METHOD DEVELOPMENT FOR THE ANALYSIS OF NUCLEAR FORENSIC SIGNATURES WITH ICP-MS

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By
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FORENSIC SIGNATURES WITH ICP-MS

Presented by Veronica C. Bradley

A candidate for the degree of Doctor of Philosophy
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Professor John M. Gahl
DEDICATION

This dissertation is dedicated to my parents, Brett and Kathleen, for all their support over the years. I am eternally grateful for everything they have done for me. I am also grateful to my siblings, Donny, Joe, and Bernie, for their support during this process. I would also like to dedicate this dissertation to my undergraduate research advisors, Drs. Mike and Corinne Deibel. Thank you for introducing me to academic research and for convincing me to undertake the process of earning a PhD. Finally, I am extremely thankful to have so many good friends who have lent me emotional support over the years.
ACKNOWLEDGEMENTS

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Nuclear forensic analysis is a field of analytical chemistry that focuses specifically on analyzing signatures of nuclear material for criminal investigation. Promising nuclear forensic signatures include rare earths element pattern and uranium and plutonium isotopes ratios. Uranium isotope ratios that deviate from natural indicates enrichment activities. The presence of plutonium and the $^{239}$Pu/$^{240}$Pu isotopic ratio indicate irradiation of uranium for weapons production purposes. Samples for nuclear forensic analysis are often urgent, and therefore must be analyzed quickly, with good accuracy and precision. Robust methodologies must be developed for analysis of samples from potential nuclear scenarios with suitable speed, accuracy, and precision.

In this dissertation, a method was developed to analyze uranium isotope ratios from solid particles on the surface of environmental swipe samples for the purpose of quickly and accurately determining whether uranium enrichment was occurring in the facility. A method to quantify rare earth impurities in uranium ore concentrates using high performance ion chromatography (HPIC) and inductively coupled plasma mass spectrometry (ICP-MS) was tested, as was a method to rapidly dissolve inorganic material using ammonium bifluoride and subsequently quantify the rare earth concentration using a newly developed high performance ion chromatography method coupled with ICP-MS detection. The method was demonstrated by accurate measurement of rare earth elements in igneous USGS minerals. Finally, the method was used to separate fresh fission products from a uranium tracer with detection by gamma ray spectroscopy.
Chapter 1: Introduction

This work explores the use of elemental and isotopic signatures for nuclear forensic analysis. The instrumental method inductively coupled plasma-mass spectrometry (ICP-MS) is employed for these measurements. ICP-MS is a mature and robust technique whose multi-element analysis and isotope analysis capabilities have made it valuable for nuclear applications. This work explores development of new ICP-MS methodologies for trace element analysis. This includes development of rapid dissolution chemistry, exploration of high-pressure ion chromatography (HPIC) for in-line and off-line separation of rare earth elements (REE) and actinides prior to HPIC analysis, and the potential of using HPIC and gamma ray spectroscopy to measure fresh fission products.

1.1 Nuclear Forensics

The field of nuclear forensics originated in the early 1990’s in response to the increased detection of illicit nuclear materials at international borders. To investigate and counter this problem, analytical tools and methods were created and adapted to study the forensic signatures of nuclear material[1]. The goal of technical nuclear forensic analysis is to support investigations by providing information linking nuclear material with processes, people, events, and locations. Nuclear forensics is generally split into two categories: pre-detonation and post-detonation. Pre-detonation nuclear forensics investigates the signatures of nuclear material that have not been detonated, whereas post-detonation nuclear forensics analyzed nuclear debris following the explosion of a nuclear weapon to discover the type of weapon and the origin of the nuclear material. Nuclear material could carry signatures either from the starting material (i.e. its origin) or the
Signatures are measurable parameters or a combination of parameters that can be investigated to make conclusions about the origin and history of the nuclear material, such as the mine the uranium ore came from and the chemical processes the material underwent. These signatures can include the trace metal impurities in the material, the uranium and plutonium isotope ratios, concentration of uranium or plutonium daughter products, which is used to determine the time elapsed since the last chemical purification, and corrosion products from storage[2, 3]

Pre-Detonation Nuclear Forensics

Nuclear Fuel Cycle and Uranium Processing

Important aspects of pre-detonation nuclear forensic efforts are to prevent material diversion through safeguards, detect or deter nuclear material diversion through treaty monitoring, and to detect material outside of control. An example would be in monitoring uranium processing in the nuclear fuel cycle. Uranium is naturally occurring in mineral deposits such as sandstone, unconformity, and hematite breccia complex[4]. The largest producers of uranium as of 2015 are Canada, Kazakhstan, and Australia, while Canada, the USA, and Kazakhstan have cumulatively produced the most uranium (shown in table 1.1)[4]. The uranium in high grade ore deposits is often in the form of uraninite and pitchblende, which contain up to 70% U by weight, but these ores are uncommon[1, 4]. More common are low-grade ores, which have a uranium concentration of approximate 0.2%. At the beginning of the fuel cycle, uranium ore is mined and chemically processes to produce uranium ore concentrates (UOCs). Yellowcake (U₃O₈) is the product of the first stage of the fuel cycle, in which the natural uranium is leached and extracted from
ore[5-7]. Yellowcake contains 60—80% uranium by weight[8]. The UOCs are eventually processed into uranium metal or uranium dioxide (UO₂) for incorporation into nuclear fuel or nuclear weapons.

**Table 1.1:** Commercial uranium production from 2010-2015 and historical uranium production for the top producing countries in tons U[4]

<table>
<thead>
<tr>
<th>Country</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>9,786</td>
<td>9,145</td>
<td>8,999</td>
<td>9,332</td>
<td>9,134</td>
<td>13,325</td>
<td>496,564</td>
</tr>
<tr>
<td>USA</td>
<td>1,660</td>
<td>1,537</td>
<td>1,596</td>
<td>1,835</td>
<td>1,919</td>
<td>1,256</td>
<td>374,896</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>17,803</td>
<td>19,451</td>
<td>21,317</td>
<td>22,574</td>
<td>23,127</td>
<td>23,800</td>
<td>268,992</td>
</tr>
<tr>
<td>Germany</td>
<td>8</td>
<td>52</td>
<td>50</td>
<td>27</td>
<td>33</td>
<td>0</td>
<td>229,629</td>
</tr>
<tr>
<td>Australia</td>
<td>6,203</td>
<td>5,983</td>
<td>6,991</td>
<td>6,350</td>
<td>6,350</td>
<td>5,672</td>
<td>200,556</td>
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<tr>
<td>Russian Federation</td>
<td>3,562</td>
<td>2,993</td>
<td>2,872</td>
<td>3,135</td>
<td>3,135</td>
<td>3,055</td>
<td>161,906</td>
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<tr>
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<td>583</td>
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<td>540</td>
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<td>393</td>
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<tr>
<td>Niger</td>
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<td>4,351</td>
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<td>4,528</td>
<td>4,528</td>
<td>4,116</td>
<td>139,432</td>
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<tr>
<td>Uzbekistan</td>
<td>2,400</td>
<td>2,500</td>
<td>2,400</td>
<td>2,400</td>
<td>2,400</td>
<td>2,385</td>
<td>135,891</td>
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<tr>
<td>World Production</td>
<td>53,663</td>
<td>53,494</td>
<td>58,344</td>
<td>59,637</td>
<td>56,252</td>
<td>60,496</td>
<td>2,802,267</td>
</tr>
</tbody>
</table>

Uranium containing ores must be milled, then chemically oxidized to ensure hexavalent uranium before being purified through ion exchange, solvent extraction, or precipitation techniques[1]. Even after purification metal impurities remain in the UOC that are dependent on the type of ore the uranium was derived from, milling method
employed, and the chemical purification procedure[9]. The elemental impurity of UOCs and isotopic abundances of uranium and contaminants such as lead and strontium can be used to facilitate identification of the origin of interdicted UOC[6, 8, 10, 11]. The presence of processing chemicals in the samples can be used to support forensic studies. Anions like phosphorus, sulfur, bromine, and iodine, as well as relative distribution and isotopic composition of REE have been shown as useful signatures for origin assessment[7, 8, 12-14]. REE have similar chemical behavior due to the non-bonding nature of their 4f valence electron shell, and therefore the REE pattern does not change significantly during the purification process[8]. It has been shown that deposit types have distinctive REE patterns, which refers to the concentration of each element in comparison to that of the other REEs. Relative distribution patterns can be used as a complementary forensic signature, along with uranium and lead isotope ratios and other trace element concentrations, for origin assessment[5, 15, 16].

Trace elements, including REEs, are generally analyzed using mass spectrometry, especially ICP-MS and thermal ionization mass spectrometry (TIMS), because mass spectrometry has a much lower detection limit (by several orders of magnitude) for atomic analysis than other instruments, like inductively coupled plasma – optical emission spectroscopy (ICP-OES), flame atomic absorption spectroscopy, or graphite furnace atomic absorption spectroscopy[17]. Rare earth elements can be difficult to quantify through mass spectrometry however, as they have many isobaric overlaps with each other, and light REEs will form oxides with the same mass as heavier REEs. To overcome these interferences, separations are often performed prior to mass spectrometric analysis using
high performance ion chromatography (HPIC) which separates rare earths based on their binding affinity to charged functional groups.

After ore extraction UOC must be further processed into a useful chemical form of uranium for either fuel or weapons applications. First, the UOC material is heated at 700 °C in the presence of H₂ to convert the uranium from UO₃ to UO₂.

\[
\text{UO}_3 + \text{H}_2 \rightleftharpoons \text{UO}_2 + \text{H}_2\text{O} \quad (1.1)
\]

UO₂ is then reacted with HF at 450 °C to form UF₄, which can react with air to form UF₆.

\[
2 \text{UF}_4 + \text{O}_2 \rightleftharpoons \text{UF}_6 + \text{UO}_2\text{F}_2 \quad (1.2)
\]

Or UO₂ can be reacted with ClF₃ or BrF₃ through the reaction below:

\[
3 \text{UF}_4 + 2 \text{ClF}_3 \rightleftharpoons 3 \text{UF}_6 + \text{Cl}_2 \quad (1.3)
\]

The latter reaction is preferred as uranium recovery is 50% higher than that achieved in equation 1.2[1]. UF₆ is a solid at standard temperature and pressure, and sublimes above 64 °C[18]. It is used in uranium enrichment processes in its gaseous form[19]. It reacts with water in the atmosphere and hydrolyzes to form UO₂F₂, and therefore must be kept in sealed, dry environments.

There are several methods that can be used to enrich uranium using gaseous UF₆. The first method, electromagnetic isotope separation, was used by Alfred Nier in 1940 to separate $^{235}$U from $^{238}$U for fission experiments[20]. It involves ionizing atoms through electron impact, then deflecting them in an electric and magnetic field. Ions with different masses will be deflected to different extents and can then be collected as relatively pure enriched isotopes though it is not often used for uranium separation any more as it does not scale well to the quantities of enriched uranium required for the nuclear fuel cycle[21]. The most common enrichment methods currently used are gaseous diffusion and gas
centrifugation[22]. Gaseous diffusion is based on the principle that in thermal equilibrium, lighter molecules travel faster than heavier ones. When a hole in a porous membrane with a diameter smaller than the mean free path of UF₆ is placed in the wall of a container, a higher proportion of the total ²³⁵UF₆ molecules pass through the hole than ²³⁸UF₆[1]. In a different enrichment process, gas centrifugation, large centrifuges spin UF₆ gas at high speeds. Heavier ²³⁸UF₆ molecules migrate towards the outside of the centrifuge while the lighter ²³⁵UF₆ isotopes remain closer to the center of the centrifuge[23]. In both methods the enrichment process tends to be repeated many times, with the exact number of repeated processes depending on the desired level of enrichment.

While natural uranium can be used as fuel in nuclear power reactors, light water reactors are often enriched in ²³⁵U up to approximately 3% to decrease the amount of fuel needed for a given power output[1]. Nuclear weapons, by contrast, often use highly enriched uranium with ²³⁵U making up 90% - 95% of the total uranium content[24]. The isotopic composition of uranium material can indicate the intended use of the material, and therefore measuring uranium isotope ratios is vital when monitoring uranium enrichment in nuclear facilities, as is required by The Treaty on the Non-Proliferation of Nuclear Weapons (NPT)[25].

Environmental Sampling

The International Atomic Energy Association (IAEA) is responsible for verifying declared stocks of nuclear material and uranium enrichment. The IAEA uses robust sampling techniques to investigate nuclear facilities, and then sends the samples to the Network of Analytical Laboratories (NWAL) for analysis. One sampling method used by the IAEA is environmental sampling (ES). ES was implemented in 1996, and is performed
by swiping surfaces in nuclear facilities with a 10 × 10 cm piece of cloth made up of woven cotton fibers[26]. The swipe samples are analyzed for fission products and actinide content, as well as actinide isotope ratios. Swipes are either bulk digested to determine the total amount of analytes and average uranium and plutonium isotope ratios, or single particles of uranium or plutonium are taken from the swipe and analyzed for the isotopic composition of the individual particle[26]. For bulk analysis, the whole swipe is dissolved in acid and all uranium and plutonium contained on the swipe goes into solution. The total actinide content on the swipe is found this way, however only the average isotope ratios can be determined. The isotope ratio of the bulk digestate may not reflect the isotopic composition of any given particle present prior to digestion, for example, if there is both depleted and enriched uranium particles present on the swipe, the isotope ratio of the bulk digestate may appear natural. Isotopic analysis of the bulk digestate is most commonly done on multicollector (MC) ICP-MS instruments or multicollector thermal ionization mass spectrometry (MC-TIMS). Instruments with multiple detectors (called multicollector instruments) can detect multiple isotopes simultaneously, leading to higher precision compared to instruments that can only measure one isotope at a time.

Single particle analysis is especially important when looking for undeclared enrichment activities, as a bulk digestion containing both enriched and depleted U particles will average out, obscuring the unauthorized activity. Analyzing individual particles for the isotope ratios eliminates that risk. Solid particle analysis can be accomplished using secondary ion mass spectrometry (SIMS), in which a particle is isolated and loaded onto a planchet, then bombarded with a sputtering ion source which forms secondary ions on the surface of the sample. Fission track (FT) TIMS is also used for particle analysis. In this
technique, particles are collected from the surface of the swipe and irradiated. Fission tracks are measured in the particles to find particles with high quantities of fissile material, which are loaded onto a TIMS filament for isotopic analysis. The only direct surface sampling technique currently in routine use is laser ablation ICP-MS, in which a laser is directed to the surface of a sample and ablates a portion of the material. The ablated material is swept into an ICP-MS by a flow of inert gas.

Post-Detonation Nuclear Forensics

Uranium highly enriched in $^{233}$U or $^{235}$U, and the fissile $^{239}$Pu, can be turned into a nuclear weapon. Nuclear devices produce explosive energy through the exoergic nuclear reactions of fission and fusion. In a neutron induced fission reaction the target nucleus deforms to a saddle point configuration and the nucleus splits into two smaller atoms. Fission produces on the order of 200 MeV of energy per reaction. Fusion is the process by which two light nuclei combine to form a heavier atom, also accompanied by a release of energy[27]. The important fusion reaction $^3$H($^2$H,n)$^4$He reaction produces 17.6 MeV of energy and a neutron with 14.1 MeV of kinetic energy. While the design of individual devices can vary, the principle of a nuclear weapon is the inducement of fission reactions in an amount of uranium or plutonium that can sustain a chain reaction.

Following an illicit nuclear detonation, a rapid and robust response is vital to determine the parameters and origin of the device. The extreme conditions of a nuclear detonation destroys traditional forensic indicators like fingerprints, and therefore nuclear forensic methods must be relied upon for the device attribution[1]. The number of reactions increases exponentially until the device is blown apart, creating an explosion with
temperatures of millions of degrees, several orders of magnitude higher than chemical explosives[27, 28]. The energy released in the explosion is a combination of thermal energy, in the form of x-rays and photons, the kinetic energy of ions and electrons, gamma rays and neutrons that were products in the fission reactions, and excited atoms[28].

A terrestrial detonation produces localized refractory debris that may be sampled near the test sight. The dust plume from the explosion circulates debris in the atmosphere and results in world-wide fallout. The radioactive debris field includes fission products, neutron activation products produced from neutron interactions with surrounding area, and unfissioned actinides. The debris around the detonation site is a glassy matrix that is formed when local soil and minerals are taken-up in the fireball and melt in the extreme heat and interact with the nuclear debris[29]. As the fireball cools, the material in the fireball coalesce as it condenses, as the molten particles aggregate and become heavier, they fall down to earth in the aerodynamically preferred form of spheres and teardrops[30]. Some of these droplets reached the ground while molten, fusing with molten materials on the surface[29]. When the device is blown apart, the blast sends bomb components and environmental matrices in different directions leading to a heterogeneous mixing on the debris field referred to as physical fractionation[31]. Along with physical fractionation, there is chemical fractionation of the debris field since volatile elements travel further away from the blast site, while refractory elements remain near the center of the field.

To ensure a comprehensive picture of the debris components, robust sampling techniques, which collect material from all areas of the debris field, are necessary[32]. Different types of nuclear weapons can cause differences in the fission products observed in the debris field, as the fission mass yield changes depending on the isotopes that undergo
fission, and the energies of the neutrons that induce fission. For example, fusion weapons, which contain deuterium in the center of the weapon, produce 14 MeV neutrons which cause a decrease in the peak to wing ratio on the fission split curve (see figure 1.1)[1, 33]. The wings of the fission-mass yield curve, including light REEs such as La, Nd, and Pm, are most sensitive to the actinides and the neutron energy spectrum, and are therefore important analytical targets for nuclear forensic analysis[34].

**Figure 1.1:** Mass yield split for $^{235}$U fission induced with thermal neutrons and 14-MeV neutrons[1]
A variety of analysis techniques, including both nondestructive surface imaging and destructive analysis, have been used to characterize nuclear debris. Non-destructive imaging techniques that have been used include alpha and beta radiography, scanning electron microscopy (SEM) with backscatter detectors, and x-ray fluorescence (XRF) spectroscopy, and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) which have the benefit of characterizing heterogeneity in the sample, and allow for the sample to be reused for further analysis[30, 33, 35, 36]. Destructive techniques generally involve bulk sample dissolution, usually through acid digestion, prior to analysis with mass spectrometric techniques such as ICP-MS, multi-collector (MC) ICP-MS, or radiochemical methods[33]. A benefit to bulk dissolution is that a representative sample will provide a picture of the isotopic composition of the entire debris field, although if the sample is non-representative it causes analytical bias in the results.

The most common sample dissolution technique for nuclear debris analysis includes acid digestion in open vessels. This method generally consists of a mixture of nitric acid (HNO₃), hydrochloric acid (HCl), perchloric acid (HClO₄), and hydrofluoric acid (HF), and requires several days to dissolve refractory minerals as the dissolution temperature is limited by the boiling point of the acid (approximately 130 °C)[33, 36-41]. This method has drawbacks in the time required to complete dissolution, and the use of hazardous acids like HF and HClO₄ which requires special facilities and personnel training. High pressure microwave digestion can be used at higher temperatures and require a mixture of HF and HNO₃[40]. The vessels can over-pressurize, leading to sample leaks which is not ideal when working with radioactive samples. Improving the dissolution of
post-detonation debris to minimize these drawbacks is necessary for a faster, more robust analysis method to understand and respond to a nuclear attack.

Ammonium bifluoride (ABF, NH₄HF₂) fusion has been proposed as an alternative to mixed-acid digestions of post-detonation debris, as it does not require specialized equipment or hazardous chemicals, it is performed at atmospheric pressures, and can reach higher temperatures than mineral acids. Ammonium bifluoride is a solid at room temperature with a melting point of ~ 125 °C, and a boiling point of 240 °C[42, 43]. Partial decomposition of ABF into ammonia and HF (equation 1.4) has been reported between 120 and 220 °C[44].

\[ \text{NH}_4\text{HF}_2(s) \rightarrow \text{NH}_3 + 2\text{HF} \]  

The fluorides in ABF reacts with silicon oxides and can therefore be used to break down nuclear debris matrices, through equation 1.5.

\[ \text{SiO}_2(s) + 3\text{NH}_4\text{HF}_2 \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(g) + 3\text{NH}_4\text{F}(s) \]  

Other elements react with ABF and form ammonium-fluoride complexes or metal fluorides[41, 45]. ABF fusion has advantages over other dissolution methods in that it has a relatively high boiling point compared to mineral acids, and therefore dissolution temperatures can be higher, leading to faster dissolution speeds. Fusion can be accomplished on a hot plate and doesn’t require pressurized vessels or expensive equipment. After a debris sample is dissolved, the elemental make-up can be analyzed through various elemental spectroscopy techniques, with ICP-MS being one of the most common.
1.2 Mass Spectrometry

Mass spectrometers have been used in nuclear research since their creation. The first mass spectrometer was built in the early 20th century by J. J. Thompson and Francis Aston, based on his work measuring cathode rays, to measure the masses of charged atoms. Later Alfred Nier redesigned the mass spectrometer, creating an instrument that was smaller and consumed less energy, thus making it more suitable to a wide range of applications outside of fundamental physics. Nier managed to separate $^{235}$U from $^{238}$U, leading to the confirmation that $^{235}$U was responsible for fissions occurring in uranium material[46]. Inductively coupled plasma mass spectrometers were commercialized in 1983 and have since been applied to many fields, including environmental, geological, and nuclear fields[17].

![ICP-MS schematic](image)

**Figure 1. 2:** ICP-MS schematic [47]

Inductively coupled plasmas are the most common type of plasma ionization source. They consist of three main parts, the torch, the radiofrequency (RF) coil, and the
power supply. The torch is made of three concentric quartz tubes consisting of an outer tube, a middle tube, and the sample injector[48]. Ar gas flows between the outer and middle tube at a rate of 15-17 L min\(^{-1}\)[17], an auxiliary gas, generally also Ar, flows between the middle tube and the sample injector, and the nebulizer gas carries the aerosolized sample from the spray chamber through the sample injector[49]. The auxiliary gas and the nebulizer gas both flow at approximately 1 L min\(^{-1}\). The torch is positioned horizontally inside a copper coil connected to an RF generator. An alternating current is applied in the coil which causes an electromagnetic field to the area at the top of the torch[50]. A high-voltage spark strips electrons from Ar atoms. The electrons are accelerated and form a chain reaction through electron-stripping collisions with other Ar atoms[17]. The plasma ranges in temperature from 6,000 K on the outside, to 10,000 K in the center of the plasma nearest the end of the sample injector[50]. The aerosolized sample travels through the center of the plasma and is ionized as the ground state atoms in the sample collide with the energetic electrons in the plasma[17, 50].

To introduce an analyte to the ICP, a solution must pass through an aerosol generator and a droplet separator. To generate an aerosol, a liquid is pumped into a nebulizer and a gas (usually Ar) flows perpendicular to the solution, breaking up the liquid into small droplets. Larger droplets can be difficult for the plasma to dissociate to ionize single atoms[51, 52], and so solution is sent through a spray chamber, which separates out the smaller droplets in the aerosol to enter the plasma. Many designs of both nebulizers and spray chambers have been developed, each having different advantages and disadvantages over the others. Concentric nebulizers are commonly used in modern instruments for liquid analysis. The sample is sent through a capillary tube, generally at a
flow rate of 1-3 ml min⁻¹, and Ar gas surrounds the capillary and flows parallel to the solution until reaching the exit nozzle, where the aerosol is formed as the gas hits the solution[53]. Concentric nebulizers have good sensitivity and stability, however the capillary can get blocked when analyzing samples with high amounts of total dissolved solids[54].

