THESIS

ISOLATION OF REACTOR-BORNE NEPTUNIUM USING ION SPECIFIC EXTRACTION

CHROMATOGRAPHY RESINS AND DETECTION BY GAMMA SPECTROSCOPY

Submitted by

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ABSTRACT

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Although actinides are the most informative elements with respect to the nature of a

nuclear accident, plutonium analysis is complicated by the background created by fallout from

nuclear explosions. Therefore, ^{239}Np, a short-lived actinide ($T_{1/2}$ = 2.4 d) that emits several

gamma rays, is proposed herein as a suitable proxy. The most prominent photopeaks from ^{239}Np

are at 106 keV, 228 keV, and 278 keV. However, the 106 keV and 228 keV photopeaks of ^{239}Np

are also characteristic of ^{129m}Te and ^{132}Te, volatile fission products with half-lives of 33.6 days

and 3.2 days, respectively. Although not as pronounced, there is also some spectral interference

of the 278 keV peak with the 284 keV peak of ^{131}I. The aim of this study was to screen the

available ion specific resins provided by Eichrom Technologies, LLC, for the highest possible

recovery and isolation of trace amounts of ^{239}Np from samples with large amounts of fission and

activation products such as radiocesium, ^{131}I, and ^{129m}Te. The investigated environmental media

for these separations were aqueous solutions (simulating rainwater) and soil.

Aqueous solutions containing ^{239}Np and volatile radionuclides were filtered through

UTEVA, Actinide, RE, and TRU Eichrom® resin columns to ascertain the most effective means

of isolating ^{239}Np from other fission and activation products for detection. This was followed up

with isolation of ^{239}Np from a soil matrix. The resins most effective for eluting ^{239}Np from

aqueous solution were UTEVA and RE (90±13% and 50±7%, respectively, calculated via the

278 keV peak yield). Isolation of ^{239}Np from soil using these columns was found achievable

only by washing out the entire ^{239}Np-loaded stationary phase from the resin columns with acetone. This suggests that soil components can contribute to the formation of organometallic complexes within the resin matrix that enhance the retention of tetravalent neptunium.

Analysis of the tellurium, cesium, and iodine content in eluates, washing solutions, and resins was conducted. Substantial fission product exclusion from eluates was found for TRU resins, RE resins, and UTEVA resins, although exclusion varied by the eluent used. In conclusion, the RE and UTEVA resins with HNO$_3$ as a loading solution and eluent provide the best recovery of ^{239}Np from rainwater samples while suppressing volatile radionuclides. Separation of neptunium from volatile radionuclides in soil requires further investigation, although we have demonstrated that the techniques used herein are effective at extracting neptunium from a soil matrix for detection by gamma spectroscopy.

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INTRODUCTION

Background

Following a nuclear event, such as a nuclear explosion or the meltdown of a core at a nuclear power plant, there is a spectrum of radionuclides released. Many of them are easily quantified and reported to the public (e.g., ^{134,137}Cs, ^{131}I, ^{132}Te). However, these radionuclides do not reveal the ultimate causes and chronology of the nuclear event.

The most recent renowned nuclear events that caused widespread contamination by radioactive material are the nuclear accidents of Chernobyl (1986) and Fukushima (2011). These events both resulted in the release of those aforementioned radionuclides. The total releases, excluding noble gases, from the Chernobyl power plant amounted to more than an order of magnitude greater than those releases from Fukushima Dai-Ichi [1]. The actinides, especially uranium, neptunium, and plutonium, provide a clearer picture of the severity of the meltdown, including temperatures achieved within the reactor core and conditions of the pressure vessels and containment units. Release of actinides into the environment signifies core meltdown and release of nuclear fuel. Release of radiocesium, iodine, and tellurium could be indicative of cladding failure; temperatures associated with this release range from 700°C – 1100°C. Temperatures associated with actinide release from the fuel exceed 2400°C [2] [3]. Table 1 lists stages of core damage and the corresponding radionuclides that are released. In comparison to Chernobyl's release of more than 2.6 PBq of plutonium, only 2.7×10^{-4} PBq of plutonium have been reported released from Fukushima [1]. Chernobyl released 1.4% of its plutonium core inventory [4], whereas Fukushima released approximately five orders of magnitude less ($\sim 2.5 \times 10^{-5}$%) of its plutonium core inventory [5]. These numbers reflect the damages incurred to

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the Chernobyl reactor, including the steam explosions, graphite fire, and overall damage to the reactor building's integrity. In contrast, the failure of the cooling systems at Fukushima resulted in the meltdown of the nuclear fuel without compromising the safety installations (containment) of the reactors. Consequently, actinide releases by the Chernobyl reactor far exceeded those of the Fukushima reactors [1] [5] [6] [7].

Table 1: Radionuclide Releases During Stages of Fuel Damage.

Fuel Cladding Temperature	Radionuclides Released	Core Condition
>700°C	Noble gases: Xe, Kr Halogens: I, Br Alkali Metals: Cs, Rb Others: Te, Sb, Se	Cladding failure
>1600°C	Noble Metals: Ru, Rh, Pd, Mo, Tc, Co Others: Ba, Sr	Grain boundary release
>2400°C	Lanthanides: La, Zr, Nd, Eu, Nb, Pm, Pr, Sm, Y, Cm, Am Others: Ce, Pu, Np	Core melt

Information compiled from McKenna and Glitter **[2]** and Soffer et al. **[3]**.

Quantifying actinide releases requires measurement of plutonium isotope ratios. Plutonium is found ubiquitously from atmospheric nuclear explosions. Due to the natures of nuclear explosions or reactor fuel composition and irradiation, ^{238}Pu ($T_{1/2}$ = 87.74 yrs), ^{239}Pu ($T_{1/2}$ = 2.4 × 10^4 yrs), and ^{240}Pu ($T_{1/2}$ = 6563 yrs) are present in different ratios. The ^{240}Pu/^{239}Pu and ^{238}Pu/$^{240+239}$Pu isotopic or activity ratios tend to vary by source (Figure 1) [8]. In an area where the majority of contamination is from global fallout, detection of contamination from a reactor would require measurement of plutonium isotopic ratios before and after an event, or a ^{238}Pu/$^{240+239}$Pu ratio significantly exceeding 0.2. The quantification of the degree of plutonium

contamination is complicated by the inability to quantify each isotope within a sample using radiometric techniques. The alpha particles emitted from [238]Pu, [239]Pu, and [240]Pu are 5.50 MeV, 5.16 MeV, and 5.17 MeV, respectively. Alpha spectroscopy cannot be used to determine the [240]Pu/[239]Pu ratio. Either accelerator mass spectrometry (AMS) or sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) must be used, requiring extensive sample preparation. Therefore, actinide contamination from a nuclear reactor is difficult to rapidly confirm.
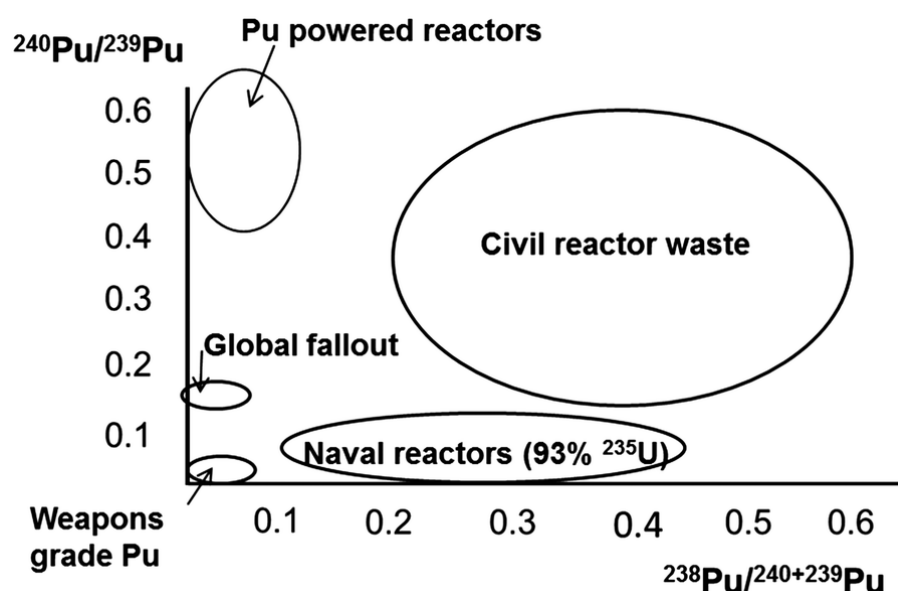
Figure 1: Plutonium Activity Ratios for Known Sources.
Reproduced from S. Cagno, K. Hellemans, O. C. Lind, L. Skipperud, K. Janssens and B. Salbu, "LA-ICP-MS for Pu source identification at Mayak PA, the Urals, Russia," Environmental Science: Processes & Impacts, vol. 16, pp. 306-312, 2014. With permission of The Royal Society of Chemistry.

