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Characterization and Validation Methods for a New Isotopic
Neptunium Spike Material

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Abstract

Neptunium-237 with a half-life of 2.1 Ma is the second most abundant anthropogenic actinide in the environment. This radionuclide has been released by nuclear weapons testing, nuclear accidents, and discharges from the nuclear industry. Global nuclear waste contains ~ 120 t ^{237}Np , which will eventually become the dominant radio-toxicity risk for long-term storage and confinement. However, ^{237}Np remains poorly studied in the general environment compared to other anthropogenic actinides. Accelerator Mass Spectrometry (AMS) excels at abundance sensitivity and background suppression and would be ideally suited to measuring ^{237}Np at ultra-trace concentrations to better understand the migration of Np and to use this radionuclide as an environmental tracer. However, the unavailability of an isotopic Np-spike impedes the normalization of raw AMS measurement data, which is necessary to accurately calculate the Np-concentrations in the original samples. With its long half-life of $1.55 \cdot 10^5$ a and lack of abundant isobars, ^{236g}Np is the most suitable candidate.

The work presented was carried out in the context of a joint project between the Universities of Vienna, Tsukuba, and Kanazawa that aimed to develop such an isotopic Np-spike material via the $^{232}\text{Th}(^7\text{Li}, 3\text{n})^{236g}\text{Np}$ -reaction. The development of methods to characterize a new isotopic Np-spike, i.e., quantify both the ^{236g}Np -content and relevant contaminants, was the central aim of this PhD project. The main challenge was posed by the co-production of the isomer ^{236m}Np ($t_{1/2} = 22.5$ h) that decays into the isobars ^{236}U and ^{236}Pu . Due to the very small nuclear charge differences $\Delta Z/Z$ relevant for established isobar suppression techniques such as degrader foils or gas-filled magnets, these isobars could not be distinguished from ^{236}Np by any accelerator mass spectrometry facility worldwide.

A first isobaric analysis of mass 236 was developed based on the element-specific formation ratio of $\text{AnF}_4^-/\text{AnF}_5^-$ of the three actinides (An) in question (U, Np, and Pu). This method enables the identification of significant isobaric interference by a deviation from the calibrated $\text{NpF}_4^-/\text{NpF}_5^-$ formation ratio on mass 236. A more sensitive and reliable method for isobaric analysis of the Np-spike was based on the unique Ion-Laser Interaction Mass Spectrometry (ILIAMS) instrumentation at the Vienna Environmental Research Accelerator (VERA). Extensive experiments demonstrated that $^{236}\text{UF}_4^-$ can be selectively suppressed via photodetachment with a 637 nm laser, whereas both $^{236}\text{UF}_4^-$ and $^{236}\text{NpF}_4^-$ can be suppressed by gas reactions in an ion cooler to enable direct measurement of $^{236}\text{PuF}_4^-$. By combining the developed techniques with AMS, a prototype ^{236g}Np -spike was characterized in the course of this thesis. The ^{236}Pu -fraction could be

constrained to < 0.3 %, and ^{236}U has been conservatively estimated at (7.5 ± 7.5) % of mass 236 in the spike. The ratio of $^{236}\text{Np}/^{237}\text{Np}$ of 6.93 ± 0.27 and the quantity of $(1.64 \pm 0.14) \cdot 10^9$ atoms ^{236}Np in the potential spike material were determined by AMS measurements at VERA.

The prototype Np-spike material was used for the quantitative analysis of ^{237}Np in environmental samples and compared with the performance of the non-isotopic ^{242}Pu -spike normalization. The sample selection included reference materials, peat bog cores, the Zurich sea water intercomparison sample, and Pacific seawater samples to assess a potential ^{237}Np source term from the releases of treated cooling water from Fukushima into the Pacific.

In testing the limits of these new methods beyond the original scope of the thesis, promising isobar separation schemes for the separation of ^{241}Am from ^{241}Pu or ^{238}U from ^{238}Pu using a 355 nm laser were explored. ^{241}Pu and ^{238}Pu play an important role in emission source identification and dating, and ILIAMS has the potential to improve and simplify their measurement.

In a complementary approach to the work on the new isotopic ^{236}Np -spike, the ^{242}Pu non-isotopic spike for the analysis of ^{237}Np in air filter samples collected in the 1960s in Vienna has been supported. These samples contain a pure signal from the atmospheric nuclear weapons tests, which were the largest source term for ^{237}Np in the environment. Contrary to earlier studies, no post-depositional migration or mixing with other source terms is possible for these samples. A well-defined $^{237}\text{Np}/^{239}\text{Pu}$ ratio for global fallout is crucial for studying Np migration, or identifying additional source terms. The dust collected in air filters was a challenging sample matrix with no previously established procedures for ^{237}Np analysis. AMS measurements performed within the scope of the thesis complemented radiometric techniques for testing and iterative optimization of the chemical sample treatment and normalization techniques, and have enabled the analysis of these valuable samples by AMS.

Zusammenfassung

Neptunium-237 mit einer Halbwertszeit von 2,1 Millionen Jahren ist das zweithäufigste anthropogene Aktinid in der Umwelt. Dieses Radionuklid wurde durch Kernwaffentests, nukleare Unfälle und Anlagen der Nuklearindustrie in die Umwelt emittiert. Radioaktive Abfälle enthalten weltweit $\sim 120\text{ t }^{237}\text{Np}$, das langfristig zum dominanten Radiotoxizitätsrisiko für deren Lagerung werden wird. Verteilung und Migration von ^{237}Np in der Umwelt sind jedoch im Vergleich zu anderen anthropogenen Aktiniden weiterhin wenig erforscht. Beschleunigermassenspektrometrie (AMS) würde sich durch ihre herausragende Sensitivität ideal zur Messung von ^{237}Np in Umweltproben eignen, um die Migration von Np in Umweltsystemen besser zu verstehen und um dieses Radionuklid als Umwelt-Tracer zu verwenden. Die Nichtverfügbarkeit eines isotopischen Neptunium-Spikes, eines anderen Np-Isotops, das Proben für Relativmessungen beigelegt werden kann, behindert jedoch die Normalisierung der AMS-Messdaten, die notwendig ist, um die Np-Konzentrationen in den ursprünglichen Proben genau zu berechnen. Mit seiner langen Halbwertszeit von $1,55 \cdot 10^5$ Jahren wäre ^{236g}Np der geeignetste Kandidat.

Die vorgestellte Arbeit wurde im Rahmen eines gemeinsamen Projekts der Universitäten Wien, Tsukuba und Kanazawa durchgeführt, das darauf abzielte, ein solches isotopisches Np-Spike-Material mittels der $^{232}\text{Th}(^7\text{Li}, 3n)^{236g}\text{Np}$ -Reaktion zu entwickeln. Die Erforschung von Methoden zur Charakterisierung eines neuen isotopischen Np-Spikes, also zur Quantifizierung sowohl des ^{236g}Np -Gehalts als auch der relevanten Verunreinigungen, war das zentrale Ziel dieses Promotionsprojekts. Die größte Herausforderung war die Mitproduktion des Isomers ^{236m}Np ($t_{1/2} = 22.5\text{ h}$), das in die Isobare ^{236}U und ^{236}Pu zerfällt. Aufgrund der sehr geringen Kernladungsunterschiede $\Delta Z/Z$, die für etablierte Techniken zur Isobarenseparation, wie Absorberfolien oder gasgefüllte Magnete entscheidend sind, konnten diese Isobaren von ^{236}Np bisher an keiner Beschleunigermassenspektrometrie-Einrichtung weltweit unterschieden werden.

Eine erste Isobarenanalyse für Masse 236 wurde auf Basis der elementspezifischen Bildungsverhältnisse von $\text{AnF}_4^-/\text{AnF}_5^-$ der drei betreffenden Aktinide An (U, Np oder Pu) entwickelt. Diese Methode würde die Identifizierung signifikanter Isobarenfraktionen durch eine Abweichung vom kalibrierten $\text{NpF}_4^-/\text{NpF}_5^-$ Bildungsverhältnis bei Masse 236 ermöglichen. Eine sensiblere und zuverlässigere Methode zur Analyse des Np-Spikes basierte auf der einzigartigen Ion-Laser Interaction Mass Spectrometry (ILIAMS)-Instrumentierung am Vienna Environmental Research Accelerator (VERA). Umfangreiche Experimente zeigten, dass $^{236}\text{UF}_4^-$ selektiv mit einem 637 nm-Laser neutralisiert werden kann, während sowohl $^{236}\text{UF}_4^-$ als auch $^{236}\text{NpF}_4^-$ durch Gasreaktionen in ei-

nem Ionenkühler unterdrückt werden können, um eine direkte Messung von $^{236}\text{PuF}_4^-$ zu ermöglichen. Durch eine Kombination der entwickelten Techniken mit AMS wurde im Verlauf dieser Arbeit ein Prototyp des ^{236g}Np -Spikes charakterisiert. Weniger als 0.3 % der Masse 236 ist ^{236}Pu , und ^{236}U wurde konservativ mit $(7.5 \pm 7.5) \%$ der Masse 236 im Spike abgeschätzt. Das $^{236}\text{Np}/^{237}\text{Np}$ Verhältnis von 6.93 ± 0.27 und die Menge von $(1.64 \pm 0.14) \cdot 10^9$ Atomen ^{236}Np im potenziellen Spike-Material wurden durch AMS-Messungen bei VERA bestimmt.

Das Prototyp ^{236}Np -Spike-Material wurde für die quantitative Analyse von ^{237}Np in Umweltproben verwendet und mit der Leistung der nicht-isotopischen ^{242}Pu -Spike Normalisierung verglichen. Die Probenauswahl umfasste Referenzmaterialien, Torfmoorkerne, ein 10 Liter Aliquot des Zurich sea water intercomparison (ZSW) Materials und Meerwasserproben aus dem Pazifik, um einen potenziellen ^{237}Np -Quellterm aus den Freisetzungen des aufgereinigten Kühlwassers aus Fukushima in den Pazifik zu bewerten.

Vielsprechende Isobaren-Trennverfahren für die Separation von ^{241}Am von ^{241}Pu oder ^{238}U von ^{238}Pu mit einem 355 nm Laser wurden untersucht. ^{241}Pu und ^{238}Pu spielen eine wichtige Rolle bei der Identifizierung und der Altersbestimmung von Emissionsquellen, und ILIAMS hat das Potenzial, ihre Messung zu verbessern und zu vereinfachen.

In einem komplementären Ansatz zur Arbeit am ^{236}Np -Spike wurde die Analyse von Proben mittels Normalisierung von ^{237}Np auf den nicht-isotopischen ^{242}Pu -Spike unterstützt. Die untersuchten Luftfilterproben, die in den 1960er Jahren in Wien gesammelt wurden, enthalten ein unverfälschtes Signal der atmosphärischen Kernwaffentests, die der größte Quellterm für ^{237}Np in der Umwelt waren. Entgegen früherer Studien ist für diese Proben Radionuklidmigration nach der Deposition und jeder Beitrag anderer Quellterme prinzipiell ausgeschlossen. Ein gut bekanntes $^{237}\text{Np}/^{239}\text{Pu}$ -Verhältnis für globalen Fallout ist entscheidend, um die Migration von Neptunium zu untersuchen oder um den Einfluss zusätzlicher Quellterme zu identifizieren. Der in den Luftfiltern gesammelte Staub war eine anspruchsvolle Probenmatrix, für die keine Erfahrungen mit der Extraktion von ^{237}Np vorhanden waren. AMS-Messungen die im Rahmen der Dissertation durchgeführt wurden, ergänzten radiometrische Techniken zur Prüfung und iterativen Optimierung der chemischen Extraktions- und Normalisierungstechniken, und ermöglichten die Analyse dieser wertvollen Proben durch AMS.

Acknowledgments

The completion of this thesis was only possible because of the support of my partner Bibiane Kaufmann and the patience of my daughter Lore Wiederin during many long evenings or weekends I spent in the lab or at the keyboard. Combining research with childcare can be challenging, and I am immensely grateful to Bibiane for enabling me to push through the more demanding phases of this PhD, and I will make up all missed time and postponed vacations after the submission. I also wish to thank my parents both for their support over many years, and for laying the groundwork for my scientific curiosity in my childhood.

I particularly wish to thank my supervisor Karin Hain for giving me the opportunity to pursue this topic, the freedom to explore it and questions beyond the original scope and for the advice, supervision and feedback that were necessary to turn those explorations into publications and a thesis. Without Martin Martschini and his support, ideas and feedback many experiments would not have been possible, and the ILIAMS experiments benefited immensely from his previous work. The measurements on the actinide beamline of VERA have similarly profited from Peter Steier's previous work, but I particularly want to thank him for his amazing support whenever technical problems rose beyond my ability to fix. Without his remote or in-person support at all hours, several measurements would have had to be aborted, and without the late-night conversations on topics ranging from history and politics to forms of representation of field theories in the accelerator hall, beam-tuning would have been a lot less enjoyable.

Besides the very successful collaboration under difficult circumstances - across continents during the pandemic restrictions - I want to thank Aya Sakaguchi for inviting me to join the irradiation experiment at RIKEN when that was possible again, for facilitating the Fukushima seawater sampling opportunity and for patiently answering many questions I had on the irradiation experiments, chemistry and Japan.

I further want to thank my (former) fellow PhD students Stephanie Adler, Oscar Marchhart, Alexander Wieser and Michael Kern for all the feedback, encouragement, fun and support over the years, Silke Merchel for explaining both finer points of chemistry and academia over countless coffees, Robin Golser for his advice, Johannes Lachner for raising the question of ^{237}U , and Helga Schmelzer-Vincro and Sigrid Lielacher for their help in navigating the bureaucracy of the University of Vienna.

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Part I.

Foundations and framework

1. Declarations

Statement of Contribution

This thesis is based on four articles or manuscripts in various stages of publication (from published to submitted) that are documented in Chapters 4, 5, 6, and 7. To comply with the regulations for cumulative PhD theses, my own contribution as a PhD student needs to be made explicit. The statement of contribution form was signed by me and my thesis supervisor and submitted to the director of doctoral studies at the Faculty of Physics, University of Vienna, in February 2026 and approved in March 2026. This form is documented in Appendix 10.2 and is the basis for the description of my contribution to the four publications presented in this thesis.

The publication “Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu, and Am in accelerator mass spectrometry measurements at VERA” [Wiederin et al. 2022], Chapter 4 is based on my original idea. I designed and performed all experiments for developing the idea into a working method, as well as the first applications, and prepared all samples. I have conducted all measurements independently as the person responsible for the respective beamtimes at the VERA Accelerator Mass Spectrometry facility, but I received help dealing with technical problems and defects at the accelerator. I developed and performed the data analysis, wrote the draft for the manuscript and collected and implemented feedback from all co-authors, before handling the submission and peer review process as the corresponding author. I was supported by my supervisor and co-authors with supervision and feedback throughout this process.

For the publication “Isobar separation of actinides in mass spectrometry by the combination of laser photodetachment with ion-gas interactions” Chapter 5, I was responsible for method development, sample preparation, beam tuning, performing all measurements, data evaluation and interpretation, as well as drafting the manuscript, implementing feedback by co-authors, and handling article submission and review as the corresponding author. I also participated in the production of the ^{236}Np -spike material at the RIKEN Nishina AVF cyclotron together with the coauthor A. Sakaguchi. Several experiments for this paper were performed in collaboration with M. Martschini, but I conducted most of them independently and was the person responsible for the beamtimes. I was supported by my supervisor K. Hain and co-authors, particularly M. Martschini, with supervision and feedback throughout this process, and received help with technical problems and defects at the accelerator when they occurred.

The third paper is “Characterization and first application of a new ^{236}Np -spike for

(A)MS measurements of ^{237}Np ” documented in Chapter 6. The selection of samples, sample preparation for most samples, beam tuning, measurements on the accelerator, data evaluation and interpretation, as well as writing the first draft and implementing feedback from co-authors and reviewers, were among my responsibilities for this paper. I also personally collected seawater samples off the coast of Fukushima, designed the experimental approach for completing the spike characterization myself with AMS and isotope addition series measurements, rather than relying on external ICP-MS data, and handled communication with the Japanese partner group to coordinate on open questions such as the ^{237}U co-production before and during drafting the manuscript. Some environmental samples were prepared under my supervision by a laboratory technician.

For the final paper “Developments of analytical techniques for the determination of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios on air filters from Vienna, Austria“ in Chapter 7, I am co-author and was responsible for some (final) steps in sample preparation, the production of external standards and tuning targets, test measurements with AMS and data evaluation, and drafting of the corresponding parts and review of the whole manuscript. I contributed to the planning of the experiments and interpretation of the data. Furthermore, I contributed to ongoing discussions on the iterative adaptation of the sample preparation, measurement procedures and data evaluation to overcome challenges and was involved in multiple rounds of internal review and revisions of the manuscript leading up to the submission of the manuscript.

Institutions and locations:

Work for this thesis was primarily conducted at the Vienna Environmental Research Accelerator (VERA) at the University of Vienna, specifically the actinide beamline [Steier et al. 2019], the Ion-Laser InterAction Mass Spectrometry setup [Martin Martschini et al. 2022] and associated laboratories operated by the Isotope Physics group at the Faculty of Physics of the University of Vienna. The production of the prospective Np-spike materials was performed at the AVF cyclotron offline beamline (e.g., described for a similar purpose in Itoh et al., 1995 [Itoh et al. 1995]) and the associated laboratory at the RIKEN Nishina Center for Accelerator Based Science in Saitama, Japan. Radiochemical purification of the spike materials and other irradiated samples was primarily performed at the University Tsukuba. The Fukushima seawater samples to investigate a potential ^{237}Np source term from treated water releases have been collected by me while supporting a sampling campaign off the coast of Fukushima. I filtered and prepared these samples for storage and transport at the radiochemistry laboratory of the University of Tsukuba.

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AI use

The partially AI based tools Grammarly and Paperpal have been used in a proofreading capacity to check the text for spelling mistakes and improve the wording or grammar for the four manuscripts before submission. I reviewed and discarded or manually implemented each suggested change to make sure the the wording actually improved and the content was not affected. Parts were checked for readability and clarity with Gemini pro and the U:AI system of the University of Vienna and while the feedback was taken into consideration, these systems were not used for text generation. The manuscripts may have undergone various plagiarism and AI based checks by editors, reviewers or publishers, and it is therefore unknown to which databases parts of the text may have been uploaded to. Outside this limited application, generative AI was not used for the manuscripts or the mantle text of this thesis. All plots and images are based on measured data (plots), human input (other images/schematics) or attributed to their external source.

Licenses

The manuscripts in Chapters 4, 5, and 6 have been published or submitted for publication as open-access articles under the CC-BY 4.0 Creative Commons license. The final status of the fourth manuscript documented in Chapter 7 has not yet been decided at the time of this writing and is under review by Journal of Environmental Radioactivity. However, the version documented here it is currently available as a pre-print, and the general Elsevier copyright agreement grants permission to authors to reuse manuscripts in academic theses under all publication models (open access or subscription).

Some images produced by the author for the IAEA Accelerator Knowledge Portal on NUCLEUS are also used in the introduction of this thesis to illustrate basic concepts of Accelerator Mass Spectrometry. The IAEA explicitly permits reusing such materials, and the image credit is attributed to me on the Nucleus portal, and Nucleus is referenced as the source in all instances.

