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Investigating the possibility of using Pu-236 as a non-isotopic tracer for Np-237
in environmental samples

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Abstract

Over the course of the past century, significant amounts of radioactive elements have been released into the environment through fallout from nuclear weapons testing and other anthropogenic activities. Among them is neptunium, a comparatively poorly researched actinide whose contribution to environmental radioactivity is predicted to rise in the long term. Quantitative determination of radionuclides from environmental matrices necessitates the use of a suitable tracer to monitor their yield during radiochemical procedure. However, in the case of ^{237}Np , neptunium's most abundant and relevant nuclide, no such isotopic tracer exists.

In this work, the concurrent determination of ^{237}Np and plutonium isotopes via ^{236}Pu , a non-isotopic tracer for ^{237}Np of similar chemical behavior, was examined. Four different sample processing techniques were carried out and compared with regard to their applicability to soil and water matrices. Investigated samples were spiked with ^{237}Np and ^{236}Pu tracer solutions and radioanalytes were solubilized by acid leaching. After adjustment of oxidation states, neptunium and plutonium were separated from the matrix via ion-exchange or extraction chromatography and sources for α -spectrometric measurements were prepared via micro-precipitation.

The best results in terms of reproducibility of recovery ratios were achieved by the VERA method, a protocol utilizing iron hydroxide co-precipitation, ascorbic acid and nitrite as redox agents and extraction chromatography with UTEVA[®] resin, for soil samples of 1 g. The good agreement of chemical yield ratios between the two tracers demonstrates ^{236}Pu 's suitability as a non-isotopic tracer for ^{237}Np . At the same time, this approach allows for simple analyses within a relatively short timeframe. The efficacy of the other methods investigated in this work was hindered by low recovery yields or insufficient decontamination from thorium and bulk matrix components.

Zusammenfassung:

Im vergangenen Jahrhundert wurde eine beträchtliche Menge an radioaktiven Elementen durch radioaktiven Niederschlag aus Kernwaffentests und anderen menschlichen Aktivitäten in die Umwelt freigesetzt. Eines dieser Elemente ist Neptunium, ein vergleichsweise wenig erforschtes Actinoid, dessen Beitrag zur Umweltradioaktivität voraussichtlich in Zukunft steigen wird. Die quantitative Bestimmung von Radionukliden in Umweltproben erfordert die Anwendung eines geeigneten Spikes, um Ausbeuteverluste während der chemischen Trennung nachvollziehen zu können. Im Falle von ^{237}Np existiert aber kein passender isotopischer Spike.

In dieser Arbeit wurde die gleichzeitige Bestimmung von ^{237}Np und Plutonium-Isotopen über ^{236}Pu , einen nicht-isotopischen Spike für ^{237}Np mit ähnlichen chemischen Eigenschaften, untersucht. Vier verschiedene Aufarbeitungsmethoden wurden mit Hinblick auf ihre Eignung für Boden- und Wasserproben analysiert und verglichen. Untersuchte Proben wurden mit ^{237}Np - und ^{236}Pu -Spikes versetzt und Radionuklide in den Proben mittels Säurebehandlung in Lösung gebracht. Nach dem Einstellen der Oxidationsstufen wurden Plutonium und Neptunium mittels Ionenaustausch- oder Extraktionschromatographie von der Probenmatrix abgetrennt. Messpräparate für die α -Spektrometrie wurden durch Mikropräzipitation hergestellt.

Die besten Ergebnisse in Bezug auf die Reproduzierbarkeit der chemischen Ausbeuten wurden mit der VERA-Methode für Bodenproben von 1 g erzielt, einem Verfahren bei dem Mitfällung mit Eisenhydroxid, Ascorbinsäure und Nitrit als Redoxmittel und Extraktionschromatographie mit UTEVA[®] Harz zum Einsatz kommen. Die gute Übereinstimmung der Verhältnisse der chemischen Ausbeuten spricht für ^{236}Pu s Eignung als nicht-isotopischer Spike für ^{237}Np . Gleichzeitig ermöglicht die Methode relativ schnelle und simple Analysen. Die Tauglichkeit der anderen in dieser Arbeit untersuchten Methoden wurde durch niedrige chemische Ausbeuten oder unzureichende Abtrennung von Thorium und Matrix-Komponenten beschränkt.

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1. Introduction

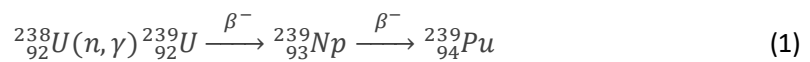
Radioactivity is a ubiquitous physical phenomenon present throughout space, the earth's atmosphere and the earth's crust. Arising from nuclear reactions or the spontaneous disintegration of unstable nuclei, it is defined by the characteristic emission of radiation in the form of electromagnetic waves or particles. The causes of environmental radioactivity can be distinguished into radioactive isotopes of natural and anthropogenic origin. Natural sources of radioactivity include extremely long-lived primordial radionuclides, their progeny and cosmogenic radionuclides. Anthropogenic radioactivity, on the other hand, refers to the presence of radioactive isotopes released artificially through human activities. Nuclear power plants, waste from industrial and medicinal applications and nuclear weapons testing are among the major contributors to man-made environmental radioactivity (IAEA, 2007). Since the introduction of anthropogenic radioactivity almost a century ago, extensive research on its impact on organisms and the environment has been conducted. Recent developments in regard to climate change and global political climate have further reinforced the need for environmental radioactivity studies. Essential to the understanding of distribution and behavior of radioactive material in the environment, these studies enable a multitude of scientific endeavors. Determination of fallout patterns, implementation of radiation protection, archeological and geological studies and climate change research are just a few examples of a long list of applications utilizing isotopic or nuclear techniques (Anagnostakis, 2015). While γ -spectrometry is broadly used to monitor radioactivity in environmental samples, α -spectrometry remains an important radioanalytical technique for determining the activity of α -emitters due to the combination of its simplicity, versatility, high sensitivity and affordability (Vajda et al., 2020).

Plutonium (Pu) and Neptunium (Np) isotopes are among the most important α -emitters released through anthropogenic activities. Due to the long half-lives of relevant isotopes (i.e., $t_{1/2} = 87.7$ y for ^{238}Pu , 24110 y for ^{239}Pu , 6561 y for ^{240}Pu and 2.14×10^6 y for ^{237}Np), they are considered persistent radioactive pollutants, consequently necessitating accurate and rapid methods of their quantitative determination to ensure appropriate environmental monitoring and risk assessment (Qiao et al., 2010). According to estimations by Beasley et al. (1998), the overall global fallout of ^{237}Np amounts to approximately 1.5 tons, based on a $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.18, a $^{237}\text{Np}/^{239}\text{Pu}$ ratio of 0.47 and the release of around 13 PBq of $^{239+240}\text{Pu}$ into the environment (Kelley et al., 1999). An $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio of 0.47 corresponds to an activity ratio of approximately 0.002, which is why accurate determination of ^{237}Np in samples of typical size (about 10 – 20 g) via α -spectrometry is virtually impossible. Presently, quantification of ^{237}Np in environmental samples necessitates the application of highly sensitive measurement techniques such as AMS (Accelerator Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma – Mass Spectrometry).

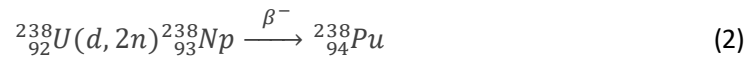
2. Theoretical Background

2.1 Plutonium

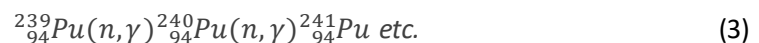
The chemical element plutonium is a radioactive metal and member of the actinide family. Approximately twenty Pu isotopes with masses ranging from 228 to 247 have been characterized, all of which exhibit nuclear transmutation. Plutonium's atomic number of $Z=94$ is the highest of any naturally originated element. Small quantities of ^{239}Pu are continuously produced via capture of fast neutrons by ^{238}U in natural uranium ore deposits, as depicted in Equation (Eq.) (1), and infinitesimal traces of ^{244}Pu , a long-lived ($t_{1/2}= 8.13 \times 10^7$ y) isotope created by rapid neutron capture processes during primordial nucleosynthesis, can still be detected today (Wallner et al., 2015).



The lion's share of Pu found in nature, however, is of anthropogenic origin and was primarily released through nuclear weapons testing during the Cold War era and nuclear energy production. The first man-made plutonium isotope was ^{238}Pu , produced during bombardment experiments of uranium with deuterons in 1940 by Seaborg, McMillan, Kennedy, and Wahl (Seaborg et al., 1946).



Due to its high energy density, the spontaneous decay of ^{238}Pu is mainly utilized in radioisotope thermoelectric generators. Anthropogenic production of ^{239}Pu , an isotope with a high cross-section for thermal neutrons, was accomplished shortly thereafter via neutron bombardment of ^{238}U , as described in Eq. (1). Its nuclear properties sparked immense interest during the then-current wartime, resulting in the construction of the plutonium production complex at the Hanford Site as part of the Manhattan Project. It is considered the most important isotope of Pu and is the main isotope employed in nuclear reactors and weapons. Elucidation of the chemical and physical properties of plutonium was largely accomplished through its utilization. The capture of fast neutrons by ^{239}Pu results in the formation of heavier plutonium isotopes.

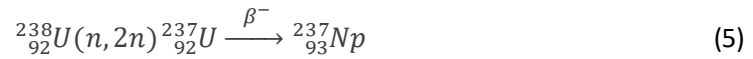
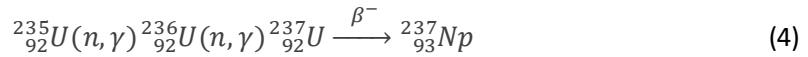


The most relevant isotopes with regard to environmental monitoring are ^{238}Pu , ^{239}Pu and ^{240}Pu . Other notable plutonium isotopes include ^{236}Pu and ^{242}Pu . They primarily find application as tracer isotopes. The physical and chemical properties of plutonium are as unique as they are complex. The solid metal can exist in six different allotropic phases of varying densities and mechanical qualities and has an unusually high resistivity for a metal. Additionally, elemental plutonium and its compounds are quite reactive and unstable with respect to the effects of their own irradiation, temperature, and chemical

reactions. In solution, plutonium exists in up to five different oxidation states, making it notoriously difficult to adjust its oxidation state for radioanalytical separations (Clark et al., 2006). Because of its prevalence in the earth's crust caused by anthropogenic input, plutonium is useful for numerous environmental studies, enabling the determination of its origin and release date through its isotopic composition, assessment of its atmospheric and geochemical mobility, and other scientific endeavors.

2.2 Neptunium

Neptunium is the first transuranic element and somewhat inconspicuous among the early actinides. The isotope ^{239}Np was the first to be identified through neutron bombardment experiments with ^{238}U in 1939 by McMillan and Abelson, as described in Eq. (1) (McMillan et al., 1940). A couple years later, ^{237}Np , the most significant isotope concerning neptunium's environmental impact, was discovered within the course of the Manhattan Project. As ^{237}Np is the parent-nuclide of the so-called 'neptunium series', the $4n + 1$ natural decay chain, there used to be natural reservoirs of primordial neptunium. Nowadays, these reservoirs are depleted since all the neptunium has decayed and the vast bulk of today's neptunium deposits is the result of neutron capture reactions of ^{235}U and ^{238}U in nuclear fuel.



Due to its lack of practical applications, most of the ^{237}Np generated during the nuclear fuel cycle is predestined to end up in nuclear waste repositories (Zhao et al., 2014). Presently, neptunium's contribution to environmental radioactivity is small since all of its isotopes are short-lived beta or X-ray emitters or, in the case of ^{237}Np , an alpha emitter with an extraordinarily long half-life and thus low specific activity. However, according to long-term projections, the extent of ^{237}Np 's radiation burden will rise to significant levels as a result of its long half-life, its constant input into the environment and the decay of ^{237}U and ^{241}Am . Additionally, neptunium exhibits higher mobility in the environment than other actinides, further necessitating its monitoring and consequently reliable analytical methods for its separation and quantitative determination (Thakur et al., 2012). Unfortunately, the accurate determination of ^{237}Np is impeded by the lack of a suitable tracer, a circumstance that will be further discussed in Chapter 3.

2.3 Alpha Spectrometry

Alpha spectrometry is a widely employed radioanalytical method in fields like environmental monitoring, nuclear forensics, geology, nuclear fuel processing and the production of radiopharmaceuticals. Detection of radionuclides is based on the specific energies of α -particles emitted during their radioactive decay. The principal setup of an α -spectrometric system consists of the detector, situated inside a vacuum chamber and connected to a bias supply, an amplification system, a multichannel analyzer (MCA) with an integrated analog-to-digital converter and a computer to operate processing software. A schematic illustration of this setup is depicted in Figure 1.

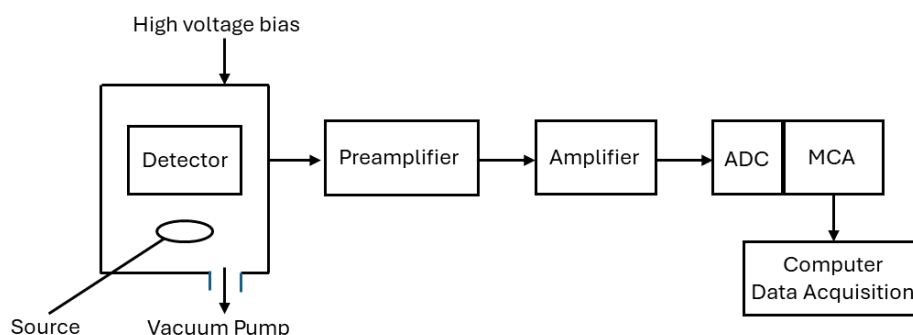


Figure 1. Schematic illustration of an alpha spectrometric system.

Different types of detectors, including ionization chambers, scintillation detectors and semiconductor detectors, find application in setups for α -spectrometric measurements. Among these, silicon semiconductor detectors are utilized most frequently due to their high resolution, sensitivity, compactness, and simplicity (Wolf, 2008). Penetration of α -particles in the depletion region of the semiconductor induces the formation of electron-hole pairs. The number of these pairs is proportional to the deposited energy, thus enabling the conversion of particle energy into measurable electronic pulses. Voltage pulses are then amplified, digitized and assigned to channels of the multichannel analyzer based on their pulse height, generating a spectrum of pulse counts plotted against energy. An exemplary α -spectrum is visualized in Figure 2. The spectrum enables qualitative and quantitative analysis via interpretation of particle energy and counts, respectively.

Alpha spectrometry is valued for several beneficial attributes. Firstly, due to the combination of the high yield of the α -decay process, the high intrinsic signal-to-noise ratio of semiconductor α -detectors, the high efficiency of these detectors for incident alpha particles and their high selectivity against beta and gamma radiation, alpha spectrometry is a highly sensitive technique, enabling very low detection limits. Secondly, the scope of determinable radionuclides is quite extensive, including almost all α -emitters with half-lives long enough compared to the necessary radiochemical procedure and measurement, as well as β -emitters with α -active progeny. Additionally, the conventional utilization of an internal, α -emitting tracer provides high reliability, as it compensates for losses during chemical

separation and for the counting efficiency of the detector. Finally, α -spectrometry is relatively inexpensive to carry out and the analysis of alpha spectra is reasonably simple. The main disadvantage of α -spectrometric measurements stems from the short range of α -particles, necessitating chemical separation of target radionuclides from the sample matrix and from other radionuclides to prepare a thin, homogenous counting source. This approach allows for the minimization of attenuation within the source and the prevention of overlapping energy ranges in the spectrum (Vajda et al., 2020).