The radionuclide [239]Np is a short-lived, β^-- and γ-emitting actinide ($T_{1/2} = 2.4$ d). It is produced by the neutron capture of [238]U in the nuclear reaction [238]U(n,γ)[239]U and subsequent disintegration of short-lived [239]U ($T_{1/2} = 23.5$ min) by beta decay. Numerous properties of [239]Np make it practical for assessing the extent of reactor core damage after a nuclear accident. Neptunium and plutonium are both actinides and, therefore, exhibit similarly low volatilities.

Since ^{239}Np has a half-life of 2.4 days, there is no background ^{239}Np in the environment. Furthermore, its emission of multiple gamma rays with energies higher than 100 keV and emission frequencies greater than 10% make ^{239}Np a suitable radionuclide for rapid detection by gamma spectroscopy. Therefore, ^{239}Np may be an ideal proxy for quantification of fuel inventory release following a nuclear accident.

Three prominent gamma rays are emitted by ^{239}Np: 106 keV, 228 keV, and 278 keV. These gamma photons are emitted with emission frequencies of 26.3%, 11.1%, and 14.4%, respectively. However, the detection of ^{239}Np following a nuclear event is complicated by the high activities of fission products, especially radioactive iodine and tellurium. The radionuclides ^{129m}Te and ^{132}Te emit 106 keV and 228 keV gamma rays, respectively, causing spectral interference with the peaks of ^{239}Np in the gamma spectrum [9]. The high activity of ^{131}I, and the consequential intensity of its 284 keV gamma ray, emitted during a nuclear event may result in some spectral interference along the 278 keV gamma peak of ^{239}Np as well. Therefore, the 278 keV photopeak is not fully undisturbed in environmental samples taken after a nuclear event and does not necessarily provide a reliable signature of ^{239}Np.

Neutron Capture, Activation, and Fission

Neutron activation is the capture of a neutron by a nucleus to form a radioactive nucleus. Neutron activation is instrumental for neutron energy measurement, chemical analysis of a sample, and neutron detection. However, neutron activation also occurs within nuclear reactors, producing nuclides such as ^{134}Cs from the ^{133}Cs fission product and ^{239}U from ^{238}U. The equation for neutron activation of an atom by thermal neutron capture is

$$^{A}_{Z}X + ^{1}_{0}\text{n} \rightarrow ^{A+1}_{Z}X + \gamma \tag{1}$$

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where A is the atomic mass number of the atom X, Z is the atomic number of the atom, and γ is a prompt gamma ray emitted by the excited nucleus. The activation of the atom sometimes results in nuclear instability and, consequently, some form of decay. Decay can be in the form of isomeric transition, where the metastable state becomes stable and emits a characteristic photon, or some other form of decay (typically beta decay).

The activity (A) associated with a sample after neutron activation is dependent on the cross section (σ) for thermal neutron capture of the nuclide being irradiated, the amount of the nuclide (N), the neutron flux ($\dot{\varphi}$), the length of time the sample is irradiated, and the decay constant (λ). The decay constant is defined as $\lambda = \frac{\ln(2)}{T_{1/2}}$, where $T_{1/2}$ is the physical half-life of the activation product. It is necessary to consider the matrix surrounding the sample, since that can also influence the neutron flux. Assuming an unshielded and uniform neutron flux within the sample, the equation used to calculate the activity following neutron irradiation is [10]

$$A(t) = N\sigma\dot{\varphi}\left(1 - e^{-\lambda t_{irr}}\right) \tag{2}$$

where

λ = decay constant of the nuclide produced (s^{-1}),

N = number of target atoms being irradiated,

σ = cross section for neutron activation (cm^2),

$\dot{\varphi}$ = neutron flux (neutrons cm^{-2} s^{-1}),

t_{irr} = irradiation time of sample (s).

If the radionuclides produced from neutron activation decay by a process involving the emission of a gamma photon, the activity of the sample following neutron activation can be measured on a gamma detector. A high purity germanium (HPGe) detector or NaI(Tl) detector could be utilized for this purpose. However, time following irradiation must be considered

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before measuring the sample. If the sample is measured too soon after activation, the activity may be sufficiently high to result in significant resolving time losses or peak summation. High activity samples sometimes are allowed to decay to reduce resolving time losses. If the sample is measured too long after activation, the activity may be too low to detect any radioactive atoms produced. Therefore, $A(t)$ can be adjusted to account for this decay time t_{rad}:

$$A(t) = N\sigma\dot{\varphi}\left(1 - e^{-\lambda t_{irr}}\right)e^{-\lambda t_{rad}} \tag{3}$$

Neutron capture may result in fission instead of activation for heavier atoms. The probability of fission is referred to as the cross section for fission σ_f. Fission results in the production of two fission products (ternary fission products, such as tritium, are also possible), kinetic energy, neutrons, and gamma rays. For ^{235}U, 2.5 neutrons on average are released per thermal fission with a total energy release of approximately 200 MeV. These fast neutrons then can either induce further fissions or can be captured after moderation to create activation products [10].

Fission products are produced with yields approximated by the curve in Figure 2. The most probable fission products have atomic masses 90-100 amu and 130-145 amu. Since these products tend to be neutron rich, they rapidly decay by beta decay along their isobar to achieve stability.
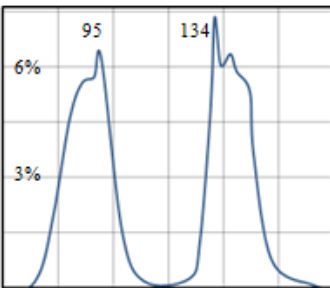
Figure 2: Fission Product Yield.
The abscissa denotes the mass numbers of the fission products produced. The ordinate is the probability of production by fission.

Quantification of fission products and activation products released following a reactor meltdown can contribute to assessment of damage within a reactor. Volatility, defined as the ability of a substance to be vaporized, varies by the chemical nature of a substance. After a reactor cooling system fails, the temperature within the core of a reactor can increase to temperatures exceeding 2400°C as a result of residual heat within the fuel elements, delayed fissions, and decay heat [2] [3]. As temperatures increase, substances are volatilized based on their chemical properties. Noble gases are the first to be released; followed by cesium, iodine, and tellurium; then semi-volatile elements such as strontium and ruthenium; and lastly elements with low volatility, including the rare earth elements and actinides such as plutonium and neptunium (Table 1).

Gamma Ray Detection and Measurement

Gamma rays are monoenergetic photons that may be emitted from the nucleus of an atom that undergoes radioactive decay. Techniques employed to measure the energies of these photons typically utilize scintillators or semiconductors. These detector types have different purposes; consequently, both were utilized in this study.

Scintillating materials can be either liquid or solid. A common scintillating crystal often used is sodium iodide doped with thallium, NaI(Tl). With a high effective atomic number and high density (3.67 g/cm^3), these scintillation counters can have rather high detection efficiencies. (However, the total detection efficiency of any system is dependent on the geometry of the source relative to the detecting medium.) Photons that interact with the crystal induce excitations and ionizations within the crystal by the photoelectric effect, Compton scattering, or pair production. Electrons liberated by these interactions release their kinetic energy in the crystal, resulting in the excitation of the atoms. The return of the atoms to their ground states

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results in the release of visible/UV photons. Photons produced within the crystal are funneled into a photomultiplier tube, where they interact with the cathode and cause a cascading amplification of electrons. The anode receives the final amplified signal, which is proportional to the energy of the initial gamma ray [10] [11].

