an emergency situation where vast number of samples are likely to be collected and in need of timely analysis.

APPENDIX A: STRONTIUM CHRONOMETRY NOT USING SR RESIN

As mentioned in section 8.6, depending on the facilities and instrumentation available for measurement, Sr Resin may not be the ideal extraction chromatographic resin to use if determination of source age is desired. At the very least, a procedure that separates the radioactive strontium and yttrium from non-radioactive zirconium would allow for a significantly larger number of locations to be utilized for measurements. To this end, an alternative separation scheme to that which was established by *Steeb et.al*[108] was investigated by *Zattoni*[110] in 2015. Unfortunately, this work did not result in a precise enough measurement and could not be verified with a source of known age. The work is briefly described here, along with results from a minor investigation on improving the precision of the procedure that was carried out at UNLV.

A.1 Separation Scheme

The resin used in this work is commercially available DGA Normal resin from Eichrom Technology. DGA Normal resin utilizes N,N,N',N'-tetra-n-octyldiglycolamide as an extractant, shown in Figure 33. This resin was chosen because the published data indicated excellent retention of strontium and yttrium in 1 M HNO_3 (k' ≈ 70 and 65000, respectively), while zirconium retention was much lower (k' ≈ 15).[109] This would allow the zirconium to be eluted through the column relatively quickly, while the strontium and yttrium were retained and recovered in lower molarity HNO_3 or a different acid altogether. When this separation scheme was tested, however, no zirconium was shown to be eluted prior to strontium. Adding a small amount of HF (0.2 M end concentration) to the 1 M HNO_3 resulted in satisfactory elution of zirconium at the beginning of the scheme.

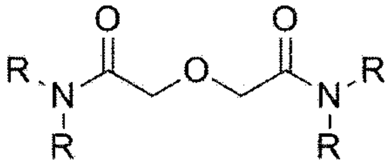

Figure 33: Structure of N,N,N',N'-tetra-n-octyldiglycolamide, in which R is a straight chain 8-carbon group[111]

A.2 Zattoni Measurement Scheme and Results

While the work by Zattoni proposed a method by which the stable ^{90}Zr could be isolated from its radioactive parent and grandparent (^{90}Y and ^{90}Sr, respectively), the amount of ^{90}Sr still needs to be known for the calculation of a source age (as described in Chapter 1.4.2). To accomplish this, the sample solution is split, with one portion being measured using LSC to quantify the strontium and yttrium present in the solution in parallel to the second portion undergoing separation and using ICP-MS to determine zirconium content. Since the source was old enough that strontium and yttrium were in secular equilibrium, the calculation of strontium concentration in the sample prior to analysis was straight forward. The elution strategy outlined in *Zattoni*[110] had the columns loaded with 250 µl of solution, with the zirconium being eluted in the first 5 ml of 1 M HNO_3 rinse solution, the strontium being eluted in the 16 – 20 ml fraction using 0.05 M HNO_3, and the yttrium staying on the column throughout. Each fraction collected (excluding the load fraction) was 5 ml.

The separation and measurement were carried out using a NIST traceable ^{90}Sr source. However, while the activity of the ^{90}Sr source used to test the separation scheme was well known, the true age unfortunately was not. The calculated age was determined to be 68 ± 11 years. The error associated with the measurement was considered too large for use in nuclear forensic applications, but was attributed primarily to solution quality. It was suggested that containers of different material and purer acids would likely improve the precision and minimize trace contamination that could skew the results.

A.3 Work at UNLV

Batch studies were carried out using ^{85}Sr and ^{89}Zr with DGA Normal resin to determine the actual retention values of the two elements in the two matrices (1 M HNO_3 and 0.2 M HF/1 M HNO_3). The general procedure followed was the same as outlined in Chapter 2.2.1 of this dissertation. The separation scheme was also tested using vacuum column chromatography using the equipment described in Chapter 2.2.3 of this work and the flow rates, acids, and volumes described in Chapter 6.7

of *Zattoni.*[110] All acids used in these experiments were described in Chapter 2.1 of this dissertation, except for the fact that TraceSELECT nitric acid (Sigma-Aldrich) was substituted to allow better trace analysis via ICP-MS. Zirconium-89 was obtained from Perkin Elmer in the form of zirconium oxalate in 0.5 M oxalic acid. The zirconium was co-precipitated with a lanthanum carrier using ammonium hydroxide, centrifuged, then rinsed with de-ionized water and centrifuged again. This precipitate was then dissolved in concentrated hydrochloric acid, resulting in zirconium chloride in solution, and this was further purified using ion exchange chromatography. A full description of the oxalate to chloride conversion procedure can be found in *Bennet*.[112] The eluted zirconium was in a 2 M HCl solution, which was then gently evaporated to dryness and reconstituted in concentrated nitric acid to convert the zirconium to the nitrate form before use. Solutions of stable strontium, yttrium, and zirconium with an internal indium standard were used to verify procedures. These were obtained in the form of ICP standards from Fluka (Sr, Y), RICCA (Zr), and VHG Labs (In). The standard Sr, Y, and Zr solutions were 1000 $\mu g\ mL^{-1}$ and In was 10000 $\mu g\ mL^{-1}$. Subsamples were taken, gently dried, and reconstituted in the appropriate acid matrix. For analysis using ICP-MS, samples were placed in 2 % v/v HNO_3/0.1 % v/v HF solutions. Hydrofluoric acid was included to ensure the solubilization of zirconium, but kept at a low enough level to not damage the glass parts of the ICP-MS.

All measurements were performed on the ICP-MS described in section 2.3.4 of this dissertation. Sample flow was kept at 1 ml $min.^{-1}$, with the nebulizer gas flow at 0.93 L min^{-1}, and RF power at 1100 W for all samples and standards.

A.3.1 Batch Studies

As mentioned previously, very little zirconium was eluted in the correct fraction when the aqueous phase for the extraction consisted of 1 M nitric acid. When investigated via batch study, the zirconium retention by the resin was significantly stronger than what was previously reported by *Horwitz et.al,*[109] which is illustrated in Figure 34. Also shown in Figure 34 is data from *Pourmand et.al*,[113] who characterized DGA Normal resin for 60 different elements in 2010. The data generated here is much more in line with that found in *Pourmand et.al* than *Horwitz et.al*.[109, 113] As suggested in *Pourmand*,[113] these differences may stem from the use of purified and (in this case) carrier free elements. Another potential source of these differences is the use of significantly smaller concentrations of elements. *Horwitz*[109] used ICP-AES for analysis, which would require at least mg L^{-1} level concentrations to carry out meaningful measurements. *Pourmand*[113] used ICP-MS, which would be amenable to μg L^{-1} concentrations, and this work utilized radiometric measurements, which could use ng L^{-1} or lower concentrations. Zirconium polymerization has been shown to occur at zirconium concentrations greater than 10^{-4} M,[107] which corresponds to roughly 10 mg L^{-1}, and could factor into the much lower retention reported via ICP-AES analysis that was not seen with the more sensitive instrumentation.