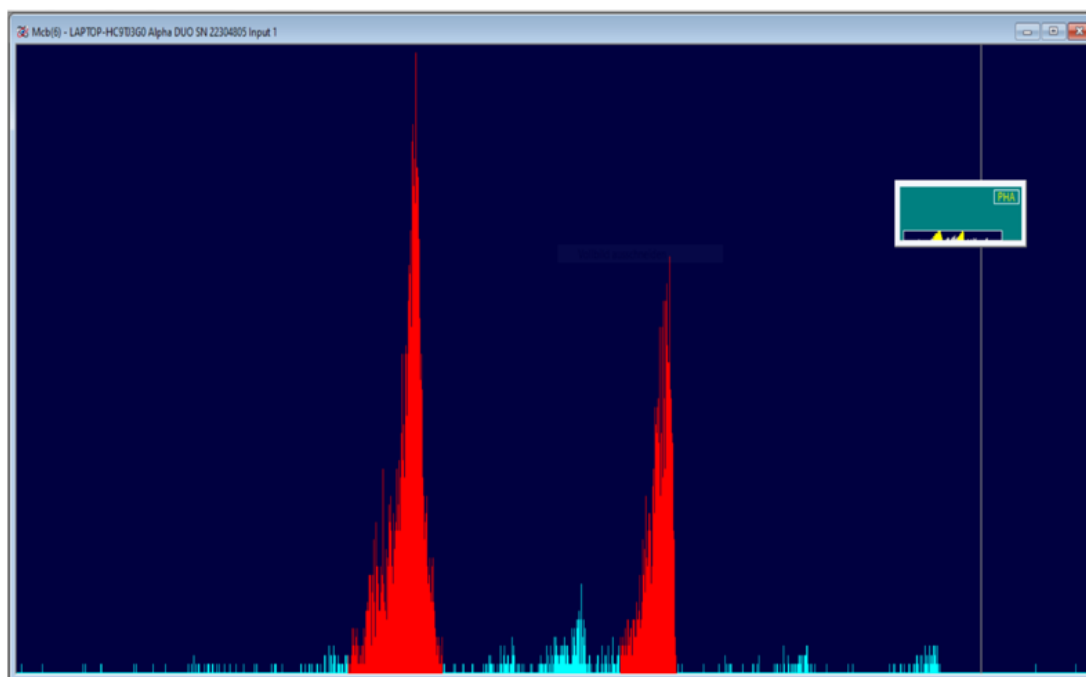


Figure 2. α -spectrum measured with an Ortec Alpha Ensemble[®] α -spectrometer with surface barrier detector. Highlighted peak areas depict ^{237}Np (left) and ^{236}Pu (right).

2.4 Radiochemical Procedure

Given the importance of environmental radioactivity studies concerning α -emitting radionuclides, it is not surprising that researchers have established an extensive repertoire of analytical methods with the goal of transforming a sample of interest into a measurable activity source. The typical radiochemical procedure for any solid, environmental sample consists of four steps:

- Complete dissolution or leaching of the radionuclides of interest
- Redox adjustment
- Chemical separation
- Sample mounting

This thesis will provide an overview of the radiochemical preparation of samples for alpha-spectrometric measurement, with an emphasis on neptunium and plutonium in soil samples.

2.4.1 Sample Dissolution

2.4.1.1 Ashing techniques

Following the application of adequate sampling methods, which are outside of the scope of this thesis, samples commonly have to undergo some sort of physical manipulation (heating, grinding, etc.) to facilitate dissolution. Organic matter, ubiquitous in almost any sample, represents a potential source of error for radiochemical analysis due to its ability to influence solubility equilibria through complex formation. While there are reports of increased recovery yields for actinides of interest in the presence of organic substances, samples are routinely ashed prior to wet digestion to avoid interference with subsequent chemical separation methods (Fujikawa et al., 2002). Among the different ashing techniques available, dry ashing finds the most application due to economic reasons as well as reasons of simplicity and safety (Andrejko et al., 1983). Sample material is placed in a ceramic container and heated in a muffle furnace for an extended period of time, at a specific temperature or with a specific thermal program. However, reported ashing temperatures in literature vary strongly, especially with regard to the accurate analysis of plutonium in soil samples. Temperatures of 300-900 °C have been used by researchers over the past decades in an attempt to achieve complete decomposition of organic material and simultaneously avoid volatilization of analytes, typically only relevant for certain species like tritium and iodine, and formation of refractory residues that are insoluble during the acid leaching process. Application of ashing aids can help to circumvent these problems through facilitation of oxidation processes and prevention of volatilization (Miller-Ihli, 1992). In consideration of the multitude of studies covering this issue, recent consensus points to the ideal ashing temperature being somewhere in the range of 300-500 °C (Veselsky, 1977; Wang et al., 2015). Other ashing methods include wet ashing, a term sometimes used interchangeably with wet digestion, where organic material is removed from a sample in an aqueous environment utilizing strongly oxidizing acids or reaction mixtures, and cold ashing, where oxidation of organic matter takes place at room temperature in the presence of activated oxygen. These techniques are less significant for radiochemical methods due to the use or formation of potentially carcinogenic or explosive substances or the need for sophisticated equipment (Andrejko et al., 1983).

2.4.1.2 Tracer

Another factor to consider prior to the application of any wet digestion chemistry is the manner in which the actual detection of analytes is conducted. Because the mass of the radionuclides of interest within a sample is negligibly small, conventional analytical tools like gravimetric determination are not applicable and measurement of the activity of isolated analytes lacks information about losses during chemical procedure. Therefore, addition of a carrier or, more commonly, a tracer is part of the initial step in the routine determination of radioisotopes. The term carrier refers to a substance that raises

the effective concentration of an analyte, enabling conventional methods not suited for micro-scale analysis. Carrier material consists of a stable isotope of the target radionuclide or a chemically similar element, usually found in the same group of the periodic table. A tracer, on the other hand, is an indicator that allows for monitoring of a target analyte on the basis of identical chemical behavior. Through addition of a known quantity of another radioisotope with different decay energy and originally non-existent in the sample, determination of an unknown amount of radioisotope in a sample is made possible (MARLAP, 2004a). Moreover, the tracer technique, pioneered by George de Hevesy in 1913, is commonly utilized in various environmental, medicinal, biological and geological studies. Technically, different isotopes of the same element exhibit slight differences in kinetic and thermodynamic behavior. However, the impact of this effect is deemed to be vanishingly small for typical experiments and only relevant for certain cases of the use of radiotracers of very low molecular weight, where large relative mass differences are present (Haba et al., 2011).

The satisfactory performance of a tracer is highly dependent on the identical behavior of tracer and analyte, requiring the equivalency of chemical forms and oxidation states. Consequently, tracer addition to the sample should occur as early as possible. Generally, this takes place shortly prior to sample dissolution in consideration of the necessary time to ensure complete equilibration of added tracer and analytes (MARLAP, 2004a). Depending on the specific task, tracer addition can be carried out prior to ashing. This approach, however, comes at the risk of potential isotopic discrimination during the ashing process (Wang et al., 2015; Krammer, 2020). A tracer's suitability for a radiochemical method is dependent on numerous factors, including the availability of a suitable isotope, radionuclidic and radiochemical purity, its behavior in the system, the necessary activity and its mode of counting as well as potential health risks. The half-life of a tracer should be long in comparison to the duration of the experiment and is considered particularly important because it has several effects on the radiochemical procedure. On one hand, appropriate tracer half-life circumvents the challenges of handling unnecessarily elevated levels of activity and the need for significant decay corrections. On the other hand, it limits the ingrowth of radioactive daughter nuclides that could interfere with the accurate determination of activity in multi-element analyses (McMillan, 1975). Due to the very low concentrations at which most radiochemical procedures are carried out, the significance of adsorption processes of radiotracers and radioanalytes onto particles and surfaces of containers is high compared to the chemistry of elements at conventional concentrations. Minimizing the degree of adsorption can be accomplished by preventing interaction with negatively charged surfaces via adjustment of low pH, complexation, selection of suitable container material and, if necessary, dilution with carrier (MARLAP, 2004a; Serne, 1992).

2.4.1.3 Acid leaching techniques

Complete dissolution of the sample matrix is essential to the successful isolation of radionuclides of interest. The actual composition of a given sample, however, is mostly unknown to the analyst, constituting the need for general and reliable methods of decomposition applicable to a broad spectrum of environmental matrices. These methods are based on the merging of reactant and solvent, creating a homogenous solution suitable for subsequent separation techniques. Due to the insolubility of most naturally occurring compounds in water, strong acids and fusion salts are utilized to enable dissolution via chemical exchange, complexation, rearrangement reactions or oxidation-reduction processes. Methods most important to modern radiochemical procedure can be categorized into three classes: acid leaching/total dissolution, fusion and microwave digestion. In consideration of aspects such as the data quality objective, the nature of the sample, economic feasibility, hazard potential, waste generation and the source term of the radionuclides of interest, each of the dissolution techniques mentioned above comes with certain benefits and disadvantages (ORTEC®, 2024).

Leaching is commonly defined as the solubilization of analytes from their carrier substance. In radioanalytical chemistry, leaching techniques enable the determination of the soluble fraction of target radionuclides under specific applied leaching conditions. Traditionally, this is done by utilizing a hot plate as heat source. Leachable radioanalytes differ depending on the applied leaching agent and complex matrices often require different methods of leaching to achieve complete dissolution of different geochemical phases (MARLAP, 2004b). Among the available acids, HNO_3 is most commonly used because of its ability to oxidize most metals to nitrates and the high solubility of those nitrates in aqueous solution. Total dissolution, usually achieved via digestion in HNO_3 and HF, is necessary when analytes of interest are highly insoluble (e.g., plutonium reactor core material) or embedded within a refractory component of the sample matrix. While generally considered preferable to partial leaching, due to the often-unknown composition of sample matrices and the feasibility of conveniently dissolving ubiquitous silicate ores, complete decomposition utilizing HF comes with its own disadvantages and the correct choice of method is dependent on several factors. Sample dissolution with HF in an open container is known to cause the loss of some elements through volatilization and certain refractory minerals (e.g., zirconium oxides) experience incomplete decomposition (Chao et al., 1992). Moreover, total dissolution is unnecessary if quantitative leaching from the sample can be demonstrated confidently (Braysher et al., 2019). In consideration of the desire for simple and fast analytical methods in routine analytics, acid leaching remains a viable dissolution technique for specific scientific endeavors.

2.4.1.4 Fusion techniques

Fusion techniques represent a sophisticated alternative to complete dissolution involving HF. Sample material, mixed with a fusing salt/flux in a crucible, is heated beyond the melting temperature of the fusion reagent, enabling the conversion of challenging environmental matrices, such as silicates, sludges and soils, to acid-soluble forms (Milliard et al., 2011). Depending on the composition of the matrix and the elements of interest, different types of fusion salts, including carbonates, alkali hydroxides, fluorides and boron compounds, find application during fusion processes. The success of a fusion reaction is dependent on a variety of factors, such as the presence of chemically bound oxygen in minerals, slow and even heating to avert premature combustion of substances preceding the fusion process, the, preferably low, melting point of the fusing reagent and the ratio of fusing reagent to sample material. In comparison to classical acid leaching with HNO_3 and HF, fusion techniques are generally less time-consuming, produce less chemical waste and exhibit superior kinetic behavior (Sahu et al., 2019). On the other hand, fusion techniques are prone to contamination of the sample as a result of the interaction of the fusing flux with the crucible or the large quantitative excess of fusing flux needed to ensure decomposition of sample material. Moreover, exceedingly high temperatures utilized during fusion processes may cause volatilization of analytes and solutions derived from fusion methods contain high concentrations of dissolved salts, which may be disadvantageous during subsequent purification steps. Therefore, dissolution by acid leaching is preferable for certain applications, such as multi-element analyses in combination with sensitive and precise mass spectrometry measurement techniques (Kasar et al., 2020).

2.4.1.5 Microwave digestion

Heating with a microwave oven, first reported in 1975, is regarded as a safe, rapid and convenient alternative to conventional hot plate dissolution (Abu-Samra et al., 1975). At its inception, the practical use of microwave techniques was limited by sample size and the corresponding pressure acting on the reaction vessel, impeding the ability to reach the necessary detection limits. This drawback has since been remedied by advances in vessel design and sensitive detection methods, making microwave dissolution an effective radioanalytical tool, providing good recovery yields with short digestion times, low potential for contamination and minimal required supervision (Alvarado et al., 1996). Microwave instrumentation can be roughly distinguished into open vessel and closed vessel systems, and while both techniques come with advantages and disadvantages, the utilization of closed pressurized vessels is especially interesting because it allows for the heating of dissolving agents beyond their boiling points at normal pressure, further facilitating the dissolution of sample material (Lamble et al., 1998). When applied without microwave instrumentation, pressure vessels are commonly referred to as acid digestion bombs, providing improved solubility based on the same principle.

In summary, recent literature entails the need for different dissolution methods for varying scientific research questions. Satisfactory digestion of a particular sample is contingent on the specific sample matrix and the radionuclides of interest, and generalizations are hard to justify considering the conflicting data in literature concerning recovery, reproducibility and efficacy of different dissolution procedures.

2.4.2 Redox Adjustment

Manipulation of oxidation states is among the most important tools applied during radiochemical procedure, as it is essential to the success of many routine separation techniques such as ion-exchange and extraction chromatography. Likewise, oxidation-reduction (redox) processes enable sufficient sample dissolution and quantification techniques like electrodeposition. Furthermore, since oxidation states of target analytes and tracer or carrier substances must be identical to ensure complete equilibration and consequently quantitative yield determination, their adjustment constitutes the basis of most quantifications carried out during radiochemical endeavors. Changes in oxidation numbers of radioanalytes may influence their chemical behavior and stability, thus emphasizing the need to control them. However, accurate adjustment of oxidation states of certain transuranic elements represents a major challenge because of their susceptibility to change caused by disproportionation reactions and other redox processes.

2.4.2.1 Oxidation states

The diversity in oxidation states at the beginning of the actinide series is a consequence of the unique electronic configuration of f-block elements and their consequently unique chemical properties. Electrons occupying 5f subshells experience elevated shielding compared to those occupying 4f subshells of the cognate lanthanides, which demonstrate homogenous redox behavior. As a result of this superior relative stabilization, energy levels of 5f, 6d and 7s electrons are in close vicinity to one another, enabling the participation of those electrons in chemical bonding and giving rise to the variety of oxidation states exhibited by earlier actinide ions in the series. Continuous filling of the 5f orbitals increases the energy gap between 5f and 6d subshells, resulting in the preference of the lower oxidation states +2 and +3 for actinides of higher atomic number, as depicted in Table 1 (Kihara et al., 1999).

Actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Oxidation State		(2)				(2)				(2)	(2)	2	2	2	
	3	(3)	(3)	3	3	3	3	3	3	3	3	3	3	3	3
		4	4	4	4	4	4	4	4						
			5	5	5	5	5								
				6	6	6	6								
					7	7									

Table 1. Overview of the oxidation states of actinides (Edelstein et al., 2011).
Bold = most stable, () = unstable

These features are best exemplified by the diverse oxidation numbers of the elements uranium (U), Np, Pu and americium (Am). Low pH generally favors lower valence states, while high pH promotes the stability of higher valence states. In addition to the multitude of possible oxidation states, these oxidation states are also susceptible to change induced by various potential redox processes that ordinarily take place during radioanalytical procedure. Moreover, for certain actinides, like plutonium, it is common for multiple oxidation states to coexist in the same solution. The combination of these attributes confers upon the early actinides a chemical behavior, unmatched in complexity by most other elements in the periodic table.

2.4.2.2 Complexation

The structures of actinide cations in acidic aqueous solution can be distinguished into four types. Tri- and tetravalent species exist in the form of M^{3+} and M^{4+} ions, exhibiting a high charge density and tendency to be affected by hydrolysis, solvation and polymerization. Penta- and hexavalent species, on the other hand, are present as the linear dioxo-cations MO_2^+ and MO_2^{2+} . Withdrawal of the metal's effective charge by the bound oxygen gives rise to stable molecular cations, more resilient in regard to chemical transformation than their tri- and tetravalent counterparts (Edelstein et al., 2011). The chemical behavior of actinides is defined by their electropositive character. Consequently, all actinide ions are hard Lewis acids, illustrated by their inclination for complexation by ligands with hard Lewis base donor atoms such as oxygen and fluorine. Actinide-ligand bonds are mainly ionic and, in many cases, kinetically unstable. Their thermodynamic stability is largely contingent on factors concerning electrostatic attraction and steric hinderance, including ion size, the effective charge of the metal center and the size, flexibility and dentaty of the ligand. Given that most commonly applied separation techniques like ion-exchange and extraction chromatography are based on the interaction of complex anions, comprehension of the complexation chemistry of actinides is of great importance when

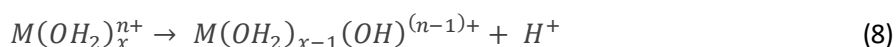
investigating them. In general, the tendency of complex formation is in alignment with the order of increasing charge density:



Among the actinides with the most multifarious redox behavior, the degree of complexation increases from U(IV) to Am(IV) and decreases from U(VI) to Am(VI), a trend approximately in agreement with the sequential filling of the 5f subshell and the consequently decreasing ionic radii (Choppin et al., 2006). The complexation power of commonly present anions increases in the following order (Paulenova et al., 2013):



The phosphate ion in particular, commonly present in environmental matrices, can pose problems with regard to sample preparation. Because of the high stability of phosphato-complexes, their formation is favored compared to the formation of, usually desired, nitrate- and chlorido-complexes, thus representing a potential source of error during anion-exchange separations. Additionally, phosphato-complexes are prone to formation of insoluble precipitates and polymerized aggregates. To avoid these interferences, phosphate scavengers like $Al(NO_3)_3$ are routinely added to sample solutions with a high phosphate content (Edelstein et al., 2011). Hydrolysis of actinide ions represents a unique form of complexation resulting from interaction with water molecules in aqueous solution. Coordination of water to acidic, positively charged cations increases the acidity of protons of the bound aqua ligands, facilitating the formation of hydroxo-complexes.