Cyclonic spray chambers are round, and when the sample aerosol and argon flow into the spray chamber it creates a vortex. Smaller droplets are carried with the gas into the injector, while larger droplets hit the walls of the spray chamber and fall to the drain[55]. Scott type double pass spray chambers consist of two concentric tubes, where the aerosol from the nebulizer is sent through the center tube, and larger droplets hit the side of the tube and fall into the drain, creating a positive pressure which in turn sends small droplets through the outer tube and into the sample injector[52, 55]. Cyclonic spray chambers have higher sampling efficiency compared to double-pass spray chambers, leading to higher sensitivity and lower detection limits, since more sample is sent into the plasma[17].

The plasma operates at atmospheric pressure (~760 torr) while the mass analyzer is under vacuum (10⁻⁶ torr). As ions travel from the plasma to the mass analyzer, they pass through an interface maintained at a vacuum of 1-2 torr using a roughing pump. The interface consist of a series of 2 or 3 cones of decreasing sized openings whose purpose is to direct the ions produced in the plasma into a cohesive ion beam while reducing the vacuum[17].

Once the ion beam passes through the interface, it is sent through a series of optics, made-up of electrostatically controlled lens that are kept at a pressure of 10⁻³ torr by a
turbomolecular pump. The optics keep the ion beam collimated as the pressure is further reduced as the ions travel from the plasma into the mass analyzer and minimizes the spread of ion energies[56]. The ion beam has a secondary function of preventing particulates and neutral species from reaching the mass analyzer and detector, because if they did enter the detector, they would increase background noise and cause signal instability[57]. A well-functioning optic system sends a collimated beam of positively charged ions into the mass analyzer of the ICP-MS at a high vacuum while ejecting undesirable species such as neutrals, photons, and particulates[57].

Figure 1.3: Quadrupole mass analyzer (A)[58] and sector field mass analyzer (B) [59]
ICP ion sources have been successfully paired with several types of mass analyzers, one of which is a quadrupole mass analyzer. Quadrupoles are made up of 4 rods of equal size (figure 1.3). A DC field and a time-dependent AC radiofrequency are placed on opposite pairs of rods, as the ion beam spirals through the center of the four rods[60]. Changing the currents placed on the rods allows the ions with the desired mass-to-charge \( (m/z) \) ratio to reach the detector, while the other ions are ejected from the quadrupole. For multi-element analyses, the AC/DC potential is applied for one \( m/z \), which passes through the quadrupole into the detector, then is switched to allow another \( m/z \), continuing until all analytes have been measured. Quadrupoles typically have resolutions of between 0.7 and 1 atomic mass units (amu)[17]. Multiple quadrupoles can be lined up in series, as is the case in a type of mass spectrometer called a triple quadrupole. In this set-up, the first quadrupole is set up to select a particular \( m/z \), which is then sent into a second quadrupole along with a reaction gas. The analyte and gas may react to form a polyatomic species of a different \( m/z \) for which the third quadrupole selects.
Another fairly common mass analyzer for ICP-MS is the sector field mass analyzer, which has a much higher resolving power compared to quadrupoles[62]. Magnetic sectors have been utilized for high resolution mass spectrometry since the 1940s but the first commercial ICP-MS that combined a magnetic sector with an electrostatic analyzer (ESA) was not available until 1989[62]. The magnetic field disperses ions based on ion energy and mass, changing the angle that the ion travels while the ESA only disperses ions with regards to ion energy[63]. When the magnet and ESA have equal energy dispersion in opposite directions, they focus the ion angle and energy of interest for analysis. This instrument achieves resolution through the use of two mechanical slits, one at the entrance to the mass analyzer and one at the exit, before the ions reach the detector[64]. Double-focusing instruments can have low, medium, and high-resolution settings, based on the slit width, with a trade-off of decreasing sensitivity as resolution increases[64, 65].

After leaving the mass analyzer, ions reach a detector. Discrete dynode electron multipliers are the most common detectors used in for ICP-MS. As an ion leaves the mass filter, it hits the first dynode, causing secondary electrons to be emitted. These electrons are accelerated into a second dynode by electron-optics, generating more secondary electrons which travel to a third dynode, and generate even more electrons. This process continues, creating an electron pulse that finally reaches the multiplier collector or anode and a pulse is sent to a digital discriminator and counting circuitry[66]. The dynamic range of the detector in pulse mode is around 5 orders of magnitude. To extend the dynamic range of the detectors, they are often used in both pulse and analog modes[67]. The analog signal is measured at the middle dynode, and if the signal reaches a certain threshold, it is
processed through the analog circuitry, and otherwise the electron cascade continues to the anode and is processed through the digital discriminator[17].

The signal read-out on the computer software is in the units of counts per second. The signal can be optimized by tuning various parameters in the ICP-MS, such as the nebulizer gas flow rate and the position of the torch with respect to the interface cones. Qualitative analysis of samples can utilize signal intensity without further manipulation, however for quantitation of signal other strategies must be employed. The method of quantitation will depend on the analytes and matrix of the sample, amount of sample available, and requirements for accuracy and precision.

Precision refers to the reproducibility of results. ICP-MS instruments often have precision specifications from the manufacturer, both for short- and long-term precision. Short-term precision is found by measuring mid-concentration solutions (1-10 ppb) 10 times with integration times (the amount of time a mass analyzer stays at a particular m/z) of 2-3 seconds[17]. Short-term precision tends to be on the order of 1-3%. To measure long-term precision, or the reproducibility of measurements over a long period of time, like the length of an analysis with many samples, the same measurements for short-term precision are repeated every 5-10 minutes over a period of 4 to 8 hours [17]. There is normally higher variability in results over longer periods of time, leading to typical long-term precision of 3-5%. For the best understanding of instrument precision, the measurements should be done with solutions containing matrices typical of the types of samples that are normally analyzed on the instrument in question.

Accuracy is a measure of how close an experimental value is to a known value. When developing methods, reference materials with certified concentrations of trace
elements are often used to determine the accuracy of the method under development.

Accuracy is generally reported in terms of error (E), which can be either absolute or relative (expressed as a percent). Relative error is a metric reported more often since it can be used to compare accuracy between components with very different concentrations. Relative error ($E_r$) can be found using equation 1.6, with $\bar{X}$ being the mean of the measured values, and $x_r$ being the reference value.

$$E_r = \frac{\bar{X} - x_r}{x_r} \times 100$$  \hspace{1cm} (1.6)

Certified reference material trace element concentrations normally have an associated uncertainty, as do measured concentrations. Uncertainty is generally a range of values in which there is a reasonable likelihood the true value falls within. Measurement precision is part of uncertainty, but uncertainty generally is a combination of all uncertainty in a given method, from the uncertainty in the mass measurement all the way to the instrumental precision. There are many ways to calculate uncertainty, software packages like metrodata GmbH GUM (Guide to the Uncertainty in Measurement) Workbench 2.4 standardize uncertainty calculations. Uncertainty can also be estimated through the standard deviation of sample replicates. Finding the accuracy of a measured value compared to a reference value with uncertainty can be done through a zeta score.

$$\zeta = \frac{X - x_r}{\sqrt{\mu_x^2 + \mu_{xr}^2}}$$  \hspace{1cm} (1.7)

In equation 1.7, X is the measured value, $X_r$ is the reference value, and $\mu_x$ and $\mu_{xr}$ are their associated uncertainties. For zeta scores of $\leq \pm 2$ the measured and reference value show good agreement, while scores $\geq \pm 3$ are seen as questionable[68]. Different quantitation techniques can have higher or lower uncertainty associated with them, and the
quantitation method chosen for any given measurement must consider the acceptable level of uncertainty needed for the analysis.

An external calibration curve can be created by analyzing a number of standards which contain analytes of known concentration over a range of concentrations that is likely to contain the unknown sample along with blanks. These are then used to create a plot of measured intensity vs concentration and fitted with a regression line. The slope and intercept of the regression line is used to find the concentration of the unknown based on the intensity of the measured signal. Calibration standards are matched to the acid matrix and generally contain between 3 and 5 concentration points, plus a matrix blank. Signal intensity can change over the course of an analysis, and therefore recalibrating the instrument is necessary, either with the full set of standards, or a midpoint standard. Uncertainty in external calibration can be propagated from the uncertainty in each individual calibration standard. External calibration works best when the matrix of the standard closely matches the matrix of the sample. Polyatomic interferences that can form from matrix ions can cause inaccurate results if the matrices do not match. Differences in pH, viscosity, total dissolved solids, and organic content between the sample and the external standard can also change conditions in the nebulizer, spray chamber, and the plasma.

When the sample matrix is difficult to match in standards, and matrix effects are high, standard addition can be used as an alternative quantitation technique. In standard addition, aliquots of the sample are spiked with different amounts of analytes and are measured along with an unspiked aliquot to create a different calibration curve for each sample. This method drastically increases the analysis time, as each sample is run 3 or
more times and is more labor intensive than external calibration. It also requires sufficient sample volumes to split the sample into 3 or more portions.

Isotope dilution mass spectrometry (IDMS) is one of the most accurate and precise quantitation techniques and is considered a primary analysis method[69]. It involves changing the isotope ratio of an analyte through the addition of a known amount of an isotopically enriched spike. The isotope ratio of the analyte will shift depending on the enrichment level of the spike, and the concentration of the sample and spike. Figure 1.5 shows the change in isotope ratio of an analyte in a sample after being spiked with a solution of the analyte enriched in isotope B. The original isotope ratio (shown in blue) and the enriched isotope ratio (orange) turn into a new ratio after mixing.

![Isotopic abundance of two isotopes of an analyte in a spiked solution](image)

**Figure 1.5:** Isotopic abundance of two isotopes of an analyte in a spiked solution

Based on the isotope ratio of the sample and spike, the mass of sample, the mass of spike added, and the concentration of the analyte in the spike solution, the concentration of the analyte in the original solution can be calculated using equation 1.8
\[ C = \frac{(A_{\text{spike}} - (R \cdot B_{\text{spike}})) \cdot W_{\text{spike}}}{R \cdot (B_{\text{sample}} - A_{\text{sample}}) \cdot W_{\text{sample}}} \] (1.8)

In this equation, \( C \) represents the concentration of the analyte in the sample, \( A \) is the abundance of the enriched isotope, \( B \) is the abundance of the other isotope, \( R \) is the \( A / B \) isotope ratio in the enriched spike, and \( W \) represents mass. Despite the high accuracy and precision associated with this method, IDMS does have several drawbacks. First, IDMS can only be done on elements with at least two isotopes. Enriched isotopic spikes can be difficult to obtain and expensive, as they require specialized facilities to enrich the isotopic solutions. Isobaric or polyatomic interferences can bias isotope ratio measurements. For example, REEs do not have multiple isotopes free from isobaric overlap from neighboring REEs, and therefore require corrections to be applied to account for isobars in the matrix unless the REEs are separated prior to IDMS analysis.

Internal standardization is a technique that is not used on its own for quantitation purposes, but rather applied in concert with another quantitation technique such as external calibration or standard addition. This technique is used to correct for variations in signal intensity over the course of an analysis caused by fluctuations in the speed of the peristaltic pump, fluctuations of gas flow, and plasma temperature. An internal standard is an element that is unlikely to be found in the sample matrix that is added to all the samples, standards, and usually the blanks in the same amount. A correction factor is applied to the samples based on the difference in intensity of the internal standard in the samples compared to the standard.

A detection limit is the smallest amount of analyte that can be reliably differentiated from a blank signal[70]. Detection limits, referred to as limits of detection or LOD, can be separated into instrumental detection limits and method detection limits. Instrumental
detection limits are the smallest measurable amount of analyte in the solution being pumped into the ICP-MS spray chamber for analysis, while method detection limits refer to the minimum amount of material that, after undergoing all sample preparation, can be detected on the instrument. Method detection limits are generally higher than instrumental detection limits, since sample preparation often involves dilution of some sort. While LODs define the lowest concentration that can be statistically differentiated from the background, this value is not able to be reliably quantified. The limit of quantitation (LOQ) gives the smallest amount of analyte that can be reasonably quantified. There are several ways of calculating LODs and LOQs, the most common of which applies a constant (k) to the standard deviation of the blank signal (s_0) which is then divided by the slope of the external calibration regression line. The value of k is different for the particular parameter being calculated[70, 71].

\[ L = k \frac{s_0}{m} \]  

(1.9)

When determining LOD, k generally is set equal to 3, which, assuming a gaussian distribution in signal detection, means that 99% of the time, when a signal of that magnitude is measured, the analyte is present[70]. For LOQ determinations k is traditionally set to be 10. When there is significant signal in blank measurements, when the y-intercept of an external calibration curve is greater than zero for instance, a blank equivalent concentration can be added to the standard deviation of the blank[72].

\[ \text{LOD} = \text{BEC} + 3s_0 \]  

(1.10)

The LOQ in this case is generally agreed to be 3.3 times the LOD[72]. Detection limits for ICP-MS varies depending on the element being measured, the sample introduction system, the type of mass analyzer and detector, and the sample matrix. For most
elements, LODs for ICP-MS are in the range of pg g\(^{-1}\). ICP-MS detection limits are several orders of magnitude lower those of atomic spectroscopy techniques like ICP-optical emission spectroscopy (ICP-OES) and graphite furnace atomic absorption spectroscopy (GFAAS). ICP-MS analysis methods have been increasingly applied to the field of nuclear chemistry[17]. Because of its broad capabilities of measuring elemental and isotopic concentrations in a wide variety of sample types, it has become an indispensable tool for nuclear forensic analyses[26].

1.3 Ion Chromatography

*Chromatography Background*

Chromatography encompasses a wide variety of separation techniques in which closely related components to be separated are dissolved in a mobile phase, and then sent through a stationary phase which is immobilized, often on a column[73]. The components in the mixture are separated based on their affinities for the two phases. Those with a stronger affinity for the stationary phase spend more time retained on the stationary phase and elute from the column later than the components with a stronger affinity for the mobile phase. Chromatography was invented in the early 20\(^{th}\) century by Russian botanist Mikhail Tswett when he managed to separate plant pigments through adsorption chromatography[73]. Chromatography today is categorized into three main areas: Gas chromatography (GC), in which the mobile phase is a gas and the stationary phase is a solid or bonded liquid, liquid chromatography (LC), with a liquid mobile phase and a solid or liquid bonded or adsorbed to a surface as the stationary phase, and supercritical fluid chromatography (SFC), which uses a supercritical fluid as the mobile phase. LC is further
broken down into several subcategories, including partition, adsorption, ion exchange, size exclusion, and affinity chromatography. In packed column chromatography, the sample starts in the mobile phase and is sent through the column. The different components of the sample are distributed between the stationary phase and the mobile phase interacting to various extents with both phases. Components can be characterized by how long it takes for them to elute from the column, called the retention time ($t_r$) or the amount of time the component spends in the stationary phase, called the adjusted retention time ($t'_r$) which can be found by subtracting the $t_r$ of an unretained component or the solvent front from the $t_r$ of a retained component (figure 1.6). The retention time is based on the affinity of the analyte with the stationary and mobile phases, therefore changing either phase will change the retention time.

![Example chromatogram](image)

**Figure 1. 6: Example chromatogram[73]**

When comparing the separation between two components of the initial sample, the relative retention, also called the separation factor, can be calculated (equation. 1.11)[71]. The greater the value of the separation factor $\alpha$, the better the separation.
Each peak in the chromatograph has an associated retention factor (k) (equation 1.12), which is the adjusted elution time divided by the time required for the mobile phase to travel through the column ($t_m$). The retention factor is used to determine the amount of time an analyte spends in the stationary phase compared to the time it spends in the mobile phase, where an analyte that has more affinity for the stationary phase has a larger k than a sample with less.

$$k = \frac{t_{r2}}{t_m} \quad (1.12)$$

Column efficiency is affected by the broadness of the peaks as the analytes elute from the column. The plate theory can be used to quantify the efficiency of a column through equation 1.13, which can be used to calculate the number of theoretical plates (N) based on the column length (L) and the plate height (H).

$$N = \frac{L}{H} \quad (1.13)$$

The plate theory was developed by Martin and Synge in 1941, comparing a column to a distillation apparatus, where a better separation was achieved with more distillation plates[74, 75]. They made the assumption that a chromatographic column was equivalent to a plate column with N theoretical plates, where more plates lead to better separations. N can be calculated based on the retention time of a peak and its peak width using equation 1.14, where W is the peak width at the base of the peak and $W_{1/2}$ is the width of the peak at half its maximum height.

$$N = 16 \left(\frac{t_r}{W}\right)^2 = 5.54 \left(\frac{t_r}{W_{1/2}}\right)^2 \quad (1.14)$$
To increase peak resolution in a separation, H should be minimized while maximizing N. Decreasing the particle size of the stationary phase also increases resolution, as it lessens peak broadening.

*Ion Chromatography Background*

Ion chromatography is a type of liquid chromatography in which the stationary phase is made up of anions like SO\(_3^-\) or cations such as N(CH\(_3\))\(_3^+\) are covalently bonded to a resin, and the mobile phase is a liquid. Ions in the sample and mobile phase are attracted to stationary phase ions of opposite charge and compete for active sites in the stationary phase. The difference in affinity of the sample and eluent (or mobile phase) ions for the active sites leads to differences in ion-exchange equilibria, and therefore to varied amounts of time spent in the stationary phase[76]. The characteristics of the eluent play a large role in the separation quality, since eluent ions compete with sample ions for stationary phase active sites. The strength of the eluent increases with increasing ionic strength. As the pH of the eluent increases towards the pK\(_a\) of the analyte, there is a decreased ability to elute anions, as the fraction of analyte in ionic form is dependent on the eluent pH. Temperature and flow rate also play a role in analyte retention. Increased temperature increases the ion exchange rate, which can result in better separation. As flow rate increases beyond the optimum value the elution times decrease but separation efficiency also decreases[77]. Greater differences in ion-exchange equilibria lead to better peak resolution. Separation problems occur when the analyte ions have small differences in ion-exchange equilibria and the selectivity of the exchange resin for metal ions is low. In cases like this, the ion-exchange equilibria differences can be expanded through chelation of the metal ion to a ligand which has differing ligand binding affinities for the different analytes, known as
chelation ion exchange chromatography[78]. The exchange mechanism for chelation ion exchange between the metal ions (M), the stationary phase (S) and the eluent ligand (E) is shown in equations 1.15 and 1.16[79].

\[
M^{a+} + nS^{-}H^+ \rightleftharpoons S_nM + nH^+ \tag{1.15}
\]

\[
S_nM + nE^- \rightleftharpoons nS^- + ME_n \tag{1.16}
\]

**High Performance Ion Chromatography**

As mentioned above, peak resolution increases as the particle size of the column packing decreases. When using gravity-flow columns, however, the elution times increases dramatically as particle sizes decrease. To separate analytes in columns with small particle sizes in reasonable amounts of time, a pressurized pump system can be used. High performance liquid chromatography (HPLC) was invented in the late 1960s to push the mobile phase through columns with particles with 1-3 µm diameters at high pressures[73]. HPIC can be accomplished using HPLC systems by substituting the typical column packed with organic stationary phases, most often C-8 or C-18 chains, with columns packed with ion exchange stationary phases. HPIC systems include mobile phase(s), a sample injector, pumps, a column, and a detector, which must all be compatible with each other and with the analytes.
Traditionally in HPIC, the mobile phase eluents are acids or bases of known concentrations, buffered to a specific pH. Prior to entering the column, the eluents can be filtered through Millipore nylon filters to prevent any solid particles from damaging the pumps or clogging the column, and degassed, as dissolved gasses can affect flow rates, interfere with detectors, and form bubbles, resulting in a loss of pressure in the system. Degassers can be vacuum pumps, distillation systems, or spargers. Sparging involves sending an inert gas, such as He, into the sample reservoir to remove dissolved gasses. HPIC systems can generally allow for the use of between 2 and 4 eluents, depending on the design of the system, which vary in affinity for the stationary phase, concentration and/or pH. Eluents are mixed through proportioning valves, and the ratio of the eluents can either be kept constant, called an isocratic elution, or can be varied over the course of the separation, called a gradient elution. An isocratic elution tends to result in longer separation times, and, especially for analytes with longer retention times, broader peaks, so a gradient elution is generally preferred when possible.

The mobile phase must be forced through the column at a high pressure, often between 1000 and 2000 psi. This is accomplished by means of a pumping system. The main criteria for an HPIC pump is that it create pressures of up to 6000 psi relatively smoothly (without pulses of the solvent which lead to baseline noise in the chromatogram), with flow rates between 0.1 and 10 mL, and high flow reproducibility (≥ 0.5% ), and be resistant to corrosive eluents. Several pump styles have been used over the years, but in modern systems the most common pump style is dual-piston in-series pumps. In this style eluent flows into the small chamber of a piston (the primary piston), which is
driven by a motor and pushes the solvent out of the chamber into a second piston (the secondary piston or high pressure piston) which then sends the eluent out of the pump[81]. Eluents can be mixed in a low-pressure environment before reaching the pump, where a single pump draws eluent from a 4-port proportioning valve and a microprocessor controls the amount of solution to be drawn from each eluent, called a quaternary pump. The other method for eluent mixing is in a high-pressure mixing pump, called a binary pump system. In this method, two pump units draw eluent from separate containers (one pump per eluent) which are mixed downstream of the pumps. Binary pumps cost more than quaternary pumps as they have two separate pumping units, and can accommodate fewer eluents, but they have the benefit of lower dwell volumes and more accurate mobile phase composition[81].

Sample injection is a contributing factor to peak broadening. The larger the amount of sample injected, the broader the peaks become. The accuracy in the amount of sample injected also contributes to uncertainty in the final quantification. Sample aliquots must be sent into a pressurized mobile phase (post-pumping unit) without depressurizing the mobile phase. HPIC systems rely on autosamplers to inject small, precise aliquots of sample into the column under high-pressure. This is done through the use of a rotary injection valve, with a sampling needle, a sample loop, an inlet from the pump and an outlet to the column (figure 1.8)[82].
Figure 1.8: Sample injection switching valve

The sample is picked up from a small vial using a sampling syringe and pushes the sample into a sampling loop. Sampling loops control the sample volume to be injected, and different sized loops can be switched out, depending on the needs of a particular analysis. The most common loop size is 100 µL. Sample loops have two fill modes, full-loop mode fills the entire sample loop, and the amount of sample injected is entirely dependent on loop size. Partial-loop mode fills between 10 and 50% of the loop with sample. Full-loop mode generally is more accurate than partial loop mode, but does not have the flexibility to have multiple injection volume options without changing the loop[82]. When the sample has been loaded into the injection valve, it switches into injection mode, sending the mobile phase through the sample loop which pushes the sample ahead of the mobile phase into the column.