2. Introduction

2.1. Np – discovery, properties, sources, and relevance

Neptunium lends its name to the $4n+1$ primordial decay chain, but with a half-life of 2.144 ± 0.007 Ma [Lowles et al. 1992] for the most stable isotope, the initial ^{237}Np inventory on Earth has long since decayed. Trace concentrations of ^{237}Np can be found in highly concentrated uranium ores such as Katanga pitchblende at $(2.16 \pm 0.11) \cdot 10^{-12}$ relative to ^{238}U [Myers et al. 1971]. Today, Np is predominantly an anthropogenic element produced and released by human nuclear activities since the 1940s. The first isotope of Neptunium to be discovered was ^{239}Np in 1940 McMillan et al. [1940], with ^{237}Np following in 1942 (published 1948) [Wahl et al. 1948]. In terms of half-life, production pathways in human nuclear activities and past releases to the environment, the α -emitting ^{237}Np is the most important isotope of neptunium.

In nuclear reactors with thermal neutrons, the main pathway for the production of ^{237}Np is via two neutron capture reactions, $^{235}\text{U}(n,\gamma)^{236}\text{U}$ and $^{236}\text{U}(n,\gamma)^{237}\text{U}$ followed by the β -decay of ^{237}U to ^{237}Np with a half-life of 6.752 ± 0.002 days [Basunia 2006]. The detonation of thermonuclear weapons produces large quantities of fast neutrons, which exceed the 6.18 MeV threshold for the $^{238}\text{U}(n,2n)^{237}\text{U}$ reaction, followed again by β -decay to ^{237}Np [Mukerji et al. 2013]. In both cases, ^{241}Pu ($t_{1/2}=14.329 \pm 0.29$ y) is produced via multiple neutron captures on ^{238}U and decays first into ^{241}Am ($t_{1/2}=432.6 \pm 0.6$ y) and then ^{237}Np [Nesaraja 2015]. Due to the half-life of ^{241}Am , this pathway is negligible for younger materials but becomes relevant over time, e.g., for long-term storage of nuclear waste.

A total accumulated inventory of ~ 54 t ^{237}Np and an annual production of 3 t have been estimated for spent nuclear fuel in the year 2003 [Albright et al. 2005]. Assuming constant production over the past 23 years would place the current total (2026) at ~ 120 t. Based on the same publication, these numbers increase significantly if ^{241}Am which decays into ^{237}Np over time is to be included for estimating long term storage inventories: The combined inventory was estimated at 140 t in 2003, increasing by 7 t per year. In the first phases of nuclear waste storage, shorter-lived radionuclides with a corresponding higher specific activity are the major concern in nuclear waste storage, but ^{237}Np will become the dominant source of potential cancer doses per ton of material after $\sim 10,000$ years and remain so for several million years [Cohen 1982]. The ^{237}Np inventory in nuclear waste can be expected to increase considerably through the decay of

^{241}Am , with an estimated inventory of 87 t (as of 2003) [Albright et al. 2005]. Significant quantities - 400 kg at the Savannah River Plant alone - of ^{237}Np have been separated from nuclear waste [Paul L. Roggencamp 1987], primarily with the goal of producing ^{238}Pu for radionuclide batteries.

^{237}Np itself is fissile and has critical mass of 56 kg, similar to highly enriched ^{235}U [Albright et al. 2005; Preston et al. 2025]. While no information on its use in nuclear weapons is publicly available, ^{237}Np potentially poses a nuclear proliferation risk for millions of years, even if by that time nuclear reactors suitable for the production of nuclear weapons have long since been discontinued.

An estimated 1500 kg of ^{237}Np have been released by nuclear weapons testing, as well as ~ 400 kg from the reprocessing plant at Sellafield and >40 kg from La Hague, making ^{237}Np the second most abundant anthropogenic actinide in the environment [Beasley et al. 1998a; Beasley et al. 1998b; Kelley et al. 1999]. While global fallout clearly is the largest source term for environmental ^{237}Np overall, locally other discharges can contribute significantly to the inventory, as has been observed in the North Atlantic Ocean or the Arctic Ocean [López-Lora et al. 2021].

Data on the actual behavior of Np in the environment is incomplete and sometimes conflicting. Overall, the valence state is the most important factor for the chemical and migration behavior of Np in the environment [Kaszuba et al. 1999]. Generally speaking, the reduced +3 and +4 oxidation states of Np are found to be more particle reactive, while the +5 state behaves more conservatively. However, the application of general principles to complex environmental matrices is difficult, particularly with sparse environmental Np data sets.

For soil, both strong attachment to particles [Röllin et al. 2009] and unexpected mobility even of the reduced Np(IV) species have been reported [Peruski et al. 2018]. The Np(IV) mobility in the latter study was attributed to a combination of partial oxidation and the formation of a reduced colloidal species. A study on the Ob River sediments (Siberia, likely influenced by the Semipalatinsk test site) indicated that Np can be remobilized from the sediment more readily compared to Pu [Kenna 2009]. This second study, Kenna et al., 2009, used sequential chemical treatments aimed to release metals from specific compounds. They reported relevant Np fractions loosely bound on the surface of iron oxides/hydroxides, humic substances or in exchangeable sites in the clay minerals while Pu was not detectable in these fractions and Np was found to be 8 times more likely to be bound to organic matter than Pu.

For seawater, a more conservative behavior, defined by low reactivity and the tendency to remain in solution, can be expected: Np should be present mainly in the +5 state in the form of NpO_2^+ and, in this dissolved state, should move with water masses [Lindahl et al. 2005]. However, the presence of certain minerals that strongly bind Np could lead to scavenging [Townsend et al. 2022] and strong bio-sorption of Np has been demonstrated [Songkasiri et al. 2002]. In a recent study, Np concentrations in surface waters decreased

by 25-30 % when in offshore vs inshore sampling stations off the coast of Namibia, in the Benguela Upwelling System, indicating significant particle reactivity of Np, while ^{236}U remained constant in these conditions [López-Lora et al. 2020]. In groundwater, mobility of the reduced Np(IV) has been demonstrated based on hydrous ferric oxide colloids [Kalmykov et al. 2007].

Overall, the chemical behavior of Np in most environmental matrices appears difficult to predict, and requires further study under real environmental conditions. Np generally behaves conservatively in ocean water, but may behave differently from established tracers like ^{236}U under specific conditions. Therefore, ^{237}Np has great potential as an environmental tracer either complementary to or combined with established tracers like ^{236}U or ^{239}Pu . On the other hand, the large quantities of ^{237}Np present in nuclear waste necessitate sensitive detection methods in various matrices from a long-term storage safety and migration perspective as well as from a nuclear security and non-proliferation perspective.

2.2. Overview of existing ^{237}Np measurement techniques

2.2.1. Radiometric detection methods

As an α -emitter with a Q_α of (4957.3 ± 0.7) keV and several prominent α emission lines, e.g., 4788.0 keV (47.64 %), 4771.4 keV (23.2 %), 4766.5 keV (9.3 %) [Basunia 2006], ^{237}Np in principle well detectable by α -spectrometry. However, the low specific activity of 2.60×10^7 Bq/g, potential interference from ^{234}U , ^{230}Th and ^{226}Ra and overlap of the different ^{237}Np α -peaks complicate the measurement for environmental samples [Nóra Vajda et al. 2011]. A clean separation of neighboring α -peaks also requires extremely thin samples to minimize depth-dependent energy losses and straggling, and consequently broadening of the measured energy distribution for a given α -line. The chemical sample preparation of α -spectrometry therefore has multiple goals: thoroughly removing the matrix, suppressing interfering α -emitters, and maximizing the ^{237}Np yield. As a final step after purification, thin samples can be produced, e.g., via electro-deposition on stainless steel [Hou et al. 2008]. Using typical Si detectors, detection limits in α -spectrometry are on the order of 0.2-0.4 mBq/sample ($2-4 \cdot 10^{10}$ at/sample), assuming no interfering peaks and a background count rate of 10^{-4} - 10^{-5} cps [Nóra Vajda et al. 2011].

Furthermore, α -spectrometry requires a suitable chemical yield tracer. With no other long-lived α -emitting isotope of Np, the main candidates are the short-lived (2.3 d) β -emitter ^{239}Np or ^{235}Np . Whereas the latter has negligible α -emission intensities, the dominant electron capture decay branch can be detected via the resulting x-ray emissions [Harvey et al. 1987] and the half-life of 396.1 d is reasonably long. Despite the short half-life of ($t_{1/2} = 2.34 \pm 0.02$ d [Connor et al. 1959]), ^{239}Np is a useful chemical yield tracer due to the possibility of using ^{243}Am generators to produce ^{239}Np solutions on a regular

basis in radiochemistry laboratories [Wenzel et al. 2002]. While there are two viable yield tracers, neither is an α -emitter, and thus converting between different activity measurements introduces additional uncertainties: An α -emitting tracer would allow the direct normalization of ^{237}Np data to the tracer count rate in a relative measurement. Instead, in the case of ^{239}Np the chemical yield has to be determined in a separate measurement (and normalization) of the ^{239}Np chemical yield via the 277.6 keV γ -line [Benedik et al. 2017], which can then be used to correct the instrumental efficiency calibrated α -spectrometry result for ^{237}Np .

The main limitation for radiometric detection of ^{237}Np at low concentrations is the very long half-life of 2.144 Ma. By comparison, that of ^{238}Np is only 2.1 days, and the cross-section of the $^{237}\text{Np}(n,\gamma)^{238}\text{Np}$ reaction is $(177.6 \pm 3.8) \text{ b}$ [Rovira et al. 2020], making Neutron Activation Analysis (NAA) a viable option for the measurement of ^{237}Np . Assuming a neutron flux of $5.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ over six h (achievable in a typical TRIGA MkII research reactor [Merz et al. 2011]), it has been estimated that 1 Bq of ^{237}Np activity could be converted into $6.8 \times 10^4 \text{ Bq}$ of ^{238}Np activity [Kim et al. 1988]. In real environmental samples, detection limits on the order of 0.01 - 0.05 mBq have been reported [Nóra Vajda et al. 2011]. Whereas NAA has thus the highest sensitivity of the radiometric detection methods of ^{237}Np , it requires a high-flux reactor and considerable chemical sample preparation both before and after the irradiation, further complicating the tracking of chemical yields and adding costs both in human resources, high purity reagents, and instrumentation. These requirements limit the suitability of NAA for the large sample batches required for environmental monitoring.

2.2.2. ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is a standard tool in the detection of anthropogenic radionuclides. The basic principle of ICP-MS is the plasma ionization of the sample using inductively coupled electrical currents at atmospheric pressure with a mass spectrometric analyzer in high vacuum. The advantages lie in high ionization efficiencies for inorganic analytes, particular heavy metals and techniques like standard addition [Kim et al. 1989] or external calibration with standard solutions [Krachler et al. 2014] enable measurements of ^{237}Np without an isotopic spike, as long as the concentrations exceed the limit of detection of the respective ICP-MS system.

Whereas basic ICP-MS would not have the required sensitivity for the detection of ^{237}Np in environmental samples, there are specialized designs that significantly improved the capabilities of this technique for ultra-trace radionuclide detection. The major difficulties arise from potential molecular (in ICP-MS publications often called polyatomic) or isobaric interferences, multiply charged ions with the same m/q ratio as the isotope of interest and tailing from neighboring masses, such as the primordial ^{238}U for ^{237}Np and ^{239}Pu . State of the art studies involving trace amounts of ^{237}Np use advanced designs. The sector field ICP-MS approach substantially improves the mass resolution, to the

point where most interferences can be resolved into separate peaks [Jakubowski et al. 1998]. On the other hand QQQ-ICP-MS introduces a chemical filter in the form of a gas reaction cell between two quadrupole mass filters, where both molecular and isobaric interferences as well as abundant neighboring masses can be significantly reduced by suitable reactive gases [Fernández et al. 2012]. ^{237}Np data is usually normalized via a non-isotopic ^{242}Pu -spike or by combining ^{239}Np as a chemical yield tracer with external standards for instrumental normalization. State-of-the-art measurements of ^{237}Np on QQQ-ICP-MS (ICP-MS/MS) [Yang et al. 2021] or sector field ICP-MS Zhang et al. [2023] achieve detection limits of 0.6 fg ($\sim 1.2 \times 10^6$ at) and $1.3 \times 10^{-3} \mu\text{Bq/l}$ (~ 50 fg or 1.3×10^8 atoms/l) respectively.

2.2.3. Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) is an ultra-sensitive method for detecting trace amounts of long-lived radionuclides. A more detailed description of the Vienna Environmental Research Accelerator (VERA) AMS instrumentation used for most measurements in this thesis can be found in Chapter 3. In the following section, the general principle and the application of AMS for ^{237}Np measurements shall be briefly introduced. The first application of accelerators for the detection of rare isotopes was the identification of ^3He in stable He by [Alvarez et al. 1939]. In 1977, the potential for using negative ion sources and (tandem) accelerators for radically improving radiocarbon dating was discovered, leading to the development of Accelerator Mass Spectrometry (AMS) [Purser et al. 1977]. In principle, an AMS facility consists of a negative ion source and two mass spectrometers linked by a tandem accelerator, as shown schematically in Fig. 2.2.1. The key advantage of AMS is the complete suppression of molecular interference through the stripping process in the tandem accelerator, which allows for interference-free single-atom detection of many rare radionuclides.

AMS is a relative measurement technique, and count rates for one isotope by themselves do not enable an absolute determination of that isotope in a sample. Varying chemistry yields, sputter yields, ion optical transmissions, detection efficiencies and other factors would have to be taken into account for quantitative results. The output of an AMS measurement are therefore isotopic ratios, or in some cases ratios of radionuclides of different elements. In radiocarbon measurements, the isotopic ratio of $^{14}\text{C}/^{12}\text{C}$ is measured and then, e.g., used as the input for a suitable calibration function to determine the age of a sample [Reimer et al. 2020]. Since the rare isotope has to be detected via single ion counting in a suitable detector, e.g., a gas filled ionization chamber, stable or primordial isotope ion currents typically range from pA to hundreds of nA and have to be measured by other means such as Faraday cups. Standard materials with well known isotopic ratios are then used to calculate correction factors to compensate for different detection yields of these different measurements.

In the high mass range of the actinides, the relative mass differences and consequently

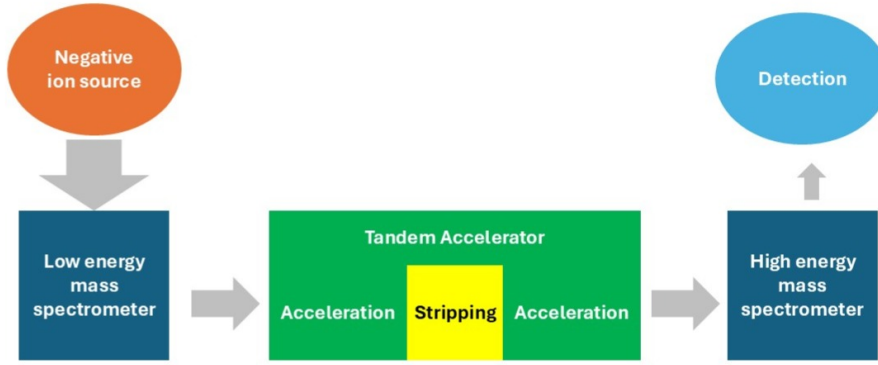


Figure 2.2.1.: The principle of AMS: Negative ion beams are generated from sample materials in the ion source. The low-energy mass spectrometer selects specific masses for injection into the tandem accelerator, where electron stripping suppresses molecular interference. Subsequently, the high-energy mass spectrometer filters the resulting atomic cations by mass for detection via single-ion counting (trace isotopes) or ion current measurement (stable/primordial isotopes).

the separation of neighboring masses is much smaller than for lighter AMS nuclides such as ^{14}C . A major challenge for actinide AMS is therefore achieving the required resolution with minimal beam losses, and minimizing both tailing from abundant neighboring masses and interference from multiple-scattering events [Steier et al. 2019]. The first measurement of a rare actinide isotope, i.e., natural ^{236}U in uranium ores, with AMS has been reported in 1994 [Zhao et al. 1994], with environmental ^{236}U following in 1997 [Zhao et al. 1997]. In 1997, AMS was used for the first time to measure ^{237}Np [Fifield et al. 1997]. A sensitivity of 10^5 atoms was reported using ^{239}Np as a chemical yield tracer, while ^{242}Pu was used to monitor the instrumental yield.

2.3. The problem of normalization and potential isotopic spikes

Whereas AMS offers exceptional abundance sensitivity (10^5 [Quinto et al. 2017] to 10^6 at/sample [López-Lora et al. 2019a]), the problem of normalization has not been solved reliably for ^{237}Np . Normalization in this context means the calculation of an absolute content or concentration from a measured trace ion count rate via a relative measurement involving a known quantity of a different ion species, ideally another isotope of the same element. For uranium measurements, the $^{233}\text{U}/^{236}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios are either the quantities of interest (e.g., for differentiating between nuclear industry and weapons fallout [Hain et al. 2020; Steier et al. 2008]), or the ^{238}U concentration of the sample has to be determined by other means to then allow quantification of ^{233}U and/or ^{236}U relative to it. In the case of Pu, no stable or primordial isotope exists, so an isotopic spike - a well-known quantity of, e.g., ^{242}Pu or ^{244}Pu can be added to each sample, so that other isotopes such as $^{239,240}\text{Pu}$ can be measured relative to the isotopic spike [Fifield et al. 1996]. Then, from the isotopic (atom) ratio of an isotope of interest to the spike isotope, e.g., $R(\frac{^{239}\text{Pu}}{^{242}\text{Pu}})$ measured via AMS and the number of added ^{242}Pu -spike atoms N_{242} , the number of ^{239}Pu atoms in the sample can be calculated as

$$N_{239} = R(\frac{^{239}\text{Pu}}{^{242}\text{Pu}}) \cdot N_{242}.$$

For the analysis of ^{237}Np , no stable or primordial isotope exists, and no isotopic spike has been readily available. Limited quantities of ^{236}Np as an isotopic have been produced previously for this purpose, as discussed in Section 2.4 and Chapter 6. However, ^{236}Np was unavailable for most laboratories, and the $^{237}\text{Np}/^{236}\text{Np}$ atom ratios achieved were in the range of 0.28189 [Goldstein et al. 2021] to 0.2182 [Efurd et al. 1991], so that ^{237}Np from the spike material can cover the environmental signal for low concentrations in environmental samples. Consequently, most ^{237}Np analyses via AMS have relied on non-isotopic spikes, typically ^{242}Pu for normalization.