An ion's tendency to undergo hydrolysis is in accordance with the principles applied for complexation in general, hence affecting tetravalent ions most significantly. Consequently, actinides in tetravalent form, their most ordinarily adjusted oxidation state with respect to separation techniques, are liable to the most significant degree of hydrolysis. Similar to the interaction of cations with other oxygen-containing ligands, hydrolyzed actinide ions can lead to the formation of insoluble precipitates and condensed species, connected by hydroxo or oxo bridges (Edelstein et al., 2011). Fortunately, the extent of actinide hydrolysis is highly dependent on the acidity of the sample solution and for acidic solutions of $pH < 1$, formation of hydrolyzed species is deemed hardly relevant (Choppin et al., 2006).

2.4.2.3 Redox potentials

Estimation of an oxidation state's stability and susceptibility to change is most reasonably accomplished by comparison of standard electrode potentials (E°). Defined as the difference in electric potential generated by an electrochemical cell reaction in which molecular hydrogen is oxidized to solvated

protons by reduction of a species to its lower oxidation state under standard conditions (100 kPa H₂ gas pressure, 298.15 K, [1mol/L] of solute reactants), standard electrode potentials are commonly utilized as reference data in various scientific disciplines as they allow for the prediction of the course of chemical reactions (IUPAC, 2006).



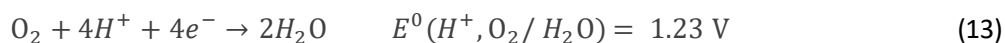
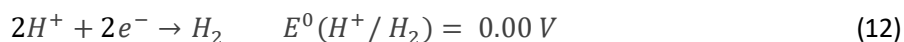
Because of the equivalency of absolute values of oxidation and reduction potential in a redox reaction, it is common practice to refer to standard electrode potentials as standard reduction potentials E^0_{red} . The transformation of any species through uptake or donation of electrons is accompanied by a change in Gibbs free energy, related to the standard reduction potential by the equation:

$$E^0 = -\frac{\Delta G^0}{nF} = -\frac{RT}{nF} \ln K \quad (10)$$

with ΔG^0 being the change in Gibbs free energy (J·mol⁻¹), F being the Faraday constant (F = 96485 C·mol⁻¹), R being the universal gas constant (R = 8.314 J·K⁻¹·mol⁻¹), T being the temperature in Kelvin, n being the number of transferred electrons and K being the equilibrium constant of the redox reaction. Naturally, the equilibrium constant of a redox reaction is dependent on the ratio of the chemical activities of the species' reduced and oxidized forms. Under the assumption that the value of E^0 of Eq. (10) corresponds to an ideal half-cell potential and that concentrations of all redox-active solutes are sufficiently low to equate them with chemical activities, the Nernst law describes the ideal half-cell potential E of an actinides redox reaction as follows:

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{[An(red)]}{[An(ox)]} \quad (11)$$

$E^{0'}$ is the formal reduction potential, specific for a chemical milieu and most commonly determined in 1M perchloric acid. The combination of its low but stabilizing proton concentration and weak complexing power provides beneficial attributes that allow for the reasonable approximation of formal and standard reduction potentials (Paulenova et al., 2013). The entirety of element-specific electrode potential data in any specific medium can be illustrated through Latimer diagrams of the formal reduction potentials of redox couples. A comparison of these values with the half-cell potentials of reduction and oxidation of water enables the estimation of an actinide's species liability to change in aqueous solution (Bard et al., 1985).



The $E^{0'}$ s depicted in Figure 3 provide an explanation of the stability trends of oxidation states of the early actinides. Species with $E^{0'} < 0 \text{ V}$, such as actinides in elemental form, U(III) and Am(II) have the reducing capability to liberate hydrogen from water, whereas species with $E^{0'} > 1.23 \text{ V}$, like Am(IV) and

(VI), are strong oxidizing agents able to release oxygen from water. Consequently, these species are not stable in acidic aqueous solution (Paulenova et al., 2013).

The exact values of E^0 s in literature may vary between publications, due to the multitude of factors limiting their accurate determination. Since the first publication of Latimer's 'Oxidation Potentials' in 1938, in which most E^0 s are based on estimations from thermodynamic data, E^0 s of actinides have been elucidated thoroughly through new methods to electrochemically determine E^0 s and new approaches to the assessment of thermodynamic data (Latimer, 1952). From a practical standpoint, however, measurement of E^0 s continues to be generally afflicted by phenomena of electrode kinetics, effects of pH and temperature, ambiguous redox behavior and so on. As a result, measured and calculated values rarely correlate. However, despite the lack of precision concerning the determination of absolute values of reduction potentials, they provide useful information in regard to the estimation of relative electrochemical changes in a system (Kihara et al., 1999).

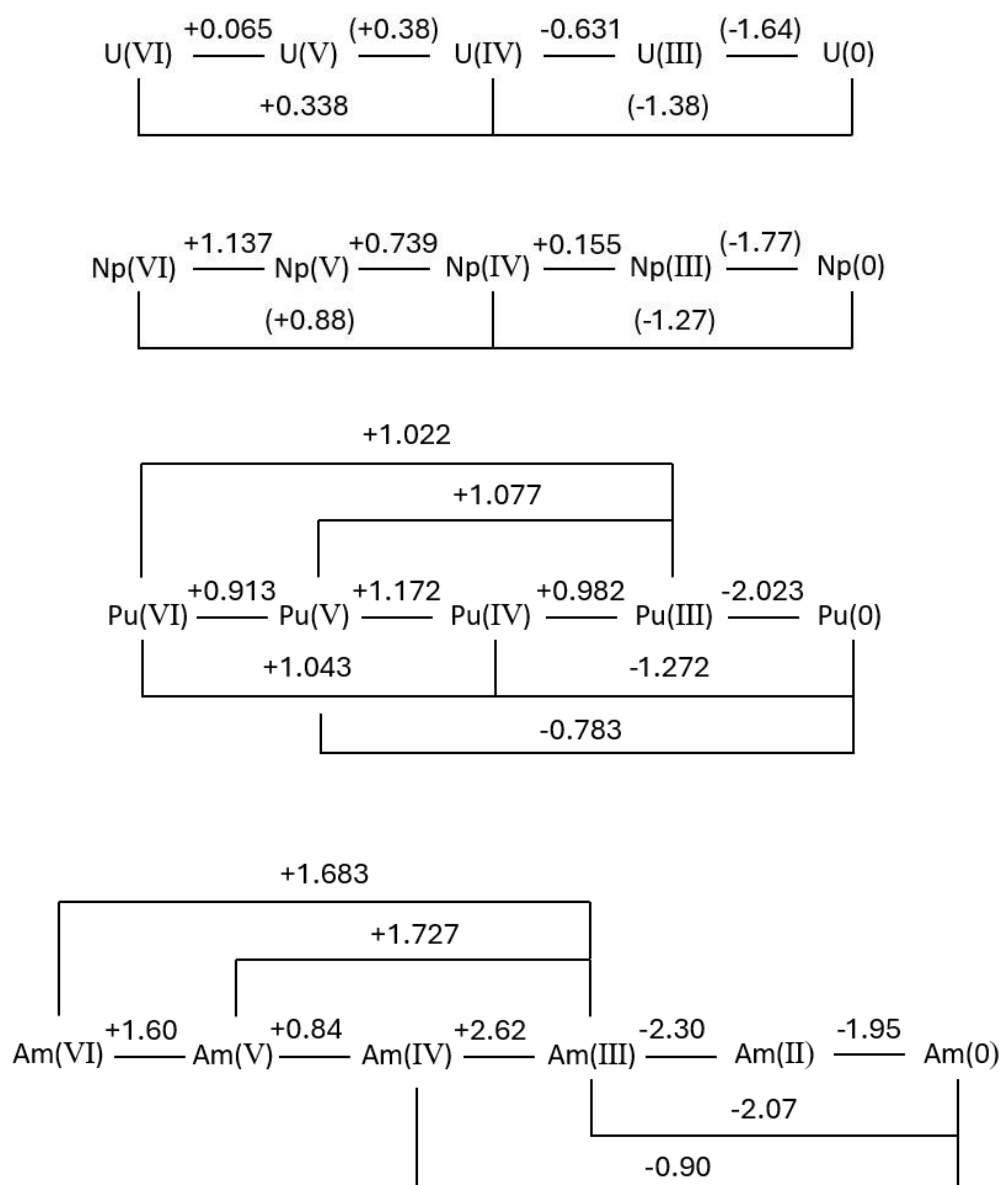


Figure 3. Latimer diagrams of formal redox potentials E° s for selected actinide redox couples in V. (in 1M HClO_4 at 25°C vs standard hydrogen electrode)
Reference data for U and Np from Kihara et al. (1999), for Pu from Clark et al. (2006) and for Am from Paulenova et al. (2013); values in brackets are standard electrode potentials E° s (Bard et al., 1985).

One major factor contributing to the varying nature of oxidation states of actinides is their tendency to undergo disproportionation reactions. Generalizations regarding the characteristics of these reactions are hard to justify since reaction rates and equilibria are dependent on pH, the presence of complexing agents and the concentration and attributes of the specific element. Small differences in the composition of the chemical medium may result in drastically altered ratios of valence states. Nevertheless, estimation of an oxidation state's proclivity towards disproportionation in a particular medium can be accomplished through calculation of the differences in formal reduction potentials between oxidation to its higher oxidation state and reduction to its lower oxidation state. Because

oxidation states from III to VI are most significant to the chemistry of actinides in aqueous solution, these potential differences are ordinarily determined for tetra- and pentavalent actinide species.

$$\Delta E(IV) = E^{0'}(An(V)/An(IV)) - E^{0'}(An(IV)/An(III)) \quad (14)$$

$$\Delta E(V) = E^{0'}(An(VI)/An(V)) - E^{0'}(An(V)/An(IV)) \quad (15)$$

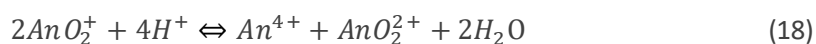
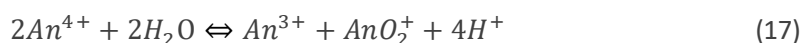
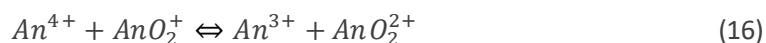
As demonstrated in Eq. (10), changes of redox potentials are accompanied by changes in Gibbs free energy ΔG^0 . Thus, ΔE represents an indicator of whether the course of a reaction is spontaneous or not. Since ΔE is proportional to the negative value of ΔG^0 , a positive value of ΔE would imply a positive value of ΔG^0 and therefore the stability of the particular actinide species. Conversely, values of $\Delta E(IV)$ and $\Delta E(V)$ close to or below zero indicate an oxidation state's tendency to undergo spontaneous disproportionation reactions. Insertion of formal redox potentials of the respective couples from Figure 3 into Equations (14) and (15) gives the ΔE values of tetra- and pentavalent U, Np, Pu and Am, depicted in Table 2. They emphasize the acknowledged susceptibility towards disproportionation of Am(IV), U(V) and Pu(V). In the case of plutonium, $\Delta E(IV)$ is also sufficiently low to allow for disproportionation, which is why plutonium exhibits the most variable redox behavior of all elements (Paulenova et al., 2013).

	U	Np	Pu	Am
$\Delta E(IV)$ [V]	1.01	0.59	0.19	-1.78
$\Delta E(V)$ [V]	-0.32	0.40	-0.26	0.76

Table 2. Differences in oxidation and reduction potentials of tetra- and pentavalent selected actinides in 1M HClO₄ (Paulenova et al., 2013).

As is apparent from the data in Figure 3, redox potentials connecting the most important oxidation states of plutonium are of similar magnitude. For this reason and the nuanced kinetics governing the plethora of possible individual disproportionation reactions, equilibrated acidic solutions containing plutonium commonly contain a mixture of species ranging from Pu(III) to Pu(VI) (Clark. et al., 2006). While these complications can impede the collection of experimental data, quantitative determination of plutonium or any other element with fluctuating redox behavior in solution is not affected, provided that establishment of a reproducible equilibrium can be confidently demonstrated. For this reason, the typical valence state adjustment during radiochemical analysis of actinide analytes involves the application of a reducing agent, adjusting all forms of radioanalytes and tracers to their lowest oxidation level momentarily (MARLAP, 2004a). Subsequent rapid redox processes will affect each species of chemically identical behavior to an equal extent, therefore generating an equilibrium mixture of analytes and tracers that constitutes the prerequisite for quantitative determination of radionuclides that exhibit multiple oxidation states.

The scope of thermodynamic and kinetic properties influencing the disproportionation reactions of neptunium and plutonium is vastly extensive, and summarized corresponding information is described elsewhere (Kihara et al., 1999; Paulenova et al., 2013; Clark et al., 2006). However, even superficial consideration of the three most typical types of disproportionation reactions in acidic aqueous solution provides crucial insight into their fundamental underlying principles.



Reactions involving the formation or rupture of Pu=O bonds with covalent character are slow and almost irreversible, due to implications attributed to the rearrangement of the solvent shell and the reaction rates of two-electron transfers (Edelstein et al., 2011). Conversely, transformations between the redox couples An^{3+}/An^{4+} and AnO_2^+/AnO_2^{2+} are fast and reversible, and therefore, the reaction in Eq. (16) is rapid compared to the reactions in Equations (17) and (18). While all actinides are affected by these reactions, the degree to which they are is dependent on the specific element, its concentration, pH, temperature and the complexing power of the solution (Paulenova et al., 2013). Upon consideration of Eq. (17), it is evident that disproportionation is discouraged by high pH and high actinide concentrations. For this reason, redox adjustment of actinides to the tetravalent state, often desired for actinide separation procedure, is commonly carried out under highly acidic conditions. Utilization of appropriate complexing agents can enhance this shift of equilibrium synergistically. In the presence of sufficient concentrations of hard ligands such as NO_3^- , An^{4+} and AnO_2^{2+} species experience more complexation than their counterparts of lower effective charge density, thus pushing the equilibrium to their respective sides in Equations (17) and (18). On the other hand, acidic conditions increase the tendency of pentavalent actinides to disproportionate, as indicated in Eq. (18). As a result, these species are highly susceptible to change under the usual conditions present during radioanalytical endeavors or nuclear fuel processing, despite their generally high thermodynamic stability in the presence of oxygen. In environmental media with very low actinide concentrations and neutral pH, however, disproportionation of AnO_2^+ ions is significantly diminished, which is why the solubility and migratory behavior of these species are of particular interest in regard to the environmental monitoring of radionuclides (Topin et al., 2016). It is important to note that these observations are generalizations, unable to predict the exact behavior of a specific actinide species in a particular milieu. For example, due to the very low reaction rate of its disproportionation, Np(V) is the most dominant form of neptunium in the presence of complexing agents at low pH, despite the favorability of tetra- and hexavalent states under these conditions (Paulenova et al., 2013).

Nevertheless, these principles explain the simultaneous coexistence of multiple oxidation states in solution and facilitate the interpretation of empirical data on redox species, whose composition is highly dependent on the reaction medium.

2.4.2.4 Important redox agents

Nitrous acid: Nitrous acid (HNO_2), though not commonly added to radioanalyte reaction mixtures, is omnipresent in aqueous solutions of nitric acid, as it is generated through the thermal or radiolytic decomposition of HNO_3 . Since the presence of HNO_2 and other redox-active nitrogen oxide species is known to affect redox equilibria of actinide ions, understanding, or ideally confinement, of their reactions is of great importance to radioanalytical separation procedure, as well as fuel reprocessing. The intricacy of HNO_2 's impact on valence state control lies in the autocatalytic nature of its reactions with actinides. In other words, nitrous acid, formed as a product of a reaction with actinide ions, will often catalyze the same reaction and therefore increase its own production until equilibrium is established. As a result, even trace amounts of HNO_2 can severely influence the valence state profiles of target analytes (McKenzie et al., 2016). To combat this issue, HNO_2 scavengers are frequently applied during radiochemical analysis.