HPIC systems are made up of at least two columns, a guard column and an analytical column, connected in series. The guard column has the same stationary phase as the analytical column but is much shorter, on the order of 5 cm. The purpose of the guard
column is to prevent impurities such as highly retained compounds and particulates from reaching the analytical column. The guard column is replaced much more frequently than the analytical column and extends the lifetime of the analytical column. The analytical column is much longer than the guard column, though the exact length is dependent on the level of resolution needed in any given separation, and the cost of the column increases as the length increases. Ion exchange columns are made up of charged functional groups covalently bonded to polymeric resins. Functional groups are either cation exchangers, which are negatively charged and used to separate cations, or anion exchangers, positively charged groups that separate anions. Cation exchangers can either be strong-acid cation exchangers or weak-acid cation exchangers. Strong acid cation exchangers are made up of sulfonate groups (-RSO$_3^-$, pK$_a$ ~ -3) and work across the whole pH range, as the pK$_a$ of the conjugate acid is so low[78, 79]. Weak-acid cation exchangers are carboxylates (RCO$_2^-$, pK$_a$ < 3)[78]. Because of their high pK$_a$, only a portion of the carboxylates are deprotonated and available as cation exchange sites. Anion exchange columns contain positively charged functional groups. Porous anion exchange groups are quaternary ammonium compounds (-NR$_3^+$) and different R groups affect the selectivity of the ion exchangers[83, 84]. Mixed-bed columns, with a combination of anion exchange sites and cation exchange sites, can act as cation or anion exchangers.

Resin capacity limits the amount of sample that can be loaded onto a column and is measured in terms of milliequivalents of exchangeable ions per gram of resin (mequiv g$^{-1}$). Ion exchange columns tend to have low capacities, of between 0.01 – 0.2 mequiv g$^{-1}$ because the ion exchange groups are mostly on the surface of the resin beads[78]. As
columns age, it is common for their capacity to decrease, as the stationary phase is
degraded, or mobile phase ions are irreversibly adsorbed to the ion exchange sites.

HPIC systems commonly have ultraviolet-visible (UV-Vis) spectrophotometers
built into them. As the mobile phase elutes from the column it enters a flow cell between
a light source, often a combination of a deuterium lamp and a tungsten halogen lamp, with
a specific wavelength and a detector. The detector measures the loss of light, or the
absorption, as the sample flows through. This type of detector has limited applicability in
trace metal analysis as analytes must absorb photons with wavelengths in the UV-Vis
range, which requires specific chelators. This can be accomplished by a post-column
derivatization with UV-Vis-active chelators such as arsenazo-III[85]. The detection limits
of these systems tend to be quite high which is a limiting factor when analyzing trace or
ultratrace concentrations.

HPIC systems can be connected directly into the nebulizer of an ICP-MS for trace
metal analysis, which has much better detection limits than a UV-Vis spectrometer and
eliminates the need for post-column complexation. The organic acids used as the HPIC
mobile phase can cause problems in the nebulizer, spray chamber, and torch leading to
system failure when used in high concentrations, so when coupling HPIC to an ICP-MS
minimizing organic concentrations and including sufficient wash-out times is necessary to
preserve the conditions of the equipment.

REE separation

REEs are made up of lanthanides, Y, and Sc, although for the purposes of this work
the focus will be on the lanthanides. Lanthanides have a 4f valence electron shell, and
when ionized electrons are first pulled from the 6s orbital, then the 5d orbital, most
Lanthanides exist in the 3+ oxidation state, leading to electron configurations of \([\text{Xe}] \, 4f^n\).

Lanthanides have a wide range of coordination numbers (6-12) but coordination numbers of 8 and 9 are most common. They preferentially bind to donor atoms with high electronegativity such as oxygen and fluorine[86]. Because of their shape f orbitals do not overlap with the orbitals of ligands and therefore do not significantly participate in bonding. Because of this, the chemistry of lanthanides is similar, making separation difficult. The main exploitable difference in the lanthanides is the decrease in the atomic radii (as well as the Ln\(^{3+}\) ionic radii) from the light lanthanides to the heavy lanthanides (table 1.2) because the effective nuclear charge on the valence electrons increases with increasing atomic number.

**Table 1.2:** lanthanide ionic radii (pm)[86]

<table>
<thead>
<tr>
<th>Ln(^{3+})</th>
<th>La(^{3+})</th>
<th>Ce(^{3+})</th>
<th>Pr(^{3+})</th>
<th>Nd(^{3+})</th>
<th>Pm(^{3+})</th>
<th>Sm(^{3+})</th>
<th>Eu(^{3+})</th>
<th>Gd(^{3+})</th>
<th>Tb(^{3+})</th>
<th>Dy(^{3+})</th>
<th>Ho(^{3+})</th>
<th>Er(^{3+})</th>
<th>Tm(^{3+})</th>
<th>Yb(^{3+})</th>
<th>Lu(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>103.2</td>
<td>101</td>
<td>99</td>
<td>98.3</td>
<td>97</td>
<td>95.8</td>
<td>94.7</td>
<td>93.8</td>
<td>92.3</td>
<td>91.2</td>
<td>90.1</td>
<td>89</td>
<td>88</td>
<td>86.8</td>
<td>86.1</td>
</tr>
</tbody>
</table>

The concentration of lanthanides in UOCs can be used as a signature that can be used for provenance studies[5, 8, 15, 16]. Light lanthanides are valuable analytical targets in post detonation analysis. Isotopes of the elements La, Ce, Nd and Pm, appear along the wing of the fission mass-yield curve and provide information on the neutron energy spectrum and the fuel type of a nuclear device. REEs have complicated mass spectra due to the presence of isobaric and polyatomic interferences, and therefore separation prior to analysis is necessary for accurate REE quantification.

The most common method of separating lanthanides for analytical applications is through chelation ion exchange chromatography. Lanthanides have been separated through both cation and anion exchange, depending on the complexing agents used in the separation. Ln\(^{3+}\) ions can be loaded onto a cation exchange column and then treated with
a complexing agent. The heavier lanthanides, with the highest charge density, bind strongest to the anionic ligand and elute from the column fastest[86]. Ln complexes with negatively charged complexing agents that have an overall negative charge will bind to positively charged anion exchange sites. Lighter lanthanides, with lower charge density bind less strongly to the anion exchange sites and are eluted faster. A variety of cation and mixed bed columns have been used to separate REEs over the years, including a camphor-10-solfonic acid cation exchange column with α-hydroxyisobuteric acid (α-HIBA) eluent[87], a Luna SCX cation exchange column with α-HIBA[88], IonPac CS10 with α-HIBA, HCl, and HNO₃[89]. The IonPac CS5 mixed bed ion exchange column with oxalic acid, lithium hydroxide, and α-HIBA mobile phases[90-92], and the IonPac CS5A with oxalic acid and diglycolic (DGA) acid[34, 93-96].

![Oxalic Acid](image1.png) ![Diglycolic Acid](image2.png)

**Oxalic Acid**
- pKₐ₁ = 1.23
- pKₐ₂ = 4.19

**Diglycolic Acid**
- pKₐ₁ = 2.70
- pKₐ₂ = 3.93

**Figure 1.9:** Structure and acid dissociation constant (pKₐ) of oxalic acid (left)[97] and DGA (right)[98]

The IonPac CS-5A mixed-bed ion exchange column has sulfonate cation-exchange sites and quaternary ammonium anion exchange sites. The column used in this work has a 50 x 4 mm CG5A guard column and a 250 x 4 mm CS5A analytical column. In dual
cation and anion separations, Ln$^{3+}$ ions generally are loaded onto the column and bind to the cation exchange sites, they then form complexes with chelates in the mobile phase. The stability constants of the complexes are affected by the effective nuclear charge of the REE ion, which in turn effect retention on the column[99]. When α-HIBA is used as an eluent, stability constants of the Ln- α-HIBA complexes increase from La to Lu, and the cationic complexes elute in order of decreasing atomic number[99]. For an oxalic acid eluent, which is generally buffered to a pH of ~4.5 so a majority of the oxalate molecules have been deprotonated (pK$_{a2}$ = 4.19), to form the conjugate base C$_2$O$_4^{2-}$, the bidentate oxalates bind to the positively charged REE ions to form negatively charged complexes$^{[100, 101]}$. The negatively charged lanthanide oxalate complexes (Ln(C$_2$O$_4$)$_3$(H$_2$O)$_2$ or Ln(C$_2$O$_4$)$_3$(H$_2$O)$_3$) have coordination numbers of 8 or 9 and the complex exchanges on the anion exchange sites. As DGA is added to the mobile phase it exchanges with the oxalates complexed with the lanthanides as Ln-DGA complexes have a higher stability constant$^{[101]}$. The heavier lanthanides have a higher charge density and therefore a higher affinity for the anion exchange resin, and are retained longer in the column while the lighter, less densely charged lanthanides elute earlier$^{[79]}$.

1.4 Conclusions

Nuclear forensic analysis requires accurate, precise, and rapid methods of analyzing signatures in nuclear material. Signatures of interest in this work are uranium and plutonium isotope ratios, trace element quantities, particularly those of REEs, in OUCs for origin assessment and post-detonation nuclear debris. The following work utilizes ICP-MS, along with various dissolution and separation techniques, to develop methods for the quantification of these signatures.
ICP-MS instruments are made up of a sample introduction system, which for liquid analysis consists of a nebulizer and a spray chamber, a torch, and interface region, a mass analyzer, and a detector. Because there are many different styles of all these components that have different advantages, ICP-MS is an extremely versatile form of atomic spectroscopy. It is advantageous over other atomic spectroscopic techniques in its low detection limits and ability to measure most elements. In chapter two of this work a microextraction system is attached to an ICP-MS for the direct analysis of isotope ratios of solid uranium particulates on environmental swipe samples which are used by the IAEA for treaty monitoring. This technique can quickly measure isotope ratios of individual particles without transferring particles to other mediums as is done in LG-SIMS and FT-TIMS analysis.

HPIC is a useful tool to separate ionic species in solution. It is made up of a mobile phase reservoir, a pumping system, a sample injector, an analytical column which houses the stationary phase, and a detector. It has been used successfully to separate REEs for quantitation purposes and can be connected to an ICP-MS for detection of analytes that are not UV-vis active (like REEs). In chapter 3 HPIC separations are performed on UOC samples spiked with enriched isotope standards to measure REE concentrations through IDMS. REE concentration patterns are one signature for origin assessment of UOC samples, and therefore accurate and precise REE analysis methods are vital for pre-detonation purposes.

Chapter 4 focuses on dissolution techniques for post-detonation nuclear debris. Difficult to dissolve refractory minerals are present in debris both from the underlying geology of the detonation site, and the high temperatures of the explosion. ABF fusion is
advantageous over other dissolution method because it can be accomplished at higher
temperatures than mineral acid digestion, doesn’t use hazardous chemicals like HF, and
doesn’t need specialized equipment like high pressure microwaves. The ABF digestate,
along with digestate from microwave digestion was separated on a conjugated HPIC-ICP-
MS to quantitate REE concentrations in the geological material in chapter 5. The material
was spiked with fission products to demonstrate the methods ability to separate the REE
fission products that will be present in post-detonation debris from complicated fission
spectra. HPIC and ICP-MS have been utilized in the course of this work to analyze REEs
and other trace elements that may be useful nuclear forensic signatures.
1.5 References


[61] NexION 300 ICP-MS Manual, Perkin Elmer.


[88] F. Guéguen, H. Isnard, A. Nonell, L. Vio, T. Vercouter, F. Chartier, Neodymium isotope ratio measurements by LC-MC-ICPMS for nuclear applications: investigation of


Chapter 2:
Direct isotopic analysis of solid uranium particulates on cotton swipes by microextraction-ICP-MS

2.1 Preface

The work described here is a method to measure the isotope ratios of uranium particulates directly from the surface of IAEA swipes without sample preparation or digestion. Small, microgram-sized particulates containing pg amounts of various uranium compounds of interest to fuel cycles and pre-detonation nuclear forensics were deposited in on cotton swipes. These particulates were extracted in 5% nitric acid and fed into an ICP-MS for analysis. The experiments were completed at Oak Ridge National Laboratory. The results of the study was presented as follows. Bradley, V. C., Spano, T. L., Metzger, S. C., Ticknor, B. W., Dunlap, D., Zirakparvar, A. N., Roach, B. D., Hexel, C. R., and Manard, B. T. Accepted by the journal Analytica Chimica Acta on April 13th 2022.

2.2 Introduction

The Treaty on the Non-Proliferation of Nuclear Materials (NPT) requires countries to declare their stocks of nuclear material, including uranium enrichment activities, and allow the International Atomic Energy Agency (IAEA) to independently verify the declarations[1]. The IAEA utilizes various analyses to safeguard these materials; one such method (implemented in 1996) employs environmental sampling (ES). Traditional ES is performed by sampling within a nuclear facility with a 10 × 10 cm swipe (typically consisting of woven cotton fibers)[2]. These swipe samples are subsequently sent to the IAEA Network of Analytical Laboratories (NWAL) for analysis of fission products and actinide content / isotopes. The measurements are ultimately divided into two categories,
bulk and particle analysis. Bulk analysis is performed to determine uranium and plutonium amounts and the average isotopic value of material collected on the entire swipe. This is achieved through laborious bulk ashing, digestion, and chemical separation, prior to analysis of purified U and Pu aliquots by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) or thermal ionization mass spectrometry (TIMS). Particle analysis is achieved by locating target particles (micrometer-sized) on a swipe, then determining the isotopic composition of individual particles[2], information which is lost during complete digestion within the bulk analysis regime. This is routinely achieved via large geometry secondary ionization mass spectrometry (LG-SIMS) and fission track (FT) TIMS[2-4]. Uranium isotope ratios that deviate from natural abundance can indicate enrichment activities within the facility. $^{235}\text{U}$ is a fissile isotope and is commonly used as fuel for nuclear power plants and in nuclear weapons[5]. Enrichment levels of $^{235}\text{U}$ are separated into four main categories: depleted (DU, $<0.3\%$ $^{235}\text{U}$), natural (NU, $0.3$-$1\%$ $^{235}\text{U}$), low enriched (LEU, $1$-$20\%$ $^{235}\text{U}$), and high-enriched (HEU, $>20\%$)[6]. Many commercial power plants use NU or LEU as fuel, while HEU could be utilized for nuclear weapons[5].

$^{234}\text{U}$ is naturally occurring at trace levels and is a secondary indicator of enrichment. $^{236}\text{U}$ is not naturally occurring, and its presence is an indication of irradiated uranium since it is only created by $^{235}\text{U}$ neutron capture[5].

Direct surface sampling could expedite analysis of swipes, bypassing lengthy ashing and digestion steps. Common surface sampling techniques for uranium particle analysis include FT TIMS, SIMS, and laser ablation (LA) ICP-MS. FT TIMS has been shown to measure $^{235}\text{U}/^{238}\text{U}$ isotopics of 0.5 to 20 μm-sized particles with uncertainties of around 2%, though it requires expensive and time-consuming sample preparation[4, 7-10].
SIMS requires the particles to be transferred from the swipe to a Si wafer prior to analysis. This technique has been successful at analyzing particles greater than 0.5 µm, with uncertainty in the $^{235}$U/$^{238}$U isotope ratio of 2-3%[9, 11]. In LA-ICP-MS, a laser is directed to the surface of the sample, thus ablating a finite amount of material. This ablated aerosol is then swept into the ICP with a flow of inert gas. For LA systems, the uncertainty in the $^{235}$U/$^{238}$U ratio depends heavily on the type of ICP-MS used; single detector ICP-MS instruments, including both quadrupole and sector field, are sequential mass analyzers, and therefore the high variability in the transient signal leads to higher uncertainty (reported uncertainty ranges from 2-7% for single detector ICP-MS)[9, 12, 13]. Multi-collector ICP-MS instruments can measure multiple isotopes simultaneously, which leads to higher precision in the isotope ratios (uncertainties between 0.2% and 4.9% have been reported)[14-16]. LA has recently also been coupled to time-of-flight (TOF) ICP-MS[17], which has advantages for transient signal analysis, as it can measure all isotopes essentially simultaneously, using a single detector. Using this system, uncertainties in $^{235}$U/$^{238}$U between 0.35% and 7% were found, depending on the enrichment level of the uranium and the size of the particle measured[17].

A more recent approach to direct solid sampling is through liquid extraction on the surface of a sample using a microextraction sampling probe[18, 19]. This technique has been used to analyze organic compounds from thin tissues sections, which were then sent to an electrospray mass spectrometer[20]. A similar sampling approach for inorganic analyses used a scanning flow cell which seals against the sampling surface. An electrolytic solution is pumped through electrodes and into the cell, and directed into the ICP-MS for the detection of the dissolved species[21-22]. They have been used over the past decade
for metal dissolution and catalytic studies[21, 23, 24]. A recent study by Manard et al., employed a microextraction probe to sample cotton swipes doped with uranium[25] and plutonium[26] and directly analyze them with ICP-MS. Solutions containing isotopic Certified Reference Materials (CRMs) of uranium and plutonium were deposited onto swipes and dried prior to extraction with the microextraction probe. This method determined the uranium isotopic composition of the doped CRMs to within 0.5 - 2% deviation from the certified $^{235}\text{U}/^{238}\text{U}$ isotope ratios[25]. Uranium microextraction from swipe samples has also been analyzed through an atmospheric pressure glow discharge microplasma coupled to an Orbitrap MS[27].

While the initial studies demonstrated the microextraction-ICP-MS method on samples deposited as solutions, the work presented here is the first demonstration of the microextraction-ICP-MS method focused on solid uranium particulates on cotton swipes. Samples were prepared such that uranium particulates were loaded onto the swipe. In many cases the samples analyzed here contained an agglomeration of particles, rather than a single discreet particle. Solid particulates of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{UO}_2\text{F}_2$ were extracted from cotton swipe surfaces using a microextraction sampling probe and analyzed on a quadrupole ICP-MS. The results provide insight into the ability of microextraction techniques to accurately and precisely measure U content and isotopics in samples analogous to those likely encountered in the real world. For example, during reprocessing of used nuclear fuel, uranium can be recovered by batch crystallization as $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$[28]. Many types of uranium processes employ UF$_6$ gas which when released into the atmosphere reacts with water to form $\text{UO}_2\text{F}_2$ particles[29]. Uranium isotope ratios in particles investigated in this work therefore could be characteristic of
activities relevant to nuclear safeguards [30]. The ability to directly measure these solid uranium particulates on the swipe surface, without lengthy dissolution steps or locating and transferring the solids off the swipe matrix may offer a rapid and cost-effective way to increase analytical throughput of environmental samples.

2.3 Materials and Methods

Materials, Reagents, and Sample Preparation

All dilutions were performed with Optima™ grade nitric acid (HNO₃) from Fisher Scientific (Pittsburgh, PA, USA) and diluted with ASTM Type I water (18.2 MΩ-cm) generated from a Barnstead™ xCAD Plus ultrapure water purification system (Waltham, MA, USA) by volume as needed. Samples of UO₂(NO₃)₂·6H₂O and UO₂F₂ (reagent grade) were obtained from International Bioanalytics (Boca Raton, FL, USA) and used as received. Samples were prepared by depositing the UO₂(NO₃)₂·6H₂O and UO₂F₂ particulates onto cotton swipes (Texwipe TX304 10 × 10 cm, Kernersville, NC, USA). Particles were transferred onto multiple swipe substrates using an AxisPro Microsupport micromanipulator (Shizuaka City, Shizuaka, Japan) with two 0.5 µm tungsten probes. Swipes were pre-stamped with the micromanipulator probe to mark location for particle placement. Particles ranging from approximately 6 µm to 40 µm in length were picked up by the probes and deposited in the center of the stamped swipe, mostly as an agglomeration of particles. Optical images of each sample were collected to enable estimation of sample size, and to ensure that the particulates were exclusively located within an area that would be contained in the microextraction probe tip. Additional images of sample material were collected to provide an overview of sample size and morphology. Swipes were loaded onto a Hitachi scanning electron microscope (SEM) SU3900 (Tokyo, Japan) for imaging prior
to extraction. The samples were imaged in variable pressure mode at 30 psi using a backscattering electron (BSE) detector. The HV was set at 5 V with a 20 µm electron beam spot size.

**TIMS analysis of uranium compounds**

A Thermo Scientific Triton (Bermen, Germany) double-focusing multi-collector thermal ionization mass spectrometer (MC-TIMS), equipped with nine faraday cups and one secondary electron multiplier (SEM), was used for analysis of $^{234}$U/$^{238}$U, $^{235}$U/$^{238}$U and $^{236}$U/$^{238}$U isotopic ratios of the same compounds investigated by the microextraction technique. A Total Evaporation (TE) method following ASTM international designation C1672-17[31] was used in which samples are analyzed to exhaustion and the summed intensities are compared to a reference standard to determine the isotope ratios. Uranium measurement by TE is a robust, mature method for determination of uranium isotopes[32-34]. Solid UO$_2$(NO$_3$)$_2$·6H$_2$O and UO$_2$F$_2$ samples were dissolved in 2% (v/v) nitric acid in leached perfluoroalkoxy alkane (PFA) vials to a concentration of 1 µg µL$^{-1}$. Isotopic reference materials from the European Commission, Joint Research Centre-Geel (JRC-Geel, formally the Institute for Reference Materials and Measurements (IRMM)) were analyzed, bracketing the samples to correct for instrumental mass bias (IRMM-3050[35]) and as quality controls (IRMM-2020[36]). Samples and standards were deposited onto double zone refined rhenium filaments and analyzed in a double filament configuration. Target filament loads were between 1-2 µg of uranium to get >500 measurement cycles. Mass calibration, amplifier gain, and baseline calibrations were performed prior to sample measurement. Uranium isotope ratios are reported, after a linear mass-bias correction, with
total uncertainty budgets calculated using the GUM Workbench 2.4 (Metrodata, Germany) software package.

Microextraction-ICP-MS

Microextraction-ICP-MS was performed with an Advion Plate Express (Ithica, NY, USA) coupled to a Thermo Scientific (Bremen, Germany) iCAP RQ quadrupole ICP-MS. The microextraction probe lowers onto the swipe, until 300 N of force has been achieved, forming a seal on the surface. Upon sealing, an extraction solvent (5% HNO₃) is delivered to the probe head at a rate of 0.2 mL min⁻¹. The solvent and extracted species are subsequently delivered to the ICP-MS. After extraction, the probe head is cleaned by performing three cleaning extractions on a 10 × 10 cm piece of Teflon. Swipe blanks were also analyzed between samples. The microextraction probe was integrated to the ICP-MS via a PFA concentric nebulizer housed within a glass cyclonic spray chamber. The nebulizer gas flow rate was predetermined via instrument tuning to be 1.059 mL min⁻¹. The ICP-MS was operated in kinetic energy discrimination mode, with a He gas flow rate of 4.953 mL min⁻¹ and a dwell time of 0.1 s for ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U.

The transient signal was integrated in the Qtegra software using the ICIS peak detection algorithm. A 15-point gaussian smoothing was applied, with 5 passes. There was a baseline window of 50 s, noise factor of 1, peak noise factor of 2, and the peak height percentage was set to 1 with a tailing factor of 4. The integrated total counts under the peak were used to determine the isotopic abundances. The mass bias correction was applied to each isotopic system, utilizing the known comparator value from a calibration standard, and described by Mathew et al[34]. External precision (EP) was defined as the standard deviation (σ) of the ten isotope ratio measurements. Internal precision (IP) was determined
for each extraction based on the expanded uncertainty of the transient signal measurement.
The percent relative difference (% RD) was defined as the percent difference of the measured value from a “true” value or “reference” value, in this case the isotope ratio determined by MC-TIMS measurement.