Semiconductor detectors can quantify the energy of photons by the number of electron-hole pairs produced in the detecting medium. The semiconducting elements used, such as silicon or germanium, have four valence electrons; doping the silicon or germanium with elements that have three or five valence electrons creates regions with an excess of holes (*p*-region) or excess of electrons (*n*-region), respectively. The detector has both an *n*-region and *p*-region, and a depletion zone in between. Applying a reverse bias to the detector, where the *n*-region is connected to the positive terminal and *p*-region to the negative terminal, generates the depletion zone, which is the sensitive region of the detector. Ionizing radiation interacts in the depletion zone to generate electron-hole pairs that are proportional in number to the energy of the incident radiation. The holes and electrons travel through the *p*-region and *n*-region, respectively, and the electrons generate an electric pulse at the read-out [10] [11].

Scintillation counters can be used to measure low-activity samples; however, they lack the high resolution of high purity germanium (HPGe) semiconductor detectors. Because of the high resolution, HPGe detectors have a greater signal-to-noise ratio, thereby reducing measurement uncertainty. Unlike scintillation counters, HPGe semiconductor detectors require cryogenic temperatures for maintenance of structural and functional integrity. The energy required to excite electrons into the conduction band of the detecting medium is a few electron volts, thereby requiring thermal control. Additionally, HPGe detectors utilize relatively low voltages (up to 300 V) in contrast to NaI(Tl) detectors, which can require over 1000 V [10] [11].

In this study, an HPGe detector was used for rapid assessment of ^{131}I and ^{239}Np activities in solution before and after suction through resin columns. After short-lived nuclides had decayed away, a NaI(Tl) detector was used for the evaluation of ^{123m}Te and ^{134}Cs expression in the eluates. The HPGe detector was then utilized to quantify the expression of ^{123m}Te and ^{134}Cs in the eluates.

Ion Specific Extraction Chromatography Resins

Four resins were evaluated for their abilities to isolate neptunium from fission and activation products. Resins vary by the stationary phase and, consequently, the acid concentrations required to form and to dissociate the complexes that are formed between the stationary phase and the metals in the mobile phase. Information about the chemical properties of each resin is available on the Eichrom Technologies website. The UTEVA, TRU, and Actinide resins are selective for actinides. The selectivity and affinity is expressed with a k' value; larger values are associated with greater retention of a target on the resin column. The RE resin has not been evaluated for actinide element retention, but was expected to behave similarly to the TRU resin.

The UTEVA resin contains diamyl amylphosphonate as the extractant. In the presence of nitrate ions, nitrato complexes are formed with the actinide elements. At 10 M HNO$_3$, the k' value is approximately 400 at 25°C. However, higher k' values are associated with high HCl concentration. At room temperature and 10 M HCl, the k' value of the UTEVA resin exceeds 1000. A 10 M HCl solution was used for loading, and a 0.1 M HCl solution was used for eluting to selectively elute the neptunium from the column. At a concentration of 0.1 M, the k' value is below 1.

The Actinide resin uses P,P'-di(2-thylhexyl)methanediphosphonic acid (DIPEX®) as the extractant and has a greater affinity for actinides at lower concentrations of HCl. Therefore, a 0.1 M HCl solution (k' = 10^7) was used for loading, and a 10 M solution (k' < 5 × 10^4) for eluting.

The TRU resin uses octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) for the extractant system. The RE resin utilizes the same extractant system as the TRU resin, but has a higher concentration of CMPO. The k' values for the actinides on TRU resin exceed 10^4 for HNO_3 concentrations exceeding 0.2 M, whereas the k' values for the lanthanides on RE resin range from 1 to 100 for HNO_3 concentrations ranging from 0.1 M to 10 M. Limited information is available regarding k' values for actinides on RE resin.

To optimize selectivity and exclusivity of a resin, pre-conditioning is required. A loading solution of required acid and pH is washed through the column prior to loading the column with the sample. The column is rinsed with the loading solution after loading the sample to maximize the purity of the elution. Lastly, an elution solution of different pH is passed through the column into a new vial to collect the ions of interest [12].

Objective

The high activities of volatile fission and activation products following a nuclear event result in difficulties detecting trace amounts of ^{239}Np in environmental samples. The objective of this study was to determine an effective means of separating reactor-borne neptunium from other reactor-borne nuclides using Eichrom® resin columns. Neutron activation was conducted at the USGS TRIGA® Reactor in Denver, Colorado, to create a panel of nuclides that are typically released as a result of a nuclear event. The radionuclides produced at the reactor were mixed in

aqueous and soil matrices to simulate samples that could be obtained following a nuclear event. Typical reactor accident nuclides include ^{134}Cs, ^{239}Np, ^{131}I, and ^{123m}Te. Activation products that were also produced include ^{239}U, ^{121m}Te, ^{121}Te, ^{125m}Te, ^{127m}Te, ^{127}Te, ^{129m}Te, ^{129}Te, ^{131m}Te, and ^{131}Te. These nuclides were then combined in solution to simulate rainwater. The solutions were then eluted through the UTEVA, TRU, Actinide, and RE resin columns to determine which columns were most effective at isolating neptunium. After determining the most effective columns for neptunium isolation, neptunium was spiked into dried soil to simulate soil samples following a nuclear event. The soil samples were leached with nitric acid, filtered, and vacuumed through those columns that were most effective. Gamma spectroscopy prior to elution through the columns, immediately following elution, and five months after elution provided information about how selective the resins were against possible fission and activation products that would contaminate environmental samples following a nuclear event.

MATERIALS AND METHODS

Nuclide and Stock Solution Preparation

^{134}Cs, ^{239}Np, ^{123m}Te, and ^{131}I, were generated by neutron activation of CsNO$_3$,

UO$_2$(NO$_3$)$_2$ · 6H$_2$O, and Te(OH)$_6$ · 2H$_2$O at the USGS TRIGA® Reactor in Denver, Colorado.

^{134}Cs was representative of all radiocesium that would be present following a nuclear event;

similarly, ^{123m}Te was a proxy for all radioactive tellurium and ^{131}I for all radioactive iodine. The

samples were irradiated in Suprasil® quartz glass vials positioned in either the reflector tube ($\dot{\varphi}$

$= 4.3 \times 10^{12}$ neutrons cm^{-2} s^{-1}) or rotary rack ($\dot{\varphi} = 1.4 \times 10^{11}$ neutrons cm^{-2} s^{-1}). Sample

quantities, irradiation times, and cooling times are listed in Table 2. The tellurium sample was

irradiated for 6 hours on the date 140319[1] and for 6 hours on 140326. The uranium and cesium

samples were irradiated for 2 hours on 140327.

Table 2: Nuclide Preparation by Neutron Activation.

Sample	Quantity	Irradiation Position	Irradiation Time	Cooling Time
CsNO$_3$	50 mg Cs	Reflector Tube	2 h	48 h
UO$_2$(NO$_3$)$_2$ · 6H$_2$O	20 mg depleted U	Reflector Tube	2 h	48 h
Te(OH)$_6$ · 2H$_2$O	30 mg Te	Rotary Rack	12 h	5 d

The peak thermal flux values within the rotary rack and reflector tube were 4.3×10^{12} neutrons cm^{-2} s^{-1} and 1.4×10^{11} neutrons cm^{-2} s^{-1}.

Stock solutions were prepared from each irradiated sample on 140331 (Day 0). The

CsNO$_3$ sample was washed from the quartz vials using 0.5 M HNO$_3$ to create a 50 mL stock

solution with a concentration of 1 mg/mL Cs. The Te(OH)$_6$ · 2H$_2$O and UO$_2$(NO$_3$)$_2$ · 6H$_2$O were

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[1] March 19, 2014

washed from the quartz vials using deionized water (dH_2O) to create 30 mL and 20 mL stock solutions, respectively.

To ascertain the activity in each stock solution, 100 µL from each solution was added to 35 mL dH_2O and measured directly on the window of the Gamma Products, Inc., HPGe roll top counting shield detector. Analysis through CANBERRA's ProSpect® revealed the following activities in 100 µL after 2 minutes:

Table 3: Gamma Ray Intensities and Activities on Day 0.