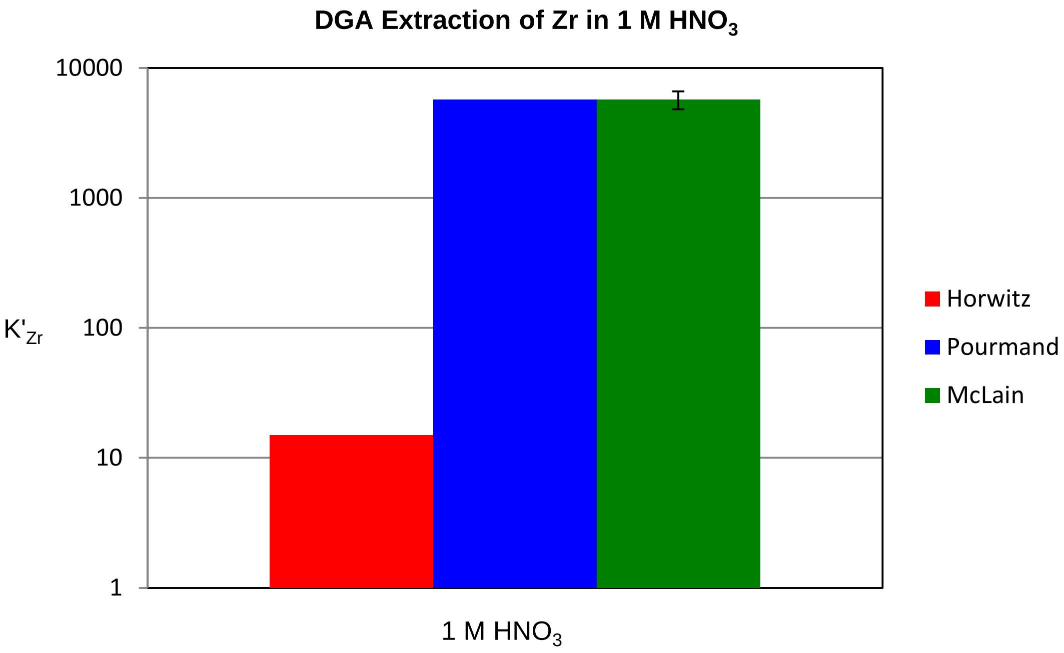

Figure 34: Zr Extraction data with DGA Normal resin from three different sources. Data from Horwitz and Pourmand do not contain error bars because values were estimated from figures.[109, 113]

The batch study in 1 M HNO_3 sheds light on why no zirconium was seen in the early fractions for the proposed elution scheme when 1 M HNO_3 was used as the load solution. The batch studies were taken one step further and the retention of strontium and zirconium in the 0.2 M HF/1 M HNO_3 mixed acid matrix was analyzed to see what the theoretical separation factor would be. The separation factor of two elements in a given acid matrix is determined using equation (12), in which k'_{Sr} and k'_{Zr} are the chromatographic capacity factors of strontium and zirconium, respectively. Chromatographically, the separation factor is the ratio of peak elution volumes with the analyte that takes longer to elute on top, which means that conventionally the factor is always greater than unity.[114] To ensure this is the case, the larger of the two k' values must always be in the numerator when determining a separation factor with batch study results.

$$SF = \frac{k'_{Sr}}{k'_{Zr}} \qquad (12)$$

Figure 35 contains the results of the batch study in 0.2 M HF/1 M HNO_3. The calculated separation factor of 39.64 ± 8.48 indicates a very clean separation, assuming a moderate amount of tailing by the first element eluted (Zr). Although not included here, Sr retention in 1 M HNO_3 was also studied via batch analysis, and the retention was found to be consistent with that established for the HF/HNO_3 mixture.

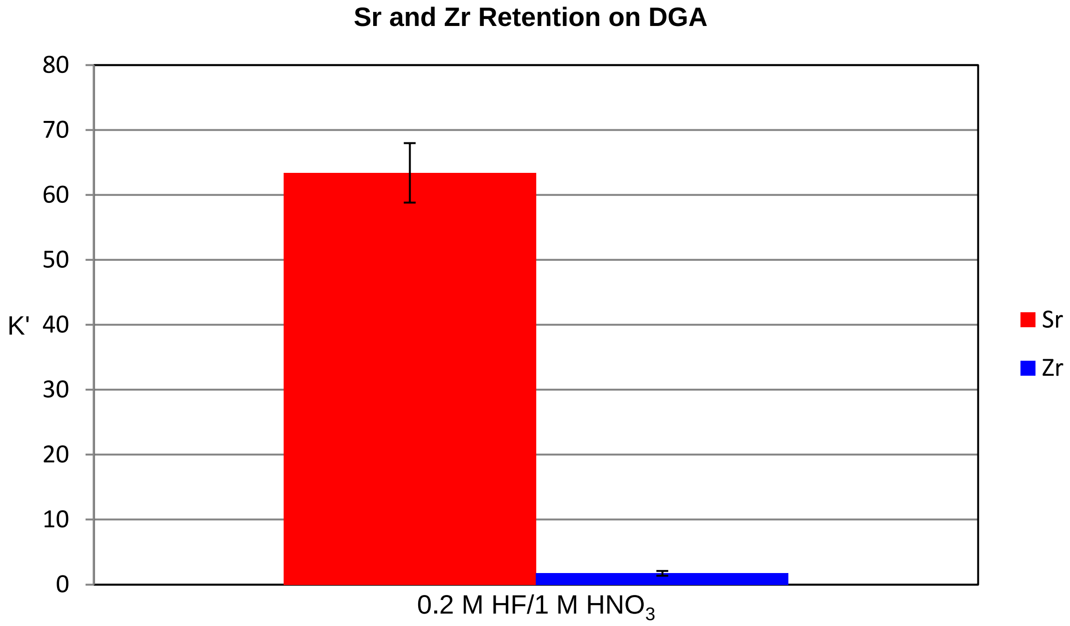

Figure 35: Retention of strontium and zirconium on DGA Normal resin in 0.2 M HF/1 M HNO3 obtained from batch study.

A.3.2 Column Studies

Initially, the procedure set forth in Zattoni was followed in its entirety using stable strontium, yttrium, and zirconium ICP-MS standards to ensure the experiments were reproducible. When this was done, however, the observed zirconium recovery was consistently in the 300 – 500 % range. This is shown in Figure 36, in which the zirconium recovery was approx. 375 %. Subsequent experimentation showed significant recovery of zirconium in the zirconium fraction even when none was added to the load solution, as shown in Figure 37. From this observation, it was determined the excess zirconium must be coming from the column. To remedy this phenomenon, the column preconditioning was changed from the rinse acid (1 M HNO_3) to the load solution (1 M HNO_3/0.2 M HF). Adequate reduction of zirconium in the sample blank was achieved by doing so, and subsequent samples have had reasonable recoveries similar to those present in Figure 38.

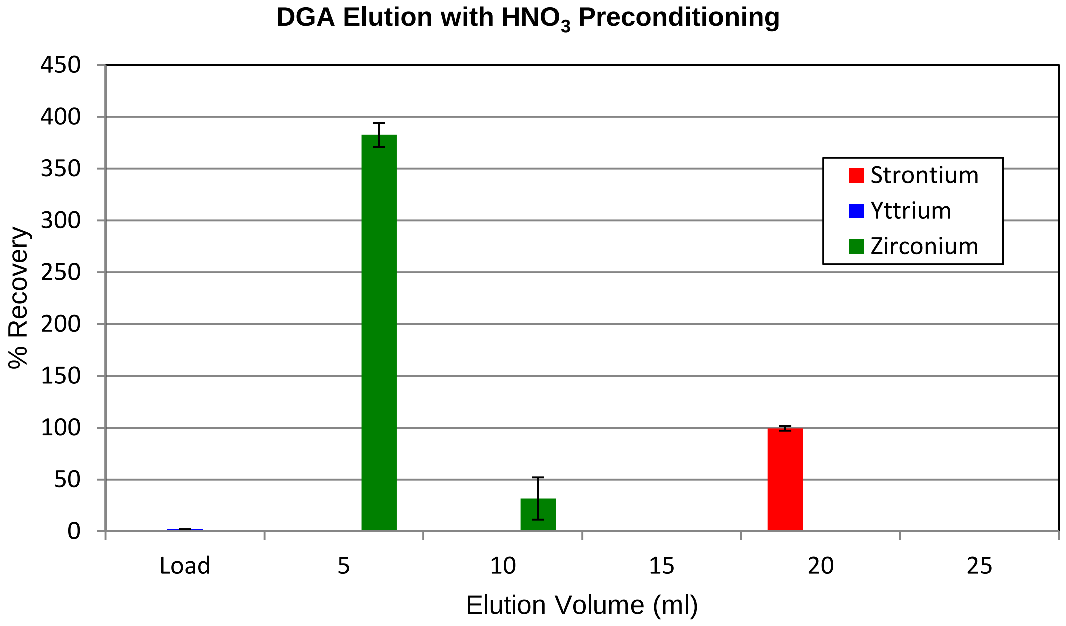

Figure 36: Elution profiles of Sr, Y, and Zr from a DGA Normal column when 1 M HNO_3 was used for preconditioning.