2.4 Results and Discussion

_Uranium Sample Optical Characterization_

Swipe samples were prepared with particulates of various sizes (<40 µm in length) of either UO$_2$(NO$_3$)$_2$·6H$_2$O or UO$_2$F$_2$. The uranium compounds were transferred to a swipe that had previously been stamped by the microextraction probe head to mark the location for deposition of the sample. Each uranium compound was characterized via SEM imaging (figure 2.1). UO$_2$(NO$_3$)$_2$·6H$_2$O and UO$_2$F$_2$ have clear distinctions in morphology that can be seen in the images, with UO$_2$F$_2$ particles possessing a higher density[37] (6.37 g cm$^{-3}$ as opposed to 2.81 g cm$^{-3}$ for UO$_2$(NO$_3$)$_2$·6H$_2$O[38]). Differences in particle morphology are attributable to variability between the crystal structures of these materials and their methods of crystallization. UO$_2$(NO$_3$)$_2$·6H$_2$O is highly soluble[39] and precipitation from aqueous solutions result in large, well-formed crystals. Conversely, UO$_2$F$_2$ is typically formed by hydrolysis of gaseous UF$_6$. The rapid kinetics of formation for this phase thus result in small, highly friable particles[40], which can easily agglomerate together into larger deposits.
Figure 2.1: Scanning electron micrograph of particulates of UO$_2$(NO$_3$)$_2$·6H$_2$O (A) and UO$_2$F$_2$ (B) representative of the typical size of extracted particulate samples.

Particles were loaded onto each swipe using an AxisPro Microsupport micromanipulator. The probes were used to pick up individual particulates via adhesion forces (Van Der Waals and electrostatic interactions)\(^\text{[41-44]}\) between the material and the probe surface, and deposit them on the prepared swipes. The length and width of the particles were measured using the micromanipulator software. These dimensions were used to estimate the total mass of the particles, or agglomeration of particles, based on the density of the compounds. The swipe containing each prepared sample was imaged with the micromanipulator microscope, although the whole area of the stamp could not be contained in one image so multiple images were taken and then stitched together (Figure 2.2). An example particulate can be seen near the center of the pre-stamp (Figure 2.2).
Particulate mass determinations were done using a multistep process. First, images taken during micromanipulation were imported into the FIJI software suite[45] and converted to black and white monochromatic images using the “split channels” function. For each image, the green channel was chosen due to these images possessing the sharpest contrast. Then, scale bars from the original micromanipulator images were used to create an internal scale within FIJI. Image thresholds were then adjusted and applied to distinguish the particles from background. The “analyze particles” function in FIJI was employed to determine the surface area of each deposit. Although likely an overestimation, 50% of the surface area calculated for each particle was chosen as an approximation of the particle depth. This is a justified assumption, as anisotropic particles are likely to orient themselves parallel to the two dimensional plane with the largest area; it is highly unlikely that the longest dimension would be orthogonal to the field of view[46]. Following volume estimations from size measurements, experimentally determined densities for each material of interest were taken from crystallographic information files for these phases (Inorganic Crystal Structure Database Collection Codes 23814[38] and 31630[37]) for UO$_2$(NO$_3$)$_2$·6H$_2$O and UO$_2$F$_2$, respectively. After using the calculated particle volumes and material density (2.81 g cm$^{-3}$)

**Figure 2.2:** Stitched microscope image of a stamped swipe loaded with a UO$_2$(NO$_3$)$_2$·6H$_2$O particulate, insert highlighted in blue showing a close-up of the particulate, including measurement of length and width.
for UO₂(NO₃)₂·6H₂O and 6.37 g cm⁻³ for UO₂F₂) to obtain approximate masses, the uranium content for each deposit was determined using the weight percent uranium obtained from the ideal formulae for each phase.

*Extraction efficiency*

Multiple extractions were performed on the same location to test the methods efficiency. Figure 3 shows the ²³⁸U recovery as a function of extraction event. Sampling time was determined based on a series of extractions of different lengths, and 15 seconds was found to be a suitable amount of time to mobilize the uranium, where ~99% and 94% of the UO₂(NO₃)₂·6H₂O and UO₂F₂ respectively, was detected within the first 15 seconds. The third through sixth extractions were not significantly above background, as shown in figure 2.3.

![Figure 2.3: Uranium recovery as a function of 15 second extraction events, with UO₂(NO₃)₂·6H₂O (orange, solid line) and UO₂F₂ (green, dashed line).](image)

While there were small amounts of uranium remaining after 1 extraction, there was not sufficient signal of the minor isotopes to measure isotope ratios, therefore the usable uranium signal was all accounted for in the first extraction. The slightly higher solubility of UO₂(NO₃)₂·6H₂O relative to UO₂F₂ is expected. Using ΔfG_m°[47], solubility product
constants ($K_{sp}$) at 25°C were calculated for both phases with values of 1.074 and 1.044 obtained for UO$_2$(NO$_3$)$_2$·6H$_2$O and UO$_2$F$_2$ and, respectively.

**The effect of uranium mass on signal transient**

A positive correlation exists between the estimated mass of U in the particle and U counts found, with higher estimated U mass corresponding to higher counts for $^{234}$U, $^{235}$U, $^{236}$U and $^{238}$U, which suggests efficient extraction and uptake of each U sample, regardless of the particulate load. Figure 4 shows the transient signal for all twenty samples for the detected U isotopes as a function of estimated U mass and extraction time for UO$_2$(NO$_3$)$_2$·6H$_2$O (Figure 2.4A) and UO$_2$F$_2$ (Figure 2.4B). The samples are arranged by uranium deposit on the z axis, and in general the larger sample load also corresponds to higher signal. The smallest particle measured had a length of 6 µm, and an estimated uranium content of 1.13 ng, while the largest sample contained three particles (within the sampling area) with lengths of 10, 20, and 40 µm, and a total uranium content of 794 ng. The transient peak width and shape remained consistent for all particle sizes, indicating a complete extraction of each sample load.
Figure 2.4: U signal (cps) as a function of extraction time and particulate size for 
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (A) and $\text{UO}_2\text{F}_2$ (B)

**Isotope Ratio Measurements**

The measured $^{235}\text{U}/^{238}\text{U}$ isotope ratio and standard deviation ($k=1$, EP, in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ after analysis via microextraction ICP-MS was 0.00230(4), with a % RD from the reference value of 1.0%. The EP (1.7%) for this ratio is comparable to those obtained by single detector LA-ICP-MS[9, 12, 13, 15, 17, 48-51]. The $^{234}\text{U}/^{238}\text{U}$ ratio was 0.000010(1) with a % RD of 0.96 %. The EP of the $^{234}\text{U}/^{238}\text{U}$ ratio was 10%, but still in
line with minor isotope ratios found with LA-ICP-MS, due to the low quantity of the minor isotopes present in the particulates compared to the higher abundance uranium isotopes\textsuperscript{49-52}. The $^{236}\text{U}/^{238}\text{U}$ ratio was determined to be 0.0000033(1) which has a 7.3\% RD compared to the reference value, and an EP of 3\%. Figure 2.5 plots measured isotope ratio (by microextraction-ICP-MS) divided by the referenced value for all 10 samples (ordered smallest to largest). Additionally, the average isotope ratio value of the 10 samples (black solid line) is presented with its EP at $\sigma$ (black dashed lines). The red line denotes the target value (referenced TIMS value). Based on the estimated mass of uranium deposited on each sample, there was between 0.02 and 8 pg of $^{234}\text{U}$ and between 0.04 and 28 pg of $^{236}\text{U}$ per particle, which shows that this method could be viable at determining isotope ratios at low levels.

![Figure 2.5: Measured uranium isotope ratios as a function of reference value for UO$_2$(NO$_3$)$_2$·6H$_2$O, with solid lines denoting average (bold) and dotted lines showing uncertainty (2 times the standard deviation. The red line shows the target (reference) ratio. Uncertainty of the individual samples is based on error propagation of the measurement.](image)

The UO$_2$F$_2$ $^{235}\text{U}/^{238}\text{U}$ ratio found with microextraction-ICP-MS was 0.00720(9), which is a 0.6\% RD from the reference value. The EP for the $^{235}\text{U}/^{238}\text{U}$ ratio was 1\%,
slightly lower than that of UO$_2$(NO$_3$)$_2$·6H$_2$O, which is reasonable since UO$_2$F$_2$ is NU, and therefore has a higher abundance of $^{235}$U compared to the DU UO$_2$(NO$_3$)$_2$·6H$_2$O sample. The $^{234}$U/$^{238}$U ratio was found to be 0.000056(4) with a 1.9% RD and an EP of 4%. The UO$_2$F$_2$ samples were estimated to have between 0.03 - 120 pg of $^{234}$U. The $^{236}$U/$^{238}$U ratio was not measured due to the low abundance of $^{236}$U in NU. Figure 6 shows the microextraction-ICP-MS isotope ratio divided by the reference value for each individual sample, sorted by mass load of uranium (lowest to highest mass load).

Figure 2. 6: Measured uranium isotope ratios as a function of reference value for UO$_2$F$_2$, with solid lines denoting average (bold) and dotted lines showing uncertainty (2 times the standard deviation. The red line shows the target (reference) ratio. Uncertainty of the individual samples is based on error propagation of the measurement.

Zeta scores ($\zeta$) are used to compare an experimental value to a certified or reference value[52-54]. The Zeta scores were calculated to assess the performance of the microextraction method based on the average microextraction ratio measurement ($X$) and its uncertainty $\mu_{(x)}$, and the reference value ($X_a$) and its uncertainty $\mu_{(Xa)}$ through the equation:
\[ \zeta = \frac{X - X_a}{\sqrt{\mu^2(X) + \mu^2(X_a)}} \]  
(2.1)

A zeta score is generally considered highly acceptable if \( \zeta \leq \pm 1 \), while scores \( \geq \pm 2 \) are considered questionable. A good zeta score indicates that the experimental is in close agreement to the reference value, and that the experimental uncertainty isn’t underestimated, since lower uncertainty leads to higher zeta scores[53]. For \( \text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O} \) the zeta score was -0.1, 0.6, and -1.6 for \( ^{234}\text{U}^{238}\text{U}, \; ^{235}\text{U}^{238}\text{U}, \; \text{and} \; ^{236}\text{U}^{238}\text{U} \) respectively. The \( ^{235}\text{U}^{238}\text{U} \) zeta score for \( \text{UO}_2\text{F}_2 \) was -0.5, and the \( ^{234}\text{U}^{238}\text{U} \) was 0.5. These zeta scores indicate that uranium isotope ratios measured with the microextraction-ICP-MS method show good agreement with ratios measured by more traditional techniques such as TIMS, and that the experimental uncertainty is consistent with the deviation from the reference value.

**Detection limits**

Blank extractions were performed on clean cotton swipes prior to each sample analysis, and the uranium values obtained were subtracted from the subsequent measurement. An average of all the blanks measured was used to determine the limit of detection (LOD) for the method based on equation 1.

\[ LOD = \frac{3\sigma}{m} \]  
(2.2)

Here, \( \sigma \) is the standard deviation of the replicate blanks and \( m \) is the slope of the linear regression line of the signal vs mass U graph, with particle sizes ranging from 6 \( \mu \text{m} \) to 40 \( \mu \text{m} \) in length. Both uranium compounds had similar uncertainty in the slope of the linear regression, and similar LODS. For \( \text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O} \) the regression line had a 4% standard error and an \( R^2 \) of 0.99 while for \( \text{UO}_2\text{F}_2 \) the regression line had a 3% standard error and an
R² of 0.99. The LODs for both UO₂(NO₃)₂·6H₂O and UO₂F₂ were similar, approximately 0.03, 2, 0.01, and 60 pg for the $^{234}$U, $^{235}$U, $^{236}$U, and $^{238}$U, respectively. These are also similar to LODs found in previous work[25]. The wide range in LODs is reasonable as the natural abundance of $^{238}$U is much higher than that of the minor uranium isotopes, leading to a higher concentration of $^{238}$U in both the cotton swipes and the reagent acids and thus a higher blank signal. The LODs are likely overestimated, since the uranium mass is based on the particulate volume estimations outlined above.

2.5 Conclusions

This work shows that microextraction ICP-MS is a sensitive and rapid method to directly measure isotope ratios of solid uranium particulates on cotton swipes. Uranium particles, or agglomeration of particles, between 6 and 40 µm in length were placed on cotton swipes using a micromanipulator. The deposited material was then mobilized from the swipe through a 15 second extraction with flowing 5% HNO₃. Particle size was shown to have a strong correlation with the ICP-MS signal, indicating efficient sample extraction.

The $^{235}$U/$^{238}$U ratio found with microextraction-ICP-MS was 0.00230(4), with a % RD from the reference value of 1.0% for UO₂(NO₃)₂·6H₂O, and 0.00720(9), with a 0.6% RD for UO₂F₂. The $^{234}$U/$^{238}$U ratio was 0.000010(1) with a 0.96 % RD for UO₂(NO₃)₂·6H₂O and 0.000056(4) with a 1.9% RD for UO₂F₂. The $^{236}$U/$^{238}$U ratio was 0.000033(1) with a 7.3% RD for UO₂(NO₃)₂·6H₂O. The LOD for this method was calculated to be 60 pg for the $^{238}$U, 0.4 pg for $^{235}$U, and 0.03 pg for $^{234}$U in UO₂F₂, indicating that this method could be applied to even smaller uranium particulates than those measured here, particularly when other more sensitive ICP-MS platforms are utilized. Extraction of particulates of different uranium compounds with applications in nuclear safeguards, such as uranium
oxides, as well as investigation of plutonium particles, will be the focus of future investigations. Additionally, improvement to the precision and sensitivity of this method may be achieved by coupling the microextraction system to a MC-ICP-MS and will be further explored.

2.6 Acknowledgements

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2.7 References


Chapter 3:
Rare Earth Element Determination in Uranium Ore Concentrates Using Online and Offline Chromatography Coupled to ICP-MS

3.1 Preface

This chapter describes a method for quantifying rare earth impurities in UOCs. It uses both an offline, fraction collection method and an online HPIC-ICPMS system and compares the strengths and weaknesses of each system in terms of accuracy, precision, speed, and limits of detection. There is not currently a certified reference material for trace elements in UOCs, but CUP-2 is a UOC that has been analyzed by a number of labs, and trace element concentrations are known within a reasonable uncertainty, therefore it was used for this experiment. Quantification was accomplished with isotope dilution mass spectrometry on both a quadrupole and a sector-field ICP-MS. These experiments were completed at Oak Ridge National Laboratory and were supported in part by the HERE fellowship from ORISE. The results from the study were published in 2016 as follows. Bradley, V. C., Manard, B. T., Roach, B. D., Metzger, S. C., Rogers, K. T., Ticknor, B. W., Wysor, S., Brockman, J. D., Hexel, C. R. R. Rare earth element determinations in uranium ore concentrates using online and offline chromatography coupled to ICP-MS. Minerals 2020. 10, 55.

3.2 Introduction

Uranium is distributed at low concentrations (1-2 \( \mu \)g g\(^{-1}\)) throughout the earth’s crust\([1, 2]\) and is commonly found in certain mineral deposits such as sandstone and quartz
pebble conglomerate[1, 3]. Mineral deposits with elevated uranium composition containing up to 2,000 µg U g⁻¹ is commonly referred to as low grade uranium ore. In rare cases uraninite ore can be found (e.g. Canada) which contain up to 70% U, by weight[2]. Most of the world’s supply of uranium comes from low grade uranium mineral deposits which needs to be extracted and concentrated[1].

After the uranium has been extracted, high levels of trace elements are commonly present. These trace elements can vary based on the mineral type, processing equipment, as well as chemical reagents used in the leaching process. Depending on the intended use of the uranium, impurities in the uranium ore concentrate (UOC) may be removed by precipitation and subsequent rinsing[1]. However, rare earth elements (REE) can persist through the production process. The REE pattern is not typically perturbed during chemical processing; hence it may provide information regarding the ore location[3-6]. For example, unconformity type ores tend to have lower concentrations of light REEs than heavy REEs[7]. Because of this, measuring the concentrations of REEs accurately is important in the field of forensics.

Additionally, other uranium materials can also benefit from the analysis of REEs. For example, weapons grade uranium has a higher tolerance for impurities with high neutron absorption cross sections (i.e. REEs) as it will only sustain a short-term reaction. The presence / absence of REEs could provide information regarding the production method. Reactor grade uranium, in comparison, must sustain a longer reaction cycle and has a lower tolerance for impurities with high neutron absorption cross sections. After fuel consumption, REEs are produced through fission (e.g. Nd and Hf) can be determined to model reactor flux in the core during operation.
REEs are traditionally measured by inductively coupled plasma - mass spectrometry (ICP-MS) through external calibration with matrix-matched standards. This methodology suffers from complexity due to matrix interferences, lack of matrix specific certified reference materials, and preparation effects which can increase measurement uncertainty[8, 9]. Isotope dilution mass spectrometry (IDMS) is an alternate quantitative approach that can reduce these uncertainties. IDMS is a primary method for quantifying elemental impurities in samples through isotopic ratios that offers high precision and accuracy and can also be traceable to certified reference materials[10, 11]. Isotope dilution consists of gravimetrically adding a known amount of an enriched isotope to perturb the analyte’s isotopic composition. This change in the isotope ratio is then measured to determine the analyte concentration using Equation 3.1.

\[
\frac{B_n}{A_s} = \frac{1-(B/A)s(A/B)_m}{(A/B)_m-(A/B)_n}
\]  

(3.1)

Where \(A\) refers to the concentration of the enriched isotopic spike, \(B\) refers to concentration of the sample, \(s\) refers to the spike, \(n\) refers to the unknown, and \(m\) refers to the mixture of the two. This method has been proven to produce accurate results in various sample matrices[8, 10-12].

The major drawback to IDMS is that multiple isotopes must be accurately measured for each analyte of interest, which can be problematic for REEs due to isobaric interferences. In order to accurately quantify REEs by IDMS, the element of interest should be separated from other mass interfering REEs and the uranium matrix[13]. Separating the analytes from the uranium matrix is especially important because heavy ions traverse more efficiently through the sample / skimmer cones of the ICP-MS than lighter ions. Therefore,
a greater population of heavy ions will depress the lighter ions and cause a reduction in sensitivity[14].

Various resins such as TRU and UTEVA are used to separate trace elements from uranium matrices[15-19], but these extraction resins do not separate the individual REEs from each other. Ion chromatography has been used to separate actinides and uranium fission products since the 1980s, and subsequently has been applied to REEs separations in environmental samples and uranium material such as nuclear fuel[12, 20-23]. Recently, methods using high performance ion chromatography (HPIC) have been developed to separate a wide variety of elements, including REEs, from various sample types including spent nuclear fuel[12], sediment and soil samples[24, 25], irradiated highly enriched uranium targets[26], and transplutonium elements created from an irradiated californium target[27]. Often HPIC uses a cation exchange column to separate lanthanides based on charge density. Elements with a higher charge density, and smaller cation radii, are more strongly retained by the anions in the column and are eluted later than elements with lower charge density[28, 29]. HPIC can be used in conjunction with ICP-MS to analyze the trace REE components after separation. The HPIC system can either be directly connected to the ICP-MS for measurements of isotopes as they elute from the column (online) or the REE fractions can be collected and subsequently analyzed (offline).

The goal of this study is to develop a methodology to separate and quantify REEs present in UOCs accurately and with low measurement uncertainty. Here, REEs were examined in a UOC reference material by IDMS. The separated analytes were measured by ICP-MS directly after being eluted from the column (on-line) and for comparison
fractions were collected and analyzed off-line. Here, the two methods, offline and online HPIC-ICP-MS, were used to compare the precision and accuracy of the methodology.

3.3 Materials and Methods

Chemicals and Reagents

All samples and reagents were prepared with Fisher Chemical Optima grade acids (nitric, HNO₃ and hydrochloric, HCl) and ultrapure water (18.2 MΩ·cm) obtained from a ThermoScientific (Waltham, MA, USA) Barnstead GenPure xCAD Plus water purification system. The reagents utilized for the HPIC separations included 0.1 M oxalic acid (C₂H₂O₄, 99.999% trace metals basis, recrystallized, Sigma-Aldrich Co., St. Louis, Mo) and 0.1 M diglycolic acid (DGA, C₄H₆O₅) (recrystallized) (>98% Acros Organics, New Jersey, USA), both buffered to a pH of 4.8 with ammonium hydroxide (NH₄OH, 20-22% as NH₃, trace metals grade, Fisher Scientific). Standard solutions for quantification were prepared from stock solutions (ICP-MS-68B-A, High Purity Standards, Charleston, SC, USA). The reference material utilized for these studies was a UOC (CUP-2) produced at the Blind River uranium refinery in Canada. This reference material (approximately 75% U by weight) has recommended values for several trace elemental impurities, none of which include REEs. CUP-2 characterization data for REEs presented here will be compared to previously reported results[30]. The high levels of REEs present, while not certified, make CUP-2 an ideal quality control sample that has been utilized in several inter-laboratory programs.
Enriched Stable Isotope Spikes

Enriched stable isotope spikes were obtained from the National Isotope Development Center at Oak Ridge National Laboratory (ORNL). These isotopes were dissolved with HNO$_3$ using a CEM Discover SP-D microwave (Mathews, NC, USA) in a polytetrafluoroethylene (PTFE) lined quartz digestion tube sealed with PTFE lined caps. Each digestion was prepared gravimetrically and weighted before and after digestion. After digestion, the spikes were diluted to a final concentration of approximately 1-2 mg g$^{-1}$ solution. For the IDMS quantification, the sample was spiked with a known amount of an isotopically enriched standard, in order to achieve approximately a 1:1 ratio between the two isotopes being compared. The standards used for spiking were enriched with the following isotopes: $^{148}$Nd (93%), $^{150}$Sm (87%), $^{151}$Eu (96%), $^{152}$Gd (28%), $^{160}$Dy (79%) $^{164}$Er (63%), $^{173}$Yb (95%), and $^{176}$Lu (83%). The concentrations of the spike solutions were determined through reverse-IDMS with a known concentration of NIST traceable, natural abundance, single element standards (High Purity Standards, Charleston, SC, USA). These isotopic measurements were determined by a Neptune (Thermo Instruments, Bremen, Germany) double-focusing multi-collector (MC-) ICP-MS, which was equipped with 9 faraday collectors and 1 secondary electron multiplier, as previously described[8].

Instrumentation

A ThermoScientific™ Dionex ICS-5000+ HPIC system utilizing an AS-AP autosampler was employed for REE separations. This autosampler is unique in that it also has fraction collector capabilities. In this configuration the autosampler needle is used initially to collect and inject the sample onto the column. After separation the eluent is
subsequently re-routed through the probe into respective fraction collection vials. This HPIC system is equipped with two quaternary gradient mixing pumps. Samples were loaded via 100 µL injection. Chromatographic separation of REEs was achieved using an IonPac CG5A guard column and a 250 × 4 mm IonPac CS5A analytical column. The CS5A column contains both cation and anion exchange sites, with sulfonic acid and alkanol quaternary ammonium functional groups.