Earlier studies often relied on a dual-spike approach with ^{239}Np as the chemical yield tracer and ^{242}Pu for the AMS measurement [Fifield et al. 1997], but recently ^{242}Pu normalization for both chemistry and instrumental yields has been successfully established (e.g., [Quinto et al. 2015, 2017][López-Lora et al. 2019a][López-Lora et al. 2021, 2020]), particularly for ground- and seawater samples. In this approach, the ^{237}Np count rates are normalized both to an internal ^{242}Pu -spike added at the beginning of the chemical sample preparation, and external $^{237}\text{Np}/^{242}\text{Pu}$ standards. The ^{242}Pu -spike traces overall yields, and the external standards provide a correction factor for differences in the ionization yields and ion optical transmissions of ^{237}Np and ^{242}Pu . Key to this approach is to ensure, that there is no elemental Np/Pu fractionation during chemical sample preparation. Extensive work has been put into optimizing the chemical sample preparation for seawater samples that focuses on ensuring quantitative co-precipitation and careful adjustment of the oxidation states of Np and Pu during anion exchange chromatography [López-Lora et al. 2019a] [López-Lora et al. 2021, 2020].

An overview of the different detection methods for ^{237}Np given in [Zhang et al. 2024], showed that the detection limit of AMS are at least an order of magnitude better than that of all competing methods. However, non-isotopic normalization is always vulnerable to chemical fractionation as discussed , e.g., in [Hain et al. 2022].

Recent works such as [Quinto et al. 2015, 2017], as discussed in [Hain et al. 2022], indicate a variability of the formation ratios for $^{237}\text{NpO}^-$ and $^{242}\text{PuO}^-$. Furthermore, the differences between the reported formation ratios for $^{237}\text{NpO}^-$ and $^{242}\text{PuO}^-$ may point to a strong matrix dependency of the anion formation, which could result in systematic errors, if the matrix of the synthetic external $^{237}\text{Np}/^{242}\text{Pu}$ standards does not match the behavior of the environmental sample matrix in the ion source. This approach is only suitable if both standards and samples have not been sputtered previously and are measured for a similar duration, since the $^{237}\text{Np}/^{242}\text{Pu}$ ratio has been observed to shift with increasing sputter-time in an AMS ion source [López-Lora et al. 2019a]. Typically, these concerns have been addressed by the demonstration of the performance of the normalization on synthetic samples or reference materials. However, extrapolating from such test samples to the performance of the normalization for each individual environmental sample may be problematic, particularly since there is no reliable way of identifying cases where the normalization failed due to elemental fractionation if only a

2.3. THE PROBLEM OF NORMALIZATION AND POTENTIAL ISOTOPIC SPIKES

^{242}Pu sample is used. In [Glückman et al. 2022] an investigation into ^{237}Np migration in clay reported overall a good performance of the non-isotopic normalization of ^{237}Np to a ^{244}Pu -spike for most samples. However, the sensitivity test samples (made from known quantities of ^{237}Np , ^{244}Pu and other actinides) shown in Fig. 1 of that publication indicate a significantly lower Np yield compared to Pu for one of these samples. A similar Np/Pu fractionation on an unknown sample would have resulted in a normalization error of an order of magnitude. Hain et al. reported the (almost) complete loss of ^{237}Np in chemical sample treatment which had not been corrected for by the ^{242}Pu -spike for an environmental reference material sample [Hain et al. 2022]. Whereas complete losses or false results on samples with known concentrations can be identified, similar scrutiny is unlikely for smaller deviations of, e.g., 50%. Another severe consequence of this lack of reliability could be confirmation bias towards expected distributions and profiles, as any truly unexpected result would be at risk of being dismissed as a normalization failure. Due to the potentially underestimated uncertainties and overestimated reliability of ^{237}Np data normalized using ^{242}Pu , this approach has been called “semi-quantitative” [Hain et al. 2022]. For more demanding sample matrices with larger variability in the chemical composition from sample to sample the potential for normalization failure increases further.

The best solution for normalization would be an isotopic spike, which greatly reduces the risk of fractionation. The remaining sources of normalization errors with an isotopic spike would mainly be losses before the addition of the spike (e.g. adsorption to container walls) or different chemical species or oxidation state for the isotope of interest and the spike (e.g. complexed vs. dissolved) that require either sufficient time for equilibration, or more aggressive sample treatment steps, e.g. to break down complexes [Lovett M. B. et al. 1990]. However, after ensuring chemical homogeneity at the beginning of sample treatment, an isotopic spike will reliably account for all subsequent losses in chemistry and measurement. A final potential source of fractionation would be differences in ion optical transmission, which have to be minimized via adequate tuning of the AMS instrumentation.

Fig. 2.3.1 shows ^{237}Np and the neighboring isotopes of U, Np and Pu on the Karlsruhe Chart of the Nuclides [Magill et al. 2006]. The beta emitter ^{239}Np , which can be separated from ^{243}Am solutions [Wenzel et al. 2002], is a useful chemical yield tracer for Np, but the half-life of 2.3 days is too short for reasonable workflows in AMS, where weeks to months can be expected to pass between the chemical preparation of the first samples and the AMS measurement. As demonstrated in [Fifield et al. 1997], the use of ^{239}Np as a chemical tracer measured radiometrically must be combined with a non-isotopic spike such as ^{242}Pu to normalize both chemical and instrumental yield factors. However, the in-growth of ^{239}Pu interferes with the measurement of this important Pu isotope in the same sample which could otherwise be determined simultaneously. Depending on the purity of the ^{243}Am generator, the unwanted addition of other radionuclides - particularly ^{237}Np from the decay of ^{241}Am is also possible [López-Lora et al. 2019b].

Whereas the half-life of ^{234}Np is slightly longer than that of ^{239}Np , it is still too short for reasonable AMS workflows, and this isotope is much harder to produce on demand since there is no ^{234}Np equivalent to the ^{243}Am generators used for ^{239}Np . All Np isotopes below ^{234}Np and above ^{239}Np decay even faster. For ^{238}Np and ^{235}Np , isobaric interference from primordial ^{238}U and ^{235}U orders of magnitude above reasonable spike quantities precludes their use for established mass spectrometric methods. There is only one isotope of Neptunium that would be suitable as an isotopic spike for the analysis of ^{237}Np for (A)MS, namely ^{236}Np with a half-life of $(1.55 \cdot 10^5) \text{ y}$.

Pu 235 25.3 m sf α 5.85 γ 49; 756; 34... e ⁻	Pu 236 2.858 a sf α 5.768; 5.721... sf; Mg 28 γ (48; 109...); e ⁻ σ _f 160	Pu 237 45.2 d sf α 5.334... γ 60...; e ⁻ σ _f 2300	Pu 238 87.74 a sf α 5.499; 5.456... sf; Si; Mg γ (43; 100...); e ⁻ σ 510; σ _f 17	Pu 239 2.411 · 10 ⁴ a sf α 5.157; 5.144... sf; γ (52...) e ⁻ ; m σ 270; σ _f 752	Pu 240 6563 a sf α 5.168; 5.124... sf; γ (45...) e ⁻ ; g σ 290; σ _f ~0.056
Np 234 4.4 d ε; β ⁺ ... γ 1559; 1528; 1602... σ _f ~900	Np 235 396.1 d ε; α 5.025; 5.007... γ (26; 84...); e ⁻ g; σ 160 + ?	Np 236 22.5 h ε; β ⁻ 0.5... γ (642...); e ⁻ g; σ _f 2700	Np 237 2.144 · 10 ⁶ a sf α 4.790; 4.774... γ 29; 87...; e ⁻ σ 170; σ _f 0.020	Np 238 2.117 d β ⁻ 1.2... γ 984; 1029; 1026; 924...; e ⁻ g; σ _f 2600	Np 239 2.355 d β ⁻ 0.4; 0.7... γ 106; 278; 228...; e ⁻ ; g σ 32 + 19; σ _f <1
U 233 1.592 · 10 ⁵ a α 4.824; 4.783... Ne 25; γ (42; 97...); e ⁻ σ 47; σ _f 530	U 234 0.0054 α 4.775; 4.723...; sf Mg 28; Ne; γ (53; 121...) e ⁻ ; σ 96; σ _f 0.07	U 235 0.7204 26 m α 4.398...; sf Ne; γ 186... e ⁻ ; σ 95; σ _f 586	U 236 2.342 · 10 ⁷ a 120 ns α 4.494; 4.445...; hy 783; sf; γ (49; 113...) e ⁻ ; σ 5...	U 237 6.75 d β ⁻ 0.2... γ 60; 208... e ⁻ σ ~100; σ _f <0.35	U 238 99.2742 298 ns α 4.198...; d hy 254; 163... e ⁻ ; σ 27; σ _f 32.6

Figure 2.3.1.: This section of the Karlsruhe nuclide chart shows the potential isotopic spikes for ^{237}Np and relevant U or Pu isobars. Only ^{235}Np and ^{236}Np have sufficiently long half-lives to be useful as an isotopic Np-spike, but interference from the primordial isobar ^{235}U prevents the use of ^{235}Np for mass spectrometry. For ^{236}Np the long-lived decay products of the isomer ^{236m}Np , ^{236}U and ^{236}Pu could also produce isobaric interference [Magill et al. 2006].

2.4. Established production pathways for ^{236}Np

^{236}Np has been produced in the past, mainly by the irradiation of various uranium isotopes with deuterons, protons or fast neutrons. A good overview for the previously attempted production reactions is given in [Jerome et al. 2017; Jerome et al. 2014]. In the following, the relevant findings on d and p irradiations of uranium targets for the production of ^{236}Np from these two publications are summarized.

The $^{238}\text{U}(p,3n)^{236}\text{Np}$ reaction was investigated and performed multiple times over the past decades, [Aaltonen 1990; Ageev et al. 1987; Bellido et al. 1994; Guzhovskii et al. 1995; Zhao et al. 1999], as was the $^{238}\text{U}(d,4n)^{236}\text{Np}$ reaction [Bellido et al. 1993; Guzhovskii et al. 1995]. However, no data quantifying isobaric interference on mass 236 or the ^{237}Np co-production has been made available for these materials. The cross-section data for all these experiments have been combined into plots in [Jerome et al. 2014] which show peaks in the 60-80 mb range for both reactions in a 15-25 MeV energy range. It is noteworthy, that the cross-sections for $^{238}\text{U}(p, 3n)^{236}\text{Np}$ reported in [Aaltonen 1990] are significantly lower ($\sim 10 \text{ mb}$ at 17.5 MeV maximum) than other cross-sections at similar

energies (23 - 80 mb for 17 -20 MeV) for this reaction in the other publications mentioned above as discussed in [Jerome et al. 2014]. Experiments reported in [Jerome et al. 2014] estimated a production of 30 Bq ^{236g}Np ($\sim 2 \times 10^{14}$ at) via $^{238}\text{U}(p,3n)^{236}\text{Np}$ which would be sufficient for the normalization of at least 10^6 AMS samples at $2 \cdot 10^8$ at per sample, or correspondingly more samples for lower amounts spiked.

The irradiation of ^{236}U targets with protons [Aaltonen 1990; Aaltonen et al. 2005] has also been explored. However, this approach would require the complete removal of macroscopic quantities of the isobar ^{236}U from trace quantities ^{236}Np produced to enable the use of the resulting material as an isotopic Np-spike.

For ^{235}U , the principal reaction investigated to date is $^{235}\text{U}(d,n)^{236}\text{Np}$ [Bellido et al. 1993; Lessler et al. 1966; Wing et al. 1959]. However, the cross-sections reported by different studies again exhibit a large variability at similar energies as shown in [Jerome et al. 2014]. For regulatory and non-proliferation reasons, macroscopic highly enriched ^{235}U targets are unavailable for almost all laboratories, particularly outside nuclear weapon states, so this pathway, while promising, is not a viable option for ^{236}Np -spike production in university and research facilities, but also generally not on large scale. For materials produced at the Los Alamos National Laboratory, Goldstein et al., 2021 reported a $^{237}\text{Np}/^{236}\text{Np}$ ratio of 0.28189 [Goldstein et al. 2021] while data in Efurd et al., 1991 results in a $^{237}\text{Np}/^{236}\text{Np}$ ratio of 0.2182 [Efurd et al. 1991]. Using a typical AMS spike amount of $2 \cdot 10^8$ at/sample would therefore introduce $4.4 \cdot 10^7$ - $5.6 \cdot 10^7$ at ^{237}Np to each sample and blank, and increase the limit of detection. While this effect can be mitigated by lowering the amount spiked, reducing the ^{237}Np co-production would be highly advantageous. The Efurd et al., 1991 publication reported a production of $6 \cdot 10^{13}$ atoms of ^{236g}Np and a $^{236m}\text{Np}/^{236g}\text{Np}$ ratio of ~ 6 which corresponds to a considerable co-production ($\sim 2 \cdot 10^{14}$ at each) of the isobars ^{236}Pu and ^{236}U .

A variety of reactions using ^{237}Np as the target, such as $^{237}\text{Np}(\gamma,n)^{236}\text{Np}$ [Yamana et al. 2001] or $^{237}\text{Np}(n,2n)^{236}\text{Np}$ [Lindeke et al. 1975] have been investigated over the years. However, using ^{237}Np as a target would place extremely high demands on isotopic purification and is unlikely to be a viable strategy for producing a ^{236}Np -spike material. The $^{237}\text{Np}(n,2n)^{236}\text{Np}$ cross-section for 13.77 MeV neutrons is very high at $\sim (540 \pm 38)$ mb [Landrum et al. 1973] (ground state and isomer combined), but the ^{237}Np matrix still prohibits the use of this reaction for a ^{236}Np -spike material for mass spectrometry.

Overall, the $^{238}\text{U}(p,3n)^{236}\text{Np}$ and $^{238}\text{U}(d,4n)^{236}\text{Np}$ reactions combine high cross-section and easily available targets, but suffer from considerable ^{237}Np co-production. High yields and low co-production of ^{237}Np could be achieved using highly enriched ^{235}U as the target material, which is generally not available. Other pathways using either ^{236}U or ^{237}Np as target materials are unlikely to yield a ^{236}Np -spike of sufficient purity, as this would require the complete removal of the macroscopic target matrix. The achieved $^{237}\text{Np}/^{236}\text{Np}$ ratios to date would significantly affect detection limits compared to pure ^{236}Np if applied to AMS measurements.

2.5. Research questions and scope of the thesis

The aim of a joint Austrian-Japanese project was to develop a new isotopic ^{236}Np -spike material, and to determine the excitation functions for the $^{232}\text{Th}(^7\text{Li}, 3\text{n})^{236g}\text{Np}$ reaction and other relevant nuclear reactions that occur in the same irradiation experiments. The irradiation experiments, the chemical purification of irradiated samples and the investigations regarding the excitation functions were the responsibility of the Japanese project partners. The central research question addressed in this thesis was the development of characterization methods for such an isotopic Np-spike material. Characterization in this context means determining the total quantity of ^{236}Np produced, and determining relevant impurities, primarily ^{237}Np , ^{236}U and ^{236}Pu . Measuring $^{236}\text{X}/^{237}\text{Np}$ ratios is possible using established AMS techniques, but analyzing the isobaric composition of mass 236 in a sample had previously not been possible at any AMS facility in the world. A electrostatic and magnetic filters used in AMS cannot distinguish between atomic isobars, and even specialized techniques that employ degrader foils [Raisbeck et al. 1984], complex multi anode detectors [Martschini et al. 2019a] or gas-filled magnets [Knie et al. 1997] that exploit the nuclear charge dependence of the energy loss or charge exchange behavior of ions are limited to much lighter ions with larger relative nuclear charge differences. The analysis of the isobaric composition in this high mass range, therefore, required the development of new approaches and techniques to enable isobar separation even in the high mass range of the actinides. The Ion-Laser InterAction (ILIAMS) instrumentation at VERA [Martin Martschini et al. 2022] is capable of isobar separation at low energies, independent of $\Delta Z/Z$ differences that limit other techniques for high Z elements. One focus of the method development was therefore to develop actinide isobar separation techniques based on ILIAMS.

After characterizing a prototype spike material, the final goal of this thesis was to validate its application for the normalization of ^{237}Np concentration using environmental reference materials and to apply the spike in the analysis of a selection of environmental samples. Whereas recent advances regarding the use of the non-isotopic ^{242}Pu normalization method for ^{237}Np have focused on seawater, a selection of sample matrices was analyzed to demonstrate the versatility of the isotopic spike. Besides the environmental reference materials IAEA-381 (Irish Sea water) [Povinec et al. 2002] and IAEA-385 (Irish Sea sediment) [Pham et al. 2008], samples from a peat bog and the new Zurich sea water intercomparison sample [Christl et al. 2025] were selected for analysis. Furthermore, a research stay in Japan with the aim of supporting one of the irradiation experiments presented the opportunity to use the new prototype ^{236}Np -spike for investigating an important radio-ecological question: are relevant quantities of ^{237}Np entering the Pacific Ocean due to the Advanced Liquid Processing System (ALPS) treated cooling water from the Fukushima Daiichi Nuclear Power Plant (FDNPP)? For this purpose, two seawater samples were collected close to an ongoing release of ALPS treated cooling water in March 2024. Besides potential environmental or human health related concerns, es-

establishing ^{237}Np as an environmental tracer requires building up a good understanding of how, where and when ^{237}Np entered the environment. Therefore, identifying or ruling out the ALPS water as a potential ^{237}Np source term was also an important question in this regard.

The success of the small prototype production experiments was uncertain, since the branching ratios and excitation functions have not been determined experimentally before. Furthermore, the regulatory framework of the countries involved in this project would not have allowed for a commercial production and export of the radionuclide ^{236}Np , so that non-isotopic ^{242}Pu normalization will still be required for most Np samples, even after a successful conclusion of this project. Complementary to the work related to the development, characterization and application of an isotopic spike material, environmental ^{237}Np samples were measured by AMS using non-isotopic normalization in a collaboration with the group of Gabriele Wallner at the University of Vienna. In this project, the goal was to measure the pure global fallout $^{237}\text{Np}/^{239}\text{Np}$ signal in air filters collected in Vienna in the 1960s. Extensive tests and validation experiments, including AMS measurements that fell into the scope of this thesis were required to optimize the sample preparation and normalization procedures and the role of external $^{237}\text{Np}/^{242}\text{Pu}$ standards.

2.6. Contribution of the individual manuscripts to this PhD thesis

The work presented in this cumulative thesis has been published in the form of four separate manuscripts that have been published (Chapter 4), accepted for publication (chapter 7) or submitted for publication (Chapters 5 and 6) in four different peer-reviewed scientific journals. In the following sections, the context and contribution of each of the four manuscripts for addressing the research questions laid out in the previous section are described.

2.6.1. Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu and Am in accelerator mass spectrometry measurements at VERA

At the beginning of this work, actinide AMS measurements that could determine the $^{236}\text{X}/^{237}\text{Np}$ ratios and monitor other contaminants such as ^{239}Pu from the decay of ^{239}Np or ^{233}U formed by neutron capture on the ^{232}Th foils was possible, but there were no capabilities to distinguish the isobaric composition of ^{236}X .

The first method capable of distinguishing isobars in this high mass (low $\Delta Z/Z$) range in AMS which was developed within the scope of this thesis is Anion Formation Isobar Analysis (AFIA). This measurement technique is based on anion formation probabilities

for various fluoride and oxyfluoride molecular anions with the aim of identifying suitable anion systems for isobar separation with ILIAMS. The rationale for this initial investigation was that the anion formation rate of an anion system in a Cs-sputter ion source should generally be closely related to the binding energy of the additional electron and therefore stability against photo-detachment. In order to separate the isobar A from the isotope of interest B with ILIAMS, finding an anion system where AX^- forms much less efficiently than BX^- would be a promising starting point.