Nitrite: Nitrite (NO_2^-) is often utilized during the oxidation state adjustment of plutonium. Its favorable redox properties allow for the simultaneous reduction of Pu(V) to Pu(IV) and oxidation of Pu(III) to Pu(IV), enabling the fixation of all plutonium in the tetravalent state. Due to the slow reaction rate of the reduction of Pu(V) to Pu(IV), another reductant, such as ferrous iron or ascorbic acid, is commonly added to accelerate the process (MARLAP, 2004a). Because Np(IV) is hardly affected at room temperature, the application of nitrite under those conditions enables the concurrent adjustment of Np and Pu to the tetravalent state (Kenna, 2002). The addition of nitrite salts to acidic aqueous solutions will result in the formation of nitrous acid, inducing a shift in chemical equilibrium. Even so, quantification is not affected as long as equilibrium between analytes and tracers is established.

Hydrogen peroxide: Hydrogen peroxide (H_2O_2) is most routinely added to sample solutions to oxidize organic matrix components or solubilized resin material after chromatographic separation. The fact that H_2O_2 is a salt-free redox agent is considered advantageous in regard to many applications. Conversely, the potential precipitation of undesirable peroxides is its biggest disadvantage. Similar to nitrous acid, H_2O_2 exhibits ambiguous redox behavior, enabling both reduction and oxidation of actinide species. Furthermore, it rapidly oxidizes HNO_2 to HNO_3 , therefore acting as a HNO_2 scavenger.

Ferrous iron: Ferrous iron (Fe^{2+}) acts as a strong and rapid single-electron reducing agent, able to convert Pu to its trivalent and Np to its tetravalent state under acidic conditions of high complexing power. Complications concerning its application may arise from interference of formed ferric iron (Fe^{3+})

with the uptake of trivalent radioanalytes during chemical separation. Pairing of Fe^{2+} with suitable ions can provide synergistic benefits like the scavenging of HNO_2 or increased stability, as is the case with ferrous sulfamate $(\text{FeNH}_2\text{SO}_3)_2$ and Mohr's salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ respectively (Paulenova et al., 2013).

Ascorbic acid: Ascorbic acid is a frequently utilized organic reductant, filling a similar role as Fe^{2+} in regard to actinide redox chemistry. Its single electron transfer is facilitated by resonance stabilization of the semidehydroascorbate radical, enabling fast reduction of actinide ions. Because many radiochemical methods introduce potentially interfering ferric iron during pre-concentration or redox adjustment, ascorbic acid commonly finds application as the agent of choice to reduce Fe^{3+} to Fe^{2+} .

Sulfamic acid: As previously mentioned, sulfamic acid is used for its ability to selectively scavenge nitrous acid while not affecting the desired valence states of investigated actinide analytes (MARLAP, 2004a).

2.4.3 Chemical Separation

Samples processed in routine radioanalytics typically contain only trace amounts of radioactive material. Consequently, adequate separation of radionuclides from the great excess of matrix components constitutes a prerequisite for their detection. Additionally, conventional methods of detection such as alpha spectrometry and mass spectrometry often require the segregation of radionuclides from one another to avoid specific interferences in the form of overlapping energy ranges and isobaric overlap, respectively. Separation techniques utilized for the analysis of radiospecies are generally subject to the same chemical and physical principles as regular analytical procedures. However, certain aspects of radionuclide behavior create challenges and opportunities unique to radioanalytical chemistry. Due to the impermanent nature of radioactive material, implications of time may become more crucial compared to ordinary analytical chemistry. Short-lived radionuclides require rapid methods of separation and decay corrections of radionuclides with moderately long half-lives demand awareness of elapsed time. The handling of radioactive material, even at lower concentrations, necessitates appropriate measures of protection in accordance with the ALARA principles and monitoring of radiation doses. High activity levels require additional consideration of the chemical effects induced by strongly ionizing radiation, such as radiolysis and the effects of generated heat. The detection of analytes through physical properties associated with their nuclide-specific radiation enables their detection regardless of their chemical form. On the flip side, sensitive detection methods employed in radioanalytical chemistry are susceptible to interference caused by contamination of surfaces and equipment (MARLAP, 2004a).

The necessity for the separation of radionuclides is as old as the discovery of radioactivity itself. Pioneers of the field like Becquerel and the Curies employed precipitation techniques to separate uranium from its progeny of higher activity, laying the foundation of our understanding of radioactive elements. In the earliest days of radioanalytical chemistry, precipitation was the only viable technique to separate actinides and remained that way until the 1940s, when the US government instituted the Manhattan Project as a consequence of World War 2. Increasing interest in radioactive elements sparked a demand for more elaborate methods of their concentration and separation, and first applications of solvent extraction and cation-exchange procedures of actinides were realized during the ensuing research efforts (Choppin et al., 1995). Inspired by the successful synthesis and isolation of neptunium and plutonium via particle irradiation in 1940, postwar research of the 1950s and 1960s, pioneered by Glenn Seaborg, led to the discovery of the remaining transuranium elements. Their identification, however, proved to be difficult due to the homogenous redox behavior of the transamericium actinides and their strong preference for the trivalent oxidation state. Moreover, every newly discovered heavy element exhibited some degree of fission, yielding high percentages of lanthanoids, similar in chemical behavior to actinides beyond americium. Because of the absence of different oxidation states and the minimal quantities of analyzed material, conventional precipitation methods lacked the selectivity required for the separation of actinides from lanthanoids and for the separation of actinides of identical charge and similar ionic radius (Nash et al., 2006). These challenges were ultimately overcome through utilization of ion-exchange materials.

Based on their underlying physical principles and mode of phase transfer, separation techniques can be roughly differentiated into several categories, including volatilization, precipitation, electrodeposition, solvent extraction and ion-exchange systems. This section will focus on ion-exchange chromatography and extraction chromatography, the main analytical tools utilized in this work and arguably the most important analytical tools in modern radioanalytical chemistry. Volatilization, while proven to be beneficial for the separation of select volatile radiospecies, is limited in the scope of its practical applications and will not be discussed in this work (Dean, 1995). Co-precipitation and electrodeposition are most significant to the preparation of counting sources and will be described in Chapter 2.4.4: Sample mounting.

2.4.3.1 Ion-exchange chromatography

Chromatography, considered one of the pillars of analytical chemistry, is a versatile separation technique for complex mixtures that takes advantage of the uneven distribution of components between two non-miscible phases. Substances dissolved in a mobile phase are moved past an immobile phase. Based on their chemical and physical behavior, components are subject to different degrees of retention on the stationary phase and separation is achieved. Depending on the attributes and state of

matter of the phase material, chromatographic separations are employed in various forms, including adsorption chromatography, affinity chromatography, gas chromatography, high-performance liquid chromatography (HPLC), partition chromatography, size exclusion chromatography and so on. Regarding their historical significance to the science of radioanalytical chemistry, however, none of the techniques mentioned above can compare to ion-exchange chromatography (IEC).

Separations based on ion-exchange take advantage of the reversible exchange of charged species between an ordinarily aqueous liquid phase and a solid phase, generally referred to as resin. Ion-exchange resins consist of inert polymers of high molecular weight containing functionalities of opposite charge and mobile counter-ions. Analytes in the mobile phase compete with these counter-ions for interaction sites, resulting in separation if selective exchange is enabled by appropriate conditions. Varying affinities of solute ions to exchange sites are affected by their charge, size and polarizability. Retention and elution of target analytes are generally achieved through control of pH and ion strength of the solution. Depending on the type of ion immobilized by resins, they can be divided into cation- and anion-exchange resins, which can be further subdivided into resins of strong and weak exchange capacity of their respective ion type. Typical anchoring points embedded into polymer particles of cation-exchange resins include sulfonate groups ($-\text{SO}_3^-$) and carboxylate groups ($-\text{COO}^-$), whereas anion-exchange resins commonly utilize quaternary ammonium groups ($-\text{R}_3\text{N}^+$). The chemical structure of the polymer backbone is especially significant to the performance of a resin, as it affects polymer-solvent compatibility and polymer-substrate interaction at the molecular level. Among the natural and synthetic options of polymeric support available, resins composed of polystyrene-divinylbenzene copolymers find the most application due to their high stability and hydrophobic nature (Rahmatpour et al., 2018). The degree of cross-linking is determined by the amount of divinylbenzene incorporated during polymerization and expressed as the percentage of weight of divinylbenzene in the reaction mixture. With increasing cross-linking, statistically distributed functionalities move into closer vicinity to one another, enhancing the resin's selectivity. On the other hand, increases in rigidity induced by high degrees of cross-linking are detrimental to the diffusion rate in the resin beads. Since the efficacy of column operations is contingent on the establishment of equilibrium between solute ions and interaction sites on the stationary phase, diffusion is the rate-limiting factor in column chromatography. Consequently, intermediate cross-linking of 4% to 8% is typically used as a compromise between selectivity and reasonable duration of operations. Utilization of small resin particles enhances diffusion rates at the cost of diminished flow rates and is therefore primarily beneficial to the performance of pressurized columns (Dean, 1995).

Both cation and anion-exchange resins have been successfully employed for the separation of actinides and other relevant radionuclides. Although many actinides exhibit large exchange constants for cation-

exchange resins, their utility is limited by the excessively strong bonding of all but pentavalent species, therefore impeding efficient separation (Nash et al., 2006). Because of the ability to influence ion exchange through exploitation of the diverse complexation behavior of actinides, anion-exchange chromatography provides more selectivity and is considered the prevalent, more broadly applicable choice in recent decades. Advances in ion-exchange technology have been instrumental to the separation and speciation of radioactive elements, including neptunium and plutonium. Strong anion-exchange resins such as Dowex® 1 can retain and elute Np and Pu, depending on the concentration of nitric or hydrochloric acid. Adjustment to the tetravalent oxidation state furthers the quick formation of nitrate- and chlorido-complexes and enhances the affinity to active centers in the resin. The presence of trivalent americium and hexavalent uranium after conventional redox treatments facilitates their separation from Np and Pu, as differently charged ions with differing degrees of complexation experience different retention behavior. Am generally passes through the column with the highly acidic loading solution while U can be eluted by moderately strong acid. Due to their similar electronic configuration, tetravalent thorium and hexavalent uranium exhibit similar elution properties in nitric acid solution. In hydrochloric media, Th is reluctant to form anionic complexes, an attribute frequently utilized in actinide separation techniques (Carswell, 1957). Elution of Np and Pu is usually carried out with dilute acids, often in combination with a stripping agent like oxalic acid or hydrofluoric acid. On-column reduction of Pu(IV) to Pu(III) with selective reducing agents like iodide or hydrazine enables sequential elution if desired.

2.4.3.2 Extraction chromatography

Extraction chromatography (EXC), sometimes referred to as partition chromatography, represents an elegant approach to the separation of radionuclides, combining the selectivity of solvent extraction with the simplicity of column chromatography (Horwitz, 1998). In essence, columns used for EXC represent a solvent extraction system with one stationary extractant immobilized on an inert, solid support. Solvent extraction, or liquid-liquid extraction, itself has been widely employed in radiochemistry from laboratory to industrial scale, due to its efficient and selective separation potential and its broad scope of applications. The technique achieves distribution based on the relative solubility of actinide complexes in two immiscible phases and allows for the separation of species of similar chemical properties over a wide range of concentrations. Though liquid-liquid extraction is still essential to nuclear fuel reprocessing methods like the PUREX process, routine laboratory usage is declining because of the large quantities of commonly toxic and flammable solvent required, and the economic and ecologic issues associated with its disposal (MARLAP, 2004a). Utilization of column chromatography can significantly mitigate this disadvantage.

The extraction chromatographic system consists of porous resin beads, composed of a liquid stationary phase adsorbed on an inert support structure, and an acidic solution as the liquid mobile phase. Addition of dilutants can facilitate solubilization of extractants and control of distribution equilibria. Addition of complexing agents is frequently employed to facilitate the elution of strongly retained analytes. In contrast to solvent extraction, where separation efficiency is described by distribution coefficients, retention on the stationary extractant is usually expressed as k' , an indicator of uptake in relation to the number of free column volumes to peak maximum (Horwitz, 1998). The combination of solvent extraction with the ease of use and intrinsically enhanced separation efficiency of column chromatography has made EXC the go-to technique for difficult actinide separations. Numerous EXC resins find frequent application, notable examples of which are listed in Table 3.

Resin	Extractant	Affinity/Applications
UTEVA® Resin	Diamylamyl phosphonate (DAAP)	Affinity for tetravalent actinides, U(VI) and Zr(IV) over commonly interfering constituents such as Al, Fe, alkali metals, etc.
TEVA® Resin	Trialkylmethylammonium nitrate (or chloride) (Aliquat® 336)	Affinity for tetravalent actinides and Tc(IV) Separation of Am(III) from lanthanides possible
TRU Resin	Carbamoyl methyl phosphine oxide (CMPO) and tri-n-butyl phosphate (TBP)	Separation of tetra- and hexavalent actinides and trivalent ions including Am(III), Bi(III), Fe(III), etc.
DGA Resin	N,N,N',N'-tetra-n-octyl diglycolamide (TODGA)	Determination of Am(III) in complex matrices Preconcentration of actinides from complex matrices
Sr Resin	4,4'(5')-di-t-butyl cyclohexano-18-crown-6	Determination of Sr in environmental samples and of Sr/Pb isotope ratios

Table 3. Examples of extraction chromatographic resins commonly used in radioanalytical chemistry (Triskem, 2018).

In the context of this thesis, TEVA® and UTEVA® EXC resins employed in this work deserve special consideration. TEVA® resin demonstrates interesting properties for an EXC resin, as its separation is based on electrostatic attraction between nitrato-complexes of analytes and Aliquat® 336, a quaternary ammonium compound very similar in structure and function to the functionalities typically utilized in strong anion-exchange resins. However, the mobility of the extractant, caused by the liquid form of the stationary phase, enables comparatively superior exchange capacity and improved uptake.

The retention of relevant metal ions plotted against the concentration of HNO_3 and HCl is depicted in Figure 4. Uptake as a function of HNO_3 concentration illustrates the preference of **TEtraVA**lent Th(IV), Np(IV) and Pu(IV) against U(VI) and Am(III) at moderate acid concentrations and, consequently, the ability to separate tetravalent actinides from other actinides. Contrary to other IEC and EXC resins, uptake of actinides decreases at HNO_3 concentrations above 4 M due to competition from nitrate ions for interaction sites. Separation of Th(IV) is readily achieved at HCl concentrations above 6 M, as it is poorly retained under those conditions (Eichrom Technologies, 2021a).

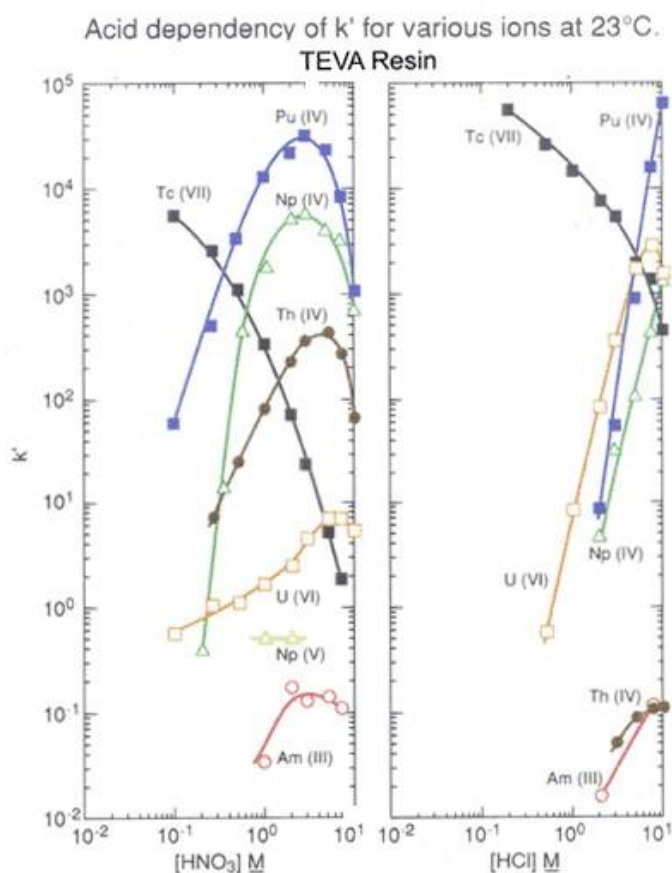


Figure 4. Dependencies of uptake (k') for selected elements on TEVA® resin in nitric and hydrochloric acid (Eichrom Technologies, 2021a).