Offline analysis of the separated REE fractions was performed by ICP-MS. The iCAP RQ (Thermo Scientific, Bremen, Germany) was used to optimize the initial separations and collection times. The Element 2 (Thermo Scientific, Bremen, Germany) was utilized for high precision isotope ratio measurements to quantify the REEs within the reference material by IDMS. Final separated fractions were introduced through a self-aspirating nebulizer (100 µL min⁻¹) into a stable sample introduction (SSI) dual quartz spray chamber housed within a PC³ Peltier Cooler (Elemental Scientific Inc., Omaha, Nebraska).

Online separations were performed on a hyphenated HPIC-ICP-MS system comprised of a Dionex ICS-5000+ HPIC system coupled to a Thermo Scientific iCAPQ quadrupole ICP-MS. This chromatographic system consisted of a metal-free HPIC pump gradient mixing capabilities for up to four eluents, a 50 µL injection loop, an IonPac CS5A column with an IonPac CG5A guard column, and a thermal compartment set at 35°C to ensure consistent elution times. Throughout the experiment the eluent flow rate was at a fixed rate of 1 mL min⁻¹. The columns were connected to the nebulizer of the ICP-MS using poly ether ether ketone (PEEK) tubing via a mixing tee-piece. Nitric acid (HNO₃, Optima, 5%) was pumped into the mixing tee-piece at 0.1 mL min⁻¹ to acidify the eluent,
post-column, prior to nebulization to aid in ionization and to increase analytical stability. The iCAP Q was fitted with a high solids nebulizer and a high matrix skimmer cone insert (3.5 mm).

All online measured isotope ratios reported reference the integrated isotopic peak areas in a transient signal using an m/z trace and a pre-determined elution time. Thermo Fisher Scientific Qtegra software package was employed for the analysis, signal smoothing, and peak fitting. Signal smoothing enabled the fitted peak areas between isotope peaks from the same element to be compared, yielding isotopic ratios in atom percent. The peak fitting and smoothing settings applied to determine peak area, found within the “Peak Detection” settings of the Qtegra software, are as detailed previously[25, 26, 31]. Where slight peak overlap occurred for Yb and Lu the isobaric peaks were statistically deconvoluted using the “multiple peak fitting” function of the OriginLab® OriginPro® 2018 graphing software. A gaussian function together with a Levenberg Markquardt iteration algorithm were employed and a natural mixed lanthanide standard was employed as a control.
**HPIC Separation**

**Offline separation protocol**

The HPIC separation was adapted from Roach et al[26]. Each injection had ~30 min separation (1 mL min\(^{-1}\)) which included a 5 min washing step (5% oxalic acid and 95% water) at the end of the separation. The sample was loaded onto the column in water and then followed an elution profile seen in Figure 3.1 to separate the REEs. The uranium matrix was subsequently removed. Fractions were collected in 30 sec increments starting at 6 min, which is when the oxalic acid eluent was first introduced to the column, for a preliminary screen to determine elution time. Subsequently fractions were collected only at the times that each element was eluted from the column.

![Figure 3.1](image.png)

**Figure 3.1:** High performance ion chromatography (HPIC) separation profile employed for rare earth elements

**Online Separation protocol**

Due to the requirement of complete peak resolution and cleaner baselines for signal processing the online separation scheme employed a slightly modified version of that used...
for the offline separation. These modifications included a 15% decrease in DGA from 14-16 min, and an extended HCl column cleaning and uranium removal stage. A 5-fold dilution of the spiked UOC sample was injected and a natural lanthanide standard was employed to calculate mass bias similar to previous work[31].

3.4 Results and Discussion

Chromatographic Separations

The separation of REE within a U sample is vital due to the amount of isobaric and polyatomic interferences which could be present (Table 3.1). For IDMS measurements two isotopes of each element are needed making the separation of these interferences even more important. For example, the measurement of $^{164}$Er has a direct isobaric interference with $^{164}$Dy (28% natural abundance). In addition to isobaric interferences, polyatomic interferences ($^{148}$Nd$^{16}$O) are created which increase the complexity with the $^{164}$Er measurement. While there are other polyatomic interferences that could be present (i.e. hydrides), oxides are the predominant species which hinder the measurement. The REE suite have significant isobaric and polyatomic interferences, hence a separation is vital for precise isotope ratio measurements.
Table 3.1: Inductively coupled plasma–mass spectrometry (ICP-MS) isobaric and polyatomic interferences (* denotes the enriched spiked used).

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<th>Element</th>
<th>Isotope</th>
<th>Natural Abundance %</th>
<th>Isobaric Interference (natural abundance %)</th>
<th>Polyatomic Interferences</th>
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<td>130\text{Ba}^{16}\text{O}, 98\text{Ru}^{16}\text{O}_3</td>
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<td>148 *</td>
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<td>Nd (5.64)</td>
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<tr>
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<td>Er (1.60)</td>
<td>Dy (28.26)</td>
<td>148\text{Nd}^{16}\text{O}</td>
</tr>
<tr>
<td></td>
<td>166</td>
<td>Er (33.50)</td>
<td></td>
<td>150\text{Sm}^{16}\text{O}, 150\text{Nd}^{16}\text{O}</td>
</tr>
<tr>
<td>Yb</td>
<td>173 *</td>
<td>Yb (16.10)</td>
<td></td>
<td>157\text{Gd}^{16}\text{O}</td>
</tr>
<tr>
<td></td>
<td>174</td>
<td>Yb (32.03)</td>
<td></td>
<td>158\text{Gd}^{16}\text{O}</td>
</tr>
<tr>
<td>Lu</td>
<td>175</td>
<td>Lu (97.40)</td>
<td></td>
<td>159\text{Gd}^{16}\text{O}, 159\text{Tb}^{16}\text{O}</td>
</tr>
<tr>
<td></td>
<td>176 *</td>
<td>Lu (2.60)</td>
<td>Yb (13.00)</td>
<td>160\text{Dy}^{16}\text{O}</td>
</tr>
</tbody>
</table>

To eliminate the interference effects for the IDMS measurement, the REE are separated by an ion exchange column and elute in order of their atomic radii (largest to smallest)[25, 29]. A representative chromatogram of the elution profile of the REEs of
interest can be seen in Figure 3.2. The blue boxes around each peak indicate where each fraction was targeted, if offline analysis was warranted. There are two elemental systems where slight coelution in the fractions was observed. The first, Eu and Gd, does not suffer from isobaric interferences between these elements (Table 2) and thus the IDMS calculation is not affected. The second, Yb and Lu ($^{176}$Yb and $^{176}$Lu), requires a correction to remove the Yb counts from the Lu fraction. This correction is made using Equation 3.2.

$$C_x = \frac{C_y \cdot A_y}{A_x}$$  \hspace{1cm} (3.2)

In this equation, $C_x$ refers to the counts of the isotope of interest, $C_y$ is the counts from the interfering analyte at an unperturbed mass and its respective abundance ($A_y$), and $A_x$ is the abundance of the isotope interfering with $C_x$ at the same mass. It is assumed that the isotopes are present in natural abundance. Fraction collection times were set-up with the aim to reduce interferences with the elements of interest. For example, Lu was collected later in time with partial loss of Lu recovery. Absolute recovery is not necessary for quantification as the IDMS ratio being monitored is unchanged.

The HPIC-ICP-MS method was verified using a multi-element solution (ICP-MS-68A-A) spiked with the corresponding REE enriched isotopes for IDMS quantification. The concentration of each REE was determined within the uncertainty of the certified values. This also served to confirm the concentration of the spike isotopes.
Figure 3.2: Representative chromatogram of rare earth elements (REE) elution profile. Shaded areas highlight approximate collection intervals of fractions for ICP-MS analysis.

This separation was also studied to determine the effects of different uranium sample loading on the chromatography robustness. The uranium samples, ranging between 10-2000 µg g⁻¹, containing µg levels of REE, were run on the HPIC using the method described above. Minor peak shifts (<30 sec) were observed in elution times for the REEs between lowest and highest amounts of U loaded onto the column. However, the resolution between REE peaks remained relatively unchanged. The successful separation of REE in a sample containing 200 µg U (100 µL injection), suggests that samples do not need to be diluted prior to separation, which maintains higher concentrations of REEs.
Offline UOC separations

A sample of CUP-2 (~4000 µg U g⁻¹ sample) was spiked with various enriched isotopes of REEs, in order to achieve a 1:1 ratio between the quantifying isotope pairs. Two test solutions were created from the spiked CUP-2 stock. These aliquots were made such that 80 µg and 200 µg U were injected onto the column. Method blanks comprised of 2% HNO₃ were run between samples using the same HPIC method to test for washout and were utilized as blank subtraction prior to IDMS calculation. A total of eight fractions were collected for the elements being measured, as depicted in Figure 3.2. The fractions were then diluted 10x with 2% HNO₃ to reduce matrix loading and premature wear on ICP-MS consumables. Diluted fractions were subsequently analyzed on a magnetic sector ICP-MS.

Most of the REEs were resolved from isobaric and polyatomic interferences in the CUP-2 sample. Only the Lu fraction had a significant interference present, ¹⁷⁶Yb, which comprised approximately 30% of the total ¹⁷⁶Lu counts. This interference was corrected (Eq. 3.2) to account for the Yb contribution. The REE concentrations determined were comparable (<5% relative difference, %RD) to previously reported values[30]. There was no significant difference in the determined REE concentrations for the two different sample loads as seen in Figure 3.3. There were slight issues with the Gd analysis, at the smaller sample loading, which is somewhat expected with the low natural abundances for the isotopes chosen (¹⁵²Gd and ¹⁵⁴Gd, 0.2% and 2%, respectively). The larger U loading did not negatively impact the overall methodology (separation and analysis). With larger loading, the sample can be directly injected into the HPIC, thus improving the overall method sensitivity.
Figure 3. 3: Concentrations of rare earth elements in CUP-2 shown as a ratio of determined concentration to the previously reported (thermotical) CUP-2 concentrations at different mass loadings.

**Online UOC analysis**

The 4000 µg spiked CUP-2 solution was diluted so that 40 µg of U was injected into the column. For the online analysis, there was complete resolution between the REE with the exception of the Lu / Yb pair. As with the offline separation, Lu was the only element that was not fully separated from its isobaric interferences ($^{176}$Yb) and was statistically deconvoluted prior to the IDMS calculation. The expanded uncertainty associated with the measurement (2σ) of the online analysis was higher than the offline measurements. This is due to the lack of replicate measurements during online analysis that offline analysis provides. It should be noted that the uncertainty associated with the IDMS spiking (i.e. uncertainty in the spike concentration) was not included in this expanded uncertainty determination, as the sample was the same for each measurement. In
general, the concentration of REEs calculated through the offline and online methodologies agreed closely and were similar to previously reported concentrations.

**Table 3. 2:** Concentration of REEs in CUP-2 with offline and online analysis compared to previously reported concentrations [32] with expanded measurement uncertainty at 2σ.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reported Concentration (µg g⁻¹ U)</th>
<th>Offline concentration (µg g⁻¹ U)</th>
<th>% difference</th>
<th>Online concentration (µg g⁻¹ U)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>26.29 ± 0.38</td>
<td>26.68 ± 0.37</td>
<td>+ 1.47</td>
<td>26.37 ± 1.07</td>
<td>+ 0.31</td>
</tr>
<tr>
<td>Sm</td>
<td>12.29 ± 0.13</td>
<td>12.28 ± 0.18</td>
<td>- 0.13</td>
<td>12.17 ± 0.30</td>
<td>- 1.02</td>
</tr>
<tr>
<td>Eu</td>
<td>1.01 ± 0.02</td>
<td>0.98 ± 0.04</td>
<td>- 3.00</td>
<td>0.96 ± 0.06</td>
<td>- 5.36</td>
</tr>
<tr>
<td>Gd</td>
<td>19.48 ± 0.28</td>
<td>19.16 ± 0.37</td>
<td>- 1.68</td>
<td>18.50 ± 0.67</td>
<td>- 5.0</td>
</tr>
<tr>
<td>Dy</td>
<td>24.72 ± 0.38</td>
<td>24.52 ± 0.32</td>
<td>- 0.78</td>
<td>24.45 ± 0.42</td>
<td>- 1.08</td>
</tr>
<tr>
<td>Er</td>
<td>11.50 ± 0.20</td>
<td>11.54 ± 0.12</td>
<td>+ 0.39</td>
<td>11.69 ± 0.34</td>
<td>+ 1.71</td>
</tr>
<tr>
<td>Yb</td>
<td>9.05 ± 0.10</td>
<td>9.13 ± 0.10</td>
<td>+ 0.88</td>
<td>9.08 ± 0.28</td>
<td>+ 0.31</td>
</tr>
<tr>
<td>Lu</td>
<td>1.09 ± 0.02</td>
<td>1.09 ± 0.02</td>
<td>- 0.12</td>
<td>1.05 ± 0.05</td>
<td>- 3.98</td>
</tr>
</tbody>
</table>

The REE concentrations found using the methods described here were also compared to previously reported values[30] through zeta scores (ζ) which were calculated according to Equation 3.3. They are calculated based on the experimental result (X) along with the expanded uncertainty µ(x) and the comparator result (Xₐ) and its uncertainty µ(xₐ) through the Equation 3.

\[
ζ = \frac{X - Xₐ}{\sqrt{µ²(x) + µ²(xₐ)}}
\]  

(3.3)

Scores of ± 1 are traditionally considered highly acceptable, while scores greater than ± 2 are generally considered questionable. The zeta scores for both online and offline analysis of CUP-2 are shown in Figure 4. The low zeta scores lend confidence to both analysis methods.
Limits of detection

The instrument blank, 2% HNO₃ analyzed on the ICP-MS between each sample, and the method blank, 2% HNO₃ injected into the HPIC and analyzed using the same methodology. As expected, there was more count variability in the method blanks simply due to the chromatographic separations. The method blanks were used for background subtraction. The limits of detection and quantification (LOD and LOQ respectively) for the method were calculated by applying a confidence factor (k=3 for LOD and k=10 for LOQ) to the standard deviation of the method blanks. These limits were calculated to be applicable to their corresponding concentration of REE per gram of U. The LODs and LOQs for all the elements were in the sub-ng g⁻¹ U range with the exception of the LOQ...
of Gd and Nd for the offline separation which was 1.4 and 1.1 ng g\(^{-1}\) U, respectively. The LOD and LOQ for the offline method were in general higher in comparison to the online. The lower quantification limits for the online method could be explained by considering that entire sample is injected onto the column and analyzed by the ICP-MS adding the counts via integration; however, the offline system might only collect a small fraction of the sample to minimize carryover from an interfering analyte thereby lowering the overall signal. For example, the fraction collection of Eu in offline mode collected the early portion of the peak to avoid any Gd interference. Subsequently, the Gd fraction collected the later peak to avoid any Eu interference. Additionally, for offline analysis, the sample was diluted post column in order to minimize the caustic effects of the organic matrix on the ICP consumables. This was especially important with the longer integration times necessary for precise isotopic measurements in comparison to the online analysis. Ultimately, the offline method detection limits could be hindered due to limitations associated with fraction collection as well as pre-ICP analysis dilutions. However, the offline method has the added benefit of injecting of a less dilute UOC which increases the REE concentrations and enables the measurement of more precise isotope ratios.

**Table 3.3: Calculated limits of detection and limits of quantification**

<table>
<thead>
<tr>
<th>Element</th>
<th>Offline LOD (ng/g U)</th>
<th>Offline LOQ (ng/g U)</th>
<th>Online LOD (ng/g U)</th>
<th>Online LOQ (ng/g U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>0.044</td>
<td>0.15</td>
<td>0.0084</td>
<td>0.028</td>
</tr>
<tr>
<td>Sm</td>
<td>0.0095</td>
<td>0.032</td>
<td>0.018</td>
<td>0.059</td>
</tr>
<tr>
<td>Eu</td>
<td>0.028</td>
<td>0.094</td>
<td>0.022</td>
<td>0.072</td>
</tr>
<tr>
<td>Gd</td>
<td>0.34</td>
<td>1.14</td>
<td>0.0093</td>
<td>0.01</td>
</tr>
<tr>
<td>Dy</td>
<td>0.021</td>
<td>0.069</td>
<td>0.0017</td>
<td>0.0055</td>
</tr>
<tr>
<td>Er</td>
<td>0.0085</td>
<td>0.028</td>
<td>0.0038</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Yb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>0.0052</td>
<td>0.017</td>
<td>0.00091</td>
<td>0.0031</td>
</tr>
<tr>
<td>Lu</td>
<td>0.0075</td>
<td>0.025</td>
<td>0.0015</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

3.5 Conclusions

The primary goal of this project was to develop a method that provided accurate and precise quantification of REEs in UOC through HPIC separations and IDMS. Overall, by utilizing IDMS, in comparison to external calibration-based quantification platforms, the uncertainty was minimized. In order to perform IDMS on REE, a separation was required and successfully achieved here by HPIC. The method was compared by performing the IDMS measurements offline by a magnetic sector ICP-MS as well as directing the separated eluents into a quadrupole ICP-MS. Here, while the overall measurement accuracy was relatively the same, the measurement uncertainty was indeed improved by high precision isotopic measurements achieved by the offline analysis. Overall, this method was effective at quantifying REE in a minimally processed UOC sample.

3.6 Acknowledgements

This work was supported by the Department of Energy’s National Nuclear Security Administration under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Oak Ridge National Laboratory is managed by UT-Battelle for the Department of Energy under Contract DE-AC05-00OR22725. This research was also supposed in part by an appointment to the HERE program at Oak Ridge National Laboratory.
3.7 References:


Chapter 4: Development of a high-temperature ammonium bifluoride fusion dissolution and ICP-MS analysis of elements with nuclear forensic value.

4.1 Preface

The following work optimized a method for the dissolution of inorganic material though fusion with ammonium bifluoride. Standard reference materials with certified trace elemental concentrations were digested with ABF fusion and experimental concentrations were compared to the certified concentrations. Reference materials spiked with Pu were digested and separated from naturally occurring uranium prior to quantification. The experiments were completed at the University of Missouri Research Reactor. The results were published in 2021 and were presented as the following. Bradley, V. C., Weilert, T. M., Brockman, J. D. Innovative high-temperature ammonium bifluoride fusion and rapid analysis of elements with nuclear forensic value. *Talanta* **2021**, 121622.

4.2 Introduction

This work evaluates high-temperature ammonium bifluoride (ABF) fusions to rapidly dissolve refractory minerals for nuclear forensic analysis. A ground level nuclear detonation produces radionuclides that are characteristic of the pre-detonation device, a phenomenon that is useful for post-detonation attribution analysis. The extreme temperature changes in the fireball produce vitrified, refractory debris and promote chemical fractionation of the radionuclides based on melting point and vapor pressure[1]. In an urban environment, the debris typically will be produced from concrete, steel, borosilicate glass, other construction materials, as well as minerals from the underlying geology[2, 3]. A robust sampling plan is necessary to account for the heterogeneous
distribution of radionuclides across a large debris field, and rapid analysis methods are needed to measure radionuclides in bulk samples. Established analytical methods for measurement of radionuclides levels in bulk samples include ICP-MS, TIMS, gamma spectroscopy, beta analysis, and alpha spectroscopy[4]. Prior to direct analysis by ICP-MS or radiochemical separation schemes, the debris sample must be quantitatively digested. To improve analytic outcomes, radiochemical separations are also typically used to preconcentrate the target analytes and remove interferences.

Target analytes in post-detonation nuclear forensic analysis include actinides and fission products. The actinides originate from the nuclear fuel in the weapon. The distribution of radionuclides in a debris sample is useful for monitoring mass-dependent isotopic fractionation, the fission efficiency, and the shape of the fission product mass yield curve. Mass-dependent isotopic fractionation in a debris sample can be assessed using a volatility index that is based on the ratio of refractory-volatile isotope pairs, such as $^{95}\text{Zr}/^{86}\text{Sr}$, $^{147}\text{Nd}/^{140}\text{Ba}$, $^{95}\text{Zr}/^{132}\text{Te}$, and $^{99}\text{Mo}/^{132}\text{Te}$[5, 6]. The volatility index has also been estimated in trinitite using a major element-volatility index and the trace element ratio $\text{Th}/\text{Rb}$[7]. Another useful metric is the fission efficiency, defined as the ratio of the number of fission events to the total fuel inventory. The fuel inventory of the device is proportional to the level of $^{235}\text{U}$, $^{238}\text{U}$, and $^{239}\text{Pu}$ in a representative debris sample, and the number of fissions is proportional to the level of refractory fission product[8]. This assumes that the refractory fissionogenic radionuclides ($^{95}\text{Zr}$, $^{97}\text{Zr}$, $^{99}\text{Mo}$, $^{103}\text{Ru}$, $^{144}\text{Ce}$ and $^{105}\text{Ru}$) and that the heavier rare earth isotopes behave similarly to actinides in the fireball[5, 6], which can be checked using the volatility index. A fission split analysis uses the shape of the fission-mass yield to infer the presence of $^{235}\text{U}$, $^{238}\text{U}$, $^{239}\text{Pu}$ and 14 MeV neutrons, indicative of a
fusion device[9, 10]. In a fission split analysis, the wings of the fission-mass yield curve, including isotopes of Nd, Sm, and Pm, are analytical targets because they are most sensitive to the actinide fuel and the neutron energy spectrum[10, 11]. It is also important to measure naturally occurring elements and their activation products in the debris to correct for production through neutron absorption. For example, \(^{239}\text{Np}\) is measured in post-detonation debris since it is used to correct for the fraction of \(^{239}\text{Pu}\) created by neutron interaction with \(^{238}\text{U}\)[10].