In these investigations, the formation rates of AnF_4^- and AnF_5^- were found to be very different for U, Np, Pu or Am, which was also reported by a parallel investigation on a different ion source [Zhao et al. 2022]. The key to developing this observation into an isobar analysis method was identifying the AnF_4^-/AnF_5^- ratio as an elemental fingerprint for these four actinides, given a suitable calibration of the expected values under the specific ion source conditions of a measurement. The article “Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu and Am in accelerator mass spectrometry measurements at VERA” documented in Chapter 4 details the development and first application of this technique. It was submitted on 2022-05-06, accepted for publication 2022-07-18 and published on 2022-08-23 in Nuclear Inst. and Methods in Physics Research, B [Wiederin et al. 2022]. The condensed data is available via the PHAIDRA repository of the University of Vienna [Wiederin et al. 2025]

Besides the initial analysis of prospective Np-spike materials published in [Wiederin et al. 2022], this method has also been used to investigate and confirm ^{236}U interference as the reason behind an incorrect ^{236}Np normalization of ^{237}Np data for a reference material with extremely high concentrations of anthropogenic actinides (IAEA-381). The results of this investigation are presented in the publication in Chapter 6.

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2.6.2. Isobar separation of actinides in mass spectrometry by the combination of laser photodetachment with ion-gas interactions

Whereas the AFIA method presented in the previous publication represents the first isobar analysis technique suitable for actinides in AMS, it has certain limitations. The sensitivity of the method is limited by a combination of the dynamic range and the uncertainties of the $\text{AnF}_4^-/\text{AnF}_5^-$ ratios. Unfavorable anions such as UF_4^- or AmF_5^- , in combination with restrictions on the total duration of the measurement (to minimize the effect of changing conditions as the samples are being sputtered) and the trace concentrations of the samples to be analyzed have resulted in high uncertainties for the isobaric composition of the Np-spike samples. Consequently, the method can be used primarily as a qualitative tool that would detect significant isobaric contaminations on, e.g., mass 236, whereas reliable quantification of small isobaric contaminations has not been possible. Furthermore, the method has a serious weakness for the analysis of ^{236}X that could not be overcome by more measurements or larger samples: Because $\text{UF}_4^-/\text{UF}_5^-$ is lower than $\text{NpF}_4^-/\text{NpF}_5^-$, and $\text{PuF}_4^-/\text{PuF}_5^-$ is higher, a specific ratio of U:Pu in the sample would mimic the expected $\text{NpF}_4^-/\text{NpF}_5^-$ ratio. While it is unlikely that a sample is made up of just the right combination of ^{236}U and ^{236}Pu , the method in itself is not sufficient for characterizing the isobaric composition of ^{236}X , and its results must be interpreted with caution in any situation where two isobars together could produce the expected ratio for the isotope of interest.

So while the AFIA results on prospective ^{236}Np -spike materials produced via the $^{232}\text{Th}(^7\text{Li},3\text{n})^{236g}\text{Np}$ reaction were compatible with the successful separation of ^{236}Np , an alternative isobar separation or analysis method was still required for a reliable ^{236}Np -spike characterization. The minimum requirement for this second characterization method was ruling out the specific U+Pu combination that would produce a false Np ratio with AFIA. Furthermore, AFIA can only be used to identify isobaric interference but is incapable of meaningful isobar suppression that would allow for the measurement of a rare radionuclide (e.g., ^{241}Pu) despite the presence of significant quantities of an isobar (^{241}Am) in a sample.

With the aim of overcoming the limitations of AFIA, the potential of ILIAMS for actinide isobar separation was explored. The article documented in Chapter 5 details the development of isobar separation schemes for $^{236}\text{U}/^{236}\text{Np}$, $^{236}\text{Np}/^{236}\text{Pu}$, $^{238}\text{U}/^{238}\text{Pu}$, $^{241}\text{Pu}/^{241}\text{Am}$ and $^{241}\text{Am}/^{241}\text{Pu}$ (notation: suppressed isobar/measured radionuclide) using laser-photodetachment or gas reactions inside the ILIAMS ion cooler. These schemes represent the first isobar separation capability ever achieved in AMS for this high mass range. Based on the $^{236}\text{U}/^{236}\text{Np}$ and $^{236}\text{Np}/^{236}\text{Pu}$ separation schemes, an unambiguous characterization of the isobaric composition of a prototype ^{236}Np -spike could be completed, while for the other separation schemes the potential for applications based on the achieved separation was explored.

The manuscript “Isobar separation of actinides in mass spectrometry by the combina-

tion of laser photodetachment with ion-gas interactions” documented in Chapter 5 was submitted to the journal JPhysG (IOP Publishing) on 2026-01-11, and resubmitted after moderate revisions on 2026-02-22 and minor revisions on 2026-04-02 with recommendation from both reviewers to publish. The version documented here includes all revisions. Data used in this publication is available via the PHAIDRA repository [Wiederin n.d.].

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2.6.3. Characterization and first application of a new ²³⁶Np spike for (A)MS measurements of ²³⁷Np

With the methodology for isobar analysis developed, and first materials characterized in this respect, the logical next step was to complete the characterization of prospective ²³⁶Np prototype spikes in the sense detailed in Section 2.5. After the isobar analysis had been completed in Chapter 5, this mainly meant measuring the ²³⁶Np concentration and the ²³⁶Np/²³⁷Np ratio, and combining all characterization results. A ²³⁷Np isotope addition approach using multiple aliquots of the spike material was used to complete the characterization on the VERA AMS facility. As earlier samples had been almost or completely consumed in the preliminary characterization measurements, both an increased production and a more efficient characterization were required. A multiple irradiation scheme was implemented for two ²³²Th foils to increase the total amount of produced ²³⁶Np, which were then designated as prototype spikes I and II to be analyzed, validated and used on first environmental samples. The manuscript documented in Chapter 6 details the results of these efforts, and represents the completion of the research questions related to the isotopic spike developed as laid out in Section 2.5. The results demonstrated that using ²³⁶Np for the normalization of ²³⁷Np is more robust and reliable than ²⁴²Pu, and produced valuable data on Np behavior in peat bogs and ²³⁷Np

concentrations near Fukushima during a release of treated water from the Fukushima Daiichi Nuclear Power Plant in 2024.

The manuscript was submitted to the journal *Talanta* (Elsevier) on 2026-03-13 [Wiederin et al. 2026a] and is undergoing a first round of revisions at the time of the submission of this thesis. The manuscript is available in the form of a preprint [Wiederin et al. 2026a].

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Andreas Wiederin: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Hiromitsu Haba:** Methodology, Resources, Writing – review & editing. **Martin Martschini:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Peter Steier:** Conceptualization, Methodology, Resources, Software, Writing – review & editing. **Aya Sakaguchi:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing – review & editing. **Akihiko Yokoyama:** Conceptualization, Methodology, Resources, Writing – review & editing. **Karin Hain:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

2.6.4. Developments of analytical techniques for the determination of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios on air filters from Vienna, Austria

This publication represents a parallel and complementary work to the other three publications. As the success of neither the ^{236}Np production nor the isobar separation work was assured, I also worked to support the application of the non-isotopic ^{242}Pu normalization of ^{237}Np concentrations. A collaboration with the group of Gabriele Wallner (University of Vienna) provided an opportunity to apply this normalization method to a new sample matrix. The samples analyzed in this study were collected during the peak phase of atmospheric nuclear weapons testing in large-volume air filters in Vienna and were expected to carry the undiluted global fallout $^{237}\text{Np}/^{239}\text{Pu}$ signature. Whereas earlier investigations of this global fallout signature have relied on soil samples, neither migration after deposition nor any influence from other source terms is possible for these unique samples. Understanding the $^{237}\text{Np}/^{239}\text{Pu}$ ratio provides a key baseline for interpreting environmental Np data, either with respect to post depositional migration or influence from other source terms. The method development focused on the minimization and correction of elemental fractionation between Np and Pu, both for the correct quantification of Np concentrations, and the measurement of the $^{237}\text{Np}/^{239}\text{Pu}$ ratio of the material captured by the filters. Most of the experimental work was undertaken at a time, when the ^{236}Np -spike material described in the previous manuscripts was not yet available. As laid out in Chapter 1, AMS measurements used to test and adapt the sample preparation and normalization procedures and the corresponding data evaluation were done within the scope of this thesis.

The manuscript was submitted to “Journal of Environmental Radioactivity” (Elsevier) on 2026-01-15 and was accepted for publication on 2026-03-26. The manuscript is available in the form of a preprint [Wallner et al. 2026].

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3. Instrumentation and Methods

Each of the four manuscripts documented in chapters 4, 5, 6, and 7 has a dedicated “methods” or “experimental” section relevant for the experimental work carried out for the respective study which, together with the referenced literature was intended to be sufficient for the respective publication. However, the article format demands minimalism when it comes to introducing relevant but already published techniques.

The following chapter gives a more comprehensive presentation of the applied methodology to supplement the individual experiments. The spike production and chemical separation, sample preparation at VERA for the various experiments documented in the manuscripts are explained, and a short introduction into the instrumentation of the actinide beamline of VERA and the ILIAMS system are given, followed by brief remarks on the data evaluation.

3.1. ^{236}Np Spike production 6.4.2

The $^{232}\text{Th}(^7\text{Li},3\text{n})^{236}\text{Np}$ reaction was proposed as an alternative approach to the production paths for ^{236g}Np described in Section 2.4, primarily with the aim of improving the $^{237}\text{Np}/^{236}\text{Np}$ ratios [Nakajima et al. 2026]. This type of reactions had been studied in the more general form $^{232}\text{Th}(^7\text{Li},x\text{n } y\text{p})^{239-x}\text{An}$, with An standing for Np, U or Pa and $x, y \in \{1, 2, 5, 6, 7\}$ by [Zhao et al. 1999]. The production of ^{236g}Np was not investigated in this earlier study, but with the production of both lighter and heavier isotopes of Np documented, it was reasonable to assume the formation of ^{236g}Np as well.

The production of a ^{236g}Np -spike material with this type of reaction should be configured to minimize the co-production of ^{236m}Np and ^{237}Np in particular. Initial simulations suggested favorable isomeric $^{236g}\text{Np}/^{236m}\text{Np}$ ratios of up to ~ 5 [Hayakawa et al. 2019] as well as the maximum of the ^{236g}Np cross-section [Nakajima et al. 2026] in the 35 -45 MeV range. However, the excitation functions were based on model calculations, and their experimental determination was a major focus of the overall investigation. These calculations were based on the ALICE code [Blann 1984].

For this purpose, a series of irradiation experiments was performed at the RIKEN Nishina Center for Accelerator-Based Science. The AVF (Azimuthally Varying Field) cyclotron (K=70 MeV) was primarily built as an injector for the larger RRC (RIKEN Ring Cyclotron, K=540 MeV) but can also be used to provide ion beams for the irradiation of materials at an offline beamline. The involved instrumentation has been described

in previous publications such as [Suda et al. 2016] or [Kambara et al. 2018]. For this accelerator, ${}^7\text{Li}^{2+}$ or ${}^7\text{Li}^{3+}$ beams in the required energy range of 30 - 45 MeV, and ion currents of up to 3 particle μA have been reported [Suda et al. 2016]. To investigate the excitation, stacks of typically 4 thin ${}^{232}\text{Th}$ targets were irradiated in each experiment. The energy loss from one foil to the next resulted in effective ion energies in the range from 24 MeV to 42 MeV, which enabled the collection of multiple data points with different energy ranges in each irradiation. Typically, no spacers were placed between the Th foils, but in some experiments high-purity aluminum foils were added to further adjust the energies. The ${}^{232}\text{Th}$ targets were either produced via electrodeposition [Teranishi et al. 2023] or commercial foils purchased from the Company Goodfellow Cambridge Ltd (12.5 μm thickness, >99% purity) [Nakajima et al. 2026].

For the experiments presented here, the foil stacks have been irradiated with ${}^7\text{Li}^{2+}$ beams at an initial energy of 42 MeV for 15 - 18 h. A major difficulty with the foil stack approach was managing the thermal load deposited onto the thin foils. To avoid fusing the foils, the irradiations took place in a He-cooled chamber sealed off from the beamline with a Be window. An actively cooled sample holder was used and the ion current was limited to 0.7 - 1 particle μA with the aim of delivering an equal dose over the available surface area [Nakajima et al. 2026]. Fig. 3.1.1 A) shows the irradiation setup, while the assembly of the irradiation targets is shown in 3.1.1 B).

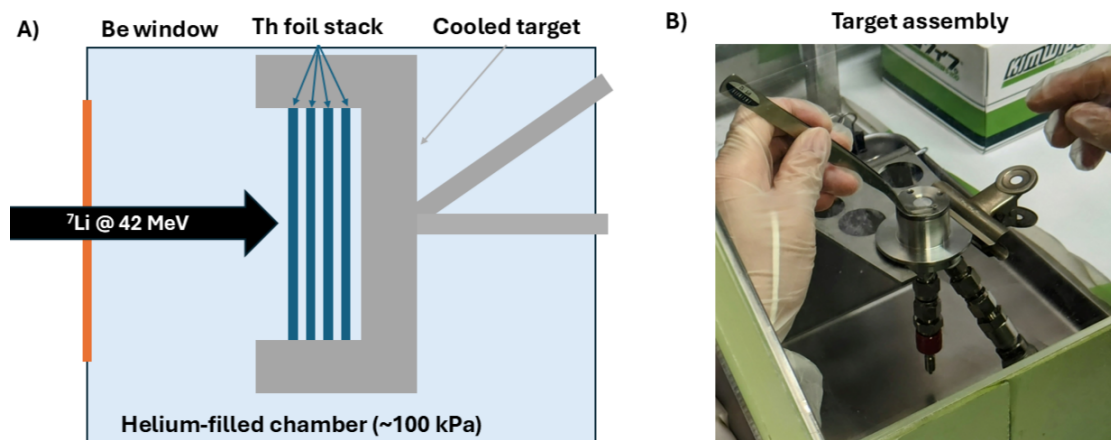


Figure 3.1.1.: The incoming ion beam enters the He cooled chamber via a Be window, and hits the Th foil stack (A). The foils (center) were clamped (outer metal ring) onto an actively cooled target holder with no spacers, with optional Al foils for adjusting the ion energy (B).

3.2. Chemical separation of the ${}^{236}\text{Np}$ spike material

The development of the chemical separation of Np from the irradiated material and also its application to the irradiated foils was not carried out within the scope of this thesis but the procedure is summarized here for completeness. The initial steps have been described elsewhere for measurements of ${}^{236m}\text{Np}$ [Nakajima et al. 2026]. In short, the irradiated foils were dissolved, prepared for ion exchange chromatography via suitably

adjusting the oxidation states and loaded onto TEVA resin (Eichrom technologies) from which various fractions could be removed selectively, before eluting the Np fraction with 16 ml of 0.1 M HCl. In a second separation step TK400 resin was used to separate Pa which interferes with the γ -emission lines from ^{236m}Np . The Np fraction was eluted with 9 M HCl and measured via γ -spectrometry in liquid form.

For AMS, the material must be prepared in solid form, typically an iron oxide matrix, which can be mixed with PbF_2 for specific applications. Furthermore, the short-lived ^{236m}Np isomer measured via γ -spectrometry in the Nakajima et al., 2026 study is the very source for the isobaric interference on mass 236 via its decay into ^{236}Pu and ^{236}U . These two interferences therefore still must be removed from any ^{236}Np -spike material. The remaining steps for the preparation of the ^{236g}Np prototype spike materials from the Np fraction after the TK400 resin are described in the supplementary information of the manuscript “Characterization and first application of a new ^{236}Np -spike for (A)MS measurements of ^{237}Np ” (Chapter 6) documented in Appendix 10.3. The major steps are summarized briefly in the following: Since the primary aim of the final separation steps is the removal of the ingrown isobars ^{236}U and ^{236}Pu , as a first step all ^{236m}Np ($t_{1/2} = 22.5 \pm 0.4$ h) had to be allowed to decay before the solution was dried and re-dissolved in 3 M HNO_3 . Then 125 μg ferric iron and 279 mg ascorbic acid were used to adjust the oxidation states for loading the solution onto an UTEVA (Eichrom technologies) column. Pu was removed by passing 4 ml ascorbic acid in 3 M HNO_3 through the column, before eluting Np with 0.2 M oxalic acid in 2.5 M HNO_3 . This Np fraction then was cleaned in several steps to remove oxalates and organic residue from the resin. Then, either suitable solutions for ICP-MS or solid AMS samples were produced. For the latter, two different options were available, depending on the desired final matrix mass. For regular AMS measurements, 2 mg of Fe(III) and a sufficient quantity of NH_3 to raise a dilute HNO_3 sample solution to pH 8.5 were added to co-precipitate Np with iron hydroxide. The precipitate was repeatedly washed, dried and calcined at 800 °C to produce the final iron oxide matrix. For ILIAMS (Chapter 5) and AFIA (Chapters 4 and 6), the iron oxide matrix was mixed with PbF_2 in a 1:9 mass ratio ($\text{Fe}_2\text{O}_3:\text{PbF}_2$). To avoid excessive dilution of Np in this matrix and, the amount of Fe used had to be reduced to 300 μg which led to inconsistent co-precipitation yields. A solution to this problem has been developed for uranium measurements [Kern et al. 2022] and successfully applied to U, Np, Pu and Am for the AFIA measurements [Wiederin et al. 2022] (Chapter 4): after adding the small quantity of Fe, the sample solution is slowly evaporated in PTFE/PFA tubes at 80 °C. The resulting pellet was dried, calcined and mixed with PbF_2 and pressed into an AMS sample holder.

3.3. The AMS facility VERA

The Vienna Environmental Research Accelerator (VERA) is an Accelerator Mass Spectrometry facility in Vienna that is optimized for versatility and expanding the reach of

the AMS method to new applications. [Martin Martschini et al. 2022; Priller et al. 1997; Steier et al. 2002, 2004, 2019]. The full layout is shown in Fig. 3.3.1. All AMS measurements presented here that did not involve the Ion-Laser InterAction Mass Spectrometry (ILIAMS) instrumentation were performed on the main AMS beamline of VERA spanning from Source 1 to the heavy isotope detector system. All ILIAMS experiments were performed on Source 2 and the associated extension of the injector beamline. After the removal of isobaric interference using ILIAMS, the remaining beam is merged into the low-energy mass spectrometer of the main AMS beamline. Consequently, all components after the beamline junction (see Figure 3.3.1) were identical. Here, the instrumentation of the actinide beamline for regular AMS and Anion Formation Isobar Analysis (AFIA) measurements (see Chapter 4) is introduced, followed by an introduction to the ILIAMS setup in Section 3.4. The actinide beamline has been previously described and characterized by [Steier et al. 2019].