Nuclide	Energy (keV)	CPS in 100 µL	Activity (Bq/100µL)
^{123m}Te	159	9.5±1.2	93±12
^{239}Np	278	15.3±0.8	1244±62
^{131}I	365	146.6±5.3	2576±93.7
^{134}Cs	605	6.0±0.4	132±10

Measurements were taken on Gamma Products, Inc., HPGe roll top counting shield detector for 120 s (live time) and analyzed with CANBERRA's ProSpect® software. Uncertainties are expressed to 3σ.

The Eichrom® resin columns are more selective for Np(IV) than Np(V). Therefore, reduction of neptunium is required prior to loading the samples onto the columns [13]. Stock solutions of Fe(II) and ascorbic acid were prepared to reduce Np(V) to Np(IV). A 1.5 M ascorbic acid solution was prepared using 13.2 g ascorbic acid and 50 mL dH_2O. A 5 mg/mL Fe(II) solution was prepared using 0.025 g $FeSO_4 \cdot 7H_2O$ in dH_2O for a total volume of 10 mL.

Rainwater Sample Preparation

Rainwater analogue samples were 24.87 mL in volume and varied by the resin that each sample would be eluted through. Each solution contained (in the order in which they were added) 1.25 mL 1.5 M ascorbic acid, 0.1 mL 5 mg/mL Fe(II), 20 µL 1 mg/mL U (^{239}Np) stock solution, 20 mL loading solution, 1 mL 1 mg/mL tellurium, and 2.5 mL 1 mg/mL cesium

(reduced to 0.5 mL on Day 4). These volumes simulated contaminated rainwater sample activity concentrations, where ^{239}Np activity concentrations are exceeded by those of radioactive iodine and cesium. Loading solutions varied by acid type and concentration, both of which were dependent on the resins. Solutions and their quantities are outlined in Table 4. Loading solutions and volatile radionuclides were added last to the rainwater analogue samples to ensure complete reduction of neptunium. Samples were run in quadruplicate. Trials I and II for each resin were conducted on Day 1, and trials III and IV on Day 2.

Table 4: Rainwater Analogue Sample Composition.

Resin	Ascorbic Acid 1.5 M (mL)	5 mg/mL Fe(II) (mL)	1 mg/mL U (^{239}Np) (µL)	Loading Solution (20 mL)	1 mg/mL Te (mL)	1 mg/mL Cs (mL)[*]
Actinide	1.25	0.1	20	0.1 M HCl	1	2.5
RE	1.25	0.1	20	8 M HNO$_3$	1	2.5
TRU	1.25	0.1	20	3 M HNO$_3$	1	2.5
UTEVA	1.25	0.1	20	10 M HCl	1	2.5

[*]Volume reduced to 0.5 mL on Day 4.

Activities of the samples before and after elution were measured on a Gamma Products, Inc., HPGe detector and calculated by algorithms in CANBERRA's Genie 2000® software. Samples were measured for 300 s (live time) before they were loaded onto the resin columns. These measurements provided the initial counts from which percent recoveries were calculated.

An Eichrom® Vacuum Box System was set up to pull samples through the resin columns. Yellow outer tips were placed through the holes of the vacuum box, and white inner tips were placed within the yellow tips. Resin columns (colored blue in Figure 3) were secured to the white inner tips. A cartridge reservoir (colored purple in Figure 3) was required for the TRU, RE, and UTEVA resins. Unused openings on the vacuum box were sealed (colored red in

Figure 3). The vacuum was adjusted to a pressure that allowed samples to flow at a rate of approximately 1 mL/min through the columns.
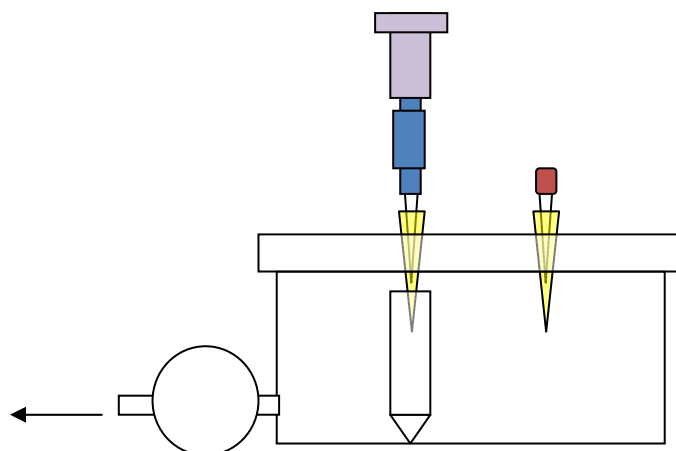
Figure 3: Vacuum Box Diagram.
The arrow denotes the airflow through the system. Airflow is monitored with the gauge (circle).

Columns were pre-conditioned with 5×1 mL loading solution[2] prior to administering the samples. After the samples were pulled through the columns by the vacuum, the columns were rinsed with 10×1 mL loading solution. The total volume collected from pre-conditioning to rinsing is referred to as the load.

Elution solutions were then passed through the columns to remove neptunium. The Actinide resin was eluted with 10 M HCl (ACT[HCl]), RE resin with 0.01 M HNO_3 (RE[HNO_3]), TRU resin with 0.1 M HNO_3 (TRU[HNO_3]), and UTEVA with 0.1 M HCl (UTEVA[HCl]). Elution solutions were administered in 10×1 mL increments. The samples were brought up to 25 mL using their respective elution solutions to ensure constant geometry when measuring them on the HPGe detector. The eluates were then measured on the HPGe detector for 300 s (live time).

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[2] 1 mL was added five times.

For UTEVA, TRU, and RE resins, different eluents were evaluated for their abilities to remove neptunium from the resin columns. The TRU, RE, and UTEVA resins were all eluted with water after having been loaded with their normal loading solutions (TRU[H$_2$O], RE[H$_2$O], and UTEVA[H$_2$O], respectively). The UTEVA resin was also loaded using 8 M HNO$_3$ and eluted using 0.1 M HNO$_3$ (UTEVA[HNO$_3$]). These trials were conducted in duplicate.

Table 5: List of Resins and Corresponding Loading and Elution Solutions.

Resin[Eluent]	Loading Solution	Eluent	Trials
ACT[HCl]	0.1 M HCl	10 M HCl	4
RE[HNO$_3$]	8 M HNO$_3$	0.01 M HNO$_3$	4
RE[H$_2$O]	8 M HNO$_3$	dH$_2$O	2
TRU[HNO$_3$]	3 M HNO$_3$	0.1 M HNO$_3$	4
TRU[H$_2$O]	3 M HNO$_3$	dH$_2$O	2
UTEVA[HCl]	10 M HCl	0.1 M HCl	4
UTEVA[HNO$_3$]	8 M HNO$_3$	0.1 M HNO$_3$	2
UTEVA[H$_2$O]	10 M HCl	dH$_2$O	2

Extraction from Soil Samples

Spectroscopic analysis of eluates and columns from rainwater analogues revealed that neptunium could be reliably eluted from RE and UTEVA columns only. Thus, these resins were used for the evaluation of the ^{239}Np recovery and fission product decontamination when applied to soil samples. On Day 3, four soil samples were collected on the Colorado State University campus, spiked with 20 μL of U (^{239}Np) solution, and dried overnight in an incubator at 38°C. The soils were then leached on Day 4 using 10 mL 8 M HNO$_3$ solution. Leaching was done for 30 minutes while boiling in reflux. After cooling the flasks, the soil extracts were filtered using a vacuum flask and a Büchner funnel (Figure 4). The filter cakes, flasks, and vacuum flasks were washed with acids of concentrations that corresponded to those used in loading solutions of respective resins (Table 4). The round-bottomed boiling flasks were washed with 2 × 3 mL

loading solution onto the filter cake. Filter cakes were then washed with 10×1 mL loading

solution. 1.25 mL 1.5 M ascorbic acid solution and 0.1 mL 5 mg/mL Fe(II) solution were added

to the filtrates prior to loading onto the columns to ensure complete reduction of neptunium in

the filtrate. After loading the filtrates onto the resin columns pre-conditioned with 5×1 mL of

respective loading solutions, the decanted vacuum flasks were washed with 4 mL loading

solution. The soil masses and washing solutions are listed in Table 6.

Table 6: Soil Samples and Washing Procedures.