Dissolution methods carried over from evaluating nuclear debris from nuclear weapons tests used open vessel acid digestions containing mixtures of HNO\(_3\)-HCl-HClO\(_4\)-HF with multiple evaporation steps[9, 12-14]. The HF was required to attack silicates and other refractory minerals; however, it interfered with downstream radiochemical processes and was therefore removed by evaporating the digestate to white fumes with HNO\(_3\) and HClO\(_4\)[10]. Open-vessel acid digestion methods can require several days to completely dissolve a refractory sample and cannot be speeded up because of temperature restrictions imposed by the boiling points of the acids (<130 °C)[12, 15]. Furthermore, the use of HF and the evaporation of HClO\(_4\) requires specialized facilities and personnel training that may not available in a field laboratory. Sample dissolution times can be reduced using pressurized digestion bombs that are heated in an oven or a microwave to temperatures of 250 °C. However, for refractory geological materials, HF is still required in concentrations greater than 35% and long digestion times of 16 hours have been reported[16]. In addition, bomb digestion vessels can become over-pressurized and leak, a significant disadvantage for a radioactive sample.
In recent years, low temperature fusion with ammonium bifluoride (ABF) has been explored for dissolution of geological materials and surrogate nuclear detonation debris[16, 17]. ABF is a fluorinating agent with a boiling point of 240 °C and a decomposition temperature of ~120 °C, at which point it partially decomposes into HF and NH₃ gas[15]. ABF replaces HF in mixed-acid digestions and is capable of attacking silicates and other refractory minerals[17]. Sample decomposition by ABF fusion is attractive because it has less hazardous chemical properties than HF, can be obtained in high purity for trace element analysis, and can be used at higher temperatures than mixed acids in open vessels[15, 17, 18]. Low temperature, open vessel ABF fusions that do not include HClO₄ have been used to dissolve felsic and mafic geological materials and soils[19, 20]. Hubley, et. al. reported an open vessel ABF fusion method for dissolution of surrogate nuclear debris samples, trinitite, and geological reference materials[19-21]. The method required 3 hours of fusion time at 230 °C, followed by an hour of reflux in HNO₃, and an evaporation step. The total dissolution time was reported to be over 5 hours. Low Zr recovery was reported in SDC-1 but not in NIST 278 or QLO-1a and was hypothesized to be due to the presence of a refractory zirconium mineral. O’hara et al., reported on a closed vessel dissolution ABF fusion method for a variety of reference materials which indicated fusion times of up to 24 hours were required for complete dissolution of some geological materials[15]. A low temperature method used a 30-minute ABF fusion to dissolve soil with successful separation of Pu from the digested sample using TEVA extraction chromatography. The total method, including the chemical separation and final ICP-MS measurement required 8 hours to complete[18].
The recent work on ABF fusion dissolution has focused on low temperatures that are compatible with PFA and PTFE labware. This work will examine an open vessel ABF fusion dissolution method for nuclear forensic analysis conducted on a hotplate at 400 °C and 540 °C in a Pt-Au alloy crucible. The higher temperatures are expected to reduce the fusion time and the total dissolution time. Potential loss of analytical targets, including Mo, Tc, Sr, REE, U, Np, and Pu through the formation of precipitants or volatile fluorides was evaluated[22]. Separation of U and Pu from the digestate was examined using extraction chromatography methods to demonstrate compatibility with downstream radiochemical separation methods.

4.3 Materials and Methods

Materials

Trace metal grade ammonium bifluoride (99.999% purity) was obtained from Sigma-Aldrich, and Trace Metal Grade acids were purchased from Fisher Scientific. Ultrapure water with a resistivity of 18.2 MΩ/cm was obtained from a Milli-Q water purification system. The geological reference materials acquired from the US Geological Survey and the National Institute of Standards and Technology used evaluate the effectiveness of the fusions were: USGS SDC-1 Mica Schist, USGS QLO-1a Quartz Latite, and NIST 278 Obsidian. The Pt-5%Au crucible was purchased from Claisse. Pre-packed 2 mL extraction chromatography cartridges containing TEVA (part no. TE-R50-s, lot no. TESR18B) and UTEVA (part no. UT-R50-s, lot no. UTSR14A) with 50 to 100 μm pore sizes were purchased from Eichrom Technologies (Lisle Il, USA). Solutions were filtered using 0.45 μm filters (MFTM Membrane Filters, Millipore).
**Instrumentation**

A Perkin Elmer NexION 300x quadrupole ICP-MS was used for sample analysis. This instrument was equipped with an HF-resistant sample introduction system from ESI, and included a PFA nebulizer, a PFA Scott double-pass spray chamber, and a torch with a sapphire injection tube. The ICP-MS was run in kinetic energy discrimination (KED) mode, with a He gas flow rate of 2.5 L min\(^{-1}\) to minimize polyatomic interferences. Standard solutions of Sc, In, and Tl were purchased from Inorganic Ventures and used as internal standards. The REE elements and the actinides were corrected using Tl and the transition metals were corrected using Sc or In.

**ABF Fusion Sample Dissolution**

**Examination of Fusion Temperature and Time**

Experiments were performed to evaluate the ABF fusion temperature, fusion time, reflux time, evaporation temperature, and filtration step in sequence. The first set of experiments examined the ABF fusion temperature and the fusion time. ABF fusions were conducted at 400 °C and 540 °C. 50 mg of USGS QLO-1a reference material and 500 mg of ABF were weighed into a platinum crucible. The Pt crucible was covered with a Pt lid and placed on a pre-heated hot plate. The ABF fusions were carried out for 5, 10, and 30 minutes at 400° C, and also for 5 and 10 minutes at 540 °C. The fusion residue was diluted with 2 mL of 8 M HNO\(_3\) and evaporated to dryness at 140 °C, based on parameters used by Zhang *et al.*[17] The evaporated sample was diluted to 45 mL of 2% HNO\(_3\) for ICP-MS analysis.
Examination of Reflux Time

A second set of experiments examined the reflux time on quantitative dissolution. The reference material QLO-1a was fused with ABF at 540 °C for 10 minutes. The sample was refluxed in 2 mL of 8 M HNO₃ at 80 °C for 5 min, 10 min, 15 min, and 20 min, and then evaporated to dryness at 140 °C. The goal of the reflux step was to dissolve fluoride containing precipitants in nitric acid prior to evaporation. The samples were filtered the day of ICP-MS analysis.

Examination of the Final Evaporation Step

The third set of experiments examined the evaporation step. Following the reflux step, samples in the crucible without a lid were heated using the hot plate to 140°C or 300 °C. The sample residue was then dissolved in 45 mL of 2% (v/v) HNO₃.

Examination of the Filtration Step

A fourth set of experiments examined the filtration step. The filtration step was carried out at three times following the sample dissolution: immediately following the ABF fusion dissolution procedure, following a 2-hour reflux step of the final dissolved sample, and immediately prior to ICP-MS analysis. A Nalgene™ filtration system with a 0.45 μm filter was used for filtration. The vacuum flask was acid washed between samples. Prior to filtration, the 0.45 μm filter was dried in an oven at 75 °C for 30 minutes and weighed using an analytical balance. The solution was filtered under vacuum and returned to its vial, and the filter was subsequently oven dried and re-weighed. Precipitate trapped on the filter was qualitatively evaluated using x-ray fluorescence spectroscopy (XRF).
**Dissolution of Pu-Spiked Samples and separation of U and Pu**

To evaluate post dissolution radiochemical separation, 50 mg of QLO-1a was spiked with 6 ng of $^{239}$Pu (0.6 mL of 10 ppb $^{239}$Pu in 2% HNO$_3$) in a Pt crucible. The sample was heated at 130 °C to dryness on a hotplate (about 10 minutes) and immediately dissolved by ABF fusion or heated in a muffle furnace to 850 °C for 4 hours. A second spike of 6 ng of $^{242}$Pu was added to the sample, which was again evaporated to dryness on a hotplate. 500 mg of ABF was added, and the sample was fused. After dissolution, the sample was reconstituted in approximately 20 mL of 6M HNO$_3$. Pu and U were then separated using TEVA and UTEVA extraction chromatography[23-25]. A 2 mL aliquot of this sample was taken, and 6 mL of 6 M HNO$_3$ was added. The sample was then prepared for the Pu separation on a TEVA column by addition of 8 mL of 2 M Al(NO$_3$)$_3$. Valence adjustment was conducted by the addition of 0.5 mL of 1 M sulfamic acid to oxidize nitrite, followed by 0.2 mL of 5mg/mL Fe(NO$_3$)$_3$ and 1.25 mL of 1.5 M ascorbic acid to reduce Pu to the 2$^+$ oxidation state. The Pu was adjusted back to Pu$^{4+}$ for separation on the TEVA column by addition of 1 mL of 3.5 M NaNO$_2$.

The TEVA resin was stacked on top of the UTEVA resin and they were placed on a vacuum box. The resins were rinsed with 40 mL of 0.1 M HNO$_3$ to remove residual U and other potential contaminates from the columns. They were next rinsed with 10 mL of 3 M HNO$_3$ to equilibrate the column. The solution was then loaded onto the TEVA/UTEVA resins with a 1 mL/min flow rate. The Pu was eluted from the TEVA resin with a solution of 0.0001 M TiCl$_3$, 0.02 M HCL, and 0.005 M HF. The U was eluted from the UTEVA resin with a solution of 0.02 M HNO$_3$ and 0.005 M HF.
Analysis of method viability with Np and $^{235}$U fission products

A tracer solution of fresh fission products and $^{239}$Np was produced by irradiation of 200 μg of a 1000 μg g$^{-1}$ natU standard (Inorganic Ventures) for 30 seconds in a neutron flux of $5 \times 10^{13}$ n/cm$^2$/s using the pneumatic tube system at the University of Missouri Research Reactor. The sample was allowed to decay for 24 hours, then 150 μg of the tracer sample was spiked into 50 mg of QLO-1a geological reference material in a Pt crucible. The sample was dried at 130 °C, then 500 mg of ABF was added, and the ABF fusion method described above was followed. Finally, the sample was counted on an HPGe detector for 20 minutes. A geometrically matched calibration standard for the HPGe detector was made from the remainder of the irradiated U solution.

4.4 Results and Discussion

Optimization of Fusion Time

The reference material USGS QLO-1a was used to examine the capability of ABF fusion to dissolve refractory minerals and recover elements relevant to nuclear forensic analysis. The fusion temperature, fusion length, reflux time, and evaporation temperature were optimized in sequence as described in the methods section. The results for the ABF fusion dissolution of QLO-1a at 400 °C for 5, 10, and 30 minutes and at 540 °C for 5 and 10 minutes are reported in Figure 4.1.
Figure 4.1: Optimization of fusion temperature and fusion length using USGS Quartz Latite (QLO-1a). The reported uncertainties were propagated from the standard deviation of 5 replicate instrument readings of the sample.

Following the 10-minute fusion at 540 °C, it was observed that ABF was no longer visible in the bottom of the Pt crucible. ABF fusion lengths longer than 10 minutes at 540 °C were not examined. It is observed in Figure 1 that increased the fusion time or the fusion temperature did not change the recovery of elements measured in QLO-1a. These initial results demonstrate excellent recovery for rare earth elements and alkaline earth metals, each of which can form insoluble fluorides. The observed high recovery of Mo and the relatively large uncertainty was attributed to the measurement being conducted near the instrument’s detection limit. Mo is an important fission product with isotopes near the peak of the fission mass yield that could form volatile MoF$_6$. A spike recovery experiment was performed to check Mo recovery. 10 µg of Mo was spiked onto a 50 mg sample QLO-1a in the Pt crucible and dried. The Mo recovery measured after the ABF fusion dissolution was 100 ± 5%. Loss of U and Mo through formation of a volatile fluoride did not occur in
the high temperature, open vessel fusion method. The recovery of monitored elements was in agreement with previous work using a 3-hour open vessel fusion conducted at 230 °C[20]. Based on these results, subsequent fusions were carried out at 540 °C for 10 minutes.

**Optimization of Reflux Time**

The goal of the reflux step is to disassociate sparingly soluble metal fluorides. Samples of QLO-1a were fused with ABF for 10 minutes at 540 °C. The residue was dissolved in nitric acid and the reflux step was conducted at 80 °C for 5, 10, 15, and 20 minutes and then evaporated to dryness at 140 °C, as described in section 2.3.2. It was observed that longer reflux times did not significantly change the recoveries for measured elements (see figure 4.2). A 5-minute reflux step was used for subsequent dissolutions.

![Figure 4.2](image)

**Figure 4.2:** Dissolution of USGS QLO-1a Quartz Latite with 80 °C reflux times of 5 minutes (blue), 10 minutes (orange), 15 minutes (grey), and 20 minutes (yellow). The reported uncertainty was determined from the standard deviation of 3 replicate samples (n=3).
Optimization of Evaporation Temperature

The evaporation step requires the most time in the ABF fusion method. To minimize the total dissolution time, the temperature of the evaporation step in the Pt crucible was increased from 140 °C to 300 °C. The time required for evaporation at 300 °C was 15 minutes, while the time required for evaporation at 140 °C was 60 minutes. As presented in Figure 4.3, the increase in evaporation temperature showed little difference in recovery, indicating that a higher temperature did not result in loss caused by production of volatile fluoride species for all examined elements, apart from Si, which forms SiF₄[16, 17]. Figure 3 also illustrates that there is not a significant change in recovery for elements that form insoluble fluorides, despite the evaporation temperature.

![Figure 4.3](image.png)

**Figure 4.3:** Comparison of the recovery of various isotopes contained in USGS QLO-1a Quartz Latite for an HNO₃ evaporation at 140 °C (blue) and at 300 °C (orange) following a 5-minute reflux step. The uncertainty was determined from the standard deviation of 3 replicate samples (n=3).
**Optimization of the Filtration Step**

During the experiments to optimize fusion length, fusion time, reflux time, and evaporation temperature, the samples were filtered several days after the fusion, immediately prior to ICP-MS analysis. To minimize the total time to ICP-MS analysis, the fused materials were instead filtered immediately following the final dilution to 45 mL. Solutions filtered immediately after the fusion dissolution had lower elemental recoveries and the filter collected visible precipitant that ranged in color from white to brown. The precipitate was not present on filters in sample solutions that were filtered two or more days after the fusion dissolution. The X-ray fluorescence spectra of the precipitate was dominated by Fe, which has been reported to react with ammonium bifluoride to produce FeF$_3$ at 300 – 400 °C[26]. Iron fluorides are sparingly soluble in water and may be dissolved through dilution, stirring, and warming the solution[27, 28]. The presence of solids in the solution are not compatible with downstream radiochemical separation methods. To increase the rate of dissolution of the Fe containing precipitant, the final solution was heated to 105 °C for 2 hours using a hot block. Figure 4.4 shows the results from three methods: waiting a minimum of 2 days prior to filtration and ICP-MS analysis, filtering immediately after ABF fusion, and filtering after heating the solution for 2 hours.
Figure 4.4: QLO-1a recovery when filtered immediately post-fusion (grey), when filtered after heating (blue) and when left for 2 days without filtering (orange). The uncertainty was determined from the standard deviation of 3 replicate samples (n=3).

Following the 2-hour heating step, element recoveries were quantitative for NIST 278 and QLO-1a when solutions were filtered after heating, while SDC-1a had lower recovery of Zr, Ce, and Nd. The low recovery of Zr in SDC-1 has been observed in previous work and was attributed to highly refractory Zr minerals, such as zircons[20]. The Ce and Nd are thought to coprecipitate with the iron fluoride and the decreased recovery in SDC-1 following the two-hour heating step is likely related to incomplete dissolution of the iron containing precipitant. The reference material SDC-1 contains 4.91 wt% Fe which is higher than both NIST 278 (1.43 wt% Fe) and QLO-1 (3.04 wt% Fe). Improved recoveries of Ce and Nd were measured when the samples were filtered two days later, supporting the hypothesis that REEs coprecipitated with the iron containing precipitant.
The optimized parameters for rapid ABF fusion dissolution were a 540 °C fusion for 10 minutes, a 5-minute reflux of the residue in 2 mL of 8 M HNO₃, evaporation at 300 °C, and final dilution into 45 mL of 2% HNO₃. The final solution was heated for 2 hours at 105 °C prior to filtration and ICP-MS analysis. This method was further evaluated by measuring recovery of elements in the following reference materials used to examine low-temperature ABF fusions: USGS QLO-1a Quartz Latite, USGS SDC-1 Mica Schist, and NIST 278 Obsidian glass. Table 4.1 reports the recovery of certified elements in the three standard reference materials, after filtration. In the USGS certificate of analysis for QLO-1a, the Nd concentration is only an “informational value” of 26 µg/g. Rosenberg et al., analyzed QLO-1a using instrumental neutron activation, and determined the Nd concentration to be 23 ± 2 µg/g [29]. As the USGS certificate of analysis did not provide a certified concentration of Nd with an associated error, the Nd concentration obtained in this work, of 22.3 ± 0.3, was compared to that reported by Rosenberg et al.

The recovery of monitored elements in NIST 278 and USGS QL0-1a was between 90 and 105%. A few common metals, such as copper, showed greater than 100% recovery. This is attributed to contamination that could have occurred during the filtration step. The dissolution method was reproducible, with standard deviations below 6% for most elements being analyzed. The low recovery of Zr in SDC-1 is attributed to the presence of a refractory Zr containing mineral such as zircon, and has been reported in previous studies[20]. In SDC-1 samples that were filtered two days after the ABF fusion method the measured percent recoveries of La Ce, Nd and Sm were 92 ± 3, 96±2, 91±2, 99 ±3, and 96±3, respectively. The Zr and Nb percent recovery was unchanged at 33 ± 4 and 79 ± 3.
This data indicates that La, Ce, Nd, and Sm coprecipitate with the iron precipitant while Zr and Nb are in the form of a refractory mineral that has not been fully dissolved.

Table 4. 1: Recovery of USGS QLO-1a Quartz Latite, NIST 278 Obsidian, and USGS Mica Schist. The uncertainty was determined from the standard deviation of 3 replicate samples (n=3)

<table>
<thead>
<tr>
<th>Element</th>
<th>QLO-1a</th>
<th>NIST 278</th>
<th>SDC-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99 ± 2</td>
<td>98.3 ± 0.7</td>
<td>94 ± 7</td>
</tr>
<tr>
<td>Ti</td>
<td>93 ± 1</td>
<td>94.7 ± 0.7</td>
<td>88 ± 5</td>
</tr>
<tr>
<td>Mn</td>
<td>N/A</td>
<td>100.2 ± 0.6</td>
<td>103 ± 1</td>
</tr>
<tr>
<td>Fe</td>
<td>97 ± 4</td>
<td>96.2 ± 0.4</td>
<td>102 ± 2</td>
</tr>
<tr>
<td>Co</td>
<td>106 ± 5</td>
<td>105 ± 2</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>Cu</td>
<td>111 ± 5</td>
<td>117 ± 24</td>
<td>95 ± 4</td>
</tr>
<tr>
<td>Rb</td>
<td>93 ± 3</td>
<td>99 ± 1</td>
<td>95 ± 2</td>
</tr>
<tr>
<td>Sr</td>
<td>94 ± 2</td>
<td>96 ± 1</td>
<td>94 ± 5</td>
</tr>
<tr>
<td>Zr</td>
<td>95 ± 1</td>
<td>N/A</td>
<td>37 ± 4</td>
</tr>
<tr>
<td>Nb</td>
<td>94 ± 1</td>
<td>N/A</td>
<td>80 ± 1</td>
</tr>
<tr>
<td>Mo</td>
<td>107 ± 19</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cs</td>
<td>88 ± 4</td>
<td>91 ± 2</td>
<td>97 ± 1</td>
</tr>
<tr>
<td>La</td>
<td>100 ± 5</td>
<td>N/A</td>
<td>83 ± 14</td>
</tr>
<tr>
<td>Ba</td>
<td>99 ± 2</td>
<td>N/A</td>
<td>94 ± 3</td>
</tr>
<tr>
<td>Ce</td>
<td>97 ± 4</td>
<td>101 ± 3</td>
<td>84 ± 11</td>
</tr>
<tr>
<td>Nd</td>
<td>100 ± 5*</td>
<td>N/A</td>
<td>90 ± 9</td>
</tr>
<tr>
<td>Sm</td>
<td>95 ± 2</td>
<td>100 ± 4</td>
<td>91 ± 10</td>
</tr>
<tr>
<td>U</td>
<td>100 ± 1</td>
<td>101 ± 2</td>
<td>90 ± 1</td>
</tr>
</tbody>
</table>

* number compared to literature value from Rosenberg et al (1980)

The concentrations of various elements were also compared to the certified values using zeta scores. Zeta scores are calculated based on the experimental concentration (X) and its standard deviation (µ(X)), and the certified value (X_a) along with the associated error of the certified value µ(X_a) according to equation 4.1.

$$\zeta = \frac{X - X_a}{\sqrt{\mu^2(x) + \mu^2(x_a)}}$$ (4.1)
Zeta scores of ± 1 are considered highly acceptable, while scores greater than ± 2 are generally seen as questionable. The zeta scores for the three reference materials are reported in Figure 5. All scores for QLO-1a had scores between ± 2, as did SDC-1, with the exception of Zr, which has already been discussed. NIST 278 had only one zeta score greater than 2 which was Sr with a score of -4.6. This is due to a low uncertainty for the certified value of Sr in NIST 278. Despite the high zeta score for this element, the recovery for Sr is 96% which is reasonable. This is an important result because accurate concentrations are needed for many elements that form insoluble fluorides, such as the lanthanides, in nuclear forensic analysis. Lanthanides especially are along the wing of the uranium fission curve and are necessary for peak-to-wing analysis, which provides information for the fission split analysis described by Moody et al[10].

![Zeta Score Chart](image)

**Figure 4.5:** Zeta scores for USGS QLO-1a Quartz Latite (blue), NIST 278 Obsidian Rock (orange) and USGS SDC-1 Mica Schist (grey)
The recovery of monitored elements agreed with the reported recovery from 3-hour open vessel fusion experiments conducted in PFA-ware at 230 °C[20]. The low temperature ABF fusions required a total method time of more than 6 hours per sample. The current ABF fusion method was completed in less than 30 minutes, with an additional 2 hours to heat the final solution if samples are to be analyzed immediately.

_Actinide Separation_

To simulate the actinide concentration in post detonation debris, an aliquot of the geological reference material was spiked with $^{239}$Pu and $^{242}$Pu, and then dissolved using the ABF fusion method described in section 3.5. At temperatures above 400 °C, plutonium can form a refractory mineral that is resistant to dissolution[10]. In order to ascertain whether the dissolution method could dissolve refractory Pu minerals, $^{239}$Pu was spiked onto the geological reference material, dried, and heated at 850 °C for 4 hours. The resulting sample was then spiked with $^{242}$Pu, dried, and dissolved using the fusion method discussed above. The U and Pu were then separated with TEVA/UTEVA extraction chromatography columns. As Table 2 shows (QLO-1a 850 °C), there is no significant change in recovery for Pu that was heated to 850 °C when compared to Pu that was spiked into the sample after heating, or between the Pu in the samples that were not heated prior to dissolution. Following filtration, the TEVA/UTEVA separation of U and Pu and ICP-MS analysis required 2-hours.
Table 4.2: U and Pu percent recoveries following ABF fusion and extraction chromatography (± indicates 1 STD, n=3)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>U-238</th>
<th>Pu-239</th>
<th>Pu-242</th>
</tr>
</thead>
<tbody>
<tr>
<td>QLO-1a</td>
<td>109 ± 13</td>
<td>99 ± 7</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>278</td>
<td>94 ± 2</td>
<td>97 ± 1</td>
<td>99 ± 1</td>
</tr>
<tr>
<td>SDC-1</td>
<td>96 ± 1</td>
<td>93 ± 2</td>
<td>94 ± 4</td>
</tr>
<tr>
<td>QLO-1a 850°C C</td>
<td>88 ± 6</td>
<td>92 ± 4</td>
<td>93 ± 9</td>
</tr>
</tbody>
</table>

*Irradiated uranium tracer*

A spike recovery standard containing $^{239}$Np, $^{97}$Zr, $^{97}$Nb, $^{99}$Mo, $^{99m}$Tc, $^{133}$I, $^{132}$I, $^{143}$Ce, and $^{149}$Pm was prepared by irradiation of a natural I standard. A sample of USGS QLO-1a was spiked and subsequently dissolved using the ABF fusion method. The spike recovery results are presented in Table 3.3.