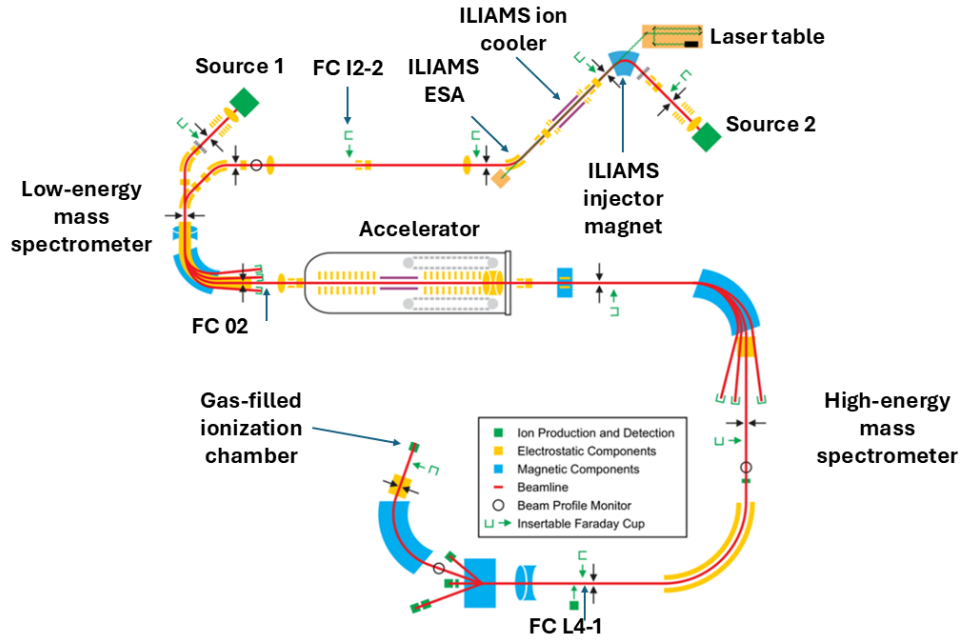


Figure 3.3.1.: A simplified schematic of the VERA facility. The actinide beamline used for all experiments without ILIAMS spans from Source 1 to the Gas-filled ionization chamber, whereas the ILIAMS system has a dedicated low-energy beamline (Source 2) and is merged into the actinide beamline in the Low-energy mass spectrometer.

Negative ions for AMS measurements are most commonly produced in a Source of Negative Ions by Cesium Sputtering (SNICS) [Middleton 1983], also called Middleton-type sputter ion source. This type of ion source is also used for both beamlines at VERA. The basic principle of this type of ion source is illustrated in Fig. 3.3.2. Samples can be mounted on 40-position sample wheels, so that one sample at a time is exposed. Cs vapors from a heated reservoir are thermally ionized on the hot metal surface of the ionizer and accelerated towards the sample by a voltage of several kV. The Cs cations impact the target material, and neutral atoms, clusters, and molecules are sputtered,

and a fraction of these neutrals binds an additional electron to form negative ions. As Cs is deposited on the sample, the work function is lowered, which leads to an exponential increase in formation probability of negative ions in this process [Gnaser 1996]. The best way of operating these ion sources and some of the physical processes involved are still debated and active fields of research, e.g., [Andersson et al. 2013; Lobanov et al. 2023; Martschini et al. 2022; Vogel 2015, 2019].

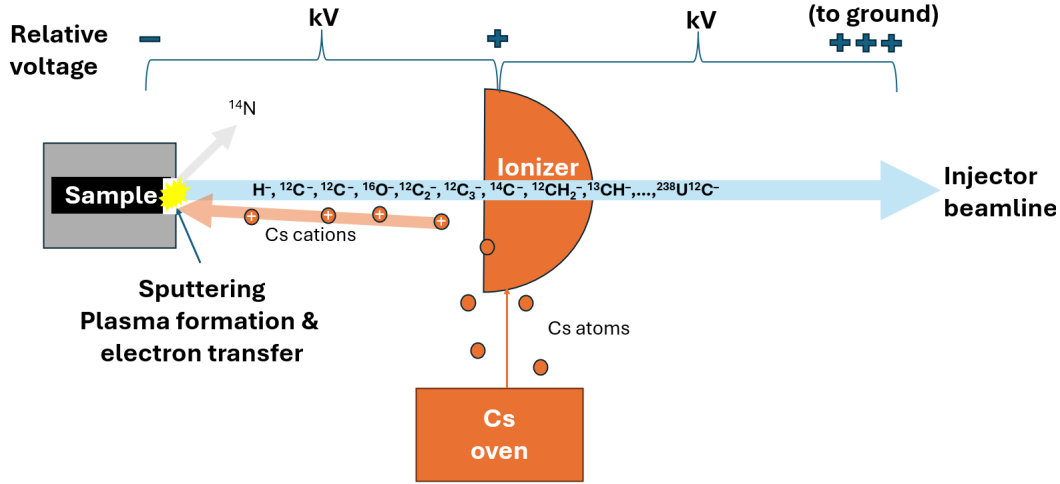


Figure 3.3.2.: Thermally ionized Cs^+ cations impact the sample and transfer electrons to atoms, molecules or clusters sputtered in this process, which are then accelerated in multiple stages towards the injector beamline. Anion beams on the order of tens of μA are formed, containing a wide range of anion species, illustrated here for a carbon target [Wiederin 2026a].

The formed anion beam passes two filters, the Electrostatic Analyzer (ESA) and the Injection Magnet. The ESA acts as an energy over charge filter, with a radius of 300 mm and a nominal deflection angle of 45° . The injection magnet is a momentum over charge filter with a radius of 457.2 mm and achieves a mass resolution of $M/\Delta M (FWHM) \sim 500$, assuming a 2 mm slit aperture [Steier et al. 2019]. These two components form the low-energy mass spectrometer of VERA and are used to select specific masses - atomic or molecular anions - for injection into the accelerator.

VERA is built around a Pelletron type tandem accelerator from the National Electrostatic Corporation (NEC) (model 9SDH-2). Chains made of metal pellets with insulating links are used to transport charges to the terminal to produce a terminal voltage of up to +3 MV. Incoming anions are accelerated towards this positive high voltage. Near the terminal, a differentially pumped stripper canal enables gas stripping, a process in which the incoming $\sim\text{MeV}$ ions interact with a thin gas (typically He for actinides). These interactions can remove electrons (typically, but not necessarily one per interaction) from the incoming particles. Subsequently, positively charged ions can also pick up electrons and the resulting charge state distributions can be calculated via systems of analytically solvable differential equations [Suter et al. 2018]. Overall, the distribution depends on the projectile velocity and the nuclear charge z of both medium and

projectiles [Schiwietz et al. 2001]. The stripper medium thickness only influences the distributions up to the point where an equilibrium between the removal and capture of electrons is reached. While the distribution is not affected, further increases in thickness (or gas pressure) would come at the cost of higher ion optical losses. For actinides, the use of He and the selection of a charge state of 3+ has been shown to be advantageous at lower energies (1.2 MV in Vockenhuber et.al., 2011, 1.65 MV at VERA) in terms of a higher charge state yield and lower collisional losses [Vockenhuber et al. 2011]. These effects resulted in high overall transmissions, and the He-stripping approach has also been implemented at VERA [Winkler et al. 2015]. However, it has been shown, that triply charged actinide-hydrides, particularly UH^{3+} and ThH^{3+} cations, can survive for the time required to reach the detector in an AMS measurement [Lachner et al. 2012]. Increasing the stripper gas pressure by approximately a factor of 3 above the optimum for the transmission, efficiently removes the hydrides. However, this solution comes at the cost of increased residual gas molecules in the beamline, which in turn can produce a background for the detection of trace radionuclides. Ion-gas interactions can result in irregular paths or charge exchange reactions with the ion beam, enabling a small number wrong masses to pass e.g., the high-energy ESA [Steier et al. 2019].

Whereas the accelerator is capable of generating a terminal voltage of 3 MV, for He stripping and the optimal yield in the 3+ state the terminal voltage must be set close to 1.65 MV, to enable the high-energy analyzing magnets to deflect the nominal beam by 90°. The design of the accelerator allows for shorting 3/9 beamline tubes to optimize the ion optical configuration for this lower terminal voltage, so that for actinides transmissions of up to 20 % ($^{238}\text{UO}^-$ to $^{238}\text{U}^{3+}$) can be achieved [Steier et al. 2019].

The high-energy mass spectrometer of VERA consists of two 90° analyzing magnets with a radius of 1.270 m and a magnetic rigidity of 176 MeV amu separated by a 90° electrostatic analyzer with an electric rigidity $E/q = 4.4$ MeV and a radius of 2.000 m. The second analyzing magnet is mainly used for the analysis of actinides, where due to the small relative mass differences a clean separation of ^{232}Th , ^{235}U or ^{238}U from neighboring trace radionuclides can otherwise be challenging. The second analyzing magnet efficiently suppresses background from other masses that have interacted with residual gas molecules and passed the first magnet and electrostatic analyzer on irregular paths or with altered energies as discussed in the previous paragraph [Steier et al. 2019]. A switcher magnet is used to direct the ion beams to the last part of the actinide beamline which consists of the second analyzing magnet, a magnetic quadrupole and the detector. Whereas macroscopic ion currents are typically measured in the Faraday cup FC L4-1 between the high-energy ESA and the switcher magnet, for trace ions a 30 mm long Bragg-type gas-filled (isobutane) ionization chamber is used. In addition to the registration of counting events, the detector also provides information on the pulse height and width of the signal generated for each event, which can be used to discard events from lower charge states that reach the detector as well as pile-up or electronic noise. For actinides measured in the 3+ state, this is particularly relevant for ^{237}Np ,

^{240}Pu and ^{243}Am whose masses are all divisible by 3.

Whereas some experiments involving the ILIAMS setup were controlled manually, both AFIA and oxide measurements using Source 1 (see Fig. 3.3.1) utilized the high degree of automation possible at VERA once a measurement is correctly set up. For the measurements presented here $^{238}\text{UX}^-$ beams ($X \in \{\text{C}, \text{O}, \text{F}_2\text{O}_2, \text{F}_4, \text{F}_5\}$) on the low-energy side and $^{238}\text{U}^{3+}$ on the high-energy side, were used to tune the beam from the respective ion source to the detector. The initial setups were then extensively optimized both manually and using a sophisticated multi-dimensional optimization algorithm to maximize ion-optical transmission [Steier et al. 2002; Steier et al. 2000]. From these optimized configurations, the machine setups for trace ion measurements can be calculated, although the accuracy and reliability of scaled setups decrease with increasing mass difference. As a consequence, complex measurements spanning large mass ranges (e.g., the AFIA measurements with masses between 306 u to 338 u on the low-energy side) require the separate optimization of multiple pilot beams. Each setup, defined by a low-energy mass and a high-energy mass, is a configuration of all machine parameters for the measurement of a specific combination of injected molecular anion and high-energy 3+ cation. To minimize the time required to switch between setups, the low-energy injector magnet chamber can be put on a variable potential of up to 12 kV, so that the injected mass can be adjusted without much slower changes to the magnetic field. For the high-energy side, the terminal voltage of the accelerator and other electrostatic components can be adjusted to switch between masses, while the magnetic fields are kept unchanged.

Programs allow the automated configuration of VERA for various masses and subsequent data acquisition. For each sample, a sequence defines which setups are to be used for which duration so that one isotope of interest after the other can be measured automatically. Samples are mounted in 40-position wheels and can be switched automatically, so that up to 40 samples, tuning targets or standards can be measured one after the other, which can be repeated until either the desired precision and accuracy are reached, or the samples have been consumed. The output files then contain all current and count rate measurements that were performed for each sample, with an automated evaluation of the regions of interest for the peak height to peak width ratio for the ionization chamber. These can then be used for further evaluation as described in the individual manuscripts.

3.4. ILIAMS instrumentation

The ILIAMS method has been described in detail in several publications [Forstner et al. 2015; Martin Martschini et al. 2022; Martschini et al. 2019b, 2017], and the introduction to this method presented here is based on these previous works. The Isobar Separator for Anions (ISA) is a similar method focused on gas reactions developed at the André. E. Lalonde National Facility for Accelerator Mass Spectrometry [Alary et al. 2022; Alary et al. 2015; Eliades et al. 2010; Flannigan 2024; Flannigan et al. 2022, 2025] that has pioneered the low-energy isobar separation in AMS. The following section aims to provide

a motivation and basic introduction to this powerful new technique. The fundamental idea of Ion-Laser InterAction Mass Spectrometry is to add a filter that depends on the electronic configuration of (molecular) anions in the beam to the mass filter of the AMS beamline to overcome interference from atomic isobars. Various processes can potentially be used to selectively remove ion species from the beam, the most relevant are photo-detachment of the (typically weakly bound) additional electron in an anion, photo-detachment of individual atoms from a molecular anion, detachment of either the electron or an atom from a (molecular) anion through collisions of the anions with gas molecules or chemical anion-gas reactions that either add, remove or replace atoms to, from or in an anion species. As long as the interaction results in a change of either charge state (removal of an electron) or mass (chemical change via removal, exchange or addition of an atom) of the anion in question, it will subsequently be removed from the ion beam. In order to be useful for isobar separation, the respective process has to be selective, so that the unwanted isobar is removed from the ion beam, while the isotope of interest remains (at least mostly) unaffected. Fortunately, aside from the noble gases, most elements can be extracted in various (molecular) anion beams with reasonable efficiency [Middleton 1989] so that there are often several options, which increases the chances of finding an anion system that fulfills the requirements for selective isobar separation.

If a process has been found to be suitable in principle to deal with a specific isobaric interference, the efficiency of the separation must be increased to the point where the isobaric interference while measuring the isotope of interest becomes negligible. Laser-photodetachment, the removal of an electron from an anion via photon interaction, can only occur if the energy of the photon exceeds the binding energy of the electron. Above the threshold, the number of surviving ions at time t , $N(t)$, is determined by the photon-anion reaction cross-sections σ (typically on the order of $\sim 10^{-17} \text{ cm}^2$) and the photon flux Φ (up to $10^{21} \text{ cm}^{-2} \text{ s}^{-1}$ for cw lasers with $\sim \text{W}$ of power output) [Martschini et al. 2017]:

$$N(t) = N_0 \cdot e^{-\sigma \Phi t}. \quad (3.4.1)$$

Therefore, $N(t)$ can be decreased via finding the optimal photon energy to maximize σ , maximizing the effective photon flux Φ (high-powered lasers or optimized ion-laser overlap), and increasing the interaction time t . Several lasers are available at VERA, and those relevant for the actinide separation experiments have been described in the “Materials and Methods” section of Chapter 5.

The velocities of ion species even on the low-energy side of an AMS facility vary depending on the applied accelerating potentials and their mass, so that ^{12}C pre-accelerated to 70 keV travels at $\sim 1000 \text{ km/s}$ while $^{238}\text{UF}_5^-$, at 24 keV, has a velocity of $\sim 120 \text{ km/s}$. These velocities result in residence times on the order of 1 - 10 μs for a 1 m segment of the beamline. The ILIAMS setup at VERA is equipped with an ion cooler that aims to increase the interaction time by three orders of magnitude. A combination of electrostatic deceleration and gas collisions is used to decelerate the ions to thermal energies,

while a gas-filled radio-frequency quadrupole (RFQ) provides radial confinement. The design of the ion cooler is described in detail in [Martschini et al. 2017], and illustrated in a 3d-model adapted from [Gaggl 2021] in Figure 3.4.1.

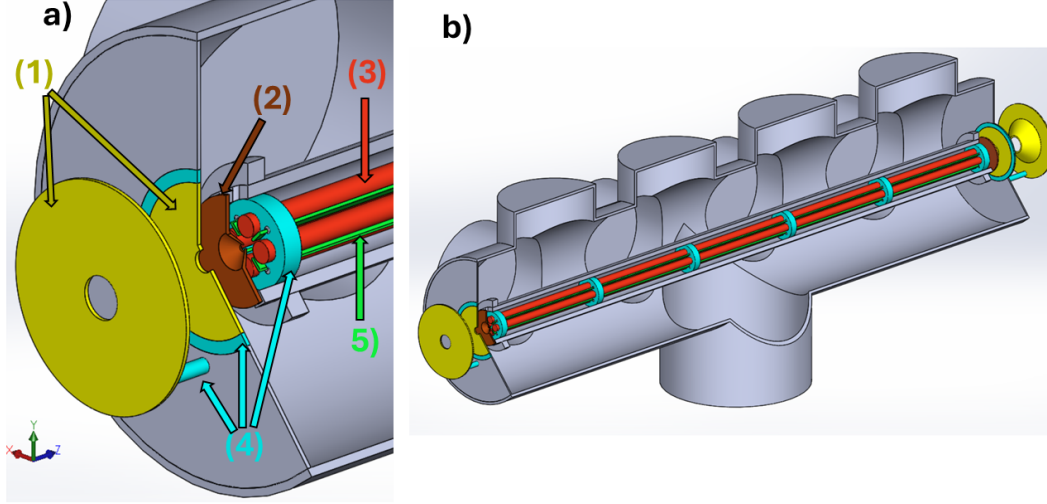


Figure 3.4.1.: 3d-model of the injection side (a) and the entire length (b) of the ILIAMS ion cooler adapted from [Gaggl 2021]. The entire casing is insulated from the beamline and set to a potential for decelerating the incoming ion beam, which is shaped with electrostatic lenses (1) for optimal transmission through the aperture of the ion cooler (2). The RF-electrodes (3) provide the radial confinement, while the guide-electrodes transport ions through the cooler. Both are held in place by six insulators (4) resistant to RF-fields over the full length of 951 mm. The extraction side is mostly identical to a) except for the use of conical lenses instead of the flat aperture lenses shown in a) .

The electrodes of the RFQ have a length of 951 mm with a radius of $r = 5.00$ mm for each rod, and an inscribed radius of $r_0 = 4.35$ mm. Four guiding electrodes (1.5 mm thick plates) provide an electric field to guide the cooled ion beam along the beam axis. A Stanford Research Systems DS345 function generator produces a sine wave signal, which is subsequently amplified in a Electronics & Innovation, Ltd. model 1020 L 200 W RF power amplifier and transferred via a ferrite transformer to two resonant circuits, providing 400 V peak voltage for frequencies of 0.9 - 6.0 MHz. Optimal beam cooling and confinement is possible in a mass range of 14 u - 350 u.