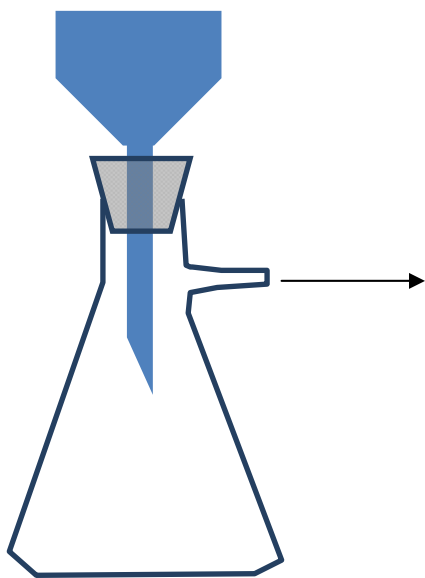| Sample	Mass (g)	Resin	Washing Solution	Flask	Cake	Vacuum Flask
SoI	5.86	RE	8 M HNO_3	2×3 mL	10×1 mL	4 mL
SoII	5.80	RE	8 M HNO_3	2×3 mL	10×1 mL	4 mL
SoIII	8.74	UTEVA	10 M HCl	2×3 mL	10×1 mL	4 mL
SoIV	6.66	UTEVA	10 M HCl	2×3 mL	10×1 mL	4 mL

Figure 4: Vacuum Flask and Büchner Funnel Diagram.
The Büchner funnel (blue) is inserted through a rubber stopper (gray) into the vacuum flask. The
arrow denotes the flow of air through the system.

After the filtrates passed through the columns, the columns were rinsed with 10×1 mL of loading solutions, and then eluted into separate vials with 10×1 mL of their respective elution solutions. After observing minimal elution of neptunium from the columns with elution solutions, water, 0.05 M oxalic acid, and 30% H_2O_2, we eluted the entire stationary phase from the resin beads using acetone.

To determine if a soil matrix would affect the retention of tellurium and cesium on the Actinide and TRU resins, 100 µL of each solution was added to soil samples that were dried overnight in an incubator at 38°C.[3] The dry masses of the samples are listed in Table 7, as well as whether ascorbic acid and Fe(II) solutions were included in amounts corresponding with previous soil samples. The samples were boiled for 30 minutes in 10 mL 8 M HNO_3, filtered on a vacuum flask, and eluted through their respective columns. A total of 12 mL of loading solution (listed in Table 4) was used in the washing process for each sample; the washing process corresponded with the regimen outlined in Table 6.

Table 7: Soil Samples for Actinide and TRU Resins.

Sample	Mass (g)	Resin	Ascorbic Acid and Fe(II)
A	10.30	Actinide	No
B	11.61	TRU	No
C	6.40	TRU	Yes
D	7.08	Actinide	Yes

Beginning on Day 155, NaI(Tl) scintillation counters were used to gather the spectra from all loads, eluates, and columns. All samples were measured for 7200 s (live time). This allowed for effective tracing of ^{123m}Te, and transitively other tellurium isotopes, through the elution process.

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[3] Addition of tellurium and cesium was conducted on Day 188. The activities were approximately 0.3 Bq/µL ^{123m}Te and 1.1Bq/µL ^{134}Cs.

RESULTS AND DISCUSSION

Four Eichrom® resins were evaluated for their effectiveness in isolating neptunium from volatile radionuclides released during nuclear events. Solutions containing ^{131}I, radioactive tellurium, [239]Np, and [134]Cs were eluted through UTEVA, RE, TRU, and Actinide resins. UTEVA and RE resins were the most effective at recovering neptunium from solution (Figure 5). All yields are calculated from ratios of 278 keV peak intensities before and after elution; uncertainties are expressed to 3σ.

To seek higher and more precise yields, different eluents were tested on Day 4. The UTEVA resin protocol requires elution with 0.1 M HCl. The efficiency of extraction from solution was also assessed using water (UTEVA[H_2O]) and 0.1 M HNO_3 (UTEVA[HNO_3]) as eluents. Elution with water appeared comparable to elution with 0.1 M HCl, and both seemed more effective than elution with 0.1 M HNO_3 (Figure 5). Similarly, the RE resin isolation efficiency was assessed using water for elution (RE[H_2O]). Elution of neptunium from RE resin using water as an eluent was as effective as using 0.01 M HNO_3 as an eluent (Figure 5).

There was no detectable [239]Np activity eluted from the four Actinide resins, two of the four TRU resins eluted with 0.1 M HNO_3 (TRU[HNO_3]), and one of the two TRU resins eluted with water (TRU[H_2O]). The other two TRU[HNO_3] resins eluted $6\pm2\%$ of the original [239]Np activity (calculated using 278 keV peak yield). Gamma spectra of the resin columns placed directly on the HPGe detector window revealed that neptunium had remained on the columns for both the TRU and Actinide resins. Therefore, TRU and Actinide resins are not as reliable as RE and UTEVA resins for neptunium elution.
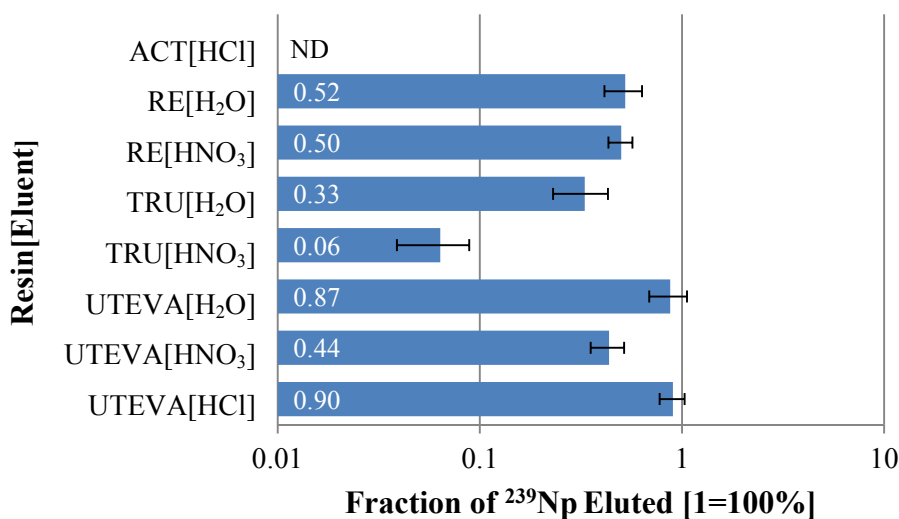
Figure 5: Percent Yield of ^{239}Np from Rainwater Analogues.
The resins ACT[HCl], RE[HNO3], TRU[HNO3], and UTEVA[HCl] were tested in quadruplicate. The resins RE[H2O], TRU[H2O], UTEVA[HNO3], and UTEVA[H2O] were tested in duplicate.

Although UTEVA[HCl] and UTEVA[H$_2$O] had the best neptunium yield, they eluted the most iodine and tellurium (Figure 6). ^{123m}Te, which has a half-life of 119 days and a 159 keV gamma emitted during 84% of isomeric transitions, was found in UTEVA eluates, resins, and loads when HCl was used as the loading solution. The ^{123m}Te isotope could not be detected in UTEVA resins and eluates when HNO$_3$ was used for the loading solution. Gamma spectra of RE resins and eluates did not show any ^{123m}Te activity as well, independent of the eluent used. Therefore, UTEVA and RE resins loaded with HNO$_3$ are the best resins for neptunium isolation.