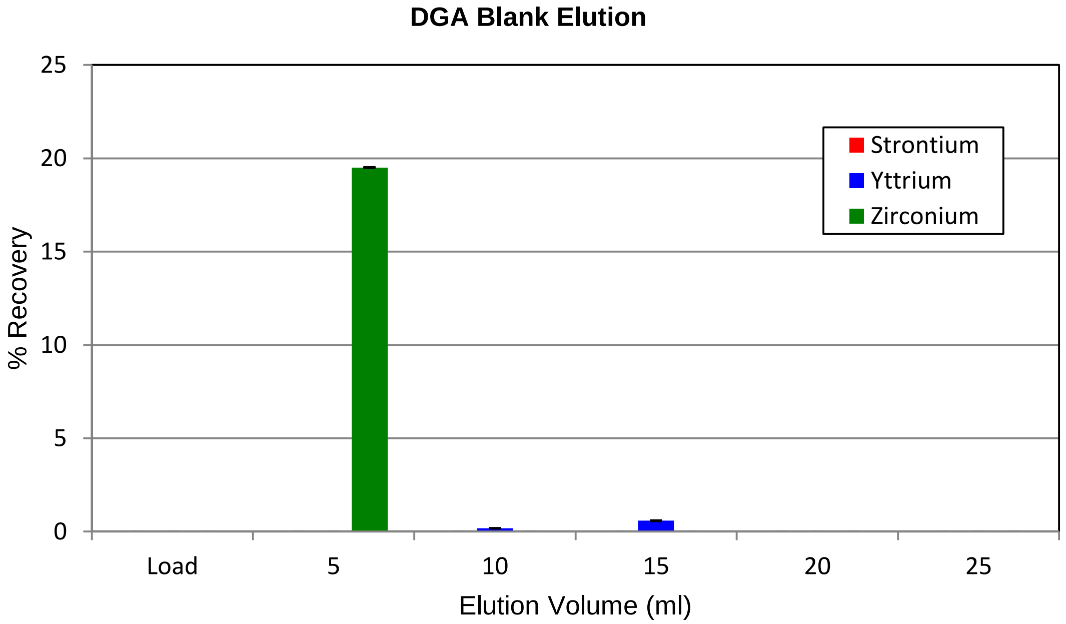

Figure 37: Elution of Sr, Y, and Zr when loaded with a blank solution. Recovery is based on the concentration of the load solution used in previous trials.

Regardless of the zirconium recovery observed, there has always been significant separation between the zirconium and strontium peaks, with little or no cross contamination by the other element or yttrium. This is illustrated by Figure 37 and Figure 38, and lends further credence to the separation factor calculated with the batch study results. While the separation factor calculated from the actual elution profile generated is much lower, this is the result of the acid matrix being changed to elute strontium quickly and in a single fraction.

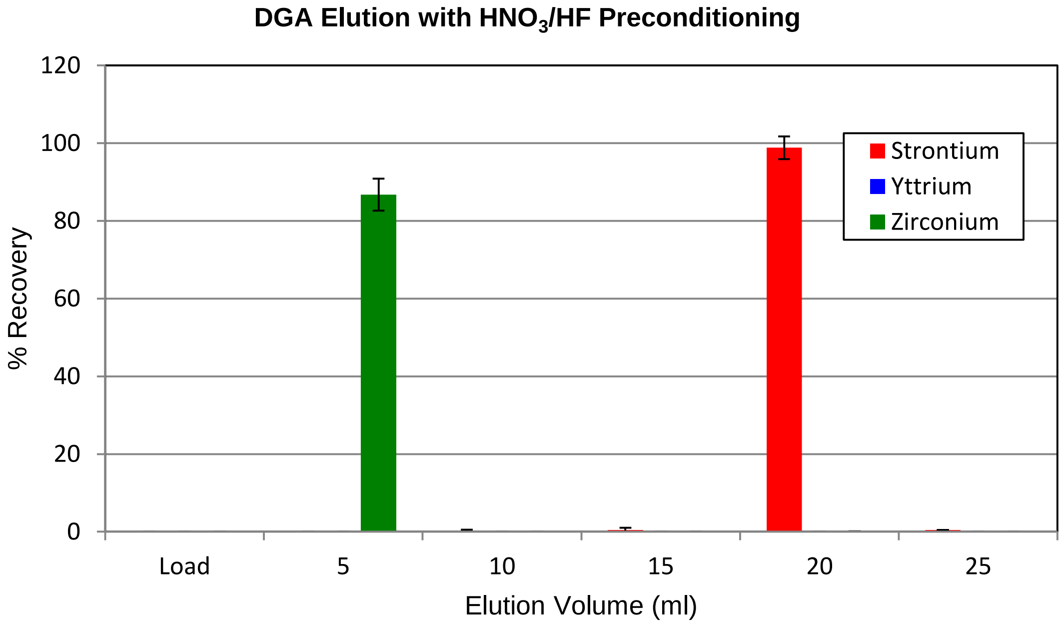

Figure 38: Elution profiles of Sr, Y, and Zr from a DGA Normal column when 1 M HNO3/0.2 M HF was used for preconditioning.

A.4 Conclusions & Future Work

Unfortunately, due to time restrictions and lack of access to a ^{90}Sr source with known provenance, it was impossible to carry out the revised procedure on a real sample. The work accomplished at UNLV showed that the separation factor for zirconium and strontium using the loading matrix identified in *Zattoni*[110] is roughly 40 and confirmed that it provides excellent separation between the two elements. It was also shown that DGA Normal resin cartridges can contain zirconium at levels significant enough to cause problems with low-level nuclear forensic measurements when used as obtained from the manufacturer. Calculations based on the observed ICP-MS data for ^{90}Zr and abundance ratios from *Baum et.al.*[115] indicate 8.38 ± 0.03 ng of zirconium present in each column, though this number is based only on one lot of columns. The source of the zirconium cannot be readily identified when examining the synthesis method for the ligands used in DGA Normal and DGA Branched resins, but it is possible, given the resin's high affinity for zirconium in nitric and hydrochloric acids, that the resin leached it from some solution or glassware used in the synthesis or storage.[109, 113]

In general, the studies at UNLV verified the work previously done at Laval University.[110] Additionally, assuming measurements on a real source would have the same fidelity achieved on the inactive solutions used in the work done at UNLV, the small changes to the Zattoni procedure resulted in a reduction in error that would correspond to a relative standard deviation (RSD) of 11 % on an age calculation. In comparison to the approx. 14 % RSD achieved at Laval,[110] this is only a marginal improvement, but is still a step in the right direction. Further improvement could likely be achieved with the use of an ICP-MS with a PTFE nebulizer, PTFE containers and flasks, and isotopically enriched zirconium and strontium standards. This would reduce any contamination associated with leaching from the nebulizer and glass used in preparation of solutions, and would reduce the variability associated with "natural" zirconium and strontium standards for recovery determination.