Anionic complexants can significantly impact the uptake behavior of TEVA® resin, a circumstance potentially detrimental to reproducible analyses and, at the same time, potentially beneficial to separation efficiency. Common matrix constituents like phosphate need to be removed via precipitation or scavenging with aluminum ions prior to chromatography. Oxalic acid, on the other hand, is routinely utilized as a stripping agent, inducing elution of all retained actinides due to its strong complexing power (Horwitz et al., 1995).

EXC utilizing TEVA® resin is an effective method for actinide separation. Due to the strong and similar retention of tetravalent Np and Pu, the resin is frequently employed for their analysis. The versatile resin is often used in combination with other resins, though many researchers have successfully conducted separations of Np, Pu and other actinides on solely a TEVA® column (Kenna, 2002; Kim et al., 2004; Qiao et al., 2010; Maxwell et al., 2010). Selective reduction of Pu enables its separation from Np on a single column. Compared to conventional IEC resins, TEVA® demonstrates several advantageous properties, such as the exceptionally high uptake of Pu(IV) and minimal tailing of Th and U (Thakur et al., 2012). Additionally, the operation of columns at relatively low concentrations of HNO_3 facilitates redox control of Pu and reduces the amount of acid waste generated (Horwitz et al., 1995).

UTEVA® is another example of a versatile resin, comprised of diamylamyl phosphonate active components sorbed on an Amberlite XAD-7 polymer backbone. Inspired by the success of tri-*n*-butyl phosphate in solvent extraction procedures, the structurally similar DAAP aims to achieve similar extraction properties while exhibiting significantly lower solubility in aqueous solution. Originally intended primarily for the preconcentration and separation of uranium, it finds frequent application as a means to separate **U** and **TEtraVA**lent actinides (Horwitz et al., 1992). DAAP extracts nitrate-complexes of actinides, therefore enabling the control of retention and elution behavior via modulation of HNO₃ concentration.

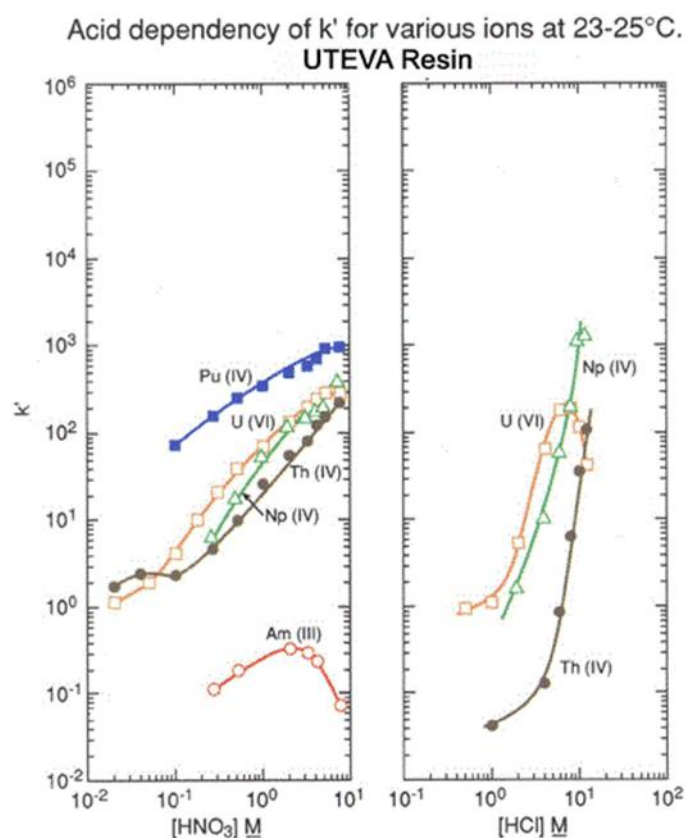


Figure 5 shows the concentration-dependent uptake of relevant actinides in nitric and hydrochloric acid. Th(IV), Np(IV), and Pu(IV), as well as U(VI), exhibit strong retention ($k' > 100$) at HNO₃ concentrations of 5 M and above while Am(III) is not retained at all. Similarities in uptake may hinder selective separation, which is why UTEVA® resin is often applied in combination with other resins. However, simultaneous determination of Np and Pu, as desired in this work, is facilitated by thorium's reluctance to form complexes in HCl and the limited effect of oxalic acid on the elution of U(VI).

Figure 5. Dependencies of uptake (k') for selected actinides on UTEVA® resin in nitric and hydrochloric acid (Eichrom Technologies, 2021b).

As is evident from Figure 5, Th can be readily removed from the resin at 4-6 M HCl concentrations. Subsequent addition of oxalic acid in HNO₃, at HNO₃ concentrations high enough to still ensure strong retention of U(VI), enables the selective elution of Np(IV) and Pu(IV) while U is retained on the column. Stripping of uranium is usually carried out with very dilute HNO₃ of 0.01-0.05 M or approximately 1 M HCl (Eichrom Technologies, 2021b). It is noteworthy that successful, selective separations of the most relevant actinides have been carried out by various researchers (Perna et al., 2001; Morgenstern et al., 2002; Vajda et al., 2009). The susceptibility of UTEVA® resin to interference by matrix components is similar to that of TEVA® resin and the same principles of its limitation apply (Eichrom Technologies,

2021b). Overall, UTEVA® resin's selectivity for actinides and their satisfactory sorption over a wide range of acid concentrations provides an effective approach to the separation of actinides. Concurrently, the uptake of many unwanted matrix elements, such as iron and alkali and earth alkaline metals, is essentially negligible (Horwitz et al., 1992).

2.4.3.3 Precipitation

Preconcentration of radionuclides via precipitation and coprecipitation is an old and established technique in radioanalytical chemistry, enabling the efficient and scalable concentration of analytes in an inexpensive manner. Separation is achieved through addition of suitable counter-ions to target analytes, resulting in the formation of an insoluble precipitate from a supersaturated solution. Due to the extremely low concentrations of radionuclides present during ordinary radioanalytical procedure, solubility limits are hardly exceeded by conventional means of precipitation. Therefore, radionuclides are almost exclusively coprecipitated with a carrier by exploiting similarities in chemical properties. In the context of radiochemistry, coprecipitation is defined as the inclusion, occlusion or adsorption of one target compound, generally soluble under the conditions of precipitation, by one or multiple other compounds that precipitate under those conditions. The multi-agency radiological laboratory analytical protocols manual (MARLAP) provides a detailed summary of factors influencing precipitation and common co/precipitation methods. Precipitating agents are usually employed in excess to ensure quantitative precipitation (MARLAP, 2004a).

The most commonly used anions for coprecipitation purposes are hydroxides, phosphates, fluorides and oxalates, all of which are capable of forming insoluble species with at least the tri- and tetravalent forms of all actinides. Reliable coprecipitation of penta- and hexavalent AnO_2^+ and AnO_2^{2+} cations is hindered by their distinct coordination geometry. The acidic nature of actinide cations facilitates their coprecipitation as hydroxides, normally carried out via addition of an excess amount of ferric iron chloride to the acidic sample and subsequent adjustment of pH with aqueous ammonia solution to 5-8. Hydroxide formation is easily reversed through addition of mineral acids, therefore enabling a simple and fast exchange of anions. Complications may arise from the precipitation of Pu(IV) hydroxide because of its low solubility, though the impact on redissolving can be minimized through rapid reacidification. Furthermore, the presence of strong complexants can seriously affect hydroxide precipitation (Nash et al., 2006). Iron hydroxide coprecipitations are a versatile tool in radiochemistry, covering a wide range of applications from initial preconcentration of complex sample matrices after dissolution to mass spectrometry sample preparation with pre-nuclear iron. Phosphates of actinides are generally insoluble, but their suitability for coprecipitation is dependent on the structural properties of the carrier precipitate's crystal lattice. The bismuth phosphate process, arguably the most historically significant coprecipitation technique utilizing PO_4^{3-} , was used for the separation of tri- and

tetravalent actinides from their penta- and hexavalent counterparts and allowed for the first large-scale concentration of Pu from U at the Hanford site during the Manhattan Project. An(III) and An(IV) species can also be effectively carried via oxalate or fluoride precipitation. Coprecipitation with lanthanoid fluorides, in particular, is regularly carried out in modern radioanalytical chemistry. However, due to the limited selectivity with respect to actinides and potentially difficult redissolving at larger scales, the method is almost exclusively employed for the preparation of counting sources for alpha spectrometry and will be discussed in the next chapter (Clark et al., 2006).

2.4.4 Sample Mounting

Successful determination of radionuclides via alpha spectrometry requires the preparation of an extremely thin counting source, as inappropriate thickness of the sample layer or the presence of carrier material and other impurities will lead to self-absorption and energy losses of particles. The quantitative, reproducible and uniform mounting of sample material constitutes the necessary prerequisite for such an endeavor (Krmpotić et al., 2018). In pursuit of efficient procedure and enhanced spectral resolution, researchers have developed a variety of sample mounting techniques that fulfill these necessary conditions. Among them, micro-precipitation and electrodeposition undoubtedly hold the most significance, while methods based on volatilization, sublimation, etc. are mostly suitable for very specific elements and research questions, thus limiting their potential applications.

2.4.4.1 Micro-precipitation

Micro-coprecipitation is an effective approach to the preparation of counting sources, utilizing the co-crystallization of actinides with lanthanoids due to similarities in chemical properties like charge, size and solubility (Sawant et al., 2019). The rare-earth carrier is most commonly precipitated with conc. HF, which enables the formation of insoluble fluorides from acidic solution, but other precipitates such as hydroxides are described in literature (Sill et al., 1981; Hindman, 1983). The method's main advantages lie in its simplicity, rapidity and cost-efficient nature, allowing for high sample throughput compared to electrodeposition. Drawbacks include the use of dangerous HF and the limited selectivity towards actinides, which may cause the carrying of interfering ions. Therefore, micro-coprecipitation is usually applied following an extensive separation procedure to exclude as many interferences as possible. Conventional lanthanoid carriers include La^{3+} , Ce^{3+} , and Nd^{3+} , all of which show almost identical performance in terms of yield and energy resolution. The amount of added carrier needs to be in the microgram range since significant deviations will negatively affect the method's efficacy. Insufficient quantities of carrier will lead to incomplete precipitation, whereas excess amounts of carrier promote the formation of a precipitate of undesired thickness. Other parameters, like temperature and the time required for complete precipitation, have more leeway and small deviations have no significant effect on recovery or resolution. Nevertheless, 30 minutes at room temperature

have been independently determined as the optimal conditions regarding temperature and standing time by different researchers in recent history (Sawant et al., 2019; Kelly, 2009). Deviations in the volume of HF to a reasonable extent have a similarly insignificant impact on the quality of the formed precipitate. Sawant et al. (2019) showed that the recovery of Am remained unchanged over a range of 0.3 to 1 mL conc. HF addition. If determination of U is desired, preceding reduction to U(IV) with a strong reducing agent like TiCl_3 is necessary since the precipitation of lanthanoid fluorides only carries tri- and tetravalent actinides. Overall, micro-coprecipitation is a convenient, rapid and broadly applicable method to analyze radionuclides without the need for sophisticated instrumentation. Additionally, its intrinsic simplicity entails high reliability and reproducibility, a valuable feature in any analytical discipline, but especially in radiochemistry, where accurate analysis of a large number of samples during a nuclear emergency may affect the well-being of the population.

2.4.4.2 Electrodeposition

In electrodeposition, sometimes referred to as electroplating, radionuclides are electrochemically accumulated from an electrolyte solution onto a cathode planchet, usually made of stainless steel or platinum. The technique is usually carried out at constant current and low voltage for several hours, and numerous organic and inorganic electrolytes find application (Thakur, 2005). Deposition may occur spontaneously, induced by a conducive potential difference between electrode and specific ions in solution, or non-spontaneously, through application of external voltage. The inclination to undergo spontaneous plating can be derived from the Nernst equation (Eq. (11)), which describes the relationship between the reduction potential of an electrochemical reaction and the activities of the species involved in this reaction. Electrodeposition allows for the deposition of extraordinarily thin, homogenous sample layers, resulting in potentially excellent energy resolution (MARLAP, 2004a).

However, adequate performance of the technique is dependent on various parameters, many of which are not trivial to control. Non-spontaneous deposition is primarily governed by differences in potential and is therefore not necessarily selective towards specific analytes. Consequently, interferences caused by insufficient separation or contaminated electrolyte solutions may negatively affect the quality of the prepared source, resulting in decreased count rates and lowered spectral resolution. This circumstance is especially relevant with respect to iron, an abundant impurity in soil and sediment samples. Conversely, micro-coprecipitation with lanthanoid fluorides does not assimilate iron species. Additionally, the electrochemical cell and its associated equipment are challenging to maintain properly and susceptible to several potential sources of error. The technique is sensitive to changes in pH and current, as well as leakage of cells (Kelly, 2009). Moreover, due to the peculiar attributes of actinides described in Chapter 2.4.2, precise adjustment of their chemical form may be difficult, resulting in the simultaneous presence of different species of the same element exhibiting different chemical behavior

during the electrolysis process. Other factors influencing the electrochemical behavior of an element are its concentration, the nature of the electrolyte, composition and design of the electrode and features of the electrochemical cell (MARLAP, 2004a). Examples of features implemented by researchers to improve deposition yields of target analytes include rotating disc cathodes (Tsoupko-Sitnikov et al., 2000) and the use of magnetohydrodynamic convection (Panta et al., 2010). In consideration of the numerous potential issues listed, it is not surprising that measurements of alpha sources prepared via electrodeposition tend to be subject to large variations compared to micro precipitation, which is why the latter is considered the more reliable and reproducible technique (Kelly, 2009). The most notable application of electrolytic source preparation is the separation of polonium via spontaneous deposition on copper, silver or nickel from hydrochloric acid solution.

3. Motivation of this thesis

Like many other alpha-emitting radionuclides, ^{237}Np has been and is continuously released into the environment through nuclear weapons testing of the 1950s and 1960s, nuclear accidents and other anthropogenic nuclear activities. However, unlike most other long-lived, alpha-emitting radionuclides, whose quantification requires the use of a tracer for yield determination after, ^{237}Np is difficult to quantify because no suitable isotopic tracer exists (Qiao et al., 2010).

The few neptunium isotopes that have been explored with regard to quantitative ^{237}Np determination by researchers come with notable drawbacks. Due to the lack of alpha-emitting Np tracers, the beta emitter ^{239}Np has traditionally been utilized, since it is relatively readily available via neutron irradiation of ^{238}U or through milking of an ^{243}Am - ^{239}Np generator. However, its short half-life of only 2.36 days necessitates regular preparation and rapid radiochemical procedure and analysis, which may be difficult to realize. Moreover, the ingrowth of ^{239}Np 's daughter, ^{239}Pu , increases the background of ^{239}Pu in the sample which is detrimental to many radioanalytical endeavors. (Qiao et al., 2014) ^{236}Np is a long-lived ($t_{1/2} = 1.55 \times 10^5 \text{ y}$) potential tracer for ^{237}Np , though its application is restricted by its difficult production and therefore limited availability. ^{235}Np represents another potential tracer in terms of its adequate half-life ($t_{1/2} = 396.1 \text{ d}$) compared to the usual duration of conducted experiments. However, preparation of ^{235}Np requires particle irradiation of uranium target material, which results in the formation of ^{237}Np as an impurity (Harvey et al., 1987). Moreover, its applicability is hindered by its decay modes (99.997% electron capture, 0.003% α -decay) and its lack of suitable γ -rays or X-rays (Qiao et al., 2010). Only when it comes to atom counting (by ICP-MS or AMS) the decay mode is irrelevant. Therefore, since no readily available neptunium spike isotope exists, the next logical strategy would be the utilization of a non-isotopic tracer with similar chemical behavior, such as plutonium. The similarities in chemical behavior of tetravalent Np and Pu regarding their interaction with chromatographic resins in the most commonly used acidic media enable the potential to achieve the same chemical yield or the same ratio of chemical yields for both species during radiochemical separation.

This thesis was carried out to establish whether the simultaneous determination of ^{237}Np and Pu (with its spike ^{236}Pu) is possible in a reproducible manner. Constant ratios of $^{237}\text{Np}/^{236}\text{Pu}$ would indicate synchronism between Np and Pu during the separation procedure. Different radiochemical procedures were tested on soil and water samples. Among the potential plutonium tracers of low natural abundance, ^{236}Pu was selected due to its availability and because of the overlap in α -energies of ^{237}Np and ^{242}Pu . If possible, the $^{237}\text{Np}/^{236}\text{Pu}$ ratio would allow for the determination of ^{237}Np via ^{236}Pu tracer in various samples.