Actinide resin and TRU[HNO$_3$] resin spectra showed tellurium only in the loads, although trace amounts of radiocesium had been eluted. There were no detectable quantities of tellurium in the eluates and resins of the Actinide and TRU resins, indicating minimal retention of tellurium and cesium by these two resins as well.
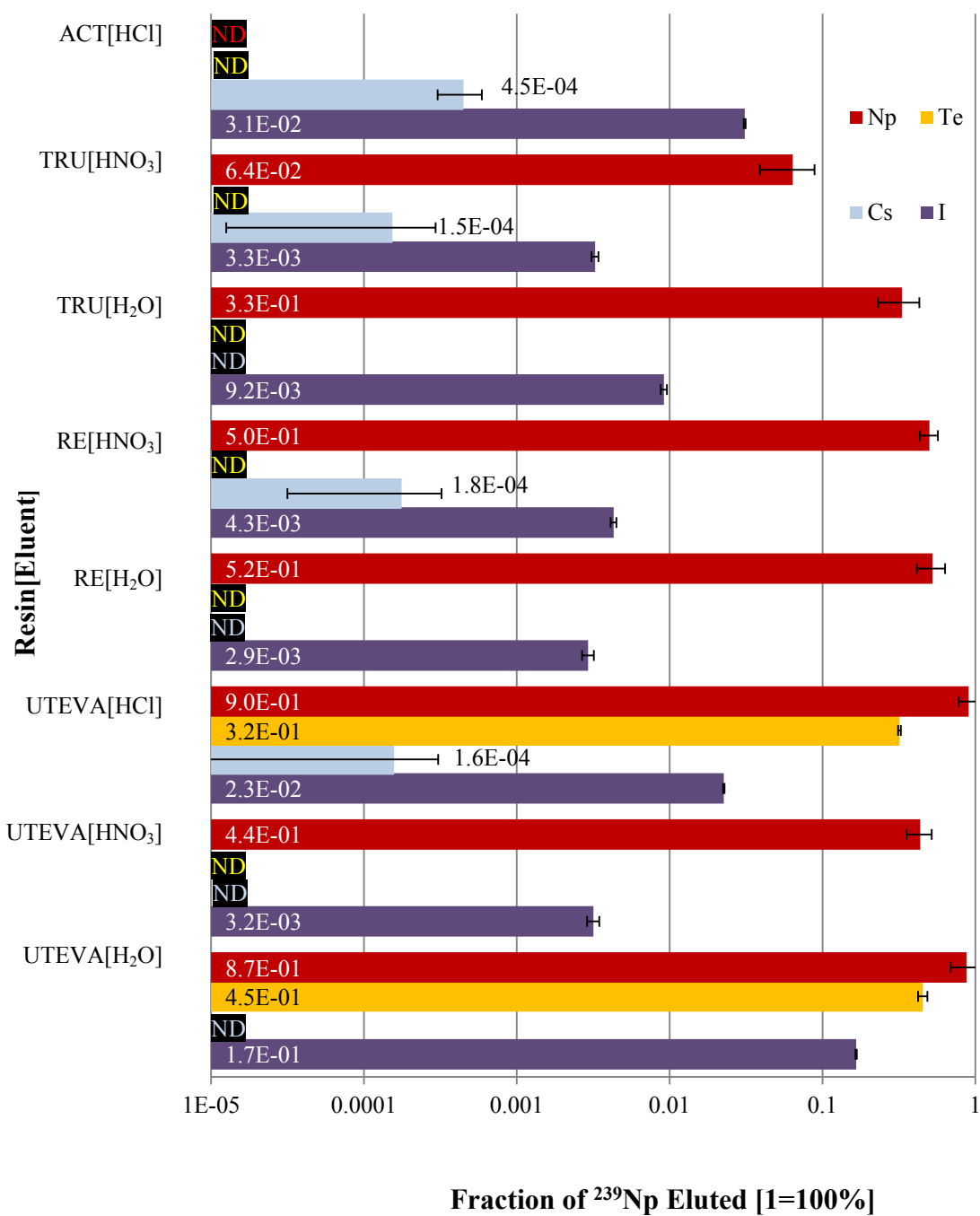
Figure 6: Extraction Efficiencies from Solution.
ACT[HCl], TRU[HNO₃], RE[HNO₃], and UTEVA[HCl] were tested in quadruplicate.
TRU[H₂O], RE[H₂O], UTEVA[HNO₃], and UTEVA[H₂O] were tested in duplicate.

There were difficulties eluting neptunium from the TRU and Actinide resin columns. No detectable quantities of neptunium were eluted from the Actinide resin column using 10 M HCl; therefore, removal of neptunium from the column may need to be done with acetone for the Actinide resin. HNO_3 solutions with concentrations less than 0.1 M may be required for effective elution of neptunium from the TRU resin column, justifying the yield of TRU[H_2O] being more than five times higher than the yield of TRU[HNO_3].

ACT[HCl], UTEVA[HCl], and UTEVA[H_2O] resins eluted more than 1% of the initial ^{131}I in the rainwater analogue samples. TRU resins, RE resins, and UTEVA[HNO_3] effectively excluded more than 99% of the ^{131}I (and transitively all iodine) from their eluates. The percent of ^{131}I activity that was removed by each resin is outlined in Appendix C, Table 16. Very high ^{131}I activities were expressed on all resin columns following treatment with eluents; therefore, elution with acetone (especially for the Actinide resin) for aqueous matrices is not recommended.

Neptunium from soil could not be eluted from UTEVA and RE resins using conventional eluents such as HNO_3, HCl, water, 0.05 M oxalic acid, and 30% H_2O_2. The only alternative was to remove the stationary phases from the column beads by dissolution using acetone. This method proved successful, as no neptunium could be detected on the columns by gamma spectroscopy following elution with acetone. Since the UTEVA soil samples had an average of 32% more dry mass than the RE soil samples, there may have been more binding sites within the soil that resulted in incomplete leaching. No neptunium remained on the columns following elution with acetone; therefore, the difference in yields may be a result of the difference in soil masses used (Figure 7). However, it has been shown that ^{239}Np can be leached from soil and extracted into solution for detection by gamma spectroscopy.

Figure 7: Extraction Efficiencies of ^{239}Np from Soil using RE and UTEVA Resins.
RE and UTEVA resins were tested in duplicate.

Soil samples containing tellurium and cesium were eluted through Actinide and TRU resins. The ascorbic acid and iron solutions used to reduce Np(V) to Np(IV) were variable to assess if these solutions contribute to any complexes between the resins and these nuclides. Spectroscopic analysis revealed non-detectable quantities of these radionuclides in the eluates and on the columns. The activities of ^{123m}Te and ^{134}Cs were concentrated on the filter cakes and in the loads. Since the Eichrom® resins tested (UTEVA, RE, TRU, and Actinide) are selective for primarily tetravalent species, the selectivity against monovalent cesium and the several oxidation states of tellurium can be assumed translational between aqueous samples and soil samples.

Tellurium, iodine, and cesium do not exist as monatomic or polyatomic ions with +4 charges. Cesium will behave chemically as an alkali metal, although it will bind very well to soils with high clay content. Therefore, if cesium is separated from the soil during the dissolution process, it will pass through the resin column with the rest of the loading solution. Such behavior was observed for the two TRU resins and two Actinide resins tested. Similarly, tellurium does not exist predominantly in an ionic form in aqueous solution that exhibits a +4 charge; the solubility of tellurium oxides and oxyacids in HNO_3 ensures exclusion from the resin

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columns [14] [15]. Analogously, Np(IV) exists as Np^{4+} in solution, whereas Np(V) exists as NpO_2^+ [16]. The coordination chemistry exhibited by tetravalent neptunium is different than that of Np(V), resulting in k' values on the TRU resin that are up to four orders of magnitude greater for the tetravalent form [12].

Further investigation of isolation of neptunium from fission products and activation products in soil samples is required. Due to the potential formation of organometallic complexes within the RE and UTEVA resin columns, this effect may be translational to the other resins. Since the RE resin and TRU resin use the same extractant system, the TRU column may behave similarly with respect to soil samples. Therefore, acetone would be the required eluent for all resin columns for soil sample analysis. If we assume significant losses of radioiodine during refluxing and minimal retention of cesium and tellurium on the resin columns, our method of isolating neptunium from soil using acetone as an eluent may be viable.

CONCLUSIONS

The presence of ^{239}Np in an environmental sample is indicative of the state of the fuel in a nuclear reactor following an accident. Although the state of the fuel can be ascertained using ^{240}Pu/^{239}Pu and ^{238}Pu/$^{240+239}$Pu isotopic ratios, the use of ^{239}Np as a proxy is rapid because of its short half-life and the distinct gamma rays it emits during radioactive decay. Using UTEVA, RE, TRU, and Actinide extraction chromatography resins from Eichrom Technologies, LLC, on rainwater analogue samples and soil samples has demonstrated that ^{239}Np can be isolated from volatile radionuclides, ensuring minimal spectral interference from volatile radionuclides during spectroscopic analysis.