Table 4.3: Recovery of various activation and fission products after ABF fusion and filtration (± indicates one standard deviation, assuming Poisson counting statistics)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Energy (keV)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{97}$Zr</td>
<td>743.41</td>
<td>112 ± 8</td>
</tr>
<tr>
<td>$^{97}$Nb</td>
<td>658.32</td>
<td>90 ± 7</td>
</tr>
<tr>
<td>$^{99}$Mo/$^{99m}$Tc</td>
<td>140.62</td>
<td>102 ± 13</td>
</tr>
<tr>
<td>$^{132}$I</td>
<td>667.85</td>
<td>33 ± 12</td>
</tr>
<tr>
<td>$^{133}$I</td>
<td>529.99</td>
<td>51 ± 6</td>
</tr>
<tr>
<td>$^{143}$Ce</td>
<td>293.4</td>
<td>102 ± 12</td>
</tr>
<tr>
<td>$^{149}$Pm</td>
<td>285.43</td>
<td>97 ± 11</td>
</tr>
<tr>
<td>$^{239}$Np</td>
<td>277.62</td>
<td>101 ± 1</td>
</tr>
</tbody>
</table>

Apart from the volatile iodine isotopes, the recovery of all radioisotopes was quantitative within error. In the future, the method should be evaluated with test-shot debris or, if available, a surrogate nuclear debris reference material. It is also of interest to couple this
dissolution method with the Rapid Analysis of Post-Irradiation Debris (RAPID) ion chromatography method developed by Roach et al [30].

4.5 Conclusions

The results demonstrate that high-temperature ABF fusion is capable of rapid dissolution of geologic materials with quantitative recovery of non-volatile fresh fission and activation products, as well as many naturally occurring elements. Limitations of the high temperature ABF fusion method included poor recovery of Zr in SDC-1 and reduced recovery of REEs in the presence of an iron containing precipitant. The REE recovery improved in SDC-1 when the final solution was heated and when the solution could sit for two days prior to filtration. The ABF fusion method was demonstrated to be compatible with the TEVA/UTEVA extraction chromatography separation of U and Pu. The total time required to dissolve samples, separate U and Pu, and analyze by ICP-MS was less than 4 hours and 30 minutes.

4.6 Acknowledgements

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4.7 References


Chapter 5:
Rapid dissolution of surrogate nuclear debris and analysis of rare earth elements using HPIC with ICP-MS and gamma ray spectroscopy

5.1 Preface

The work presented below explores the dissolution and analysis of surrogate nuclear debris, focusing specifically on rare earth elements (REE) in the material. Two high performance ion chromatography (HPIC) separation methods were developed over the course of this work. The first is an inline separation method that uses a binary pump HPIC coupled directly to an ICP-MS detector. This method was used to measure stable REE isotopes in solutions of dissolved geological material. The second method was done on a quaternary HPIC connected to a fraction collector. The column eluate was collected as fractions for subsequent analysis of fission product by gamma ray spectroscopy. This project was completed at the University of Missouri Research Reactor. Bradley, V. C. and Brockman, J. D. Rapid dissolution of surrogate nuclear debris and analysis of rare earth elements using HPIC with ICP-MS and gamma ray spectroscopy. Submitted to the journal *Talanta* on April 8th, 2022.

5.2 Introduction

Nuclear detonations at ground level produce fission products characteristic of the pre-detonation device. The shape of the fission product mass-yield is sensitive to the fissionable actinide and the neutron energy spectrum. Changes to the shape of the fission mass-yield are greatest at the wings relative to the peak and can be used to infer the relative fission contributions of $^{235}\text{U}$, $^{238}\text{U}$, and $^{239}\text{Pu}$ and the presence of 14 MeV neutrons[1, 2].
Isotopes of the light rare earth elements Nd, Sm, and Pm are considered to be useful fissiogenic monitors on the wing of the high mass-yield curve for post-detonation debris analysis[3].

Radionuclides with diagnostic value can be measured using mass spectrometry or gamma-ray spectroscopy. The light REEs are present intrinsically in the environment at low concentrations and nuclear debris analysis requires deconvolution of fission product nuclides from natural REEs and their activation products. Isotopic analysis by mass spectrometry is valuable for measurement of natural REEs and accuracy is improved by chemical separation of REEs from nearest neighbors to minimize isobaric and polyatomic interference. The REEs produced through fission or activation have relatively short half-lives and can often be measured by gamma-ray spectroscopy. Separation of fission products of interest reduces the gamma-ray spectrum complexity and lowers detection limits.

Prior to chromatography, post-detonation debris must be dissolved. Nuclear debris produced in an urban environment is expected to contain glassy minerals produced from terrestrial materials, concrete, steel and borosilicate glass[4, 5]. A robust sample dissolution method must be capable of dissolving refractory minerals, including silicates, and couple with ion chromatography. Dissolution methods currently in use have been developed for diagnostic analysis of weapons testing. These methods employ open vessels
using mixtures of HNO₃, HCl, HClO₄ and HF, include multiple evaporation steps and require several days to complete[2, 6, 7]. Modern dissolution methods of refractory minerals commonly employ high-pressure microwave digestion with HNO₃, HCl, and H followed by a secondary digestion with boric acid to sequester flouride[8]. An alternative to pressurized microwave digestion is fusion with ammonium bifluoride (ABF) [9-11]. Recently, our group has demonstrated that ammonium bifluoride (ABF) fusion is a viable digestion technique for surrogate nuclear debris samples and trinitite[12]. ABF fusion is relatively fast (reported dissolution times range from 2 to 8 hours), does not require hazardous HF acid or a microwave, and avoids an additional fluoride complexation step with boric acid[9, 10, 12]. The ABF fusion method has previously been shown to dissolve obsidian rock (NIST 278), quartz latite (USGS QLO-1a), mica schist (USGS SDC-1), Hawaiian basalt (USGS BHVO-2), dolerite (USGS DNC-1a), andesite (USGS AGV-2) [9-12].

This work describes a novel high pressure ion chromatography (HPIC) method that was developed for online REE separation with mass spectrometry analysis and off-line gamma-ray spectrometry. Ion exchange separation of REEs was first developed during World War II to separate REE fission products[13-15]. Early ion exchange methods were laborious and took many hours to complete[16]. Use of high-pressure ion chromatography systems were used to separate REEs by Campbell and Buxton in 1970[17]. Since then
HPIC REE separation methods have been applied to nuclear fuel[17-22] and environmental matrices[23, 24].

The most common ion exchange columns that have been reported for use in REE separations are mixed bed cation and anion exchange columns such as the Dionex CS5a and CG5a[20-25] and cation exchange columns like the Luna SCX[26]. Mixed bed columns, like CS5A, elute REEs from highest z to lowest by using α-hydroxyisobutyric acid_(α-HIBA) as the mobile phase, or from lowest to highest with an oxalic acid mobile phase[27]. Separation methods using oxalic acid, diglycolic acid (DGA), and water have been reported with separation times of 30 minutes with good resolution for light lanthanides, using quaternary pump HPLC systems[28]. Transition metals have been separated alongside lanthanides from environmental matrices using the CS5a column, through the addition of 2,6-pyridinedicarboxylic acid to the separation[29].

High performance ion chromatography (HPIC) can be coupled directly to an inductively coupled plasma mass spectrometer (ICP-MS) for transient signal analysis[24, 26, 27] or fractions can be collected from the column and analyzed individually for better accuracy and precision, particularly for isotope ratio analysis[28]. Uranium fission products have been measured through HPIC-ICP-MS[3] with ICP-MS instruments in radioactive laboratories. Pairing the HPIC to a fraction collector and counting separated
fractions by gamma-ray spectroscopy can also be used to quantify fission products and can be more sensitive for short half-life radionuclides.

In this work we explore ABF fusion and microwave digestion to dissolve several igneous United States Geological Survey (USGS) geological reference materials followed by REE separation using online and offline HPIC. USGS G-2 granite was chosen based on its quartz, plagioclase, and feldspar content[30] USGS QLO-1a quartz latite is a fine-grained silicate rock made up mainly of quartz and feldspar[31], AGV-2 andesite contains high amounts of sodium-rich plagioclase[32], and BHVO-2 basalt has high pyroxene content. These four reference materials contain refractory minerals formed from cooling lava containing iron, magnesium, silicates, calcium, and other elements similar to those found in an urban environment[33]. The novel HPIC method used a binary pump, inline HPIC-ICP-MS with a mixed bed Dionex CS-5a column. The gradient was composed of oxalic acid and DGA. An offline HPIC method with a fraction collector was developed to separate REE fission products into fractions for analysis by high purity germanium (HPGe) gamma detector. The offline method was also modified to allow for separation of U and Pu from the sample matrix. The method presented here can be applied to nuclear forensic analysis of stable and radioactive REE content in inorganic material.
5.3 Materials and Methods

Materials and Reagents

Ultrapure water with a resistivity of 18.2 MΩ was made with a milli-Q water purification system. Trace metals grade nitric acid (HNO₃), Hydrofluoric Acid (HF) and ammonium hydroxide (NH₄OH) were purchased from Fisher Scientific (Pittsburgh, PA). Diglycolic acid (DGA) (98%) and oxalic acid (99.9%) were purchased from Acros Organics (Fisher Scientific, Pittsburgh, PA). Trace metals basis boric acid was purchased from Sigma-Aldrich (St. Louis, MO). Labware was leached with 2% trace metal grade nitric acid for 12 hours and then rinsed with ultrapure water. The ammonium bifluoride fusions took place in 15 mL PFA tubes purchased from Savillex. Trace metal grade ammonium bifluoride (99.999%) was obtained from Sigma-Aldrich. Geological materials were acquired from the United States Geological Survey (USGS) standard reference materials (SRMs) and used to evaluate the effectiveness of the method. The SRMs used were G-2 granite, AGV-2 andesite, BHVO-2 basalt, and QLO-1a quartz latite. A calibration curve was made for REEs using Inorganic Ventures CMS-1 mixed lanthanide standard (Christiansburg, VA).

Fission product tracer production and modeling

A fission product tracer was produced at the University of Missouri Research Reactor (MURR) to separate fresh fission products. A 200 µL of a 1000 µg/g natural U
standard (Inorganic Ventures) was irradiated for 3 minutes in the Row 1 pneumatic tube irradiation position and then decayed for 16 hours before use. The activity of the fission products in the standard were measured using gamma-ray spectroscopy. The activities of the fission products in the sample and standard were decay corrected using the code ORIGEN 2.2[36].

Instrumentation

A dual-pump Perkin Elmer NexSAR inert HPLC was attached to a Perkin Elmer NexION 300x quadrupole for online sample analysis. The ICP-MS used a glass nebulizer and spray chamber. A Milestone Ethos Plus high-pressure microwave was used in microwave digestions.

For the offline analysis and fission product separation, a Perkin Elmer Flexar quaternary pump HPIC was attached to a BioRad fraction collector and placed inside a fume hood. Gamma spectroscopy was performed on a high purity germanium detector (HPGe) with 38% relative efficiency. The spectra were analyzed using Canberra Genie 2000.

Dissolution of SRMs

G-2 granite, AGV-2 andesite, BHVO-2 basalt, and QLO-1a quartz latite were dissolved via ammonium bifluoride fusion (ABF) using the method described by Hubley et. al[12]. Briefly, 50 µg of a SRM was combined in a 1:10 ratio with ammonium bifluoride
in a PFA vial with the cap loosely placed and heated on a hotplate at 230 °C for 60 minutes. Subsequently, 2 mL of concentrated HNO₃ was added and the solution was refluxed for 60 minutes with the cap off at 160 °C. The solution was then evaporated to dryness at 160 °C. 

The residue was dissolved in 2 mL of 8 M HNO₃ and heated at 120 °C for one hour, and finally was diluted to 50 mL with 2% HNO₃. An aliquot of this solution was diluted 1:3 in mobile phase A.

The same SRMs were also dissolved by microwave digestion (MWD). In this procedure, 200 µg of material was combined with 2 mL of concentrated HF and 2 mL of concentrated HNO₃ in a high-pressure microwave vessel. The microwave was run at 190 °C for 180 minutes. After it cooled, 23 mL of 4% w/v H₃BO₄ was added, and the microwave was run at 180 °C for 180 minutes. The boric acid is included to complex fluorine, forming tetrafluoroboric acid. This solution was diluted to 50 mL with 2% HNO₃, an aliquot of which was then diluted 1:11 in mobile phase A.

**Separation of REEs**

The Perkin Elmer NexSAR HPLC was fitted with a Dionex CS-5a 4x250 mm ion exchange column coupled with a CG-5a 4x50 mm guard column. Mobile phase A was 80 mM oxalic acid and mobile phase B was 36 mM DGA, both were buffered to a pH of approximately 4.5 with ammonium hydroxide. The gradient elution profile is shown in figure 5.1.
Figure 5. 1: Inline separation scheme for a binary pump HPIC-ICPMS

A four-point external calibration curve was made by diluting the mixed REE standard to concentrations such that the expected concentration of the sample was near the middle of the concentration range. An intermediate-concentration standard was analyzed after every three samples to correct for ICP drift during the analysis. The samples were analyzed over a 1-week time period.

Pu and U separation

An offline HPIC method was developed using a Perkin Elmer quaternary pump HPLC, which can make gradients with up to 4 mobile phases, placed in a fume hood and connected to a BioLogic fraction collector. The mixed REE standard was spiked with 10 ng of Pu-239. $^{239}_{\text{Pu}}$ was oxidized to Pu(VI) by adding 0.2 mmoles of KMnO$_4$ and left to
equilibrate for 12 hours. The gradient separation scheme was adjusted based on a separation reported by Wanna et al[27] to include an initial 5-minute flow of 1 M HNO₃, where An (VI) should elute.

![Quaternary Pump HPIC Gradient](image)

**Figure 5. 2:** offline actinide/REE separation scheme for a quaternary pump HPIC, where mobile phase A was 1 M HNO₃ B was H₂O, C was 80 mM oxalic acid and D was 36 mM DGA. Flow rate was 1 mL/minute.

To test the separation and recovery of REE fission products using the offline HPIC method with a gamma detector a fresh fission product tracer was utilized. A 50 µL aliquot of the irradiated U was diluted to 1 mL to geometrically match the collected fractions and used as a standard, another 50 µL aliquot was injected onto the HPIC column and separated using the offline method shown in figure 5.2. The fraction collector was used to collect 1 mL fractions every minute. These fractions, along with the unseparated standard were then
counted on a HPGe detector for 6 hours each. An ORIGEN 2.2 calculation was used to predict the activity of the REE fission products in the separated sample, and recovery was found based on these calculations.

5.4 Results and Discussion

Separation and Quantitation of REEs with the Nexsar Binary-pump HPIC

In this work, the dissolved samples were first diluted in 0.8 M oxalic acid and then injected onto the column, similar to work published by Roach et al[29]. Poor separations were achieved, especially for the higher matrix samples dissolved by microwave digestion. During optimization, the method was modified to dilute the dissolved sample with 80 mM oxalic acid (pH 4.5). A 50 µL aliquot of the diluted sample was loaded onto the analytical column for the separation and baseline separation of all REEs was achieved. The REEs are likely loaded as Ln-Oxalate\(^3^-\) complexes instead of Ln\(^3+\) cations. As the concentration of DGA is increased, the complexes convert to Ln-DGA\(^3^-\) since Ln-DGA complexes have higher stability constants than Ln-oxalate complexes[37], and are eluted from the column as DGA complexes. The difference in the DGA stability constants is higher for the heavy lanthanides than light lanthanides, so the DGA gradient improves the resolution of the later peaks. As the concentration of DGA in the mobile phase increased, the REEs were eluted from minute 6 to 20. With the Clarity v8.5 software, 8 isotopes could be monitored simultaneously during in each experiment. The nuclides \(^{143}\)Nd, \(^{147}\)Sm, \(^{153}\)Eu, \(^{157}\)Gd, \(^{159}\)Tb,
$^{163}$Dy, $^{165}$Ho, and $^{167}$Er were chosen for analysis. The chromatograms of the separation of USGS G-2 granite for both dissolution methods (ABF fusion and microwave digestion) are shown in figure 5.3. The resolution of the peaks was sufficient to measure each isotope without applying correction factors for isobars or polyatomic interferences.

In this work, only a binary HPIC pump was available for the in-line HPIC-ICP-MS experiment. The REE separation method from Bradley et al.[28] used four mobile phases, water, oxalic acid, DGA, and HCl. The samples were loaded in 2% HNO$_3$ and the DGA was not introduced to the gradient until minute 6. This separation took a similar amount of time but did not achieve total separation between Eu and Gd, and Ho and Tb were not monitored. The REE separation by Wanna et al.[27] was focused on resolving the early lanthanides and did not include DGA in the gradient. The gradient used 0.1 M oxalic acid, 0.3 M oxalic acid, and water, and had good separation for early lanthanides, but the heavy lanthanides were not separated from each other. This work demonstrates that baseline separation of all REEs can be achieved by loading the samples onto the column as anionic oxalates followed by addition of DGA to the gradient.
**Figure 5.3:** Chromatograph of REE separation in USGS G-2 Granite after dissolution through ABF fusion (A) and microwave digestion (B).
Quantitation was achieved through a 5-point external calibration curve using a mixed lanthanide standard with concentrations that bracketed the concentrations of the sample REEs. The linear regression line for each element had correlations ≥ 0.999. A midpoint standard was analyzed after every 4 separations and used to correct for instrument drift over the course of the analysis. The REE concentrations obtained from external calibration were compared to reference values from the USGS. Most of the REE recovery for the SRMs were between 90 and 110 %, although Er recovery ranged from 65 to 138% (table 5.1). Taking uncertainty of both the measured concentrations and reference concentrations into consideration, zeta scores were calculated using the average and uncertainty of the measured concentration (X and µx) and the reference concentration and uncertainty (Xa and µxa) (equation 5.1).

\[ \zeta = \frac{X - X_a}{\sqrt{\mu^2(X) + \mu^2(X_a)}} \]  

(Z5.1)

Zeta scores are used to compare two values when both have associated uncertainty. If the score is \(\leq \pm 2\) the measured value is considered acceptable, scores \(\geq \pm 3\) are seen as questionable[39]. Zeta scores were all below \(\pm 2\) with the exception of the ABF fusion concentration of Er in QLO-1a and AGV-2. The overestimation of Er in these samples could be for a number of reasons. First, the USGS recommended amount of starting material to ensure a representative sample is 200 mg, while in this fusion method only 50 mg of material was used. Secondly, the USGS values for Er in these materials were informational values, and a range of concentrations have been reported in the literature for Er, which has been shown to be dependent on dissolution method[40-43]. There was not a significant difference in the recovery for the samples dissolved through ABF fusion vs
those dissolved through microwave digestion, showing that the HPIC method is compatible with both digestions, and that ABF fusion is comparable to microwave digestion.

**Table 5.1:** recovery from 4 USGS reference materials dissolved 2 ways, through ammonium bifluoride fusion (ABF) and microwave digestion (uncertainty 2σ of triplicate samples)

<table>
<thead>
<tr>
<th>QLO-1a</th>
<th>USGS Concentration (µg g⁻¹)</th>
<th>ABF Fusion</th>
<th>Microwave Digestion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (µg g⁻¹)</td>
<td>% Recovery</td>
<td>Zeta</td>
</tr>
<tr>
<td>Nd</td>
<td>23 ± 2</td>
<td>24 ± 2</td>
<td>104</td>
</tr>
<tr>
<td>Sm</td>
<td>4.9 ± 0.2</td>
<td>4.7 ± 0.3</td>
<td>97</td>
</tr>
<tr>
<td>Eu</td>
<td>1.4 ± 0.1</td>
<td>1.3 ± 0.03</td>
<td>91</td>
</tr>
<tr>
<td>Gd</td>
<td>-</td>
<td>4.3 ± 0.2</td>
<td>n/a</td>
</tr>
<tr>
<td>Tb</td>
<td>0.71 ± 0.07</td>
<td>0.61 ± 0.05</td>
<td>86</td>
</tr>
<tr>
<td>Dy</td>
<td>3.8 ± 0.3</td>
<td>4.2 ± 0.1</td>
<td>110</td>
</tr>
<tr>
<td>Ho</td>
<td>-</td>
<td>0.80 ± 0.03</td>
<td>n/a</td>
</tr>
<tr>
<td>Er</td>
<td>2.2 ± 0.1</td>
<td>3.1 ± 0.1</td>
<td>135</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>G-2</th>
<th>USGS Concentration (µg g⁻¹)</th>
<th>ABF Fusion</th>
<th>Microwave Digestion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (µg g⁻¹)</td>
<td>% Recovery</td>
<td>Zeta</td>
</tr>
<tr>
<td>Nd</td>
<td>53 ± 8</td>
<td>51 ± 6</td>
<td>96</td>
</tr>
<tr>
<td>Sm</td>
<td>7.2 ± 0.6</td>
<td>6.8 ± 0.4</td>
<td>94</td>
</tr>
<tr>
<td>Eu</td>
<td>1.4 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>89</td>
</tr>
<tr>
<td>Gd</td>
<td>4.1 ± 0.8</td>
<td>3.9 ± 0.1</td>
<td>95</td>
</tr>
<tr>
<td>Tb</td>
<td>0.48 ± 0.07</td>
<td>0.40 ± 0.03</td>
<td>83</td>
</tr>
<tr>
<td>Dy</td>
<td>2.5 ± 0.5</td>
<td>2.1 ± 0.1</td>
<td>89</td>
</tr>
<tr>
<td>Ho</td>
<td>0.37 ± 0.02</td>
<td>0.31 ± 0.02</td>
<td>84</td>
</tr>
<tr>
<td>Er</td>
<td>1.2 ± 0.3</td>
<td>1.3 ± 0.4</td>
<td>110</td>
</tr>
<tr>
<td>AGV-2</td>
<td>USGS Concentration (µg g⁻¹)</td>
<td>ABF Fusion Concentration (µg g⁻¹)</td>
<td>ABF Fusion % Recovery</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------</td>
<td>-----------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Nd</td>
<td>30 ± 2</td>
<td>33 ± 2</td>
<td>109</td>
</tr>
<tr>
<td>Sm</td>
<td>5.7 ± 0.3</td>
<td>5.9 ± 0.3</td>
<td>103</td>
</tr>
<tr>
<td>Eu</td>
<td>1.5 ± 0.1</td>
<td>1.61 ± 0.03</td>
<td>104</td>
</tr>
<tr>
<td>Gd</td>
<td>4.7 ± 0.3</td>
<td>4.7 ± 0.3</td>
<td>100</td>
</tr>
<tr>
<td>Tb</td>
<td>0.64 ± 0.04</td>
<td>0.61 ± 0.02</td>
<td>95</td>
</tr>
<tr>
<td>Dy</td>
<td>3.6 ± 0.2</td>
<td>3.5 ± 0.2</td>
<td>98</td>
</tr>
<tr>
<td>Ho</td>
<td>0.71 ± 0.2</td>
<td>0.64 ± 0.02</td>
<td>91</td>
</tr>
<tr>
<td>Er</td>
<td>1.8 ± 0.2</td>
<td>2.31 ± 0.01</td>
<td>129</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BHVO-2</th>
<th>USGS Concentration (µg g⁻¹)</th>
<th>ABF Fusion Concentration (µg g⁻¹)</th>
<th>ABF Fusion % Recovery</th>
<th>ABF Fusion Zeta</th>
<th>Microwave Digestion Concentration (µg g⁻¹)</th>
<th>Microwave Digestion % Recovery</th>
<th>Microwave Digestion Zeta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>25 ± 2</td>
<td>22.7 ± 5</td>
<td>91</td>
<td>-1</td>
<td>23 ± 2</td>
<td>94</td>
<td>-0.6</td>
</tr>
<tr>
<td>Sm</td>
<td>6.2 ± 0.4</td>
<td>5.9 ± 0.4</td>
<td>94</td>
<td>-0.6</td>
<td>6.1 ± 0.3</td>
<td>98</td>
<td>-0.2</td>
</tr>
<tr>
<td>Eu</td>
<td>2.07 ± 0.07</td>
<td>1.9 ± 0.3</td>
<td>93</td>
<td>-0.5</td>
<td>2.03 ± 0.05</td>
<td>98</td>
<td>-0.5</td>
</tr>
<tr>
<td>Gd</td>
<td>6.3 ± 0.2</td>
<td>6.16 ± 0.03</td>
<td>98</td>
<td>-0.7</td>
<td>6.0 ± 0.3</td>
<td>95</td>
<td>-0.9</td>
</tr>
<tr>
<td>Tb</td>
<td>0.9*</td>
<td>0.84 ± 0.05</td>
<td>94</td>
<td>-1</td>
<td>0.903 ± 0.008</td>
<td>100</td>
<td>0.4</td>
</tr>
<tr>
<td>Dy</td>
<td>5.2 ± 0.2</td>
<td>5.3 ± 0.4</td>
<td>101</td>
<td>0.1</td>
<td>5.28 ± 0.06</td>
<td>101</td>
<td>0.3</td>
</tr>
<tr>
<td>Ho</td>
<td>1.04 ± 0.04</td>
<td>0.91 ± 0.06</td>
<td>88</td>
<td>-1</td>
<td>0.97 ± 0.03</td>
<td>93</td>
<td>-0.1</td>
</tr>
<tr>
<td>Er</td>
<td>2.5 ± 0.2</td>
<td>2.6 ± 0.4</td>
<td>102</td>
<td>0.1</td>
<td>2.43 ± 0.09</td>
<td>96</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

The RAPID method published by ORNL used isotope dilution to find concentrations of REEs rather than external calibration, and though they only looked at the recovery of four rare earth elements (Nd, Sm, Eu, and Gd) they found recoveries between 99 and 103%, with uncertainties ranging from 2% to 16%[29], and did not dilute samples
in their initial mobile phase prior to separation[29]. External calibration tends to have higher uncertainty than isotope dilution mass spectrometry, which is a primary analysis method. Despite the external curve, the measurement uncertainty found with this method was comparable to that found with IDMS.