4. Experimental Part

4.1 Materials and methods

Alpha spectrometric measurements were performed using a Canberra Model 7401® or an Ortec Alpha Ensemble® alpha spectrometer with semiconductor detector. Efficiencies of detector chambers are depicted in Table 4. Measurement of blank samples was omitted due to the very low intrinsic background of the detector chambers. Tested soil samples, if not already ashed, were ashed at 300-360 °C for about 3-4 hours. Radiotracers (^{236}Pu , $E_\alpha = 5.7$ MeV; ^{237}Np , $E_\alpha = 4.7$ MeV) were added to the sample prior to any radiochemical procedure and quantified by weight using an analytical balance. Deionized water was used for all dilutions, washing and rinsing. Chromatography was carried out using Dowex® 1X4 chloride form resin (100-200 mesh) and UTEVA® and TEVA® extraction chromatography resins. Different separation approaches were carried out to compare their suitability with regard to the simultaneous determination of neptunium and plutonium. Leaching and source preparation procedure remained identical for all applied methods.

Spectrometer	Detector	Efficiency	Error
Canberra Model 7401®	Chamber 3	0.346	0.036
	Chamber 4	0.284	0.037
	Chamber 6	0.345	0.059
Ortec Alpha Ensemble®	Chamber 1	0.25	unknown
	Chamber 2,3,4	0.28	unknown

Table 4. Efficiency of detectors used for alpha spectrometric measurements.

General leaching procedure: Each investigated sample was spiked with 100 or 200 μL of ^{237}Np and ^{236}Pu standard solution of known activity concentration (Table 5) and submerged in 7.2 M HNO_3 . The acidic suspension was equilibrated for 16 to 24 h. In order to achieve dissolution of radionuclides from the soil, the mixture was heated on a hot plate for 1.5 h under frequent stirring. Evaporation was limited by placing a watch glass onto the beaker and compensated with additional acid. After cooling to room temperature, insoluble residues were separated via filtration.

General sample mounting procedure: Following chromatographic separation, each fraction containing neptunium and plutonium was evaporated to dryness and the residues were fumed three times with 5 mL conc. HNO_3 + 10 drops 30% H_2O_2 as well as 5 mL conc. HCl in that order. The remaining residue was dissolved in 2 mL 1 M HCl , transferred into a small plastic tube, and the beaker was rinsed twice with 1 mL 1 M HCl . Addition of 100 μL 0.5 mg/mL Nd^{3+} solution and subsequent addition of 0.5 mL 40%

HF yielded a fine NdF_3 micro-precipitate containing neptunium and plutonium. After 30 minutes, the precipitate was sonicated in an ultrasonic bath for 1 minute before filtration through a moistened cellulose nitrate membrane filter (Whatman®, 0.1 μm pore size). The tube was rinsed with 2 mL 0.58 M HF and 2 mL dist. H_2O and the rinsing solutions were filtered through the same filter before the filter was dried and activity was determined via alpha spectrometry.

Spike	Activity concentration [mBq/100 μL]
^{237}Np	35.0
^{236}Pu	62.1 (November 1, 2018)

Table 5. Activity concentrations of applied spike solutions. Activity of ^{236}Pu is decay-corrected for each α -spectrometric measurement.

4.2 Baglan method

(simultaneous elution in hydrochloric medium using Dowex® 1X4 resin)

Each prepared sample of roughly 10 g soil or 50 mL water was spiked with 100 or 200 μL of ^{237}Np and ^{236}Pu standard solution and treated according to the general leaching procedure described in Chapter 4.1. After cooling to room temperature and the removal of insoluble residues via filtration and evaporation to dryness, a slightly adapted separation procedure from Baglan et al. (2002) was applied. The radionuclide-containing residue was dissolved in 25 mL 32% HCl and 200 mg NaNO_2 was slowly added at 70 °C under constant stirring. The reaction mixture was stirred until the formation of NO_x -gases ceased. Subsequently, the hydrochloric solution was loaded onto a preconditioned DOWEX® 1X4-column of 1.3 cm diameter and approximately 6 cm resin bed height. The beaker was rinsed twice with 15 mL 10 M HCl. A decrease in hydrochloric acid concentration from 10 to 4 M (50 mL) enabled the simultaneous elution of Np(V) and Pu(IV) while U(VI) remained fixed on the resin. Finally, the neptunium- and plutonium-containing eluate was evaporated to dryness and the alpha source was prepared as described in the general sample mounting procedure in Chapter 4.1.

4.3 AGES method

(simultaneous elution at low concentrations of HCl - HF using Dowex® 1X4 resin)

This approach is based on a procedure devised by the Austrian Agency for Health and Food Safety, originally designed as a quick method to determine strontium content in soil samples. Investigated soil samples of approximately 10 g were prepared, leached and filtered as described in the general leaching

procedure in Chapter 4.1. Next, the filtrate was evaporated to dryness and the residue taken up in 20 mL 1 M HNO_3 . 100 mg of Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, was dissolved in the warm solution of moderate NO_3^- -concentration under constant stirring before addition of an equal amount of conc. HNO_3 . After cooling to room temperature, 0.2 g NaNO_2 was slowly added to the stirring solution and stirring was continued until no indication of NO_x -gases was observable.

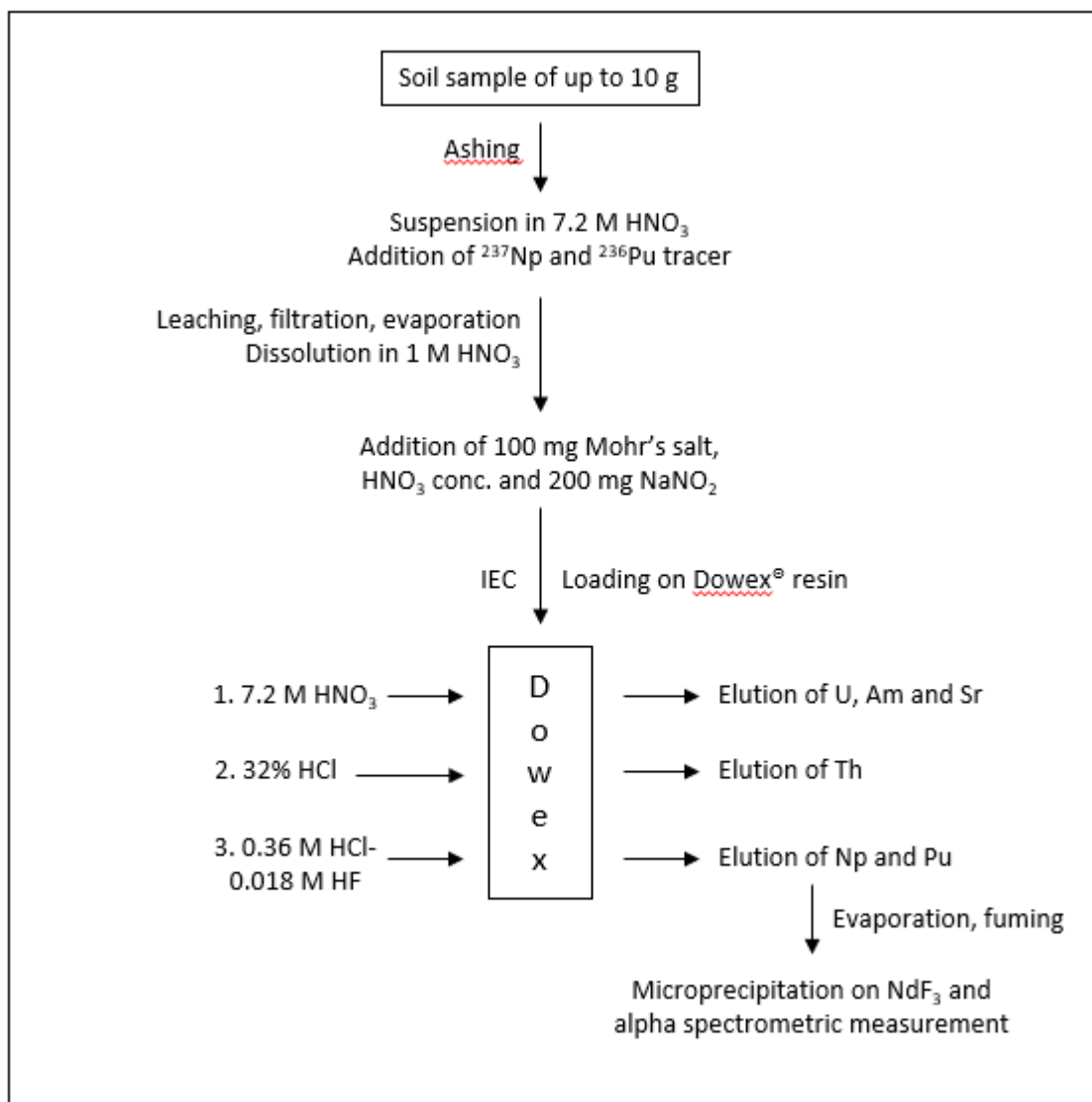


Figure 6. Chemical separation procedure for the simultaneous determination of neptunium and plutonium via alpha spectrometry using Dowex® resin.

Ion exchange chromatography was carried out using Dowex® 1x4 resin, preconditioned in 7.2 M HNO_3 . The sample solution was loaded onto a column of 1.3 cm diameter with a resin bed of around 6 cm height and the corresponding beaker was rinsed twice with 15 mL 7.2 M HNO_3 , eluting americium, strontium and uranium. Removal of thorium from the column was achieved with 3 washing steps of 15 mL 32% HCl . In the final washing step, neptunium and plutonium were eluted with 50 mL of 0.36 M

HCl- 0.018 M HF solution. Subsequently, the eluate of the final washing step was treated according to the general sample mounting procedure described in Chapter 4.1 and the source was measured via alpha spectrometry.

4.4 VERA method

(simultaneous elution with oxalic acid using UTEVA® resin)

A method devised by the Institute of Isotope Physics (running the Vienna Environmental Research Accelerator) at the University of Vienna was tested in regard to its suitability for the simultaneous determination of neptunium and plutonium in soil samples. Each ashed soil sample of either approximately 1 or 10 g or water sample was spiked with 100 µL of ^{237}Np and ^{236}Pu standard solution and leached according to the general leaching procedure described in Chapter 4.1. After cooling to room temperature, insoluble residues were separated via filtration and 2 mg/mL FeCl_3 solution (0.65 mL for 1 g samples and 1 mL for 10 g samples) was added to the filtrate. $\text{Fe}(\text{OH})_3$ precipitation was performed by adjusting the pH to 7-8 via dropwise addition of 25% NH_3 solution at 100 °C and the precipitate was allowed to cool to room temperature. pH was kept under 8.5 to avoid unwanted precipitation of other salts. Subsequently, the solution containing the precipitate was centrifuged at 4000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was washed with H_2O with pH 8. This step was repeated at least twice, until the supernatant liquid was colorless. Afterwards, the precipitate was taken up in conc. HNO_3 and evaporated to dryness.

Redox adjustment was carried out according to Maxwell et al. (2010). The residue was dissolved in 12 mL 3 M HNO_3 - 0.5 M $\text{Al}(\text{NO}_3)_3$ and 0.5 mL 1.5 M sulfamic acid solution and 1.25 mL 1.5 M ascorbic acid solution were added in that order and under constant stirring. 220 mg of NaNO_2 was slowly added at room temperature and stirring was continued until the formation of NO_x -gases stopped.

Separation of the target actinides plutonium and neptunium from other actinides was achieved by extraction chromatography using UTEVA® resin. Prior to application, the resin was soaked in distilled water for at least several hours and preconditioned on column with 3 M HNO_3 . The sample solution was loaded onto a column of 0.9 cm diameter and approximately 4 cm height and the corresponding beaker was rinsed twice with 3 mL 3 M HNO_3 , immobilizing the target actinides on the resin. 24 mL 5 M HCl was used for the removal of thorium. Finally, neptunium and plutonium were stripped from the column using 20 mL 2 M HNO_3 - 0.1 M oxalic acid. The fraction eluted with oxalic acid was treated as described in the general sample mounting procedure in Chapter 4.1 and activity was determined via alpha spectrometry.

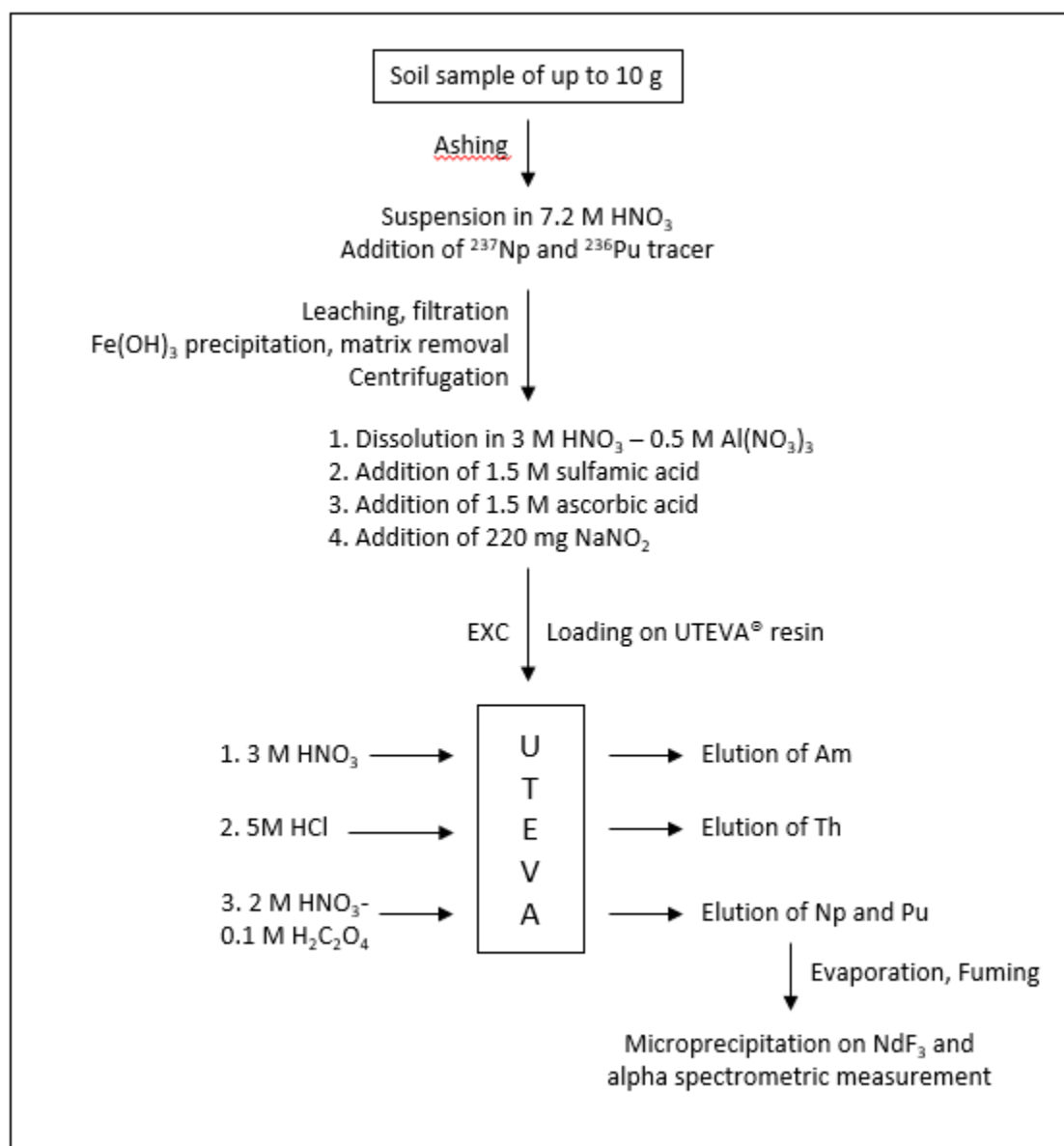


Figure 7. Chemical separation procedure for the simultaneous determination of neptunium and plutonium via alpha spectrometry using UTEVA® resin.

4.5 TEVA/VERA method

(VERA method, but simultaneous elution with oxalic acid using TEVA® resin)

Based on its uptake behavior described in Chapter 2.4.3.2, TEVA® resin is well suited to separate neptunium and plutonium from other actinides. For that reason, a slightly modified approach to the VERA method was carried out, utilizing TEVA® instead of UTEVA® resin during chromatographic separation and enabling comparison of the two resins separation efficiency under the applied conditions.

Each ashed soil sample of approximately 10 g was leached and filtered in accordance with the general leaching procedure described in Chapter 4.1. Ferric hydroxide precipitation and redox adjustment was

performed following the VERA method's procedure. Extraction chromatography was carried out using TEVA® resin, preconditioned in 3 M HNO₃. The chromatographic procedure remained identical to the VERA method's chromatography step, with the exception of an increase in HCl concentration from 5 M to 8 M to maximize the difference in uptake between thorium and the target analytes, neptunium and plutonium. HCl volumes ranging from 16 to 24 mL were applied. The eluate of the final washing step was processed as described in Chapter 4.1.