APPENDIX B: RAW DATA FOR FIGURES

Table 10: Raw data for Figure 8

Column 1		Column 2		Column 3	
Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)
0.0546	< MDA	0.0525	< MDA	0.0532	< MDA
0.1621	< MDA	0.1580	< MDA	0.1595	< MDA
0.2681	< MDA	0.2637	< MDA	0.2649	< MDA
0.3741	< MDA	0.3694	< MDA	0.3699	< MDA
0.4801	< MDA	0.4761	< MDA	0.4750	< MDA
0.5863	< MDA	0.5817	< MDA	0.5803	< MDA
0.6919	< MDA	0.6866	< MDA	0.6866	< MDA
0.8104	< MDA	0.7923	< MDA	0.7927	< MDA
0.9294	< MDA	0.8975	< MDA	0.8972	< MDA
1.0349	< MDA	1.0025	< MDA	1.0014	< MDA
1.1404	< MDA	1.1078	< MDA	1.1062	< MDA
1.2465	< MDA	1.2132	< MDA	1.2114	< MDA
1.3525	< MDA	1.3193	0.60 ± 0.08	1.3170	< MDA
1.4580	2.78 ± 0.16	1.4259	10.67 ± 0.32	1.4217	< MDA
1.5632	19.15 ± 0.43	1.5311	32.54 ± 0.56	1.5266	0.20 ± 0.04
1.6684	37.93 ± 0.60	1.6365	42.06 ± 0.63	1.6325	3.40 ± 0.18
1.7731	35.83 ± 0.59	1.7555	34.05 ± 0.51	1.7384	12.34 ± 0.34
1.8778	22.80 ± 0.47	1.8748	21.90 ± 0.45	1.8437	21.85 ± 0.45
1.9828	14.23 ± 0.37	1.9805	11.95 ± 0.34	1.9488	25.01 ± 0.49
2.0873	9.72 ± 0.31	2.0848	6.90 ± 0.26	2.0537	23.07 ± 0.47
2.2055	7.37 ± 0.24	2.1900	3.94 ± 0.19	2.1592	18.73 ± 0.42
2.3237	5.46 ± 0.23	2.2955	2.54 ± 0.16	2.2642	14.62 ± 0.38
2.4290	4.42 ± 0.20	2.4002	1.62 ± 0.13	2.3683	11.91 ± 0.34
2.5347	3.32 ± 0.18	2.5050	1.21 ± 0.11	2.4735	9.33 ± 0.30
2.6402	2.45 ± 0.15	2.6096	0.87 ± 0.09	2.5794	7.74 ± 0.27
2.7457	1.77 ± 0.13	2.7146	0.76 ± 0.09	2.6853	6.00 ± 0.24
2.8511	1.63 ± 0.12	2.8207	0.61 ± 0.08	2.7910	4.92 ± 0.22
2.9566	1.35 ± 0.11	2.9268	0.51 ± 0.07	2.8958	4.31 ± 0.20
3.0621	1.12 ± 0.10	3.0328	0.44 ± 0.07	3.0009	3.52 ± 0.18
3.1679	1.06 ± 0.10	3.1441	0.23 ± 0.05	3.1064	3.01 ± 0.17

Table 11: Raw data for Figure 9

Column 1		Column 2		Column 3	
Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)
0.0509	< MDA	0.0494	0.03 ± 0.02	0.0503	0.02 ± 0.01
0.1497	0.02 ± 0.01	0.1451	0.004 ± 0.006	0.1507	0.006 ± 0.008
0.2470	0.04 ± 0.02	0.238	0.02 ± 0.01	0.2488	0.02 ± 0.02
0.3461	0.03 ± 0.02	0.3305	0.02 ± 0.02	0.3454	0.03 ± 0.02
0.4454	0.02 ± 0.01	0.4217	0.04 ± 0.02	0.4432	0.04 ± 0.02
0.5448	0.02 ± 0.01	0.5135	0.04 ± 0.02	0.5427	0.001 ± 0.003
0.6449	0.04 ± 0.02	0.6083	0.05 ± 0.02	0.6418	0.04 ± 0.02
0.7452	0.02 ± 0.01	0.7065	0.01 ± 0.01	0.7439	< MDA
0.8461	0.04 ± 0.02	0.8092	0.01 ± 0.01	0.8518	0.01 ± 0.01
0.9487	0.02 ± 0.01	0.9134	0.02 ± 0.01	0.9621	0.01 ± 0.01
1.0526	0.05 ± 0.02	1.0130	0.01 ± 0.01	1.0700	0.04 ± 0.02
1.1557	0.02 ± 0.01	1.1066	0.05 ± 0.02	1.1777	0.03 ± 0.02
1.2576	0.48 ± 0.07	1.1991	0.11 ± 0.03	1.2867	0.47 ± 0.07
1.3586	3.95 ± 0.20	1.2948	0.99 ± 0.10	1.3940	4.64 ± 0.21
1.4596	14.28 ± 0.37	1.3931	5.78 ± 0.24	1.5012	16.29 ± 0.39
1.5602	28.09 ± 0.53	1.4955	17.80 ± 0.41	1.6081	29.18 ± 0.53
1.6614	35.13 ± 0.59	1.6010	28.85 ± 0.52	1.7143	34.74 ± 0.57
1.7644	31.37 ± 0.55	1.7060	31.99 ± 0.55	1.8229	28.51 ± 0.51
1.8697	19.74 ± 0.43	1.7936	27.03 ± 0.62	1.9344	16.57 ± 0.38
1.9741	9.60 ± 0.31	1.8804	17.65 ± 0.42	2.0437	7.71 ± 0.27
2.0756	3.78 ± 0.19	1.9801	8.68 ± 0.30	2.1513	2.94 ± 0.17
2.1776	1.40 ± 0.12	2.0792	4.69 ± 0.22	2.2594	1.22 ± 0.11
2.2800	0.56 ± 0.07	2.1822	2.56 ± 0.16	2.3672	0.59 ± 0.07
2.3832	0.29 ± 0.05	2.2875	1.31 ± 0.11	2.4763	0.34 ± 0.06
2.4876	0.20 ± 0.04	2.3941	0.73 ± 0.08	2.5872	0.23 ± 0.05
2.5913	0.12 ± 0.03	2.4714	0.38 ± 0.09	2.7162	0.17 ± 0.03
2.6950	0.09 ± 0.03	2.5501	0.22 ± 0.05	2.8444	0.12 ± 0.03
2.7975	0.09 ± 0.03	2.6606	0.13 ± 0.03	2.9548	0.07 ± 0.03
2.9002	0.08 ± 0.03	2.7709	0.12 ± 0.03	3.0619	0.07 ± 0.03
3.0054	0.05 ± 0.02	2.8776	0.07 ± 0.03	3.1642	0.07 ± 0.03

Table 12: Raw data from Figure 10 (continued on next page)

Column 1		Column 2		Column 3	
Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)
0.0376	< MDA	0.0389	< MDA	0.0397	< MDA
0.1235	< MDA	0.1246	< MDA	0.1215	< MDA
0.2107	< MDA	0.2152	< MDA	0.2164	< MDA
0.3072	< MDA	0.3054	< MDA	0.2801	< MDA
0.3951	< MDA	0.4408	0.07 ± 0.02	0.4030	0.16 ± 0.03
0.5205	1.0 ± 0.1	0.5764	1.7 ± 0.1	0.5253	0.6 ± 0.2
0.6654	7.6 ± 0.3	0.6647	5.6 ± 0.3	0.6221	6.5 ± 0.2
0.7642	15.6 ± 0.4	0.7648	13.9 ± 0.3	0.7541	15.5 ± 0.4
0.8656	24.7 ± 0.5	0.8645	23.7 ± 0.5	0.8598	22.7 ± 0.4
0.9697	30.5 ± 0.5	0.9633	31.0 ± 0.5	0.9675	27.5 ± 0.5
1.0272	29.6 ± 1.6	1.0610	32.3 ± 0.6	1.0680	30.4 ± 0.5
1.1102	28.2 ± 0.4	1.1568	28.6 ± 0.5	1.1656	26.9 ± 0.5
1.2033	23.8 ± 0.9	1.2675	20.2 ± 0.4	1.2580	20.7 ± 0.5
1.3038	15.5 ± 0.3	1.3743	12.5 ± 0.3	1.3625	13.4 ± 0.3
1.4032	8.9 ± 0.5	1.4738	7.3 ± 0.3	1.4668	7.8 ± 0.3
1.5156	5.7 ± 0.2	1.5702	4.2 ± 0.2	1.5651	4.3 ± 0.2
1.6232	2.2 ± 0.3	1.6701	2.4 ± 0.2	1.6661	2.2 ± 0.1
1.7195	1.9 ± 0.1	1.7754	1.3 ± 0.1	1.7273	0.2 ± 0.1
1.8104	< MDA	1.9207	0.3 ± 0.0	1.8234	0.8 ± 0.1
1.9054	0.5 ± 0.1	2.0617	0.4 ± 0.1	1.9605	0.25 ± 0.05
2.0088	< MDA	2.1581	0.13 ± 0.04	2.0663	0.06 ± 0.02
2.1112	0.17 ± 0.03	2.2595	0.02 ± 0.02	2.1667	< MDA
2.2482	< MDA	2.3617	< MDA	2.2658	< MDA
2.3166	< MDA	2.4613	< MDA	2.3616	< MDA
2.4084	< MDA	2.5594	< MDA	2.4519	< MDA
2.5456	< MDA	2.6584	< MDA	2.5678	< MDA
2.6575	< MDA	2.7555	< MDA	2.6840	< MDA
2.7489	< MDA	2.8528	< MDA	2.7819	< MDA
2.8393	< MDA	2.9560	< MDA	2.8427	< MDA
2.9105	< MDA	3.0656	< MDA	2.9372	< MDA