Rainwater analogues were the simplest matrix from which ^{239}Np could be isolated. Addition of 20 mL of loading solution to approximately 4 mL of sample (includes volumes from our radionuclide stock solutions only) ensured consistent pH between the preconditioned resin columns and the sample, thereby optimizing retention of the neptunium by the resin. The use of 1 mL 1.5 M ascorbic acid and 0.1 mL 5 mg/mL Fe(II) solutions should be sufficient for reducing enough neptunium within an aqueous sample to the tetravalent state to be detected by gamma spectroscopy. RE and UTEVA resins loaded with 8 M HNO_3 and eluted with 0.01 M HNO_3 and 0.1 M HNO_3, respectively, have been shown effective at both excluding volatile radionuclides from the eluate and eluting neptunium. The exclusion was either through retention on the column (observed for radioiodine) or lack of retention after loading (observed for radiotellurium and radiocesium).

Soil samples were more complicated, as elution of neptunium from the resins could only be done by dissolution of the stationary phase. Elution by acetone may be attributed to organic

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and refractory soil components. However, since refluxing precedes elution, volatile

radionuclides (especially radioiodine) may be driven off in sufficient quantities, minimizing their

presence in the filtrates that are loaded onto the columns. Our eluates from soils spiked with

volatile radionuclides without neptunium confirm the selectivity of resins against cesium and

tellurium from a soil matrix. Therefore, extraction of neptunium from soils by leaching with 8 M

HNO_3 is plausible.

Additional tests would utilize Eichrom® TEVA resins, as these were not evaluated in this

study. Since HCl and HNO_3 can be used to bind and elute neptunium from this column, separate

tests should be conducted for fission product exclusion efficiency for each acid. Furthermore,

isolation of neptunium from soil contaminated with volatile radionuclides should be conducted to

assess the effects of potential organometallic complexes on tellurium, cesium, and iodine

retention on the columns.

Eichrom® extraction chromatography resins have been shown to be effective at isolating

neptunium from volatile radionuclides released during a nuclear event. The state of the fuel in a

reactor core can be rapidly ascertained from aqueous and soil samples taken from within and

around the reactor facility. If neptunium is detected, there is certainty that the integrity of the

core cladding has been jeopardized. Detection of the short-lived anthropogenic ^{239}Np outside of

the reactor core warrants concern and rapid action. Continuous monitoring can reveal the time at

which the core elements have melted and enable further understanding of what occurs during the

meltdown of a reactor core.

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APPENDIX A: EXPERIMENTAL PROTOCOL

I.   **Stock Solution Preparation**

1. Seal the salts $UO_2(NO_3)_2 \cdot 6H_2O$ (20 mg depleted U), $Te(OH)_6 \cdot 2H_2O$ (30 mg Te), and

    $CsNO_3$ (50 mg Cs) into Suprasil® quartz glass vials.

2. Irradiate the salts at the USGS TRIGA® Reactor in Denver, Colorado. Fluxes,

    irradiation times, and cooling times are outlined in Table 2.

    a. Irradiate the tellurium sample for 6 hours twice. Cool for 7 days after first

        irradiation and for 5 days after second irradiation.

    b. Irradiate the uranium sample for 2 hours. Cool for 4 days.

    c. Irradiate the cesium sample for 2 hours. Cool for 4 days.

3. Wash the salts from the vials to create 1 mg/mL solutions of Te, U (^{239}Np), and Cs.

    a. Wash $Te(OH)_6 \cdot 2H_2O$ from the vial using 30 mL dH_2O.

    b. Wash $UO_2(NO_3)_2 \cdot 6H_2O$ from the vial using 20 mL dH_2O.

    c. Wash $CsNO_3$ from the vial using 50 mL 0.05 M HNO_3.

4. Pipet 100 μL from each stock solution into separate 60 mL Nalgene® jars from Sigma-

    Aldrich (style 2117). Bring volumes up to 35 mL with dH_2O.

5. Place jars on the window of the Gamma Products, Inc., HPGe roll top counting shield

    detector and measure for 120 s (live time) to determine activities of each sample.

6. Prepare 1.5 M ascorbic acid solution.

    a. Add 50 mL H_2O to 13.2 g ascorbic acid. Heat while stirring to ensure complete

        dissolution.

7. Prepare 5 mg/mL Fe(II) solution.

a. Add 8 mL dH$_2$O to 0.025 g FeSO$_4 \cdot$ 7 H$_2$O. Bring the total volume up to 10 mL with dH$_2$O.

II.   Vacuum Box

1. Place 50 mL Greiner centrifuge tubes from Sigma-Aldrich in the Eichrom® Vacuum Box System centrifuge tube rack for waste collection.

2. Insert yellow outer tips through the holes of the vacuum box lid for support.

3. Insert white inner tips through the yellow tips to provide a seal.

4. Attach resin columns (colored blue in Figure 3) to white inner tips.

5. For RE, TRU, and UTEVA resins, attach a cartridge reservoir (colored purple in Figure 3) to each resin column.

    a. A cartridge reservoir is not necessary for the Actinide resin.

6. Seal unused openings on the lid of the vacuum box with manifold plugs (colored red in Figure 3). These are to be inserted into the white tips.

7. Attach the vacuum gauge to the vacuum source and evacuate the box.

8. Precondition each resin with 5 × 1 mL respective loading solution. Adjust the vacuum pressure to be approximately 1 mL/min flow rate.

III.   Rainwater Analogues

1. Add to a 60 mL Nalgene® jar, in order, 1.25 mL 1.5 M ascorbic acid, 0.1 mL 5 mg/mL Fe(II), 20 µL 1 mg/mL U (^{239}Np), 20 mL loading solution (identified in Table 5), 1 mL 1 mg/mL Te, and 2.5 mL 1 mg/mL Cs.[4]

2. Obtain the radionuclide activities in each sample.

    a. Place the sample on the window of the HPGe roll top counting shield detector.

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[4] A volume of 0.5 mL 1 mg/mL Cs can be used to conserve the stock solution.

b. Measure for 300 s (live time).

c. Analyze the spectrum using either CANBERRA software program ProSpect® or Genie 2000.

3. Load the samples onto their respective preconditioned resin columns.

4. Rinse the columns using 10×1 mL of respective loading solutions.

5. Replace the 50 mL Greiner centrifuge tubes with new tubes to collect the eluates.

6. Rinse the columns with 10×1 mL of respective eluents.

7. Measure the activities in the eluates for 300 s (live time).

a. Empty the eluate from each Greiner centrifuge tube into 60 mL Nalgene® jars.

b. Rinse each tube with 25 mL dH_2O to bring the total volume in each jar up to 35 mL.

c. Obtain the radionuclide activities in each eluate using the same geometry from Appendix A III.2.

IV. Soil Samples

1. Spike soil samples with radionuclides.[5]

a. Spike 20 μL 1 mg/mL U (^{239}Np) solution into soil samples designated for RE and UTEVA resin columns. These samples are dried overnight at 38°C after spiking.

b. Spike 100 μL 1 mg/mL Te solution and 100 μL 1 mg/mL Cs solution into soil samples designated for TRU and Actinide resin columns. These samples are dried overnight at 38°C before spiking.

2. Reflux the soil samples in 8 M HNO_3 for 30 minutes.

a. Use approximately 10 mL 8 M HNO_3 for every 5 g soil (dry mass).

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[5] Preferably, all soil samples are spiked with 20 μL 1 mg/mL U (^{239}Np), 100 μL 1 mg/mL Te, and 100 μL 1 mg/mL Cs.

3. Filter the soil samples using a vacuum flask and Büchner funnel.

    a. Rinse the round bottom flask with 2 × 3 mL of loading solution respective to the designated resin.

    b. Wash the filter cake with 10 × 1 mL of the same loading solution.

4. Add 1.25 mL 1.5 M ascorbic acid and 0.1 mL 5 mg/mL Fe(II) solution to the filtrate.

5. Load the filtrates into their respective cartridge reservoirs.

6. Rinse the columns using 10 × 1 mL of respective loading solutions.

7. Replace the 50 mL Greiner centrifuge tubes with new tubes to collect the eluates.

8. Rinse the columns with 10 × 1 mL of respective eluents.

    a. If elution of neptunium is unsuccessful, as determined by gamma spectroscopy of the eluate, use acetone as the eluent for the resin column loaded with neptunium.