4.6 IAEA-TERC-2022-02

Interlaboratory comparisons of environmental samples are routinely conducted by the IAEA as a means to certify reference materials and verify nuclear activities. Additionally, these environmental sampling analyses function as proficiency tests, allowing partnered laboratories to assess the accuracy of their measurements. Such an environmental water sample, IAEA-TERC-2022-02, was investigated with regard to its ²³⁹⁺²⁴⁰Pu content. Each sample of 20 or 50 mL was spiked with 100 or 200 µL of ²³⁷Np and ²³⁶Pu standard solution, equilibrated, and evaporated to dryness. Redox adjustment and chromatographic separation were carried out following the AGES method's procedure described in Chapter 4.3. Source preparation was carried out as described in Chapter 4.1. Addition of neptunium spike enabled assessment of the method's applicability to water matrices.

5. Results and Discussion

Stated experimental standard deviations s are 1σ errors of count rates. Lower error thresholds are set at 5% to account for errors during sample preparation.

5.1 Baglan method results

Results of samples (one water and two soil samples) prepared with the Baglan method and analyzed by alpha spectrometry are given in Table 6.

Sample	m [g]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found A $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1σ)
B_H ₂ O	50	35.21	26.41	96.4	82.9	1.33	1.55	1.16	0.06
B_20	1.05	35.38	26.14	78.6	38.1	1.35	2.79	2.06	0.11
B_49	9.25	71.96	26.59	95.5	74.3	2.71	3.48	1.28	0.06

Table 6. Recovery of ^{237}Np and ^{236}Pu determined via Baglan method.

^{236}Pu activities are decay-corrected for the day of measurement.

This approach was chosen because of its simple radiochemical procedure, enabling a presumably fast, reliable and selective separation of actinides with high recovery percentages. The presence of neptunium's most stable valence state, Np(V), during chemical separation facilitates the simultaneous redox adjustment of the target radionuclides and supports high neptunium recovery percentages. Indeed, average neptunium recovery yields were high (>90%) and roughly in agreement with the data reported by Baglan et al. (2002), a circumstance potentially beneficial to the analysis of environmental samples where neptunium has a very low abundance.

However, several complications arose during the first attempts of applying the Baglan method, which is why it was dismissed at an early stage in favor of other chemical procedures. Separation of the target nuclides from other actinides was moderately effective and exclusion of matrix impurities in soil samples B_20 and B_49 was insufficient, indicated by visible, yellowish precipitates obtained after source preparation. Following redox adjustment and the formation of NO_x -gases, these samples also exhibited the formation of foam, which most likely negatively impacted chromatographic separation. Obviously, additional purification steps would combat these issues, though at the cost of simplicity and recovery yield of neptunium, the method's main advantages. Additionally, the method did not yield reproducible ratios of $^{237}\text{Np}/^{236}\text{Pu}$ recovery. However, given the small sample number, further experiments need to be conducted to verify this finding with certainty.

5.2 AGES method results

Activity yield ratios of added spikes ^{237}Np and ^{236}Pu were determined in 15 soil and water samples. The results are depicted in Table 7.

Sample	m [g]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found A $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1σ)
A_H ₂ O	1000	35.56	26.94	72.6	63.1	1.32	1.52	1.15	0.04
A_H ₂ O_2	1000	35.18	26.74	55.2	44.5	1.32	1.63	1.24	0.06
A_H ₂ O_SK	1400	34.23	26.57	36.1	40.2	1.29	1.16	0.89	0.03
A_H ₂ O_W	1000	35.32	26.44	56.1	48.8	1.34	1.54	1.15	0.06
A_18	8.10	35.88	26.39	10.0	48.1	1.36	0.28	0.21	0.02
A_19	7.40	35.56	25.67	56.2	52.3	1.39	1.49	1.07	0.03
A_20	3.25	34.58	25.92	57.6	61.8	1.33	1.24	0.93	0.03
A_16	8.69	35.56	26.52	54.7	70.4	1.34	1.04	0.78	0.05
A_17	8.17	36.19	26.59	48.9	72.6	1.36	0.92	0.67	0.03
A_18_2	8.07	35.56	26.57	52.9	46.7	1.34	1.52	1.13	0.06
A_18_3	7.78	35.95	26.72	24.2	24.8	1.35	1.32	0.98	0.05
A_18_4	8.86	35.84	26.84	48.6	53.8	1.34	1.20	0.90	0.04
A_18_5	8.86	35.84	26.84	46.4	61.9	1.34	1.00	0.75	0.05
A_19_2	8.02	36.05	26.64	28.8	79.5	1.35	0.49	0.36	0.01
A_19_3	8.02	35.88	26.94	30.9	62.8	1.33	0.66	0.49	0.02
Avg.				45.2	55.4			0.97	0.05

Table 7. Recovery of ^{237}Np and ^{236}Pu determined via AGES method.

^{236}Pu activities are decay-corrected for the day of measurement.

The ratio of ^{237}Np and ^{236}Pu before and after the radiochemical procedure is 0.82 ± 0.04 . However, a Grubbs's test revealed that activity yield ratios of samples A_18, A_19_2 and A_19_3 are significant outliers ($P = 0.05$), thus, their values were excluded from the mean value calculation.

$$G = \frac{\max|X - \bar{X}|}{s} \quad \text{Ref: (Grubbs, 1969; Stefansky, 1972)} \quad (19)$$

(Eq. 19: Grubbs's test; X = suspected outlier, $\bar{X}$ = mean value, s = standard deviation of the arithmetical mean value) Exclusion of these outliers gives an average activity yield ratio of 0.97 ± 0.05 . While these results look promising, the individual errors of the activity yield ratios for each sample are deceptively small compared to the standard deviation of 0.18 within the whole data set. Obtained chemical recoveries ranged from 10 to 80%. Noticeably, samples excluded via the Grubbs outlier test had low ^{237}Np recovery yields, most likely due to inconsistencies in preparation time and the time-sensitive

nature of valence adjustment with nitrite. Oxidation of Pu(III) to Pu(IV) via NaNO_2 under retention of tetravalent Np(IV) is a commonly applied strategy in actinide redox adjustment and can be carried out in 10 - 15 min. However, if the reaction time was increased to 25 min, Qiao et al. (2010) reported the formation of Np(V) in the loading solution, resulting in large differences in Np and Pu recovery yields. In consideration of the slower than average flowrate exhibited by the respective sample solutions, as well as the large loading volumes of around 50 mL applied in this method, it is likely that the timeframe of the valence adjustment and the sample loading sequence was too long to prevent undesired oxidation of tetravalent neptunium.

5.3 VERA method results

Analysis of samples via VERA method was separated into two categories: soil samples of 1 g and samples of up to 10 g, plus two additional water samples. Measured recovery yields of spikes ^{237}Np and ^{236}Pu in 10 g and 1 g samples are given in Tables 8 and 9, respectively. Samples V_38, V_41, V_51 and V_51_2 were measured with an Ortec Alpha Ensemble® at the Austrian Agency for Health and Food Safety (AGES).

Sample	m [g]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1 σ)
V_19	6.69	35.00	26.30	75.9	78.4	1.33	1.29	0.97	0.03
V_H2O	50.0	35.88	26.13	24.0	72.9	1.37	0.45	0.33	0.02
V_H2O_2	50.2	35.28	25.96	13.6	46.6	1.36	0.40	0.29	0.02
V_49	8.41	35.63	26.11	10.9	35.4	1.36	0.42	0.31	0.01
V_49_2	9.48	36.19	26.28	9.8	41.3	1.38	0.33	0.24	0.02
V_49_3	6.89	35.07	25.84	54.3	65.9	1.36	1.12	0.82	0.03
V_48	9.16	36.16	26.28	49.4	51.9	1.38	1.31	0.95	0.05
V_48_2	10.01	35.21	26.11	24.3	45.5	1.35	0.72	0.53	0.02
V_51	9.46	35.32	22.99	54.3	42.8	1.54	1.95	1.27	0.10
V_51_2	9.50	35.32	23.10	46.5	40.1	1.53	1.77	1.16	0.08
V_38	9.90	35.00	22.50	38.5	28.0	1.56	2.14	1.37	0.13
V_41	9.69	35.98	23.04	14.6	16.1	1.56	1.42	0.91	0.12

Table 8. Recovery of ^{237}Np and ^{236}Pu in soil samples up to 10 g and water samples determined via VERA method. ^{236}Pu activities are decay-corrected for the day of measurement.

Data obtained from the analysis of 10 g samples is inconclusive, with widely spread recovery ratio values. The large deviations in recovery yields indicate a varying degree of interfering matrix

components or significant differences in redox capacities of individual samples, resulting in inconsistent inter-element fractionation. Recovery yields of ^{237}Np and ^{236}Pu were between 10 - 76% and 16 - 78%, respectively.

Sample	m [g]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1 σ)
V_37	1.00	35.35	19.89	58.6	31.0	1.78	3.35	1.76	0.11
V_38_2	0.99	36.26	19.62	75.0	40.9	1.85	3.39	2.05	0.12
V_56	0.98	35.63	19.97	49.7	24.7	1.78	3.58	2.64	0.17
V_57a	0.97	34.13	20.08	56.6	30.3	1.70	3.18	2.12	0.13
V_37_2	0.98	34.93	19.40	50.7	27.8	1.80	3.28	2.02	0.10
V_41_2	0.98	34.02	19.97	8.8	4.4	1.70	3.38	2.08	0.24
V_37_3	0.98	34.30	19.73	38.9	22.6	1.74	3.00	1.63	0.07
V_38_3	0.96	34.58	20.02	28.5	17.2	1.73	2.86	1.58	0.07
V_56_2	0.99	35.21	19.56	48.6	26.6	1.80	3.28	1.81	0.10
V_57a_2	0.98	35.91	19.84	66.1	32.8	1.81	3.65	1.71	0.09
V_51_3	0.93	34.06	19.47	58.0	33.0	1.75	3.07	1.66	0.09
V_54	0.93	34.06	20.06	67.1	36.7	1.70	3.11	1.77	0.10
Avg.				51.0	27.3			1.83	0.11

Table 9. Recovery of ^{237}Np and ^{236}Pu in soil samples of 1 g determined via VERA method. ^{236}Pu activities are decay-corrected for the day of measurement.

The recovery data of the 1 g samples, on the other hand, looks very different. Radiochemical recoveries ranged from 9 - 75% for ^{237}Np and from 4 - 41% for ^{236}Pu . Despite this large difference in yields between the two analytes, obtained recovery ratios remained steady, with an average value of 1.83 ± 0.11 . Suspected outlier sample V_56 was excluded from the mean value calculation due to very broad and peculiar peak area of the ^{237}Np counts, indicating significant contamination. The good agreement of the chemical yield ratios between ^{237}Np and ^{236}Pu is depicted in Figure 8.

These findings suggest that ^{236}Pu is a suitable tracer for the quantitative determination of ^{237}Np and $^{239+240}\text{Pu}$ in environmental samples of 1 g soil, though further investigations into the cause of the unequal $^{237}\text{Np}/^{236}\text{Pu}$ recovery ratio would be appropriate. Qiao et al. (2010) reported extremely low chemical yields of plutonium when adding 300 mg of ascorbic acid directly into samples during valence adjustment, presumably due to the formation and stabilization of Pu(III). Though the subsequent addition of nitrite should mitigate this problem, reduction of the equivalent of 330 mg ascorbic acid

used during the redox treatment of this method might be beneficial to achieve equal recovery yields of Np and Pu.

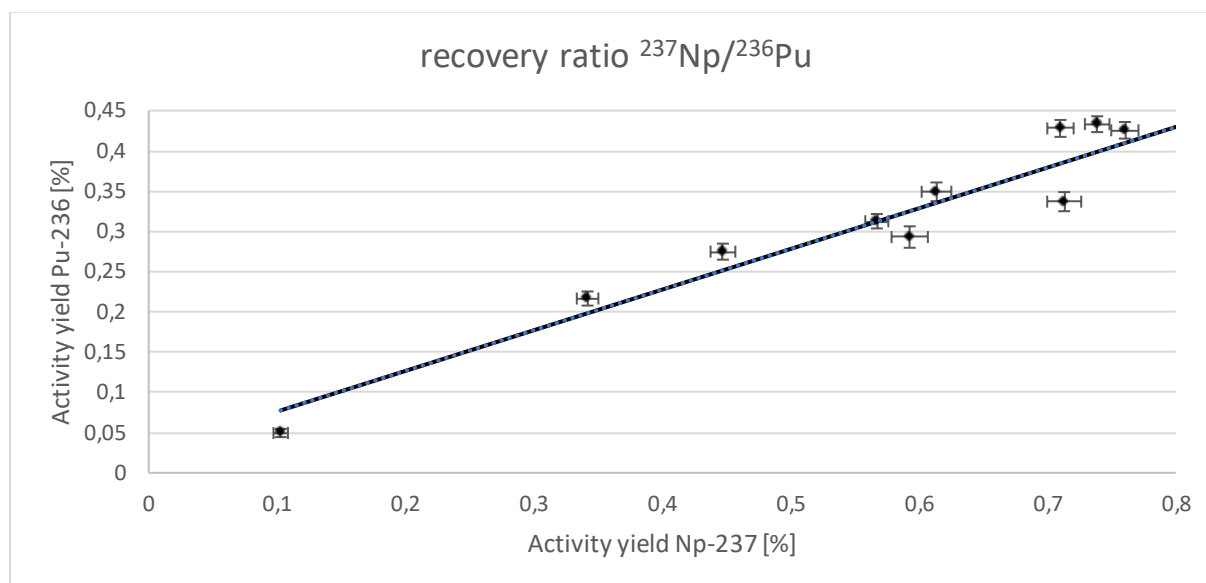


Figure 8. Chemical yield ratios of ^{237}Np to ^{236}Pu in soil samples of 1 g determined via VERA method.

On the other hand, insufficient amounts of ascorbic acid may not exert enough reducing capacity to reliably reduce the amount of ferric iron present in large soil samples (Maxwell et al., 2010). However, it is most likely that the unequal obtained recovery ratios are caused by unequal elution behavior of Np and Pu in hydrochloric acid. When omitting the HCl rinsing step during the preparation of air filter samples for measurement via AMS (here the Th masses 232, 228 and 230 do not interfere), Wallner G. (2023) obtained an average $^{237}\text{Np}/^{236}\text{Pu}$ recovery ratio of 1.04 ± 0.07 for nearly massless air filter samples (5-6 mg aerosol mass) with the same chemical separation procedure (poster presented at ENVIRA 2023).

It is evident from the combined data of 1 g and 10 g experiments that sample size had a significant impact on the efficacy of the method. Increases in sample size generally result in improved reliability of data. However, the handling of large soil samples on small chromatographic columns may lead to interferences caused by matrix components, which may have a detrimental effect on chemical recovery. For instance, Kim et al. (2004) reported degradation of chemical recoveries of Np and Pu for sample masses greater than 4 g when carrying out a chemical purification method with a similar, ascorbic acid-based redox adjustment on TEVA® columns. Further experiments are necessary to extrapolate this assumption onto separation techniques using UTEVA® resin. According to Hain et al. (2022), normalization of ^{237}Np activity concentrations to a non-isotopic Pu spike yielded satisfactory results for water samples only, when carrying out the exact same preconcentration and separation procedure to determine the Np content in ocean water samples. In consideration of this assessment,

it is not surprising that the realization of reproducible $^{237}\text{Np}/^{236}\text{Pu}$ recovery ratios is more manageable in soil samples of 1 g than 10 g. Interestingly though, the results of the two analyzed water samples did not match the results of the 1 g soil samples.

Owing to the effective separation of tetravalent Np and Pu from hexavalent U via UTEVA resin using oxalic acid, the VERA method achieved good decontamination from U. For 1 g samples, the method achieved decent decontamination from Th, though further purification would be beneficial to eliminate all peak overlap of ^{230}Th and ^{237}Np at 4.77 MeV.

5.4 TEVA/VERA method results

Recovery yields of target analytes ^{237}Np and ^{236}Pu are given in Table 10.