Column 4		Column 5	
Elution Volume (ml)	Cs Activity (CPM/µl)	Elution Volume (ml)	Cs Activity (CPM/µl)
0.0245	< MDA	0.0235	< MDA
0.0939	< MDA	0.0814	< MDA
0.1685	< MDA	0.1720	< MDA
0.2534	< MDA	0.2921	< MDA
0.4068	0.26 ± 0.04	0.3879	< MDA
0.5125	< MDA	0.5073	2.0 ± 0.1
0.6117	8.3 ± 0.2	0.6460	9.3 ± 0.3
0.7460	19.4 ± 0.5	0.7436	16.7 ± 0.4
0.8436	25.3 ± 0.5	0.8332	22.2 ± 0.5
0.9471	28.2 ± 0.5	0.9310	27.8 ± 0.5
1.0417	27.0 ± 0.5	1.042	26.9 ± 0.5
1.1400	21.4 ± 0.5	1.1406	23.0 ± 0.5
1.2317	19.2 ± 0.5	1.2371	18.3 ± 0.4
1.3256	11.8 ± 0.3	1.3505	12.7 ± 0.3
1.4264	8.6 ± 0.3	1.4545	8.7 ± 0.3
1.5213	5.6 ± 0.2	1.5561	6.1 ± 0.2
1.6185	3.6 ± 0.2	1.6169	2.7 ± 0.6
1.7106	2.4 ± 0.2	1.7093	3.4 ± 0.1
1.8114	1.5 ± 0.1	1.8351	1.7 ± 0.2
1.919	0.9 ± 0.1	1.9407	1.0 ± 0.1
2.0188	0.6 ± 0.1	2.0609	0.6 ± 0.1
2.1172	0.3 ± 0.1	2.1595	0.2 ± 0.1
2.2162	0.15 ± 0.04	2.2595	0.16 ± 0.04
2.3196	0.09 ± 0.03	2.3627	0.01 ± 0.01
2.4203	< MDA	2.4613	< MDA
2.5140	< MDA	2.5680	0.06 ± 0.02
2.6108	< MDA	2.6709	< MDA
2.7129	< MDA	2.7661	< MDA
2.8161	< MDA	2.8643	< MDA
2.8892	< MDA	2.9715	< MDA

Table 13: Raw data for Figure 11

	Vacuum	Pre-Packed	Slurry Packed
Elution Volume (ml)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)
0.1	< MDA	< MDA	< MDA
3	0.57 ± 0.60	0.026 ± 0.001	0.009 ± 0.008
8	6.31 ± 1.58	3.74 ± 0.37	< MDA
13	21.9 ± 3.6	40.3 ± 2.3	12.7 ± 15.4
18	30.2 ± 3.3	39.6 ± 2.3	58.1 ± 16.7
23	21.8 ± 1.5	8.2 ± 2.0	22.3 ± 18.5
28	10.6 ± 2.1	1.06 ± 0.34	3.0 ± 2.2
33	4.1 ± 1.3	0.29 ± 0.07	0.87 ± 0.50
38	1.50 ± 0.47	0.15 ± 0.03	0.41 ± 0.21
43	0.63 ± 0.16	0.09 ± 0.01	0.24 ± 0.14
48	0.33 ± 0.06	0.07 ± 0.01	0.13 ± 0.06

Table 14: Raw data for Figure 12 and Figure 13

	UNLV 1 ml/min	UNLV 4 ml/min	ANL 4 ml/min
Elution Volume (ml)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)
0.1	< MDA	0.023 ±0.003	< MDA
3	0.03 ± 0.02	1.33 ± 0.79	0.57 ± 0.60
8	0.76 ± 1.27	5.06 ± 2.13	6.31 ± 1.58
13	6.44 ± 2.95	9.81 ± 0.54	21.9 ± 3.6
18	17.8 ± 2.9	14.5 ± 2.2	30.2 ± 3.3
23	27.8 ± 5.8	17.5 ± 2.8	21.8 ± 1.6
29	22.1 ± 0.9	16.3 ± 1.3	10.6 ± 2.1
34	11.2 ± 2.2	12.6 ± 0.3	4.11 ± 1.25
39	4.49 ± 1.49	8.32 ± 0.71	1.50 ± 0.47
44	1.53 ± 0.63	4.83 ± 0.67	0.63 ± 0.16
49	0.64 ± 0.25	2.61 ± 0.51	0.33 ± 0.06

Table 15: Raw data from Figure 14 and Figure 16

	Nickel		Copper		Manganese		
Salt Concentration (M)	k' Sr		k' Sr		k' Sr		Ionic Strength
1	69.5	± 1.1	89.7	± 1.0	99.7	± 4.7	6
0.5	66.3	± 0.8	74.2	± 0.9	79.1	± 1.1	4.5
0.25	63.4	± 1.0	65.4	± 1.6	68.6	± 1.5	3.75
0.1	63.1	± 1.2	61.5	± 0.5	64.3	± 1.1	3.3
0.05	61.3	± 1.3	61.9	± 1.1	63.1	± 1.0	3.15
0.01	60.9	± 0.4	59.8	± 0.7	62.1	± 1.2	3.03
0.005	61.5	± 1.0	59.8	± 0.8	60.8	± 0.9	3.015
0.001	61.5	± 0.8	59.4	± 1.1	59.5	± 1.2	3.003
0	59.1	± 1.1	59.1	± 1.1	59.1	± 1.1	3

Table 16: Raw data from Figure 15 and Figure 16

	Aluminum		Chromium		Iron		
Salt Concentration (M)	k' Sr		k' Sr		k' Sr		Ionic Strength
1	127.3	± 4.2	123.0	± 3.3	127.8	± 0.7	9
0.5	93.3	± 2.0	88.9	± 2.2	92.0	± 2.1	6
0.25	75.3	± 1.0	73.7	± 1.4	75.6	± 1.6	4.5
0.1	64.9	± 0.7	64.7	± 1.7	65.6	± 1.4	3.6
0.05	61.9	± 1.8	61.5	± 1.0	63.2	± 0.8	3.3
0.01	59.0	± 0.9	58.7	± 0.4	61.7	± 1.1	3.06
0.005	59.1	± 1.3	58.6	± 0.9	61.8	± 0.8	3.03
0.001	58.6	± 0.7	58.2	± 0.8	62.1	± 1.3	3.006
0	59.1	± 1.1	59.1	± 1.1	59.1	± 1.1	3

Table 17: Raw data from Figure 17 (continued on next page)

Aluminum		Chromium		Iron	
Concentration (M)	K'	Concentration (M)	K'	Concentration (M)	K'
0.0010	< LOD	0.0011	< LOD	0.0011	0.004 ± 0.015
0.0050	< LOD	0.0053	< LOD	0.0054	< LOD
0.0100	< LOD	0.0105	< LOD	0.0108	< LOD
0.0502	< LOD	0.0526	< LOD	0.0538	< LOD
0.1004	< LOD	0.1051	< LOD	0.1076	< LOD
0.2511	< LOD	0.2628	< LOD	0.2690	< LOD
0.5022	< LOD	0.5256	< LOD	0.5379	< LOD
1.0044	< LOD	1.0512	< LOD	1.0758	< LOD