The four RFQ electrodes are set to oscillating voltages with identical amplitudes but opposite signs for neighboring electrodes. A Paul trap is defined by an oscillating electric potential, optionally combined with a static potential, and the RFQ ion cooler can be seen as a linear Paul trap, assuming a single ion regime and no buffer gas. As derived in detail in [Major et al. 2005] on which the following explanations are based, such an idealized Paul trap can be described by a set of homogeneous Mathieu equations of the form:

$$\frac{d^2 u_j}{dt^2} + (a_j - 2q_j \cdot \cos(2\tau))u_j = 0 \quad (3.4.2)$$

with the parameters a_j , q_j , and the variable $\tau = \frac{\Omega t}{2}$ with the circular frequency Ω and the time t , and $j \in \{x, y, z\}$. The Mathieu parameters a_j and q_j differ between the radial directions x , y , and the longitudinal (along the beam axis) direction z . For an idealized model of a linear Paul trap with no constant DC voltage component, the parameters a_j can be set to 0 and the motion of a charged particle inside the trap is governed by

$$q_x = q_y = \frac{2QV_{RF}}{Mr_0^2\Omega^2} \text{ and } q_z = -\frac{4QV_{RF}}{Mr_0^2\Omega^2} \quad (3.4.3)$$

with the mass M and charge Q of the ion, the voltage applied to the RFQ electrodes V_{RF} and the inscribed radius r_0 of the electrodes. Within the parameter space of the q_j , there are areas of stability, where the correct combinations of ion mass, voltage and frequency result in stable, oscillating trajectories. However, instead of a single ion interacting with an ideal Paul trap in a vacuum, ion currents ranging from a few pA to hundreds of nA ($\sim 10^6 - 10^{12}$ ions per second) are injected into the ILIAMS ion cooler, which is gas-filled. The introduction of a thin buffer gas provides beam cooling, but also random scattering. Compared to positive ions, the anions injected into the ILIAMS RFQ are much less stable. To minimize collisional electron detachment, the anions have to be decelerated to tens of eV electrostatically before interacting with the buffer gas, which should consist of very light atoms or molecules. Space charge effects and ion-ion or ion-gas interactions inside the cooler are topics of ongoing research at VERA. Diagnostic capabilities at ILIAMS are very limited, and recent work has focused on simulations which show that these effects are significant and nontrivial [Baumgartner 2024]. Simplifications and model assumptions are required due to computational costs in a particle range where computing individual particles is much too slow and macroscopic models fail. So while a definitive description of the ion cooler dynamics under realistic conditions is still elusive, the stability regions in the parameter space of the Mathieu parameters q_j are still a good predictor for reasonable settings to confine an ion species. Stable trajectories theoretically exist for $q_z < 0.908$, and the optimal transverse confinement falls into the range of $0.5 < q_z < 0.6$ as verified experimentally for the ion cooler of ILIAMS [Martschini et al. 2017]. Higher q values amplify the RF-induced micro motions, so that the amplitude of the oscillations rises [Nieminen et al. 2001] which, in a system like ILIAMS, eventually leads to ion losses. A more technical discussion of the cooler parameters and ion trajectories is beyond the scope of this thesis. However, within reasonable parameters, the confinement can be interpreted as a pseudo potential of a certain depth, which sets a limit to the number of charges that can be stored under any given configuration [Martschini et al. 2017]. The simulations identified mechanisms how higher currents lead to higher amplitudes of the trajectories through ion-ion interactions [Baumgartner 2024] and experimental data showed that both transmissions and residence times are reduced for higher currents [Martschini et al. 2017]. A practical consequence of this behavior is

that the achievable suppression factors for two different ion species of the same element, but injected at very different intensities (e.g., $^{238}\text{UX}^-$ and $^{236}\text{UX}^-$), can differ significantly. Both the primary ion beam and any other ion species injected alongside the anion of interest are relevant for this effect.

Normally, the RFQ is filled with a He buffer gas at 0.04-0.06 mbar through an inlet in the center (axial) of the RFQ. Differential pumping with three turbo pumps (before, at and after the RFQ housing) reduces the pressure to $\sim 2 \cdot 10^{-5}$ mbar just outside the RFQ housing, and 10^{-6} - 10^{-7} mbar [Martschini et al. 2017] in the beamline surrounding the ion cooler. By adding reactive gases such as O_2 or H_2 to the buffer gas, the gas filled RFQ can act as a reaction cell to selectively remove isobars from the beam via chemical reactions with the admixed gas molecules. A detailed study on chemical anion - gas reactions on the ISA system, a dedicated AMS reaction cell, has been published by [Eliades et al. 2015]. Heavier gases may cause increased rates of collisional detachment during injection before the ions are sufficiently cooled, and for all chemical reactions, there is a specific probability of back reactions which can limit achievable suppression factors [Martschini et al. 2020]. By contrast, no comparable limit exists for laser photodetachment. Changing gases requires manual mixing in an external flask, and may require extensive pumping to remove residues from the previous gas and can be done on a timescale of ~ 15 -20 minutes.

As described in [Martschini et al. 2019b], after development on a test bench, the ILIAMS system has been attached to the VERA AMS facility in the form of a separate beamline that is merged into the original beamline inside the ESA of the low-energy mass spectrometer. The ILIAMS beamline has a dedicated ion source, a 90° bending magnet with a radius in front of and a 45° ESA after the RFQ ion cooler, as shown in Fig. 3.3.1 (ILIAMS ESA). Neutralized atoms or molecules are removed at this ESA, while changed masses (added, removed or exchanged ligands) are filtered out in the low-energy mass spectrometer of VERA. The ILIAMS method has been successfully applied to several isobar systems as detailed in [Martin Martschini et al. 2022]. The research presented within the scope of this thesis, particularly in Chapter 5 expanded the reach of this novel method to the actinides for the first time.

3.5. Sample preparation at VERA

3.5.1. Tuning, test- and calibration samples

Method development for both ILIAMS and AFIA required a large number of well-defined AMS targets containing the actinides of interest in various concentrations. With no matrix to remove, and no fractions to separate, these samples only required minimal preparation: the required amounts of ^{236}U , ^{237}Np , ^{242}Pu and ^{243}Am were added to dilute HNO_3 . Similar to the approach describe in Section 3.2, $300\text{ }\mu\text{g}$ Fe was then added, and the resulting solution was evaporated. Then the resulting pellet was dried,

calcined and mixed with PbF_2 in a 1:9 (sample: PbF_2) mass ratio. Finally, this material was pressed into an AMS sample holder. Details on the reagents involved are provided in the materials sections of Chapters 4 and 5.

The in-house uranium standard Vienna-KkU is based on uranyl nitrate processed before 1918 in Joachimsthal (now Czech Republic) with a $^{236}\text{U}/^{238}\text{U}$ ratio of $(6.98 \pm 0.32) \cdot 10^{-11}$ [Steier et al. 2008]. This material was available in both pure (“KkU”) and dilute (“KkU-d30”, diluted in iron 1:30) form to provide macroscopic uranium beams for beam tuning. For oxide measurements (i.e., measurements presented in Chapter 6 (with the exception of the AFIA measurement) and Chapter 7 the Vienna-KkU-d30 material was directly pressed into sample holders. For these measurements, a second in-house standard Vienna-US8 produced from the Vienna-KkU via the addition of ^{236}U resulting in a ratio of $^{236}\text{U}/^{238}\text{U}$ ratio of $(1.01 \pm 0.05) \cdot 10^{-8}$ was used for quality control of the ^{236}U measurement and a correction factor to account for differences in the detection efficiencies between the $^{238}\text{U}^{3+}$ current measurements at FC L4-1 and the $^{236}\text{U}^{3+}$ atom counting in the ionization chamber (see Figure 3.3.1). For the AFIA and ILIAMS measurements, the Vienna-KkU, Vienna-KkU-d30 and Vienna-US8 materials were mixed with PbF_2 in a 1:9 (KkU: PbF_2) mass ratio.

For optimizing the ion optics directly into the ionization chamber, $^{238}\text{U}^{3+}$ count rates on the order of 10^4 cps were used. For oxide AMS measurements, these were produced from old carbon samples and for ILIAMS and AFIA from Merck iron powder mixed with PbF_2 (1:9 sample: PbF_2 mixing ratio).

3.5.2. Preparation of environmental samples

For the preparation of environmental samples, a procedure based on the routine protocol for actinide analysis for other actinide samples at VERA in recent years was chosen. The instrumental capabilities of VERA to suppress tailing and other background from abundant neighboring masses, particularly the second high energy analyzing magnet (see Figure 3.3.1), have reduced the demands on chemical separation of e.g. ^{238}U from the Pu/Np fraction. Consequently the main separation step is comparably simple and based on the use of a single anion exchange column. The procedure has been described in previous publications such as [Hain et al. 2022]. The following section briefly introduces the general procedure. The specific reagents, spikes, quantities, and steps used are described in the materials sections of the manuscripts in Chapters 6 and 7.

Fig. 3.5.1 shows a flowchart of the general procedure. Most of the procedure was identical for all samples, only the first preparation steps differed between solid (peat, sediment, air filters) and water samples. The spikes ^{236}Np (if available) and ^{242}Pu were added before any processing and, for water samples were left overnight to equilibrate. The water samples were pre-acidified to minimize adhesion of the actinides to the sample vessels and large samples were partially evaporated to reduce the volume of water and, therefore, the amount of Fe(III) that has to be added in the next step. The salinity

of seawater samples limits the achievable concentration factors, because precipitation of the salt content has to be avoided. Typically a reduction of the water volume by a factor of 2 could be achieved by slow evaporation down to a set mass in a large (5 l) Erlenmeyer flask with a water-cooled tube for the exiting steam on a temperature-controlled, weight-triggered hot plate.

Solid samples were dried (if necessary, e.g., peat), ashed, submerged in concentrated HNO_3 - with added spikes - and placed in a PTFE microwave vessel for digestion. Then the liquid was filtrated, dried and re-dissolved in dilute HNO_3 .

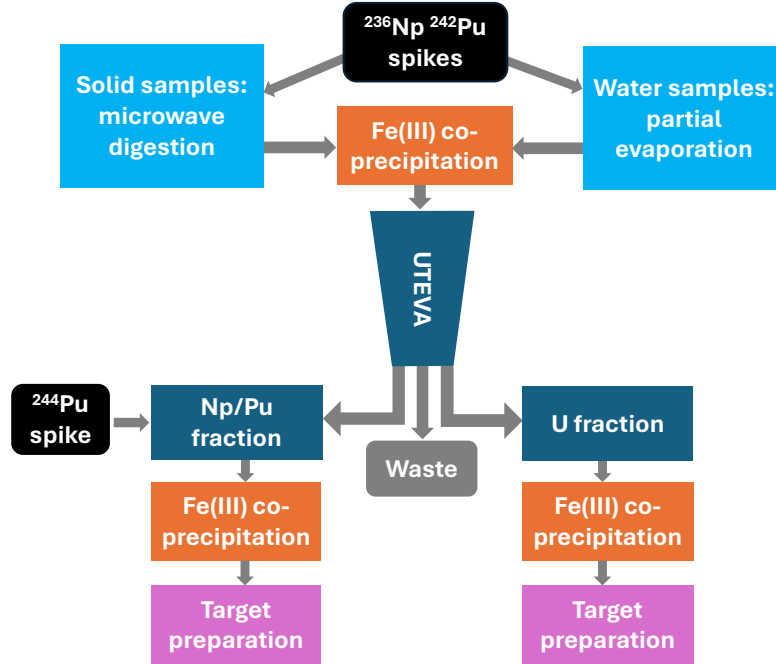


Figure 3.5.1.: Flowchart of the sample preparation and purification of environmental samples. Solid and water samples differ only in the initial steps. For all samples a first Fe(III) co-precipitation is followed by a single UTEVA column that separates the sample into waste, U, and Np/Pu fractions. After decomposing oxalates and organic compounds, the final AMS targets are produced from the precipitate formed in a second Fe(III) co-precipitation. Spikes are added at the beginning (^{236}Np , ^{242}Pu) and before the second Fe(III) co-precipitation.

All remaining steps, beginning with the Fe(III) co-precipitation, followed the same basic protocol for all sample types. After adding a sufficient quantity (typically 15 mg /l) Fe(III), the pH level was slowly raised to 8.5 under stirring by adding NH_3 until the $\text{Fe}(\text{OH})_3$ precipitate formed. After the precipitation, the supernatant was (depending on sample size) removed via decanting and/or a centrifuge. The precipitate was then washed repeatedly with ultrapure (Milli-Q) water adjusted to pH 8.5 with small quantities of NH_3 , before being dissolved in HNO_3 (conc.) and dried. By this point, most of the matrix (water, salt content,...) was removed, and the remaining material could be prepared for extraction chromatography. The procedure presented here uses only

UTEVA resin to separate the sample into three fractions: waste, Np/Pu and U. The UTEVA resin has been introduced in Horwitz et al., 1992 [Horwitz et al. 1995] and use diamyl, amylphosphonate (DAAP) to bind U(IV) and tetravalent actinides in the form of nitrate-complexes, whereas many interfering matrix elements or reagents (e.g., Fe from the previous step) pass through the resin. The various actinides retained on the DAAP extractant can then be eluted selectively, typically providing 2-3 orders of magnitude of separation. For this procedure, the column load solution had to be prepared by dissolving the dried samples 3M HNO₃ - 0.5M Al(NO₃)₃. Phosphates in the sample might complex the actinides in a form that would not be retained on the resin instead of the required nitrate complexes. The addition of aluminum to the column load solution prevents the formation of these actinide-phosphate complexes by preferentially binding the phosphate anions. Then the oxidation states had to be adjusted to Pu(IV) and Np(IV) using sulfamic acid, ascorbic acid and NaNO₂ [Maxwell et al. 2010b]. After preconditioning the UTEVA resin in 3M HNO₃ the column sample solution was passed through the UTEVA resin. Then the Np/Pu fraction could be removed from the UTEVA column using 0.1 M oxalic acid - 2M HNO₃, whereas U was eluted with 0.02M HCl. Oxalates in the Np/Pu fraction had to be decomposed either using a microwave or covered on a hot plate, and for both fractions, organic residue from the resin was removed by drying the samples, re-dissolving them in HNO₃ (conc.) and the addition of a few drops of H₂O₂. This fuming step was repeated three times. As indicated in Figure 4, a second plutonium spike, ²⁴⁴Pu was available and could be added to the Np/Pu fractions at this stage. Therefore, the ²⁴²Pu/²⁴⁴Pu ratio can provide information on chemical yields up to the final co-precipitation. The remaining steps were identical to the preparation of Np-spike samples for oxide measurements described in 3.2, beginning with the second co-precipitation. In short, the samples were co-precipitated with 2 mg Fe(III), washed, dried, calcined and pressed into the AMS sample holders.

3.6. Data evaluation

The oxide measurements in Chapters 6 and 7 are based on previously published procedures for actinide measurements at VERA [Hain et al. 2020; Steier et al. 2019] with the additional steps for the non-isotopic normalization of ²³⁷Np data described in [Hain et al. 2020]. The general approach is laid out in the AMS measurement subsection of Materials and Methods in Chapter 7, while the specifics for the spike characterization, the application of the dual ^{242,244}Pu-spike approach are stated in the Instrumentation and data evaluation section in Chapter 6. data evaluation for the experiments described in Chapters 4 and 5 differed substantially and therefore, are described in detail in the respective manuscripts, to which the reader is referred.

Part II.

Research publications

4. Relative formation probabilities for fluoride and oxyfluoride anions of U,Np, Pu and Am in accelerator mass spectrometry measurements at VERA

4.1. Abstract

Fluoride molecular anions have emerged as a potential alternative to oxides for the analysis of actinides in AMS. Research at the Vienna Environmental Research Accelerator (VERA) has focused on mixing samples prepared in an Fe_2O_3 matrix with PbF_2 for in situ fluoridation during the sputter process. The relative formation probabilities for a range of (oxy-)fluoride molecular anions of uranium, neptunium, plutonium, and americium have been found to be characteristic for each of the actinides investigated. These data can help to identify isobaric interference for the mentioned actinides. A first application is monitoring of the ^{236}U co-production with ^{236}Np during Th irradiation. Extracting these actinides in the form of tetrafluoride anions allows the suppression of U by an order of magnitude relative to Np.

4.2. Introduction

Actinides do not readily form atomic anions in Cs sputter ion sources and have to be extracted in the form of molecular anions for AMS measurements [Middleton 1974]. Over the past years, fluoride anions have emerged as an alternative to the well-established oxide anions for this purpose [Cornett et al. 2015; Kieser et al. 2012; Wang et al. 2013; Zhao et al. 2022, 2013, 1997, 2010]. A recent publication has provided a systematic study of the matrix-assisted production of oxy/fluoride molecular anions of various actinides at the AMS facility of the University of Ottawa [Zhao et al. 2022]. Whereas oxygen has three stable isotopes, fluorine is mono-isotopic. Besides the already reported potential benefits of fluoride extraction such as increased ionization yields in low cesium flux ion sources [Zhao et al. 2022], the possible reduction of hydride background [Zhao et al. 2022], some degree of elemental selectivity [Zhao et al. 2013], fluoride and oxyfluoride molecular anions can also be of use in isobar separation techniques such as Ion Laser InterAction Mass Spectrometry (ILIAMS) [Martschini et al. 2019a] or the Isobar Separator for Anions (ISA) [Eliades et al. 2010].

The efficiency of the formation of a specific anion in the sputtering process is strongly determined by the electron affinity of the corresponding neutral molecule or atom [Middleton 1974] and tends to be element specific also within groups such as the actinides [Zhao et al. 2022]. This electron affinity is in turn related to the detachment energy from the anion, a crucial property for selective photodetachment in systems like ILIAMS. We can assume, that for a given anion lower formation probabilities will correspond to lower anion stabilities and vice versa. Developing such isobar separation methods in the actinide range could open up new possibilities for the study of actinides in the environment, e.g. new potential isotopic spikes for normalization or multi-actinide analysis with simplified chemistry from a single AMS sample.

We will compare results obtained by Zhao and Francisco using a HVE Model SO110-C (High Voltage) ion source [Zhao et al. 2022] with our present results on uranium [Kern et al. 2022], plutonium, and americium using the MC-SNICS (NEC) ion source of VERA to assess the reproducibility of the anion formation for different types of ion sources. The present study presents the first experimental data on these anion formation processes for Np in AMS ion sources.

Releases from nuclear weapons testing and the nuclear industry are thought to make ^{237}Np the second most abundant anthropogenic actinide in the environment [Kelley et al. 1999]. ^{237}Np has a long half life ($t_{1/2} = 2.1 \text{ Ma}$) and exhibits conservative chemical properties under oxidizing conditions in water reservoirs, where it is present predominantly in the form of highly soluble Np(V)O_2^+ [Keeney-Kennicutt et al. 1984]. These characteristics could allow ^{237}Np to become a valuable tool for tracking environmental processes such as water mass transport [Lindahl et al. 2005; López-Lora et al. 2020]. The lack of an isotopic spike for a reliable and matrix independent normalization of Np measurements by mass spectrometric methods is the main obstacle for realizing the full

potential of ^{237}Np as an environmental tracer.

In the course of developing an such an isotopic neptunium spike, ^{236}Np was to be produced at the RIKEN Nishina Center for Accelerator Based Science via the $^{232}\text{Th}(^7\text{Li}, 3\text{n})^{236}\text{Np}$ reaction. Material chemically separated from irradiated Th by the group of the University of Tsukuba had already been measured at VERA in oxide form. This measurement had confirmed the production of nuclides of mass 236 above background and $^{237}\text{Np}/^{236}\text{X}$ ratios down to (0.07620 ± 0.00082) . Besides the desired ^{236}Np , isobaric contamination could occur either from ^{236}U produced via neutron capture on ^{235}U impurities or the decay of the meta-stable state $^{236\text{m}}\text{Np}$ into ^{236}U or ^{236}Pu , so further analysis of the mass 236 fraction was needed.

The following investigation of the formation probabilities for (oxy-)fluoride anions of actinides provided a method for this analysis: If the anion formation ratios (under otherwise identical conditions) are element-specific, and their distribution is known for external standards with known composition, then deviations from this reference distribution for a material could be used to monitor isobaric contaminations.