Sample	m [g]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1 σ)
T_48	8.75	35.25	25.56	71.9	33.0	1.38	3.00	2.18	0.11
T_48_2	9.02	35.35	25.42	56.4	24.5	1.39	3.20	2.30	0.13
T_44	9.13	35.35	23.71	72.5	57.7	1.49	1.87	1.26	0.06
T_44_2	9.13	35.49	23.92	67.6	53.6	1.48	1.87	1.26	0.06
T_44_3	10.20	35.46	25.15	68.9	69.6	1.41	1.40	0.99	0.04

Table 10. Recovery of ^{237}Np and ^{236}Pu determined via TEVA/VERA method. ^{236}Pu activities are decay-corrected for the day of measurement.

According to numerous publications and information provided by the manufacturer mentioned in Chapter 2.4.3.2, TEVA® resin's uptake behavior allows for the collective separation of Np and Pu, which is why it was tested as a substitute for UTEVA® resin in the VERA method's separation procedure. However, collected experimental data was inconsistent in terms of chemical yields and reproducibility of recovery ratios, indicating the need for additional adaptations from the original method.

In this work, fixing of radionuclides onto the resin was carried out at 3 M HNO_3 concentration, where both Np and Pu show maximum uptake. At this concentration, however, retention of Pu is almost one magnitude higher than the retention of Np, potentially altering elution profiles of the target analytes compared to the original method due to the accelerated elution of Np compared to Pu. Kim et al.(2004) reported that a constant recovery ratio of $^{237}\text{Np}/^{236}\text{Pu}$ was only achieved in concentration ranges of 4-6 M HNO_3 . Therefore, the implemented adaptation from the VERA method likely requires a loading solution of higher HNO_3 concentration or an increase in eluent volume during the last washing step to improve the generally low recovery yields of Pu. Complications regarding the valence adjustment with

ascorbic acid described in Chapter 5.3 may also be affecting Pu recovery yields. Furthermore, the method did not achieve good separation of target analytes from Th, resulting in an overlap of α -energies of ^{230}Th and ^{237}Np at around 4.7 MeV. This circumstance was particularly pronounced for samples T_48 and T_48_2, where lower volumes of HCl, 16 and 20 mL respectively, were used than the 24 mL used for the rest of the samples. Consequently, the found activity concentration of ^{237}Np in these samples is elevated. Overall, this separation strategy did not yield satisfactory results. It is likely that, similarly to the VERA method, the applied conditions were not suited to deal with high amounts of interfering matrix components, necessitating the need for further adaptations from the original method.

5.5 IAEA-TERC-2022-02 results (AGES method)

Obtained results for the analyses of sample IAEA-TERC-2022-02 are depicted in Tables 11 and 12. Quantification of the activity concentrations of $^{239+240}\text{Pu}$ was carried out via ^{236}Pu reference tracer material. Activity concentrations were compared to the reference value issued in the corresponding proficiency test evaluation report (IAEA, 2022).

Sample	V [L]	$^{239+240}\text{Pu}$ [Bq/kg]	s (1 σ)	Ref. value [Bq/kg]	Ref. unc. s (1 σ)
IAEA_1	0.05	4.52	0.27		
IAEA_2	0.02	4.77	0.34		
IAEA_3	0.02	5.06	0.25		
IAEA_4	0.02	4.49	0.19		
IAEA_5	0.02	3.86	0.27		
IAEA_6	0.02	4.17	0.25		
Avg.		4.54	0.26	5.16	0.31

Table 11. Measured and referenced $^{239+240}\text{Pu}$ activity concentrations determined in the sample IAEA-TERC-2022-02. Values and uncertainties are stated in [Bq/kg], decay-corrected for the day of measurement.

The mean value of $^{239+240}\text{Pu}$ activity concentration in sample IAEA-TERC-2022-02 was determined at 4.54 ± 0.26 Bq/kg sample material, 12 % lower than the target value of 5.16 ± 0.31 Bq/kg issued in the corresponding proficiency test evaluation report (IAEA, 2022). In order to assess the statistical validity of the results, an evaluation according to current IAEA methodology was carried out. Based on the evaluation criteria described in the report, the obtained results are considered “Accepted” in terms of accuracy, precision and z-score.

Added and measured $^{237}\text{Np}/^{236}\text{Pu}$ activity yield ratios, however, did not coincide, indicating the AGES method’s general inapplicability for the selected water samples of low volume. Interestingly, this data

did not match the results of water samples of 1 L or more described Chapter 5.2, where a higher reproducibility was achieved. These findings suggest that the efficacy of the method's redox treatment is dependent on the size of the sample, as well as the sample matrix itself. The method, originally devised for the analysis of soil samples, utilizes a robust and established valence adjustment scheme with Fe^{2+} and NO_2^- as the respective reducing and oxidizing agents.

Sample	V [L]	Added ^{237}Np [mBq]	Added ^{236}Pu [mBq]	^{237}Np yield (%)	^{236}Pu yield (%)	Added A $^{237}\text{Np}/^{236}\text{Pu}$	Found $^{237}\text{Np}/^{236}\text{Pu}$	Found/Added $^{237}\text{Np}/^{236}\text{Pu}$	s (1 σ)
IAEA_1	0.05	35.60	26.42	66.1	59.8	1.35	1.49	1.11	0.05
IAEA_2	0.02	71.19	52.86	10.4	67.2	1.35	0.21	0.16	0.01
IAEA_3	0.02	34.41	26.19	9.3	74.1	1.31	0.16	0.12	0.01
IAEA_4	0.02	35.84	53.23	9.4	58.5	0.67	0.11	0.16	0.02
IAEA_5	0.02	34.09	52.41	15.5	56.7	0.65	0.18	0.27	0.01
IAEA_6	0.02	35.42	26.74	5.1	61.3	1.32	0.11	0.08	0.01

Table 12. Recovery of ^{237}Np and ^{236}Pu determined in the sample IAEA-TERC-2022-02 via AGES method. ^{236}Pu activities are decay-corrected for the day of measurement.

Considering the high abundance of interfering matrix elements in soil matrices compared to water matrices, it is reasonable to assume that differences in ionic strength, content of organic material, and so on may influence the redox speciation of radionuclides through complexation, colloid formation or adsorption.

Low recoveries of ^{237}Np compared to ^{236}Pu for all water samples of 20 mL are indicative of an improper redox adjustment of Np to the tetravalent state. This circumstance might be explained by an excess of NaNO_2 added to the reaction mixtures of very low solute content. Very low concentrations of radioanalytes and interfering species, present in acidic water samples of small volume, further the formation of HNO_2 , which subsequently decomposes under formation of NO_x -gases. Elevated levels of exothermic NO_x -formation may lead to local increases in temperature, which in turn may increase the reaction rate of Np(IV)'s oxidation to Np(V). Moreover, due to the autocatalytic nature of HNO_2 , elevated levels of HNO_2 may result in undesired oxidation processes independently of temperature, especially considering the generally time-sensitive nature of valence adjustment with nitrite and the large loading volumes of 50 mL applied in this method.

The loss of Np(IV) during the 10 M HCl rinsing step is yet another possibility for the extremely low found Np recovery yields. Qiao et al. (2011) discovered that, when using AG-1x4 anion-exchange resin, $30 \pm 5\%$ of Np was found in the HCl fraction of high concentration. Rinsing with HCl is carried out to remove thorium, a task typically unnecessary for the analysis of water samples because of Th(IV)'s low

solubility and tendency to exist in adsorbed or precipitated form in most aquatic environments. Nevertheless, the HCl rinsing step was carried out during this analysis in order to follow procedure and assess the method's applicability to water matrices. Therefore, the large differences in chemical yields between the two analytes might be attributed to the loss of Np during the likely expendable HCl rinsing step.

6. Conclusion

In this work, four radioanalytical methods were tested with regard to the simultaneous determination of ^{237}Np and Pu in environmental soil samples. Among the formerly described methods, the VERA method showed satisfactory results regarding the reliability of recovery ratios of the added spikes for soil samples of 1 g and nearly massless aerosol samples. The good agreement of recovery ratios demonstrates that ^{236}Pu is a suitable non-isotopic tracer for ^{237}Np . To a lesser extent, the same is true for the AGES method. Both methods are characterized by their rapid and convenient chemical separation procedure necessitating only one column, therefore meeting the demanded requirements for an emergency analysis protocol in case of a nuclear incident.

Due to ^{237}Np 's low environmental abundance, at the present state these methods would be best suited for the analysis of (small) soil samples via AMS or ICP-MS, considering the adequate removal of U from the Np/Pu fraction and the insufficient Th separation. Future related endeavors could explore the possibility of increasing Np(IV)'s stability through more sophisticated redox adjustment techniques. Considering the challenges associated with the application of isotopic neptunium tracers, prospective advances in the reliable determination of neptunium will likely come in the form of improved non-isotopic tracer techniques, emphasizing the significance of this type of research.

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8. Appendix

8.1 Spectroscopic data

8.1.1 Baglan method – raw data

8.1.2 AGES method – raw data

Table 13. Alpha spectrometry data for samples prepared via Baglan method.

Sample	Counts ²³⁷ Np	Counts ²³⁵ Pu	t [s]	Canberra Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁵ Pu	File name	Date
B_H ₂ O	2534	1636	263000	Chamber 4	8416-9024	10304-10848	Baglan_H ₂ O_1	30.07.2022
B_20	4780	1712	498200	Chamber 6	8208-9008	10064-10880	Baglan_soil_20	17.08.2022
B_49	2073	596	106200	Chamber 4	8032-8356	9709-10192	Baglan_soil_49	04.09.2022

Table 14. Alpha spectrometry data for samples prepared via AGES method.

Sample	Counts ²³⁷ Np	Counts ²³⁵ Pu	t [s]	Canberra Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁵ Pu	File name	Date
A_18	216	767	175000	Chamber 6	8624-9118	10176-10832	Soil_18_1	13.07.2022
A_H ₂ O	2112	1391	237023	Chamber 6	7728-8480	9600-10256	Pr_H ₂ O	8.7.2022
A_H ₂ O_2	1096	673	163747	Chamber 6	8320-9056	10080-10784	Pr_H ₂ O_2	11.07.2022
A_H ₂ O_SK	1528	1319	435000	Chamber 4	7424-8496	9536-10144	Pr_H ₂ O-SK	15.07.2022
A_19	2427	1630	352000	Chamber 6	8416-9168	10304-10848	Soil_19_1	15.07.2022
A_20	1758	1415	256000	Chamber 6	8416-9168	10304-10848	Soil_20_1	19.07.2022
A_16_2	2796	2682	505989	Chamber 4	7808-8517	9664-10192	Soil_16_2	20.07.2022
A_H ₂ O_W	3397	2212	497033	Chamber 6	8416-9168	10304-10848	Pr_H ₂ O_Waldaq	22.07.2022
A_17	898	980	178750	Chamber 4	7775-8496	9806-10144	Soil_17_1	26.07.2022
A_18_2	829	547	155288	Chamber 4	7844-8496	9760-10176	Soil_18_2	28.07.2022
A_18_3	991	753	330000	Chamber 6	8670-9104	10368-10880	Soil_18_3	03.08.2022
A_18_4	1076	893	179200	Chamber 6	8416-9104	10368-10880	Soil_18_4	07.08.2022
A_18_5	398	398	84300	Chamber 4	8112-8464	9680-10128	Soil_18_5	08.08.2022
A_19_2	991	2026	336600	Chamber 4	8153-8464	9860-10128	Soil_19_2	12.08.2022
A_19_3	1289	1965	336600	Chamber 6	8620-9056	10304-10800	Soil_19_3	12.08.2022

8.1.3 VERA method – raw data

Table 15. Alpha spectrometry data for samples of 1 g prepared via VERA method.

Sample	Counts ²³⁷ Np	Counts ²³⁶ Pu	t [s]	Ortec Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁶ Pu	File name	Date
V_37	2820	903	520000	Chamber 1	559-706	995-1070	VERA_soil_37	14.11.2023
V_38_2	4822	1274	520000	Chamber 2	615-767	1055-1130	VERA_soil_38_2	14.11.2023
V_56	2771	588	425000	Chamber 3	537-682	963-1022	VERA_soil_56	16.11.2023
V_57a	2896	805	425000	Chamber 4	624-782	1074-1162	VERA_soil_57a	16.11.2023
V_37_2	1760	483	340000	Chamber 1	583-706	994-1067	VERA_soil_37_2	20.11.2023
V_41_2	333	94	340000	Chamber 2	640-768	1086-1135	VERA_soil_41_2	20.11.2023
V_37_3	2148	759	500000	Chamber 3	602-728	1023-1094	VERA_soil_37_3	21.11.2023
V_38_3	1655	607	500000	Chamber 4	639-788	1097-1168	VERA_soil_38_3	21.11.2023
V_56_2	3994	1223	800000	Chamber 1	572-704	997-1223	VERA_soil_56_2	24.11.2023
V_57a_2	5943	1925	800000	Chamber 2	533-769	1014-1138	VERA_soil_57a_2	24.11.2023
V_51_3	4807	1656	709800	Chamber 3	580-730	1014-1092	VERA_soil_51_3	27.11.2023
V_54	5148	1697	710000	Chamber 4	620-786	1068-1164	VERA_soil_54	27.11.2023

Table 16. Alpha spectrometry data for samples of 10 g prepared via VERA method.

Sample	Counts ²³⁷ Np	Counts ²³⁶ Pu	t [s]	Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁶ Pu	File name	Date
V_19	2090	1624	277000	Chamber 4	8676-9168	10368-10848	VERA_soil_19	19.08.2022
V_H2O	656	1453	268500	Chamber 4	7920-8416	9648-10128	VERA_H2O	23.08.2022
V_H2O_2	444	1120	268500	Chamber 6	8672-9056	10412-10800	VERA_H2O_2	23.08.2022
V_49	810	1928	605000	Chamber 6	8329-8798	10272-10800	VERA_soil_49	26.08.2022
V_49_2	310	947	253000	Chamber 6	8416-8845	10419-10864	VERA_soil_49_2	04.09.2022
V_49_3	1215	1087	185000	Chamber 6	8637-9004	10320-10864	VERA_soil_49_3	07.09.2022
V_48	1023	781	166000	Chamber 6	8128-8496	9739-10160	VERA_soil_48	08.09.2022
V_48_2	1946	2700	800000	Chamber 4	8152-8496	9802-10160	VERA_soil_48_2	10.09.2022
V_51	493	253	193370	Efficiency: 0.133			VERA_soil_51	17.03.2023
V_51_2	548	309	193390	Efficiency: 0.173			VERA_soil_51_2	17.03.2023
V_38	359	168	193320	Efficiency: 0.138			VERA_soil_38	17.03.2023
V_41	142	100	193340	Efficiency: 0.140			VERA_soil_41	17.03.2023

8.1.4 TEVA/VERA method – raw data

8.1.5 IAEA-TERC-2022-02 – raw data

Table 17. Alpha spectrometry data for samples prepared via TEVA/VERA method.

Sample	Counts ²³⁷ Np	Counts ²³⁵ Pu	t [s]	Canberra Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁵ Pu	File name	Date
T_48	1665	555	190000	Chamber 3	6671-7440	8336-8768	TEVERA_soil_48	26.09.2022
T_48_2	1306	408	190000	Chamber 6	8664-9120	10416-10784	TEVERA_soil_48_2	26.09.2022
T_44	1331	710	150000	Chamber 3	6847-7353	8336-8768	TEVERA_soil_44	28.09.2022
T_44_2	1242	663	150000	Chamber 6	8602-9104	10416-10784	TEVERA_soil_44_2	28.09.2022
T_44_3	1180	845	170000	Chamber 4	8079-8560	9835-10128	TEVERA_soil_44_3	27.09.2022

Table 18. Alpha spectrometry data for IAEA-TERC-2022-02 samples.

Sample Nr.	Counts ²³⁷ Np	Counts ²³⁹⁺²⁴⁰ Pu	Counts ²³⁵ Pu	t [s]	Canberra Detector	Channel Nr. ²³⁷ Np	Channel Nr. ²³⁹⁺²⁴⁰ Pu	Channel Nr. ²³⁵ Pu	File name	Date
IAEA_1	1386	7960	930	170719	Chamber 6	8416-9024	9088-9728	10304-10848	IAEA_03_1	28.7.2022
IAEA_2	674	5815	3223	263000	Chamber 6	8208-9008	9072-9760	10064-10880	IAEA_03_2	30.7.2022
IAEA_3	86	2023	524	95000	Chamber 4	8032-8356	8432-9040	9709-10192	IAEA_03_3	4.8.2022
IAEA_4	94	1474	874	81300	Chamber 6	8880-9184	9263-9648	10512-10800	IAEA_03_4	9.8.2022
IAEA_5	750	6217	4223	500000	Chamber 4	8056-8496	8544-9088	9648-10128	IAEA_03_5	26.8.2022
IAEA_6	96	2727	875	188000	Chamber 4	8185-8496	8496-9040	9792-10160	IAEA_03_6	6.9.2022