Copper		Manganese		Nickel	
Concentration (M)	K'	Concentration (M)	K'	Concentration (M)	K'
0.0011	< LOD	0.0010	3.5 ± 8.0	0.0010	< LOD
0.0055	< LOD	0.0051	< LOD	0.0051	< LOD
0.0109	< LOD	0.0103	< LOD	0.0102	0.0013 ± 0.0002
0.0545	0.1 ± 0.2	0.0513	< LOD	0.0510	< LOD
0.1091	< LOD	0.1027	< LOD	0.1019	< LOD
0.2726	< LOD	0.2567	< LOD	0.2548	< LOD
0.5453	< LOD	0.5133	< LOD	0.5096	< LOD
1.0905	< LOD	1.0266	< LOD	1.0191	0.001 ± 0.002

Table 18: Raw data from Figure 18

Concentration (M)	Activity (Bq/ml)	Nickel Retention (K')
1.39E-10	18.3	< LOD
2.09E-10	27.9	1.9 ± 3.2
2.97E-10	39.2	0.15 ± 0.66
4.48E-10	59.2	< LOD
5.97E-10	78.9	0.09 ± 0.40
1.48E-09	195	0.10 ± 0.48

Table 19: Raw data from Figure 19

Iron Concentration (M)	SRM 361 (k'Sr)	SRM 14f (k'Sr)	Iron Only (k'Sr)
1	113.8 ± 1.6	130.0 ± 1.1	127.84 ± 0.65
0.5	92.39 ± 0.78	95.2 ± 1.3	92.0 ± 2.1
0.25	79.79 ± 0.87	80.55 ± 0.98	75.6 ± 1.6
0.1	71.54 ± 0.80	71.71 ± 0.54	65.6 ± 1.4
0.05	69.8 ± 1.1	69.26 ± 0.58	63.23 ± 0.78
0.01	66.77 ± 0.90	67.03 ± 0.59	61.7 ± 1.1

Table 20: Raw data from Figure 20

	Nickel	Iron	SRM 361	SRM 14f
Elution Volume (FCV)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)
Load	0.012 ± 0.001	0.0144 ± 0.0001	0.0128 ± 0.0004	0.012 ± 0.001
5	0.002 ± 0.001	0.002 ± 0.001	0.001 ± 0.002	0.003 ± 0.002
10	0.03 ± 0.01	0.009 ± 0.001	0.01 ± 0.01	0.02 ± 0.03
15	0.21 ± 0.06	0.07 ± 0.008	0.07 ± 0.02	0.14 ± 0.16
20	0.66 ± 0.10	0.31 ± 0.08	0.58 ± 0.40	0.39 ± 0.48
25	1.31 ± 0.10	0.74 ± 0.17	1.69 ± 1.39	0.74 ± 0.92
30	2.07 ± 0.17	1.31 ± 0.29	2.80 ± 2.10	1.58 ± 0.86
35	90.4 ± 0.3	90.00 ± 0.03	88.7 ± 2.3	93.5 ± 4.1
40	2.71 ± 0.424	3.33 ± 0.012	1.99 ± 1.37	1.63 ± 1.10

Table 21: Raw data for Figure 21 and Figure 22

	Sodium	Potassium	Magnesium	Calcium	Zinc
Salt Concentration (M)	k' Sr	k' Sr	k' Sr	k' Sr	k' Sr
1	36.3 ± 0.6	2.0 ± 0.2	99.1 ± 1.2	28.5 ± 0.1	93.6 ± 1.1
0.5	46.0 ± 0.5	4.9 ± 0.3	78.0 ± 1.0	39.9 ± 0.5	76.1 ± 0.5
0.25	52.5 ± 0.3	10.5 ± 0.1	67.6 ± 0.4	47.1 ± 0.5	67.3 ± 0.8
0.1	57.9 ± 1.5	23.0 ± 3.4	62.5 ± 1.0	52.6 ± 0.4	62.5 ± 0.3
0.05	60.6 ± 0.7	31.9 ± 0.3	60.4 ± 0.7	55.1 ± 0.5	60.7 ± 0.3
0.01	63.3 ± 0.8	50.5 ± 0.4	59.7 ± 0.3	57.0 ± 0.5	59.9 ± 0.6
0.005	62.6 ± 1.2	55.1 ± 0.5	59.3 ± 0.5	58.3 ± 0.5	59.3 ± 0.7
0.001	63.3 ± 0.3	57.8 ± 0.6	59.4 ± 0.3	58.8 ± 0.4	59.5 ± 0.3
0	63.3 ± 0.6	63.3 ± 0.6	63.3 ± 0.6	63.3 ± 0.6	63.3 ± 0.6

Table 22: Raw ionic strength data from Figure 22, used in conjunction with k’ data from Table 21

	Na, K	Mg, Ca, Zn
Salt Concentration (M)	Ionic Strength	Ionic Strength
1	5.5	6
0.5	4.25	4.5
0.25	3.625	3.75
0.1	3.25	3.3
0.05	3.125	3.15
0.01	3.025	3.03
0.005	3.0125	3.015
0.001	3.0025	3.003

Table 23: Raw data for Figure 23

	Sodium	Potassium	Calcium	Magnesium	Zinc
Fraction (FCV)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)
Load	0.02 ± 0.01	41.8 ± 0.5	0.046 ± 0.004	0.0116 ± 0.0003	0.009 ± 0.002
5	0.22 ± 0.19	7.51 ± 0.51	0.54 ± 0.05	0.02 ± 0.01	0.01 ± 0.01
10	0.80 ± 0.64	2.10 ± 0.01	1.48 ± 0.14	0.18 ± 0.11	0.08 ± 0.09
15	1.62 ± 1.02	1.99 ± 0.03	2.51 ± 0.19	0.68 ± 0.23	0.38 ± 0.34
20	2.54 ± 0.90	1.93 ± 0.01	3.35 ± 0.11	1.50 ± 0.33	0.96 ± 0.68
25	3.93 ± 0.35	2.07 ± 0.01	4.36 ± 0.07	2.49 ± 0.40	1.93 ± 1.05
30	5.26 ± 0.70	1.95 ± 0.01	4.96 ± 0.02	3.33 ± 0.19	3.15 ± 1.05
35	67.2 ± 2.1	12.2 ± 0.5	64.5 ± 0.8	71.0 ± 0.6	71.9 ± 3.7
40	0.72 ± 0.10	0.09 ± 0.03	0.53 ± 0.05	0.583 ± 0.001	0.81 ± 0.21

Table 24: Raw data for Figure 24

	SRM 634	SRM 88B
Fraction (FCV)	Avg. Sr Recovery (%)	Avg. Sr Recovery (%)
Load	2.75 ± 1.24	0.05 ± 0.05
5	2.81 ± 0.57	0.39 ± 0.44
10	3.03 ± 0.46	1.02 ± 1.07
15	3.73 ± 0.30	1.75 ± 1.51
20	5.13 ± 0.40	3.00 ± 2.34
25	5.98 ± 0.42	4.11 ± 1.43
30	6.78 ± 0.26	4.53 ± 0.68
35	69.7 ± 4.4	85.1 ± 7.9
40	0.47 ± 0.03	0.62 ± 0.03

Table 25: Raw data for Figure 25

	HNO_3	75:25	50:50	25:75	HCl
Ionic Strength	k' Sr	k' Sr	k' Sr	k' Sr	k' Sr
11.78	82.62 ± 0.7	--	--	--	--
8.13	--	--	--	--	5.11 ± 1.09
8	80.4 ± 1.9	62.4 ± 1.5	75.0 ± 2.1	72.7 ± 4.8	--
6	73.9 ± 0.5	54.5 ± 0.5	62.8 ± 1.5	64.4 ± 0.9	--
5	--	--	--	--	2.47 ± 0.44
4	67.6 ± 0.7	51.3 ± 1.6	48.4 ± 0.4	35.3 ± 0.5	--
2.5	--	--	--	--	< MDA
2	44.1 ± 0.6	27.2 ± 0.6	19.3 ± 0.3	8.11 ± 0.4	--
1	24.3 ± 0.3	7.70 ± 0.31	4.74 ± 0.34	2.78 ± 0.06	< MDA
0.5	10.8 ± 0.3	6.23 ± 1.34	1.14 ± 0.15	1.26 ± 0.12	< MDA
0.25	4.9 ± 0.23	3.31 ± 1.19	0.62 ± 0.47	0.24 ± 0.03	< MDA
0.1	1.6 ± 0.1	0.90 ± 0.71	0.38 ± 0.16	0.17 ± 0.07	< MDA
0.05	0.60 ± 0.08	0.52 ± 0.22	0.43 ± 0.11	0.1 ± 0.07	< MDA
0.01	--	--	--	--	< MDA