This method in principle can be easily extended to other isobaric systems of interest in the mass range of actinides, such as $^{241}\text{Pu}/^{241}\text{Am}$, which is an important nuclear clock to determine the time of Pu production due to the rather short half-life of ^{241}Pu ($t_{\frac{1}{2}} = 14.329\text{ y}$). Its analysis by mass spectrometric techniques like AMS currently relies on extensive chemical separation of Pu from its daughter nuclide Am. The formation of molecular anions of americium has been included in the present study as a first step towards the development of a separation of the isobars ^{241}Pu and ^{241}Am using ILIAMS.

4.3. Materials

The ^{236}U spike was produced from 99.973 % pure ^{236}U dissolved in HNO_3 provided by the IAEA Safeguards Analytical Laboratory in Seibersdorf, Austria. An aliquot with a ^{236}U concentration of $4.842 \times 10^9\text{ at/g}$ was used for spiking the calibration samples. The ^{237}Np solution with a nominal concentration of $8.814 \times 10^9\text{ at/g}$ was provided by Radiochemistry Munich at the TU Munich, where it was prepared from a stock solution characterized by alpha-spectrometry. For ^{242}Pu and ^{243}Am , the IRMM-085 standard solution [P. Taylor 2000] and a diluted aliquot of the ^{243}Am single nuclide solution purchased from Eckert & Ziegler were used, respectively. To minimize contamination with anthropogenic actinides, supra-pure HNO_3 , previously screened PbF_2 and pre-nuclear iron were used as reagents.

Calibration samples were prepared from spike solutions by mixing a well-known number of atoms ($\sim 10^8$ atoms each of ^{236}U , ^{237}Np , ^{242}Pu and ^{243}Am) in 4 mL 4 M HNO_3 as shown schematically in Figure 4.3.1. These samples were used both to investigate the molecular anion formation distribution, and as external standards for the isobar analysis of unknown materials. Each of these calibration samples was prepared individually and

underwent the final target preparation steps currently applied for fluoride extraction as if starting from the respective purified fraction from an environmental sample. This procedure was intended to ensure a sputter matrix of the calibration samples similar to that of targets from environmental samples. After adding 300 µg of Fe, the solution was dried in teflon tubes at 80 °C.

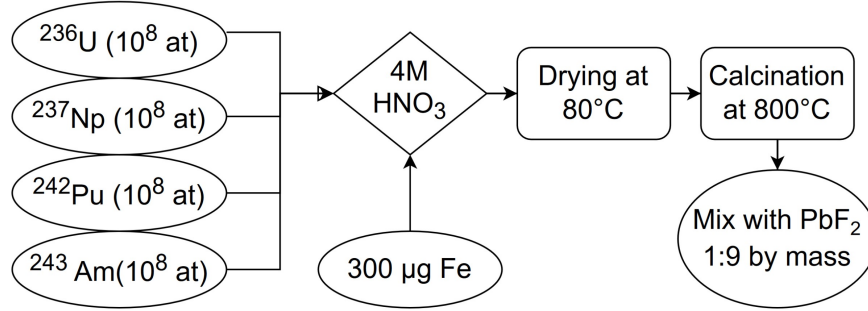


Figure 4.3.1.: Preparation of the calibration samples from spike solutions

This drying procedure was chosen instead of the usual co-precipitation to ensure quantitative recovery of the four actinides even for sub-milligram amounts of Fe [Eigl et al. 2016; Kern et al. 2022]. Drying at these low temperatures avoids element-selective losses of the actinides. Calcination at 800 °C then produced 430 µg Fe₂O₃ with embedded actinide-oxides. This oxide matrix is typically used for AMS measurements of actinides extracted as mono-oxides at VERA and most other AMS facilities [Steier et al. 2019]. For the present work, this material was then mixed with PbF₂ (Alfa Aesar PURATRONIC, 99.997%) in a mass ratio of 1:9 to ensure a sufficient fluorine supply for the in situ fluoridation in the ion source. The PbF₂ was admixed inside the quartz crucibles from the calcination step using anti-static spatulas to reduce the high transfer losses that occurred when using mortar and pestle sets for such small samples. Unfortunately, this gain may have come at the cost of more clumping and a less homogeneous blend.

Only a small aliquot of the materials from the latest irradiation experiment for the ²³⁶Np production at the RIKEN Nishina Center for Accelerator Based Science was available for AMS measurements, with the remainder being used up by other analytical methods such as ICP-MS for the characterization of the material and the chemical separation procedure. Small amounts of sample material could be recovered from the previously measured and thus already sputtered AMS targets. This material was then individually mixed with PbF₂ in a 1:9 weight ratio and pressed into copper target holders for re-measurement.

The in-house uranium standard Vienna-KkU [Steier et al. 2008] diluted in iron oxide by a factor of 30 (“D30”) and mixed with PbF₂ in a 1:9 mass ratio was used for beam tuning, as was Merck iron powder also mixed with PbF₂.

4.4. Measurement

The measurement procedure for actinides at VERA and the specifics of the actinide beamline are detailed in [Steier et al. 2019] so only the essentials and some specifics for fluoride measurements are repeated briefly in the following. In a MC-SNICS ion source built by NEC, anions were formed and extracted from the target material followed by a pre-acceleration to 41 keV. A low energy mass spectrometer consisting of an electrostatic analyzer (E/q filter) and a 90° bending magnet was used to select the desired (molecular) anion mass for injection into the tandem accelerator. At a voltage of +1.7 MV and with helium stripping, typically 15% - 20% of the ions end up in the desired 3+ charge state. The now positively charged atomic ions are then further accelerated by the positive terminal and filtered by the high energy mass spectrometer consisting of a 90° bending magnet, a 90° electrostatic analyzer, and a second 90° bending magnet for improved background suppression before being detected in a Bragg type ionization chamber.

Identification of the various (oxy-)fluoride species on each sputter target required the selection of up to 24 molecular anion species spanning a mass range from 306 u ($^{236}\text{UF}_2\text{O}_2^-$) to 338 u ($^{243}\text{AmF}_5^-$) using the low energy mass spectrometer, and the detection of $^{236}\text{U}^{3+}$, $^{237}\text{Np}^{3+}$, $^{242}\text{Pu}^{3+}$ or $^{243}\text{Am}^{3+}$ in the final ionization chamber on the high energy side of VERA. The magnetic rigidity was kept constant for all ions, and only the electrostatic components (primarily the accelerator terminal voltage and the multi beam switcher of the injection magnet) were adjusted. This approach avoided hysteresis effects on the magnets and time-consuming tuning procedures, allowing for switching times on the order of 30 seconds between setups. Two independent pilot beam *current* setups ($^{238}\text{UF}_5^-$ and $^{238}\text{UF}_2\text{O}_2^-$ from Vienna-KkU-d30+PbF₂) and two pilot *count rate* setups scaled from the corresponding *current* setup ($^{235}\text{UF}_5^-$ and $^{235}\text{UF}_2\text{O}_2^-$ from Fe+PbF₂) were used to optimize ion *current* and *count rate* measurements in each of the mass regions. Individual setups were then scaled from the closest pilot setup. For each actinide An, the ratios of the count rates in the detector after extraction as AnF_mO_n^- relative to AnF_5^- were then measured. The pentafluorides were chosen as the reference ions since they were best known and UF_5^- had been identified as the most prolific fluoride anion for uranium in previous experiments [Kern et al. 2022; Zhao et al. 2010].

Controlling the ion source is very challenging for fluorides, particularly when working with PbF₂. The formation ratios seem to be influenced significantly by factors such as the temperature of the target material, the amount and energy of the Cs ions used for sputtering and as electron donors, as well as the supply of fluorine and oxygen in the formation region. The automated source regulation aimed at a low and steady Cs flux by controlling the cesium capillary heater while keeping the ionizer at 185 W and the Cs reservoir at 200°C. Optimizing the ion source conditions and regulation for a stable output is the subject of ongoing experiments at VERA.

4.5. Results and discussion

The stability of the formation ratios $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ over time has been investigated by measuring four sequences of all 24 trace setups for a duration of 4.8 h on each of the two calibration samples I and II, which were both prepared following the procedure shown in Figure 4.3.1. The results are shown in Figure 4.5.1. Over time (i.e. from one sequence to the next) the tetrafluorides and the lighter oxyfluorides increase over the pentafluorides for U, Np, Pu and Am. A possible explanation for this trend is that, over time, the supply of fluorine is diminished which in turn impedes the formation of higher fluorides like UF_5^- . A compromise between minimizing the effect of these changing formation ratios and maximizing ion counting duty cycles had to be found. As a result, the relevant ion species were measured in two sequences of 1.2 h each and with the same ion source regulation settings for the calibration and analysis samples to ensure comparable ion source conditions.

Figure 4.5.2 shows the average $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for three beamtimes performed in February, April and June 2021. A total of ten samples spiked with ^{236}U , ^{237}Np and ^{242}Pu were measured. Four of these samples were additionally spiked with ^{243}Am . Only previously un-sputtered samples were used for the calculation of the average values shown in Figure 4.5.2.

Whereas the absolute values for the formation ratios changed from beamtime to beamtime, the $\text{AnF}_4^-/\text{AnF}_5^-$ ratio exhibited a distinct and stable pattern for U, Np, Pu, and Am in each beamtime. In all beamtimes, the $\text{AnF}_4^-/\text{AnF}_5^-$ ratios were highest for Am, followed by Pu, Np and finally U, with an order of magnitude from one actinide to the next. The separation is much less pronounced and less stable for the oxyfluoride anions investigated. The count rates of AnF_2O_2^- , AnF_3O^- and AnF_4^- with setups scaled from the pilot setup UF_2O_2^- were significantly lower in beamtime C compared to the beamtimes A and B, while the count rates for the heavier anions with setups scaled from UF_5^- were comparable. The corresponding molecular anion formation ratios were shifted accordingly for beamtime C compared to the two forgoing beamtimes. Thus, the absolute ratios for the oxyfluoride formation obtained in different beamtimes cannot be directly compared. The average count rates on $^{236}\text{UF}_5^-$ in these beamtimes ranged from 4.01 - 7.49 cps. $^{237}\text{NpF}_5^-$ produced 2.73 - 12.81 cps while $^{242}\text{PuF}_5^-$ showed large variations from 0.1 - 5.07 cps. The count rates for $^{243}\text{AmF}_5^-$ reflect the inefficient formation of this anion at 0.02 - 0.27 cps. Source effects or ion-optical losses for some of the setups could have contributed to the observed variations between beamtimes. A lower ion-optical transmission for the setups scaled from one of the pilot beams would shift the ratios but would not affect the separation of the $\text{AnF}_4^-/\text{AnF}_5^-$ ratios for the four actinides. Optimizing the setups over the required large mass range without changing the magnetic rigidity was very challenging and required the operation of several electrostatic components near or at their limit.

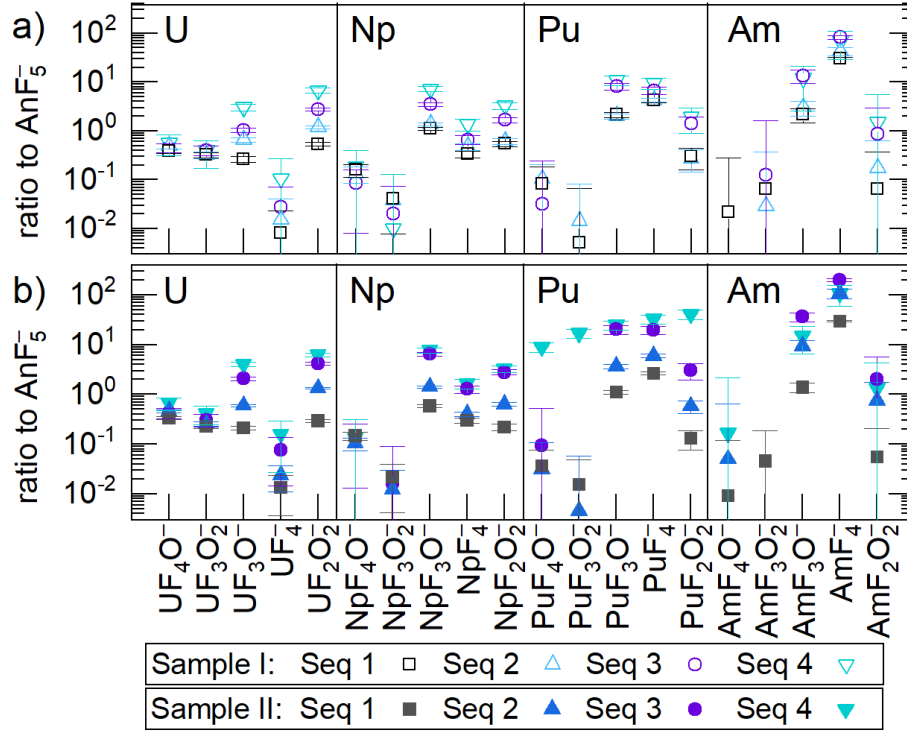


Figure 4.5.1.: On two calibration samples I (Figure a) and II (Figure b) a range of (oxy-)fluoride molecular anions of U, Pu, Np and Am were measured. For each anion species, the formation ratio relative to the pentafluoride of the respective actinide is plotted above for four 1.2 h sequences.

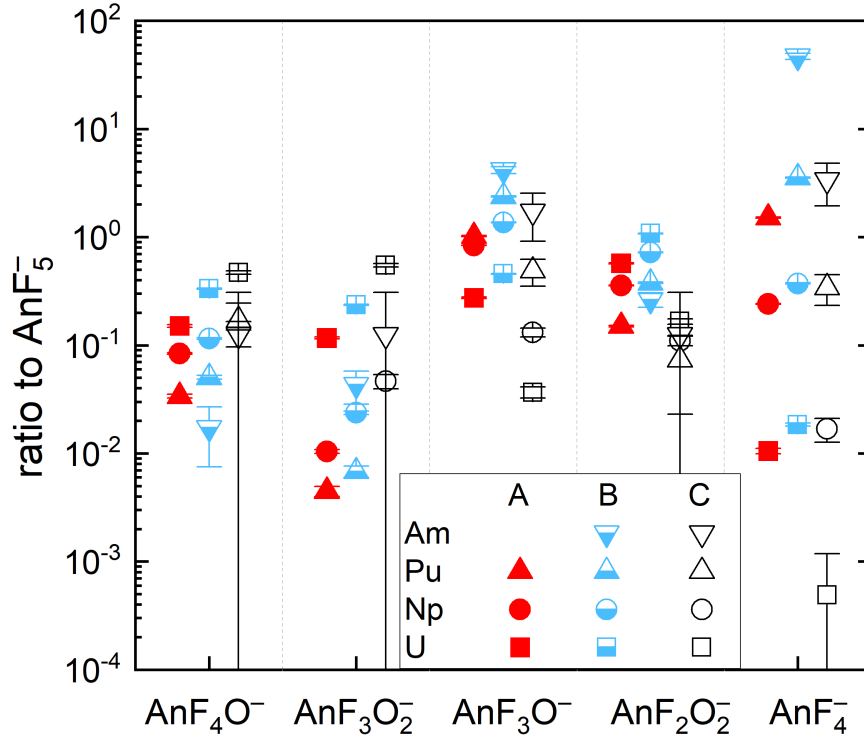


Figure 4.5.2.: The different colors show results from the three beamtimes A B and C, while the symbols indicate average $AnF_mO_n^-/AnF_5^-$ ratios for U, Np, Pu and Am. These ratios show significant shifts between beamtimes while the separation in the AnF_4^-/AnF_5^- ratios remains distinct and stable.

The observed inter-beamtime shifts necessitate the measurement of calibration samples as external standards alongside any materials that are to be analyzed for isobaric interference using the anion formation ratios.

The effect of the fluorine supply on the anion formation for U, Np, and Pu was investigated by using three different mixing ratios with PbF_2 (1:4.5, 1:9, and 1:18 by weight) as shown in Figure 4.5.3. Only samples mixed in a 1:9 ratio also included the Am spike. Both $\text{PuF}_4\text{O}^-/\text{PuF}_5^-$ and $\text{UF}_3\text{O}_2^-/\text{UF}_5^-$ are enhanced for the 1:4.5 mixing ratio by 60% and 100% respectively. For $\text{AnF}_3\text{O}^-/\text{AnF}_5^-$ and $\text{AnF}_2\text{O}_2^-/\text{AnF}_5^-$ the 1:18 mixing ratio decreased the formation ratios for all four actinides by up to 50% compared to the materials mixed in a 1:9 ratio while the 1:4.5 ratio had the opposite effect. This resulted in differences of up to an order of magnitude between the samples with 1:4.5 and 1:18 PbF_2 mixing ratios. For $\text{NpF}_4^-/\text{NpF}_5^-$ and $\text{PuF}_4^-/\text{PuF}_5^-$ ratios, the effect is less pronounced and for $\text{UF}_4^-/\text{UF}_5^-$ no difference between the mixtures was observed. However, it should be noted that the low counting statistics on UF_4^- resulted in very large uncertainties for these uranium measurements. Overall, reducing the fluorine supply appears to favor the lighter oxyfluorides (four ligands) and at least for Np and Pu the tetrafluoride anions over the heavier oxyfluorides (five ligands) and pentafluorides. The observed effect of the PbF_2 mixing ratios supports the hypothesis that a diminishing fluorine supply could explain the shift of the formation ratios over time as discussed above.

The relative anion formation ratios were then also analyzed in the irradiated material using the developed measurement procedures and compared to the results of the calibration samples. To achieve sufficient counting statistics, the results from the calibration samples in this beamtime were combined and analyzed as one material. The small amounts of recoverable material from the irradiation experiments and the low formation probabilities for some anions, such as UF_4^- made it impossible to analyze individual samples, so they were combined in the data evaluation. In future measurements, an increased U content in the calibration samples and optimization of the measurement time based on the expected count rate for each anion will improve the measurement of individual samples.

The calibration samples were measured in between the samples containing irradiated material under identical conditions. Since the irradiated material contained detectable amounts of co-produced ^{237}Np , this isotope was used for quality control of the measurement without isobaric ambiguity. As can be seen in Figure 4.5.4, the $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ ratios for the irradiated samples and the external standards were compatible within 1σ which confirms that there were no significant systematic differences between the measurement conditions for the two types of materials.

When finally analyzing ^{236}X on the irradiated samples, the averaged $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ ratio for the irradiated samples also falls within 1σ of the $\text{NpF}_4^-/\text{NpF}_5^-$ ratio for the calibration samples. This result would indicate that ^{236}Np was successfully produced and chemically separated by the groups of the Universities of Tsukuba and Kanazawa. However, on mass 236 not only ^{236}U but also ^{236}Pu could potentially contribute to the

isobaric background. The presence of just the right combination of these two isobars would mimic the $\text{AnF}_4^-/\text{AnF}_5^-$ ratio expected for ^{236}Np .