9. Measure the activities in the eluates for 300 s (live time).

    a. Empty the eluates from the Greiner centrifuge tubes into 60 mL Nalgene® jars.

    b. Rinse each tube with 25 mL dH$_2$O to bring the total volume in each jar up to 35 mL.

    c. Obtain the gamma spectra using the same geometry from Appendix A III.2.

APPENDIX B: PROPOSED PROTOCOL FOR NEPTUNIUM DETECTION

I.   **Aqueous Sample**

1. Set up the Eichrom® Vacuum Box System.

    a. Place 50 mL Greiner centrifuge tubes from Sigma-Aldrich in the Eichrom® Vacuum Box System centrifuge tube rack for waste collection.

    b. Insert yellow outer tips through the holes of the vacuum box lid for support.

    c. Insert white inner tips through the yellow tips to provide a seal.

    d. Attach resin columns (colored blue in Figure 3) to the white inner tips.

    e. Seal unused openings on the lid of the vacuum box with manifold plugs (colored red in Figure 3). These are to be inserted into the white tips.

    f. Attach the vacuum gauge to the vacuum source and evacuate the box.

    g. Precondition each resin with 5×1 mL 8 M HNO_3. Adjust the vacuum pressure to be approximately 1 mL/min flow rate.

2. Add to the sample 0.1 mL 5 mg/mL Fe(II) solution.

    a. Prepare 5 mg/mL Fe(II) solution by dissolving 0.025 g $FeSO_4 \cdot 7\ H_2O$ in 8 mL dH_2O. Bring the volume of the solution up to 10 mL with dH_2O.

3. Add to the sample 1 mL 1.5 M ascorbic acid solution.

    a. Prepare 1.5 M ascorbic acid solution by dissolving 13.2 g ascorbic acid in 50 mL dH_2O.

4. Add to the sample 5 mL 8 M HNO_3 for every 1 mL of sample.

5. Load the sample onto the resin column.

6. Rinse the column using 10×1 mL 8 M HNO_3.

7. Elute with 10×1 mL 0.01 M HNO_3 into a separate collection tube.

8. Measure 278 keV gamma ray intensity on HPGe detector for 30 minutes.

    a. If volatile radionuclide activity is too high, repeat elution procedure from step 4 using a new resin column.

II.   Soil Sample

1. Set up the Eichrom® Vacuum Box System.

    a. Place 50 mL Greiner centrifuge tubes from Sigma-Aldrich in the Eichrom® Vacuum Box System centrifuge tube rack for waste collection.

    b. Insert yellow outer tips through the holes of the vacuum box lid for support.

    c. Insert white inner tips through the yellow tips to provide a seal.

    d. Attach resin columns (colored blue in Figure 3) to the white inner tips.

    e. Seal unused openings on the lid of the vacuum box with manifold plugs (colored red in Figure 3). These are to be inserted into the white tips.

    f. Attach the vacuum gauge to the vacuum source and evacuate the box.

    g. Precondition each resin with 5×1 mL 8 M HNO_3. Adjust the vacuum pressure to be approximately 1 mL/min flow rate.

2. Reflux sample for 30 minutes in 10 mL 8 M HNO_3 for every 6 g soil.

    a. Soil can be dried overnight by heating. However, this may result in the release of volatile radionuclides from the sample.

    b. Refluxing may result in the vaporization and release of volatile radionuclides from the sample.

3. Filter the sample using a funnel and vacuum flask.

    a. Rinse the flask that used for refluxing with 2×3 mL 8 M HNO_3.

    b.   Wash the filter cake with 10×1 mL 8 M HNO_3.

4. Add to the filtrate 0.1 mL 5 mg/mL Fe(II) solution.

    a.   Prepare 5 mg/mL Fe(II) solution by dissolving 0.025 g $FeSO_4 \cdot 7\ H_2O$ in 8 mL

        dH_2O. Bring the volume of the solution up to 10 mL with dH_2O.

5. Add to the filtrate 1 mL 1.5 M ascorbic acid solution.

    a.   Prepare 1.5 M ascorbic acid solution by dissolving 13.2 g ascorbic acid in 50 mL

        dH_2O.

6. Load the filtrate onto the resin column.

7. Rinse the column using 10×1 mL 8 M HNO_3.

8. Elute with 10×1 mL acetone into a separate collection tube.

9. Measure 278 keV gamma ray intensity on HPGe detector for 30 minutes.

Table 8: ^{239}Np Yield from UTEVA[HCl] Resins.

Centroid Energy (keV) Trial:	I	II	III	IV	Avg:
106 keV	114±30%	137±37%	72±7%	75±8%	99±12%
228 keV	85±84%	86±90%	81±47%	91±59%	86±36%
278 keV	83±28%	98±34%	88±17%	92±19%	90±13%
Avg:	94±31%	107±34%	81±17%	86±21%	92±4%

Table 9: ^{239}Np Yield from RE[HNO$_3$] Resins.

Centroid Energy (keV) Trial:	I	II	III	IV	Avg:
106 keV	364±60%	48±9%	48±5%	35±4%	44±3%[*]
228 keV	34±30%	48±43%	46±23%	35±18%	41±15%
278 keV	43±14%	55±18%	58±11%	45±9%	50±7%
Avg:	38±11%[*]	51±16%	51±9%	38±7%	44±6%[*]

[*] Calculated with the exclusion of the 106 keV peak yield from Trial I.

Table 10: ^{239}Np Elution Yields by 278 keV Peak Intensities.

Trial	Actinide	TRU	RE	UTEVA
I	ND	7±4%	43±14%	83±9%
II	ND	ND	55±18%	98±11%
III	ND	6±1%	58±11%	88±6%
IV	ND	ND	45±9%	92±6%
Avg:	--	6±2%	50±7%	90±4%

Table 11: UTEVA Resin Yields with Different Eluents.

Centroid Energy (keV)	H$_2$O I	H$_2$O II	Avg:	HNO$_3$ I	HNO$_3$ II	Avg:
106	56±9%	83±15%	69±9%	46±8%	47±7%	46±5%
228	69±66%	86±95%	77±58%	69±80%	43±29%	56±42%
278	68±20%	106±31%	87±19%	44±12%	44±11%	44±8%
Avg:	62±23%	94±34%	78±20%	53±27%	45±11%	49±14%

Table 12: RE Resin Yields with Different Eluent.

Centroid Energy (keV)	H$_2$O I	H$_2$O II	Avg:
106	43±6%	33±5%	38±4%
228	50±41%	37±31%	44±26%
278	63±18%	42±13%	52±11%
Avg:	52±15%	38±12%	45±9%

Table 13: ^{239}Np Yield from TRU Resins.

Centroid Energy (keV)	Trial:	I	II	III	IV	Avg:
106 keV		6±2%	6±2%	5±1%	ND	6±1%
228 keV		3±4%	ND	6±6%	ND	5±4%
278 keV		7±4%	ND	6±2%	ND	6±2%
Avg:		5±2%	6±2%	6±2%	--	6±1%

Table 14: ^{239}Np Isolation from Soil with RE Resins.

Centroid Energy (keV)	SoI	SoII	Avg:
106 keV	76±7%	85±8%	80±5%
228 keV	71±24%	65±14%	63±14%
278 keV	74±15%	92±16%	83±11%
Avg:	70±10%	81±8%	75±6%

Table 15: ^{239}Np Isolation from Soil with UTEVA Resins.

Centroid Energy (keV)	SoIII	SoIV	Avg:
106 keV	41±5%	29±4%	35±2%
228 keV	38±10%	26±9%	32±5%
278 keV	46±11%	33±10%	39±5%
Avg:	43±5%	31±5%	37±2%

Table 16: Exclusion of Iodine.

Resin	Eluent	% ^{131}I Suppression
UTEVA	HNO$_3$	99.69±0.01%
UTEVA	H$_2$O	91.45±0.03%
UTEVA	HCl	82.54±0.03%[*]
RE	HNO$_3$	99.57±0.00%
RE	H$_2$O	99.70±0.00%
TRU	HNO$_3$	99.68±0.00%
TRU	H$_2$O	99.08±0.01%
Actinide	HCl	96.90±0.01%

[*]One of the four UTEVA resins suppressed only 67.43±0.15%; exclusion of this would result in 97.74±0.01% 131I activity suppression.