Table 26: Raw data for Figure 26

	HNO_3	5:1:1	9:3:7
Ionic Strength	k' Sr	k' Sr	k' Sr
15.11	--	--	28.1 ± 4.6
12.03	--	136.0 ± 45.7	--
11.78	82.6 ± 0.7	--	--
11.33	--	--	82.7 ± 30.7
9.03	--	127.8 ± 28.0	--
8	80.4 ± 1.9	--	--
7.56	--	--	43.0 ± 6.1
6.02	--	113.5 ± 24.9	--
6	73.9 ± 0.5	--	--
4	67.6 ± 0.7	--	--
3.78	--	--	13.8 ± 1.9
3.01	--	12.74 ± 3.33	--
2	44.1 ± 0.6	--	--
1	24.3 ± 0.3	--	--
0.5	10.8 ± 0.3	--	--
0.25	4.90 ± 0.23	--	--
0.1	1.62 ± 0.09	--	--
0.05	0.60 ± 0.08	--	--

Table 27: Raw data for Figure 27

	HNO_3	75:25	50:50	25:75	HCl
Fraction (FCV)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)
Load	0.001 ± 1.28	< MDA	< MDA	< MDA	< MDA
5	< MDA	0.02 ± 0.24	< MDA	< MDA	< MDA
10	< MDA	0.01 ± 0.37	0.06 ± 0.42	< MDA	< MDA
15	0.06 ± 0.48	0.19 ± 0.21	0.14 ± 0.27	0.17 ± 0.21	0.04 ± 1.27
20	0.22 ± 0.24	0.58 ± 0.12	0.44 ± 0.14	0.46 ± 0.13	0.18 ± 0.53
25	0.65 ± 0.14	1.14 ± 0.09	0.88 ± 0.10	0.84 ± 0.10	0.47 ± 0.31
30	1.22 ± 0.10	1.86 ± 0.07	1.48 ± 0.07	1.44 ± 0.07	0.95 ± 0.22
35	88.31 ± 0.01	86.81 ± 0.01	87.57 ± 0.01	87.05 ± 0.01	89.57 ± 0.02
40	5.61 ± 0.05	3.06 ± 0.05	3.12 ± 0.05	2.14 ± 0.06	2.40 ± 0.14

Table 28: Raw data for Figure 28

	HNO_3	75:25	50:50	25:75	HCl
Fraction (FCV)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)	Sr Recovered (%)
Load	< MDA	< MDA	0.001 ± 7.30	< MDA	54.77 ± 0.08
5	< MDA	< MDA	< MDA	0.01 ± 1.89	4.22 ± 0.28
10	< MDA	< MDA	0.07 ± 0.75	< MDA	1.22 ± 0.52
15	< MDA	0.09 ± 0.67	0.23 ± 1.19	0.21 ± 1.32	1.11 ± 0.54
20	< MDA	0.24 ± 1.18	0.40 ± 0.93	0.55 ± 0.87	1.06 ± 0.56
25	0.13 ± 1.75	0.58 ± 0.75	0.79 ± 0.66	0.82 ± 0.69	1.17 ± 0.53
30	0.41 ± 0.90	0.99 ± 0.57	1.20 ± 0.52	1.34 ± 0.50	1.23 ± 0.52
35	73.84 ± 0.07	54.98 ± 0.08	51.61 ± 0.08	52.87 ± 0.08	19.27 ± 0.13
40	18.59 ± 0.13	32.97 ± 0.10	35.95 ± 0.10	34.35 ± 0.10	2.79 ± 0.34

Table 29: Raw data for Figure 29

	5:1:1	9:3:7
Fraction (FCV)	Sr Recovered (%)	Sr Recovered (%)
Load	0.004 ± 0.002	0.29 ± 0.06
5	0.10 ± 0.03	0.79 ± 0.12
10	0.12 ± 0.04	1.32 ± 0.16
15	0.49 ± 0.10	1.98 ± 0.20
20	0.86 ± 0.13	2.35 ± 0.21
25	1.25 ± 0.16	2.80 ± 0.24
30	1.75 ± 0.19	2.75 ± 0.24
35	88.1 ± 1.4	80.0 ± 1.3
40	6.13 ± 0.35	4.71 ± 0.32

Table 30: Raw data from Figure 30

Acid Concentration (M)	Lithium Uptake k' Li
0.05	< LOD
0.1	< LOD
0.25	< LOD
0.5	< LOD
1	< LOD
2	< LOD
4	< LOD
6	< LOD
8	< LOD
11.78	< LOD

Table 31: Raw data for Figure 31

	Lithium	
Salt Concentration (M)	k' Sr	
1	70.75	± 0.62
0.5	64.99	± 0.64
0.25	61.69	± 0.54
0.1	59.97	± 0.99
0.05	58.78	± 0.64
0.01	58.78	± 0.61
0.005	59.68	± 2.69
0.001	58.05	± 0.18
0	59.1	± 1.1

Table 32: Raw data for Figure 32

	NaOH Pre-HF		NaOH Post-HF		LiOH Pre-HF		LiOH Post-HF	
Matrix	k' Sr		k' Sr		k' Sr		k' Sr	
Blue	45.9	± 0.7	54.0	± 1.0	54.1	± 1.1	46.0	± 0.8
Gold	46.2	± 1.0	46.9	± 0.7	55.7	± 1.8	50.8	± 2.0
Pink	43.7	± 0.8	41.9	± 1.2	54.8	± 2.0	46.4	± 0.8
Dolomite	60.5	± 1.2	61.5	± 1.6	59.3	± 1.8	72.9	± 0.9
Limestone	58.0	± 1.0	48.2	± 0.8	54.4	± 2.0	52.7	± 0.8

Table 33: Raw data for Figure 34

	Horwitz	Pourmand	McLain
	k' Zr	k' Zr	k' Zr
1 M HNO_3	15*	5700*	5725 ± 911

*Estimated from literature, no error provided

Table 34: Raw data for Figure 35

	k' Zr	k' Sr
1 M HNO3/0.2 M HF	1.73 ± 0.35	68.5 ± 4.6

Table 35: Raw data for Figure 36

Elution Volume (ml)	Sr-88 Recovered (%)	Y-89 Recovered (%)	Zr-90 Recovered (%)
Load (0.25)	< LOD	1.57 ± 0.35	< LOD
5	0.04 ± 0.01	< LOD	382.69 ± 11.62
10	< LOD	< LOD	31.65 ± 20.48
15	0.07 ± 0.01	< LOD	< LOD
20	99.38 ± 2.20	< LOD	< LOD
25	0.38 ± 0.01	< LOD	< LOD

Table 36: Raw data for Figure 37

Elution Volume (ml)	Sr-88 Recovered (%)	Y-89 Recovered (%)	Zr-90 Recovered (%)
Load (0.25)	< LOD	< LOD	< LOD
5	< LOD	< LOD	19.51 ± 0.03
10	< LOD	0.18 ± 0.01	< LOD
15	< LOD	0.59 ± 0.03	< LOD
20	< LOD	< LOD	< LOD
25	< LOD	< LOD	< LOD

Table 37: Raw data for Figure 38

Elution Volume (ml)	Sr-88 Recovered (%)	Y-89 Recovered (%)	Zr-90 Recovered (%)
Load (0.25)	< LOD	< LOD	< LOD
5	< LOD	< LOD	86.8 ± 4.1
10	0.08 ± 0.43	< LOD	< LOD
15	0.44 ± 0.54	< LOD	< LOD
20	98.8 ± 2.9	< LOD	0.12 ± 0.01
25	0.41 ± 0.02	< LOD	< LOD

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SPECIAL PERMISSIONS

Figure 2: Reproduced from reference 63 with permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association, and the RSC http://dx.doi.org/10.1039/b305853k