**Limits of Detection**

Limits of detection (LOD) were found using equation 5.2, where BEC is the blank equivalent concentration found from the y-intercept of the calibration curve. The instrument LOD, referring to the minimum detectible amount of analyte injected onto the column, was found, as was the method LOD, being the minimum detectible concentration in the starting material if analyzed through this method[44].

\[
\text{LOD} = \text{BEC} + 3\text{sd blank}
\]

(5.2)

The method LOD was found to be between 0.36 and 3.8 ng REE per g of geological material. This was independent of the dissolution method, as both methods had the same final dilution factor. The instrument detection limit ranged from 0.1 to 1.2 pg of REE per g of sample injected into the column. These LODs are similar to those reported by other online HPIC-ICP-MS methods[27-29].

The limit of quantitation (LOQ) is the minimum quantifiable concentration of an analyte. The LOQ is calculated through equation 5.3[44].
Table 5.2: detection limits for REEs in the final separated solution and the undissolved geological reference material

<table>
<thead>
<tr>
<th>Method LOD (ng g(^{-1}))</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Er</th>
<th>Tb</th>
<th>Ho</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method LOQ (ng g(^{-1}))</td>
<td>12</td>
<td>6.0</td>
<td>1.5</td>
<td>9.9</td>
<td>2.6</td>
<td>5.2</td>
<td>1.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Instrument LOD (pg g(^{-2}))</td>
<td>1.2</td>
<td>0.60</td>
<td>0.15</td>
<td>1.0</td>
<td>0.26</td>
<td>0.52</td>
<td>0.12</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*Pu and U separation*

The updated separation method (described in section 5.3) on a quaternary HPIC connected to a fraction collector was used to separate Pu and U from dissolved geological reference material. Adapting a method by Wanna et al.[27], the U and Pu were separated on a quaternary pump HPIC using a 1 M nitric acid gradient followed by water to flush the acid from the system prior to introduction of oxalic acid gradient for REE separation. Pu eluted early in the separation, between minutes 3 and 4. In 1 M nitric acid, Pu (VI) is present in solution as PuO\(_2^2^-\) and interacts with the anion exchange sites on the ion exchange column. After triplicate analyses, the Pu recovery was 97.4 ± 0.3 %, and showed good separation from the matrix. The addition of oxidating agents and the nitric acid portion of the separation did not seem to impact the REE resolution drastically, though it difficult to know for certain since 1 mL fractions were collected with this method.
Figure 5. 4: U and Pu separation with 1 mL fractions

Separation of U fission products

The same separation method was used for an irradiated U standard. The total number of fissions produced in the tracer was estimated to be $7.3 \times 10^8$. Low level fission products can be difficult to detect in irradiated natural uranium, since the majority of activity in the sample comes from the activation product $^{239}$Np. Separating the high activity isotopes like $^{239}$Np from the REEs allows for more accurate measurement of their activity. The separations were collected in 1 mL fractions every minute. The fractions were counted for 6 hours using an offline HPGe gamma detector. The results were compared to the geometry matched standard and corrected for decay using ORIGEN 2.2 in Table 5.3.
Separation of the REE fission products led to less complicated gamma spectra and led to a 2 order of magnitude reduction of signal at lower energies.

Figure 5.5: log of signal from a gamma ray spectra of a 6-hour count of the unseparated fraction (A) and the Ce-containing fraction (B)
The recovery of fission products was reasonable within the measurement uncertainty of the gamma spectrum, which is higher with low activity levels and long count rates. The large fraction volumes (1 mL) meant that there was not complete resolution between the fission products of interest, however complete separation from higher activity isotopes such as $^{99}$Mo, $^{131}$I, and $^{239}$Np, which have a greater impact on background levels and peak uncertainty, was achieved using this method.

**Table 5.3**: recovery and LOD of REE fission products from irradiated U ($\pm$ uncertainty) with the recovery calculated from the measured standard corrected for ingrown isotopes using MNCP-ORIGEN calculations

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Gamma Energy</th>
<th>Recovery (%)</th>
<th>LOD (Bq)</th>
<th>LOD (Bq g&lt;sup&gt;-1&lt;/sup&gt; sample)</th>
<th>LOD (pg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-140*</td>
<td>1596</td>
<td>71 ± 5</td>
<td>0.6</td>
<td>12</td>
<td>0.0006</td>
</tr>
<tr>
<td>Ce-141</td>
<td>145</td>
<td>77 ± 6</td>
<td>4</td>
<td>90</td>
<td>0.08</td>
</tr>
<tr>
<td>Nd-147</td>
<td>91</td>
<td>81 ± 9</td>
<td>30</td>
<td>680</td>
<td>0.2</td>
</tr>
<tr>
<td>Pm-151</td>
<td>718</td>
<td>114 ± 18</td>
<td>4</td>
<td>90</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Minimum detectable fissions were found based on the LOD equation above (equ 3) using the standard deviation of the background of the gamma spectrum and converted to minimum number of fissions based on ORIGEN fission split data. The instrument LOD in pg/g loaded onto the column is shown above. The detection limit for HPGe gamma spectroscopy varies widely between the isotopes monitored, based on the noise of the spectrum at the location of the peak as well as the half-life of each isotope and the yield of the gamma energy. LODs determined for REEs detected by ICP-MS ranged from 0.1 to 1
pg g\(^{-1}\), which are considerably higher than the 0.0006 to 0.2 pg g\(^{-1}\) LODs found in the gamma spectroscopy measurement, although long count times were required.

5.5 Conclusions

An inline HPIC-ICPMS method was developed for the separation of REEs from a matrix of dissolved geological material that utilizes a mixed-bed ion exchange column and diglycolic acid and oxalic acid mobile phases. Baseline separation was achieved for monitored isotopes. Measured REE concentration showed good agreement with USGS reference values, with zeta scores less than ± 2 for most elements. This method worked with both microwave digestion and ABF fusion. An offline HPIC-fraction collection method was developed to separate REE and An (VI) in surrogate post-detonation debris containing actinides and fission products. Irradiated U was separated, and fractions were measured on an HPGe gamma detector. REE fission product recovery was found to be 70 to 110% when compared to an unseparated portion of the standard. The methods developed successfully separated and quantified REEs in a variety of matrices.
5.6 References


Chapter 6: Concluding Remarks

Nuclear forensic analysis is a field of analytical chemistry that focuses specifically on analyzing signatures of nuclear material for criminal investigation. Nuclear forensic signatures include trace elements, such as rare earths, that can be used for origin assessment, isotope ratio analysis, particularly of uranium and plutonium. Uranium isotope ratios that deviate from natural indicates enrichment activities. The presence of plutonium indicates irradiation of uranium. Samples for nuclear forensic analysis are often urgent, and therefore must be analyzed quickly, with good accuracy and precision. Robust methodologies must be developed for analysis of samples from potential nuclear scenarios with suitable speed, accuracy, and precision. In this dissertation methods were developed to analyze uranium isotope ratios from solid particles on the surface of environmental swipe samples, to quantify rare earth impurities in uranium ore concentrates, to rapidly dissolve inorganic material using ammonium bifluoride and subsequently quantify the rare earth concentration in said material by separations with high performance ion chromatography.

In chapter two, direct isotope ratio analysis of solid uranium particulates on cotton swipes was achieved using a solution-based microextraction technique, coupled to a quadrupole inductively coupled plasma mass spectrometer (ICP-MS). This microextraction-ICP-MS methodology provides rapid isotopic analysis which could be applicable to nuclear safeguards measurements. Particulates of uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$·6H$_2$O) and uranyl fluoride (UO$_2$F$_2$) were successfully extracted, and $^{234}$U/$^{238}$U, $^{235}$U/$^{238}$U, and $^{236}$U/$^{238}$U isotope ratios were determined. For UO$_2$(NO$_3$)$_2$·6H$_2$O,
the measured isotope ratios had a % relative difference (% RD) from the reference isotope ratios of 0.97, 1.0, and 7.3% for $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$, respectively. The % RD of the UO$_2$F$_2$ isotope ratios were 1.9 and 0.60% for $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$, respectively. The preliminary limits of detection were determined to be 0.002, 0.4, and 60 pg for $^{234}\text{U}$, $^{235}\text{U}$ and $^{238}\text{U}$, respectively. This chapter demonstrates that microextraction ICP-MS is a rapid and sensitive method that could directly determine uranium isotope ratios of UO$_2$(NO$_3$)$_2$·6H$_2$O and UO$_2$F$_2$ particulates on cotton swipes without the need for lengthy, expensive sample preparations.

Uranium ore concentrate (UOC) is the product of dissolving and concentrating uranium from uranium-bearing ores. The concentration of various trace impurities, including rare earth elements, is a location-specific signature that can be used for origin attribution. In chapter 3, a method to separate and quantify rare earth elements in UOCs was developed. To reduce isobaric interferences, separation of the REE from the uranium matrix was achieved by high performance ion chromatography (HPIC), and the isotopic determinations were measured by ICP-MS. After separation, the target analytes were analyzed in two different modalities. For high precision analysis, the separated analytes were collected and measured by ICP-MS in an “offline” fashion. For a rapid approach, the separated analytes were sent directly into an ICP-MS for “online” analysis. These methods have been demonstrated to accurately quantify the REE content in a well characterized UOC materials.

Post-detonation debris will often consist of an inorganic matrix, and rapid, quantitative dissolution is necessary to accurately measure trace element composition. In chapter 4, high-temperature ammonium bifluoride (ABF) fusions were evaluated for
potential use in rapid dissolution of post-detonation nuclear debris. The developed dissolution method was simple, requiring only a hotplate or hotblock, and filtered samples were available for ICP-MS analysis or radiochemical separation within 150 minutes, and was found to have high (> 90%) recovery for many isotopes of interest in nuclear forensics applications. U and Pu in the dissolved material was separated using TEVA and UTEVA extraction chromatography columns, a process which resulted in > 90% recovery. An irradiated U tracer was spiked into the material prior to dissolution and analyzed for recovery of major fission products and $^{239}$Np. Besides radioiodine isotopes, a volatile element, the radionuclides that were monitored showed recovery of > 90%.

In chapter 5, the application of HPIC-ICPMS analysis of REEs was explored in materials dissolved by ABF and compared to material dissolved through the more traditional high pressure microwave digestion. The separation method used in chapter three was adapted for a binary pump HPIC system which could only contain up to two eluents. The separations were successful after the samples were diluted in the initial eluent. This separation was also adapted to include an initial separation of U and Pu in 1 M nitric acid and was applied to a separation of fission products in a uranium matrix.

This work describes many successful analysis techniques that can be applied for nuclear forensic analysis. It mainly focused on trace element analyses, isotope ratio measurements, and uranium-bearing nuclear materials through the use of quadrupole and sector-field ICP-MS. The methods developed above have been shown to be rapid and effective measurement techniques that would be useful in nuclear forensic applications.
Chapter 7:  
Future Work

The work presented here has many opportunities to be improved and added to. The microextraction system so far has been used to measure particles of uranyl nitrate and uranyl fluoride. Many uranium particles found in uranium processing facilities are in the form of UO$_2$ and U$_3$O$_8$. These can be slightly more difficult to dissolve than uranyl nitrate and uranyl fluoride and may require a different extraction solvent. A future study could be done on the extraction of uranium oxide particles with various solvents including HNO$_3$-HF of varying concentrations, a solution of ammonium bifluoride, which has been shown to dissolve uranium oxides in the past[1], and HCl solutions of various concentrations. Following successful extraction of uranium oxide, plutonium particles can be added to the swipe to test the extraction of a combination of U and Pu. $^{239}$Pu can be difficult to measure in the presence of uranium, especially when uranium is much more abundant, because $^{238}$U$^1$H has the same nominal mass. An extraction column such as TEVA could be added inline between the microextraction system and the ICP to separate U from Pu prior to analysis. Reaction cell triple quadrupole ICP-MS has been explored to shift the U up in mass to UO by reactions with various oxygen-containing gas like O$_2$, CO$_2$, and N$_2$O[2-6]. By connecting the microextraction system to a triple quadrupole ICP-MS or a MC-ICP-MS with a collision cell, U and Pu could both be extracted from the swipe surface and analyzed directly, without a separation step.

The work described in chapter 5 also has many opportunities for expansion. The exact mechanism of the REE loading and elution from the column is not well understood. This can be explored by performing the same separation while using different ion exchange
columns. When monitoring the analyte signal over the course of a separation on a cation exchange column, if the REE signal elutes at the solvent front, it proves the REE are not loaded onto the column as Ln$^{3+}$ cations, but rather are already in their anionic form prior to injection on the column. If the REE are retained by the column, then there is some cationic binding occurring between the lanthanides and the stationary phase. As no one else has diluted the sample in oxalic acid prior to column loading, it is unknown whether the REE analytes are initially bound to the column as Ln$^{3+}$ species or as Ln-oxalate$^{3-}$ species. The best way to explore the initial loading speciation is repeat the separation on single-bed cation columns and anion columns and monitor when the analytes elute from the column, as was done by Bruzzonetti et al. when exploring lanthanide loading without adding oxalic acid to the sample pre-injection[7, 8].

Nd is an especially important element for nuclear forensics as well as age-dating applications. Nd isotope ratios have been shown to be useful for provenance assessment of uranium bearing materials like UOCs[9]. Isotope ratios of Nd, along with Sm, are also used in chronometry studies[10]. Because these applications rely on isotope ratio measurements, they require Nd to be completely separated from possible isobaric interferences from Ce and other near-REEs. The separation between Nd and Ce could be improved to create even better resolution between the two peaks by altering the gradient of the mobile phase. Higher resolution of the Ce-Nd separation would lead to better Nd isotope ratio measurements for age dating or fission mass-split analysis.

Additionally, after adjusting the mobile phase gradient to optimize the resolution of the Nd peak, the Nd isotope fission yield can be explored as a monitor of neutron energy. This would involve irradiating a uranium solution in different locations in the reactor. Cd
has a high thermal neutron absorption cross section but has little absorption in the
epithermal and fast region, essentially creating a neutron energy filter. The reactor core
has a higher abundance of fast neutrons, and by enclosing the sample in Cd thermal
neutrons would be blocked from reaching the sample. Measuring Nd isotope fission yield
from uranium solutions irradiated by only epithermal and fast neutrons to those irradiated
by all neutron energies present in the reactor, the fission yield from just thermal neutrons
can be isolated.

Finally, the separation of fission products in geological material could be explored
further. Ideally the irradiated U solution would be spiked into geological material prior to
dissolution, to trace the recovery of fission products throughout the entire method. The
fractions would be collected and analyzed with gamma spectroscopy to ascertain the loss
of analyte over the course of the whole analysis, from ABF fusion through separation.
References


Appendix A:
Optimization of HPIC Separation Method

A.1 Separation of lanthanides in inorganic reference material

Lanthanides occur along the wing of the \(^{235}\text{U}\) fission split curve. When the concentration of lanthanides is compared to isotopes that occur at the peak of the curve, such as \(^{137}\text{Cs}\), it can provide information about the type of nuclear weapon or nuclear material[1].

A.2 Methods:

An offline high-performance ion chromatography (HPIC) method with fraction collection was developed to separate lanthanides in inorganic reference material that has been dissolved with ammonium bifluoride fusion, based on a separation developed by Roach et al. at Oak Ridge National Laboratory[2].

Optimization of the Separation of Rare Earth Elements through Ion Exchange Chromatography

A separation scheme by Bradley et al (2020) was optimized with regards to mobile phase pH, concentration, and flow rate, as well as mobile phase gradient[3].

\textit{pH of mobile phase}

Three separations were done, with the oxalic acid and diglycolic acid mobile phases, buffered with ammonium hydroxide (NH\(_4\)OH) buffered to pH 4, 4.5 and 5 (figure 1).
Figure A. 1: REE separation with three different mobile phase pH
The change in pH of the mobile phase caused a shift in elution time of the analytes, but did not appear to have an impact on the separation factor, therefore it was decided to use pH 4.5 going forward.

**Optimization of Flow Rate**

Three flow rates were studied to determine which would provide the best separation. The flow rates studied were 0.8 mL min\(^{-1}\) (approximately 1200 psi), 1 mL min\(^{-1}\) (~1600 psi), and 1.2 mL min\(^{-1}\) (~1900 psi). The results of these separations are shown in figure A.2.
Figure A. 2: REE separation at 3 different flow rates

The lowest flowrate (0.8 mL min\(^{-1}\)) appeared to cause some peak broadening, particularly among the heavy REEs (eluted later in the separation). The fastest flowrate (1.2 mL min\(^{-1}\)) appeared to cause a slight decrease in separation factors, particularly for the mid-mass REEs, and therefore 1 mL min\(^{-1}\) was chosen as the optimal flowrate.

Optimization of Mobile Phase Concentration

0.05 M, 0.1 M, and 0.3 M Oxalic acid and Diglycolic acid (DGA) were examined to determine the optimum mobile phase concentration, as shown in figure A.3.
The highest concentration, 0.3 M did not give a separation of the REEs. It did however separate the REEs from thorium (pale blue, eluted between minutes 16 and 17), which may be useful in the future. The lowest concentration (0.05 M) appeared to have a slight tailing effect for some of the REEs. Based on this, 0.1 M DGA and Oxalic acid were chosen as the optimum mobile phase concentration for this separation.

**Figure A. 3:** REE separation with 3 mobile phase concentrations
A.3 Results

The final separation gradient can be seen in figure A.4. The final flow rate was 1 mL/min, with mobile phase concentrations of 0.1 M, and mobile phase pH of approximately 4.0.

![REE separation Gradient](image)

**Figure A. 4:** The HPIC mobile phase gradient

The separation gradient was further adjusted to be used with a hyphenated HPIC-ICP-MS system with a binary pump system that could only utilize two mobile phases. This was accomplished by decreasing the concentration of oxalic acid and DGA and eliminating the H₂O eluent.
A.4 References


Appendix B:
List of Abbreviations

ABF: Ammonium bifluoride
AC: Alternating current
amu: Atomic mass units
α-HIBA: α-hydroxyisobutyric acid
BSE: Backscatter electron
CRM: Certified reference material
DC: Direct current
DGA: Diglycolic acid
DU: Depleted uranium
EP: External Precision
ES: Environmental sampling
ESA: Electrostatic analyzer
FT-TIMS: Fission track thermal ionization mass spectrometry
GC: Gas chromatography
GUM: Guide to the Expression of Uncertainty in Measurement
HEU: High-enriched uranium
HPGe: High purity germanium
HPIC: High performance ion chromatography
HPLC: High performance liquid chromatography
IAEA: International Atomic Energy Association
IC: Ion Chromatography
ICP-MS: Inductively coupled plasma-mass spectrometry
IDMS: Isotope dilution mass spectrometry
IP: Internal Precision
IRMM: Institute for reference materials and measurements
KED: Kinetic energy discrimination
LA: Laser ablation
LC: Liquid chromatography
LEU: Low enriched uranium
LG: Large geometry
Ln: Lanthanide
LOD: Limit of detection
LOQ: Limit of quantification
MC-ICP-MS: Multicollector inductively coupled plasma mass spectrometry
NIST: National Institute of Standards and Technology
NPT: Treaty on the Non-Proliferation of Nuclear Weapons
NU: Natural uranium
NWAL: Network of Analytical Laboratories
PEEK: Poly ether ether ketone
PFA: Perfluoroalkoxy
PTFE: Polytetrafluoroethylene
RAPID: Rapid Analysis of Post-Irradiation Debris
REE: Rare earth element
RF: Radiofrequency
SEM: Scanning electron microscope
SIMS: Secondary ion mass spectrometry
SFC: Supercritical fluid chromatography
SRM: Standard Reference material
SSI: Stable sample introduction
TE: Total evaporation
TIMS: Thermal ionization mass spectrometry
TOF: Time of flight
UOC: Uranium ore concentrate
USGS: United States Geological Survey
XRF: X-ray fluorescence
% RD: Percent relative difference
VITA

Veronica was born in South Bend, Indiana in 1996. She attended Earlham College in Richmond Indiana from 2014 to 2018. While there she participated in archaeometry research to determine trace elements in ancient Chinese pottery sherds and attended the Nuclear Chemistry Summer School program sponsored by the Department of Energy. She graduated with departmental and college honors with a Bachelor of Arts in Chemistry in May 2018. In August of 2018 Veronica began graduate school at The University of Missouri in Columbia, where she joined Dr. John Brockman’s research group to earn her PhD in Chemistry, with a focus on radioanalytical chemistry. While there she completed an internship at Oak Ridge National Laboratory.