Figure 3: Reprinted from Talanta, 62, Dietz, M.L.; Jensen, M.P., "EXAFS Investigations of Strontium Complexation by a Polymer-Supported Crown Ether, 109-113, Copyright 2004 with permission from Elselvier http://dx.doi.org/10.1016/S0039-9140(03)00422-3

CHAPTER 3: Journal of Radioanalytical and Nuclear Chemistry, "A Performance Comparison of Commercially Available Strontium Extraction Chromatography Columns," 307, 2016, 1825-1831, McLain, D.R.; Mertz, C.J.; Sudowe, R. with permission of Springer http://dx.doi.org/10.1007/s10967-015-4634-z

CURRICULUM VITAE

Derek McLain

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EDUCATION

University of Nevada, Las Vegas	Las Vegas, NV
• Ph.D. in Radiochemistry	Expected December, 2016
University of Wisconsin-Milwaukee	Milwaukee, WI
• B.S. in Chemistry	May, 2011
• Certificate in Forensic Science	May, 2011

AWARDS/HONORS

- American Nuclear Society Student Conference Best Paper, Radiochemistry Session, (April 2013)
- Nuclear Forensics Graduate Fellowship Program fellow, Medical University of South Carolina, (September 2012)
- Summa Cum Laude, Graduating class of 2011, University of Wisconsin-Milwuakee, (May 2011)
- McFarland Award 1st place undergraduate research poster, UW-Milwaukee Department of Chemistry & Biochemistry (April 2011)
- Outstanding Senior Award for chemistry majors, UW-Milwaukee Department of Chemistry & Biochemistry (April 2011)
- Outstanding Performance in Analytical Chemistry Award for outstanding work in the classroom and lab, UW-Milwaukee Department of Chemistry & Biochemistry (April 2010)
- Eagle Scout (January 2007)

SKILLS

- Handling radioactive material
- Radiochemical separations, in particular extraction chromatography
- Radiation measurements (Liquid scintillation counting, gamma spectroscopy)
- Concise report writing
- Competent at performing literature searches
- Routine laboratory practices (pipetting, weighing, record keeping, data analysis)
- SEM/EDX analysis
- Fundamentals of reactor operation (attended UC Irvine Reactor Operator School)
- Fundamentals of alpha spectroscopy

LABORATORY EXPERIENCE

University of Nevada, Las Vegas
Graduate Assistant Las Vegas, NV
Supervisor/Advisor: Ralf Sudowe (Nov. 2011-Present)
Interference Effects of Urban Materials on Radioanalytical Separations (2012-Present)
Investigated interference seen in radioanalytical separations caused by urban materials. Investigated various urban material components and simulated urban material mixtures for effects on strontium uptake. Tested Sr resin for use with mixed acid systems.

Intragroup Separation of Trivalent Actinides: Americium and Curium (2011)
Primary Graduate Student Investigator: Narek Gharibyan
Characterized extraction chromatography resins for Am(III) and Cm(III) in an effort to establish new separation methods.

Joint Research Center – Institute for Transuranics
Trainee Karlsruhe, Germany
Supervisors: Klaus Mayer, Jean-Yves Colle (Nov. 2015 – Jan. 2016)
Investigation of $CsCl/BaCl_2$ Partitioning in Aerosols Simulating A Radiological Dispersion Event
Performed decay calculations and prepared solid samples corresponding to different "age" sources, ablated them using a Nd:YAG laser, collected the particulate using a Radiological Dispersion Events Set-Up (RADES), and performed SEM or ICP-MS analyses on the resulting particles.

Argonne National Laboratory
Guest Graduate Lemont, IL
Supervisor: Carol Mertz (May – Sept. 2015)
Comparison of Strontium Extraction Chromatography Methods Using Commercially Available Products
Characterized and evaluated the elution profiles of three different commercially available extraction chromatography products.

Guest Graduate
Supervisor: Carol Mertz (May – Aug. 2013)
Extraction Chromatography Programming
Revised existing and developed new programs to simulate extraction chromatographic methods based on published retention data.

Student Research Program (Intern)
Supervisors: Carol Mertz, Mike Kaminski (May – Aug. 2010)
Characterizing Microfluidic Systems for Field Deployment (2010)
Characterized commercial extraction chromatographic material for use in a gas-pressurized extraction chromatographic microfluidic system to be used in the separation of plutonium from uranium in purified waste streams.

University of Wisconsin-Milwaukee
2009-2011, Undergraduate Researcher Milwaukee, WI
Supervisor/Advisor: Mark Dietz (Jan. 2009 – Aug. 2011)
Effects of Chain Length on Ionic Liquids' Abilities to Dissolve Materials (2011)

Investigated the ability of various ionic liquids to dissolve HDEHP and 4,4'(5')-di-(t-butyl-cyclohexano)-18-crown-6.

Designing Novel and More Environmentally Friendly Laboratory Exercises (2009-2011)
Replaced existing laboratory exercises with newer, more relatable, and environmentally friendlier exercises.

PUBLICATIONS

1. McLain, D.R.; Mertz, C.J.; Sudowe, R.; "A Performance Comparison of Commercially Available Strontium Extraction Chromatography Columns," *J. Radioanal. Nucl. Chem.,* 307:3, p. 1825 (2015).

2. Garvey, S.L.; Shahmohammadi, G.; McLain, D.R.; Dietz, M.L.; "Determination of Calcium in Dietary Supplements: Statistical Comparison of Methods in the Analytical Laboratory," *J. Chem. Ed.*, 92, p. 167 (2014).

3. Gharibyan, N.; Dailey, A.; McLain, D.R.; Bond, E.M.; Moody, W.A.; Happel, S.; Sudowe, R.; "Extraction Behavior of Americium and Curium on Selected Extraction Chromatography Resins from Pure Acidic Matrices," *Solvent Extr. Ion Exch.*, 32:4, p. 391 (2014).

PRESENTATIONS

Oral Presentations

1. McLain, D., Sudowe, R., "Using Sr Resin with Mixed Acid Matrices," ACS Fall Meeting, Philadelphia, PA, August 2016

2. McLain, D., Liu, C., Sudowe, R., "Using Sr Resin with Mixed HCl/HNO_3 Matrices," Radiobioiassay & Radiochemical Measurement Conference, Iowa City, IA, October 2015.

3. McLain, D., "Matrix Effects of Urban Material on Extraction Chromatographic Strontium Separations," Academic Lab Collaboration Meeting, Livermore, CA, August 2015

4. McLain, D., Mertz, C., Sudowe, R., "A Comparison of Strontium Extraction Chromatography Methods Using Commercially Available Products," MARC X Conference, Kona, HI, April 2015.

5. McLain, D., Amato, V., Sudowe, R., "Effects of Steel on Separations Using Sr Resin," ACS Fall Meeting, San Francisco, CA, August 2014.

6. McLain, D., Sudowe, R., "Effects of Urban Materials on Separations Using Sr Resin," Radiobioassay & Radiochemical Measurement Conference, Rohnert Park, CA, October 2013.

7. McLain, D., Sudowe, R., "Interference Effects of Steel on Sr Resin Separations," ANS Student Conference, Boston, MA, April 2013.

8. McLain, D., Sudowe, R., “Effect of Elemental Interferences on Radionuclide Analysis in Urban Rubble Samples,” ACS Spring Meeting, New Orleans, LA, April 2013.

Poster Presentations

1. McLain, D., Sudowe, R., “Separating Sr from Urban Materials Using Extraction Chromatography,” University-Industry Technical Interchange, Raleigh, SC, June 2016.

2. Mclain, D., Mertz, C., Sudowe, R., “A Comparison of Strontium Extraction Chromatography Methods Using Commercially Available Products,” MARC X Conference, Kona, HI, April 2015

3. McLain, D., Amato, V., Sudowe, R., “Effects of Steel on Radioanalytical Separations Using Sr Resin,” Academic Lab Collaboration Meeting, Lemont, IL, August, 2014.

4. McLain, D., Sudowe, R., “Effect of Elemental Interferences on Radionuclide Analysis in Urban Rubble Samples,” University-Industry Technical Interchange, Oakland, CA, December 2011.