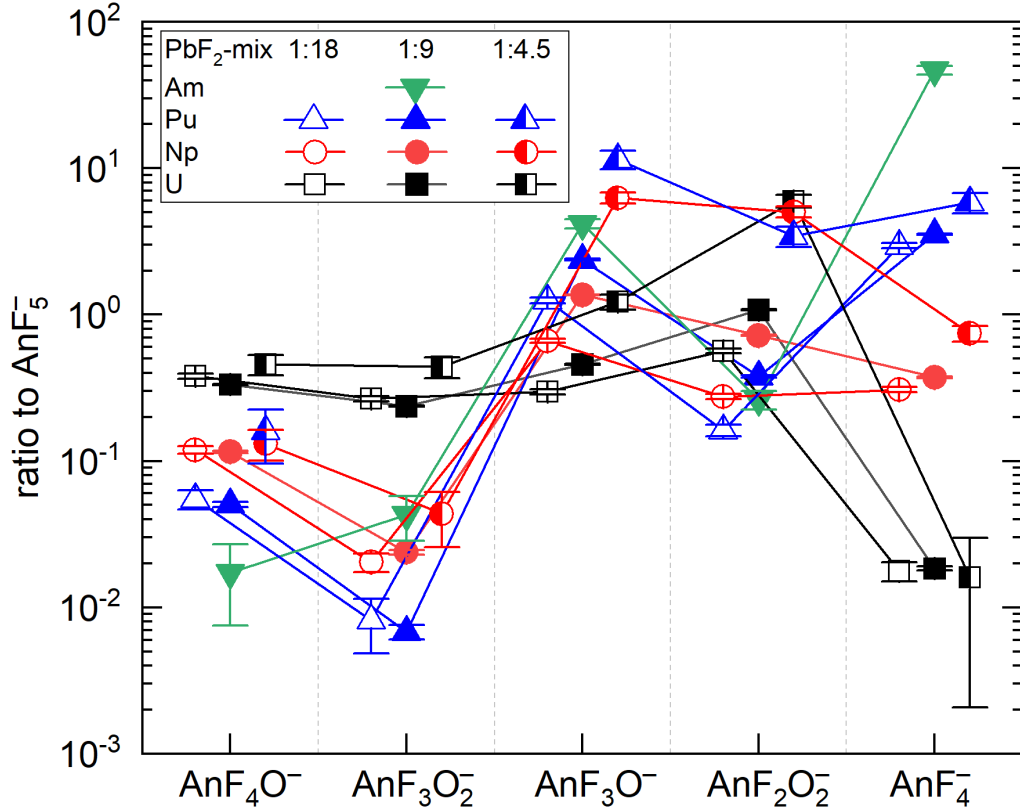


Figure 4.5.3.: Average $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for spiked calibration samples with different PbF_2 mixing ratios. A reduced PbF_2 supply favors the formation of lighter oxyfluorides for U, Np, and Pu as well as tetrafluorides for the latter two actinides.

This ^{236}Pu could only have been produced via one branch of the decay of ^{236m}Np , which was estimated to be produced at a much lower rate than the ground state ^{236g}Np in simulations using the EMPIRE code [Herman et al. 2007]. In contrast, ^{236}U could also be produced via neutron capture on ^{235}U in addition to the second branch of the decay of ^{236m}Np . Since the Pu separation procedure used for this experiment has been found to be less reliable than expected, the possibility of a non-negligible contribution from ^{236}Pu presently cannot be excluded. Further measurements on a new batch of irradiated samples will be required to confirm the tentative findings of this initial analysis. The chemical separation has been optimized for Pu suppression in the meantime and a ^{242}Pu -spike will be used to monitor its effectiveness.

The uranium data shows that UF_5^- was formed much more readily than UF_4^- , but compared to the Zhao and Francisco results [Zhao et al. 2022] the oxyfluorides were more prominent and highly variable in the present study, with UF_2O_2^- formation even overtaking UF_5^- in one measurement. For Np, the anions NpF_5^- , NpF_3O^- , NpF_2O_2^- and NpF_4^- were relevant. However, the formation ratios changed significantly between

measurements, within a measurement over time and with the PbF_2 mixing ratios. The first data on Np extraction using PbF_2 for in situ fluoridation presented here is in good agreement with the hypotheses that Np is close to a chemical tipping point within the actinide group [Zhao et al. 2022]. This would explain that the formation pattern is spread out over several anions and why it is highly sensitive to small changes in ion source conditions. For Pu, the next higher actinide, the situation is similar. The anions PuF_4^- , PuF_5^- , PuF_3O^- and PuF_2O_2^- all were formed efficiently at least in some of the measurements, and the Pu anion formation ratios observed at VERA were even more dispersed than in [Zhao et al. 2022]. In contrast to the complicated situation for Np and Pu, the formation of AmF_4^- outperformed all other selected anions in all Am measurements.

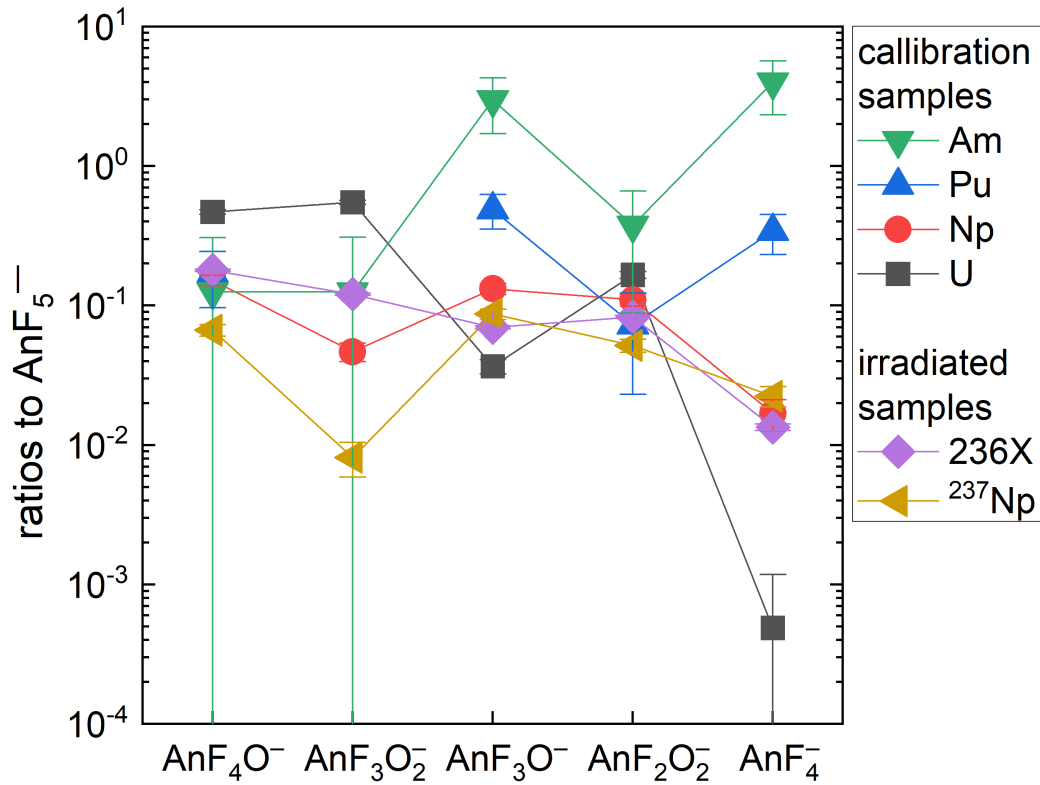


Figure 4.5.4.: Comparison of the results on relative oxyfluoride formation obtained from irradiated material with external standards containing ^{236}U , ^{237}Np , ^{242}Pu and ^{243}Am spikes. The $\text{AnF}_4^-/\text{AnF}_5^-$ ratio of mass 236 on the irradiated samples is compatible with that of ^{237}Np on the external standards.

Whereas Zhao and Francisco found the fluoride anions to dominate the extraction [Zhao et al. 2022], some oxyfluorides performed close to or sometimes even above the highest fluoride anions of the same actinide in our measurements. The oxygen supply in the target matrix should have been significantly lower in the VERA samples due to the additional calcination step which is expected to turn $\text{Fe}(\text{OH})_3$ as used in the previous study into Fe_2O_3 . Whether the more prominent formation of oxyfluorides in the present study originates in the target preparation or the ion source itself (e.g. via increased

competition for O via the formation of OH^- ions from $\text{Fe}(\text{OH})_3$ is unclear and will be explored with further experiments in the future. A notable departure from established target preparation procedures was replacing the co-precipitation of the $\text{Fe}(\text{OH})_3$ with drying the spikes dissolved in 4M HNO_3 together with 300 μg of dissolved iron, but it is not apparent how this could significantly affect the oxyfluoride formation. The coprecipitation procedure typically uses several mg of Fe to ensure quantitative recovery, which due to the high mixing ratios with the fluorine donor resulted in 40 mg - 120 mg total sample sizes in the study [Zhao et al. 2022]. The drying approach with sub mg amounts of Fe can be directly applied to individual environmental samples with a total resulting mass after mixing of 4.3 mg or less, easily fitting within a single AMS sample.

Preliminary tests at VERA with FeF_3 , the fluoridating agent chosen by the Ottawa group for its higher output stability [Zhao et al. 2022], showed significantly lower U and Np count rates overall compared to the use of PbF_2 . On this lower level, the relative prominence of the lighter oxyfluoride (4 ligands) and tetrafluoride anions was increased.

4.6. Conclusions and Outlook

The extraction of actinides using PbF_2 as a fluoridating agent has been found to be highly element specific, which confirms the previous findings reported in [Zhao et al. 2022]. Whilst some general trends such as the dominance of AmF_4^- appear to be stable, the overall distributions and the formation of oxyfluorides in particular appear quite sensitive to changes in ion source conditions or types, and hence differ significantly from those in [Zhao et al. 2022].

The $\text{AnF}_4^-/\text{AnF}_5^-$ ratios for the actinides U, Np, Pu and Am have been shown to be element specific within each measurement, and the factor of one order of magnitude separating these ratios from one actinide to the next is robust and reproducible. Based on these findings, the $\text{AnF}_4^-/\text{AnF}_5^-$ ratio can act as an elemental fingerprint. A significant amount of an interfering isobar would result in a shift of this formation ratio relative to the corresponding ratio measured on the calibration samples. The prospective neptunium spike material provided a first application for this kind of isobar analysis, and the tentative first results are compatible with a successful production of ^{236}Np .

Choosing the tetrafluorides instead to the pentafluorides for extraction of Np and U already suppresses $^{236}\text{UF}_4^-$ by an order of magnitude compared to $^{236}\text{NpF}_4^-$ in the ion source. The multitude of (oxy)fluoride anions of the various actinides greatly increases the probability of finding a suitable molecular ion system for isobar separation using methods like element selective photodetachment in ILIAMS.

Acknowledgments:

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5. Isobar separation of actinides in mass spectrometry by the combination of laser photodetachment with ion-gas interactions

5.1. Abstract

Isobaric interference is a major limitation of mass spectrometric measurements of trace radionuclides. For Accelerator Mass Spectrometry (AMS), isobaric separation is only available up to the mass range of fission products. The present work explores the potential of Ion-Laser InterAction Mass Spectrometry (ILIAMS) for trace analysis of anthropogenic actinides with isobaric interference. Such capabilities are crucial for characterizing a highly sought-after isotopic spike material for ^{237}Np measurements and for accessing additional anthropogenic actinides with AMS, which could serve as environmental tracers, emission source signatures, or for determining the age of nuclear materials. ILIAMS is a novel low-energy isobar separation technique that combines a gas-filled ion cooler with reactive gases or high-power lasers to suppress isobars selectively. In this study, we demonstrate that UF_4^- can be selectively suppressed by two orders of magnitude using a 637 nm laser without affecting NpF_4^- . Initial results indicate the potential for the selective suppression of AmF_5^- to measure PuF_5^- or, in reverse, the suppression of PuF_4^- to measure AmF_4^- using a 355 nm laser. The admixture of O_2 with the buffer gas of the ion cooler can be used to suppress UF_4^- by up to seven and NpF_4^- by up to three orders of magnitude against PuF_4^- . The first application of these separation schemes for the characterization of a prototype ^{236}Np -spike demonstrated the successful chemical removal of the co-produced isobars ^{236}U and ^{236}Pu , and similar measurements can now be performed for other prospective Np-spike materials. The isobar separation schemes developed here can also enable the measurement of ^{241}Pu without chemically removing ^{241}Am or ^{242m}Am in the presence of ^{242}Pu . Even measuring ^{238}Pu using AMS has become feasible for suitable sample matrices, despite the presence of the primordial isobar ^{238}U . These are important isotopic signatures for attributing environmental contamination to potential sources of emissions.

5.2. Introduction

Significant inventories of anthropogenic actinides, such as an estimated 2400 tons of plutonium [Albright et al. 2015] have been produced by human nuclear activities and partially released into the environment through nuclear bomb tests, nuclear accidents, reprocessing plants, and, in some areas, the direct deposition of nuclear waste [Runde et al. 2011]. Artificial origin and well-defined source terms have made it possible to use some of these radionuclides as tracers for various environmental transport processes [Casacuberta et al. 2014; Hain et al. 2020; Lindahl et al. 2010; Quinto et al. 2009; Steier et al. 2008].

Neptunium is generally very mobile under oxic conditions and can complement existing actinide tracers for ocean water mass transport, such as ^{236}U . The most relevant isotope of Neptunium, ^{237}Np , is thought to be the second most abundant anthropogenic actinide in the environment [Beasley et al. 1998b; Kelley et al. 1999]. Owing to its long half-life, it will eventually become a dominant radionuclide in nuclear waste [Ewing 1999]. The associated necessity for risk assessment and radioecological studies emphasizes the significance of analyzing ^{237}Np in environmental samples [Qiao et al. 2011]. No sufficiently pure isotopic Np-spike, i.e., a known quantity of another long-lived Np isotope that can be added to samples to quantify ^{237}Np in relative measurements, had been available, which hindered the quantification of ^{237}Np by mass spectrometric techniques. The associated analytical challenges have resulted in much less scientific attention being devoted to ^{237}Np compared to the even less abundant ^{236}U , and ^{237}Np has been called “the neglected actinide” [Thompson 1982]. The established method for the quantification of ^{237}Np in ultra-trace measurements by Accelerator Mass Spectrometry (AMS) is to use ^{242}Pu as a non-isotopic spike [Fifield et al. 1997]. Significant advances regarding the ^{242}Pu normalization of seawater Np samples have been made in the past decade [López Lora 2019; López-Lora et al. 2019a,b]. However, this non-isotopic approach is matrix-specific and carries a high risk of elemental fractionation during chemical sample preparation because the oxidation states of both Pu and Np must be carefully controlled. ^{236g}Np ($t_2 = 1.55 \cdot 10^5 \text{ y}$) was proposed as an isotopic spike for ^{237}Np to provide a robust and reliable normalization method for ^{237}Np [Jerome et al. 2014]. While ^{236}Np has been produced in the past via irradiation of ^{235}U , ^{236}U , or ^{238}U with deuterons or protons at various energies, the resulting materials typically contain high $^{236}\text{Np}/^{237}\text{Np}$ ratios [Landrum et al. 1969]. An overview of the production pathways and challenges of such legacy ^{236}Np materials, along with more recent experiments at the National Physical Laboratory (NPL) in the UK, was compiled in 2014 [Jerome et al. 2014]. Some of these irradiations explicitly aimed at the production of the isobar ^{236}Pu or used another isobar, ^{236}U , as the irradiation target, with ^{236}Np formed as a byproduct, but no data on the isobaric contamination of separated ^{236}Np materials have been published [Jerome et al. 2014]. Besides the potential co-production of interfering isobars or ^{237}Np , some of the required target materials, such as $>99\%$ enriched ^{235}U , are unavailable for regulatory

reasons. Recently, a new material distributed by the US Department of Energy (DOE) was announced [National Isotope Development Center 2025]. A total of $\sim 1.1 \cdot 10^{16}$ atoms were produced via a $^{238}\text{U}(\text{p},3\text{n})^{236}\text{Np}$ reaction using depleted uranium. However, at the time of writing, no characterization data were made available on the Isotope Program web page of the DOE or in the form of a publication. An alternative production path via the irradiation of ^{232}Th foils with a ^7Li beam in the 30-40 MeV range to minimize the co-production of ^{237}Np has been explored in collaboration by the Universities of Tsukuba, Kanazawa, and Vienna [Hayakawa et al. 2019]. However, alongside the desired ^{236g}Np , short-lived metastable ^{236m}Np ($t_{1/2}=22.5$ h) is also produced, which decays into isobaric interferences, namely ^{236}Pu and ^{236}U . For ^{236}U , in principle, there is a direct production pathway via the capture of secondary neutrons by ^{235}U impurities in irradiated foils. However, a parallel investigation recently (after the completion of the experimental work for this study) estimated a production of 26 atoms of ^{236}U via this path per foil and irradiation [Nagai et al. 2025]. While the chemical purification of the irradiated foils (to be published elsewhere) aims to remove these isobars, it is necessary to verify that the chemical suppression, typically two orders of magnitude, was sufficient, or to quantify the remaining isobaric interference.

Besides ^{236}Np and its isobars, there are also other actinide isobar systems where new separation schemes could be of great interest: ^{236}Pu with its short half-life of 14.3 yrs can serve to differentiate between old (global fallout), intermediate (e.g., Chornobyl), and young (e.g., Fukushima) anthropogenic releases via the $^{241}\text{Pu}/^{239}\text{Pu}$ ratio (referred to as “nuclear clock” in this context). Radiometric measurements of the low-energy (21 keV) beta emitter ^{241}Pu at environmental concentrations, e.g., 10^3 - 10^4 at/L in Pacific Ocean Waters [Hain et al. 2017], are challenging and require the separation of all other beta emitters [Ikäheimonen 2000]. Mass spectrometric measurements of ^{241}Pu rely on chemical separation of the interfering isobar ^{241}Am . However, in older source terms, such as global fallout, most of the ^{241}Pu has already decayed to ^{241}Am . Therefore, older samples require a higher detection efficiency and are more demanding regarding ^{241}Am suppression, which can be difficult to achieve by chemical means.

The $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio is a powerful emission fingerprint [Lindahl et al. 2010]. With its longer half-life (87.7 years), ^{238}Pu could substitute ^{241}Pu for dating or distinguishing older source terms. As an alpha emitter with a relatively short half-life, ^{238}Pu is well-suited for radiometric analysis. However, the preparation and low-level measurements of alpha sources are time-consuming. Using mass spectrometric methods, ^{238}Pu can be determined along with other source-specific Pu isotope ratios, such as $^{240}\text{Pu}/^{239}\text{Pu}$, in a single measurement. The abundant primordial isobar ^{238}U has prevented the measurement of environmental concentrations of ^{238}Pu by AMS. Sufficiently strong U suppression could enable AMS measurements of ^{238}Pu along with several other Pu isotopes. During the finalization of the present work, a new paper on measuring ^{238}Pu using a reaction-cell Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been published, demonstrating the interest in developing new mass spectrometric measurement techniques for

^{238}Pu [Peng et al. 2025]. This technique adds a collision or reaction cell before the mass filter of an ICP-MS system to remove or reduce isobaric or molecular interferences from the positive ion beam [Koppenaal et al. 2004]. This recent ^{238}Pu publication provides both a benchmark for the isobaric separation and a very effective chemical U/Pu separation procedure that would be beneficial, regardless of the instrumentation used.

The VERA (Vienna Environmental Research Accelerator) AMS facility has demonstrated sufficient sensitivity and background suppression to detect ultra-trace amounts of several anthropogenic actinides [Steier et al. 2019], including ^{237}Np , in environmental samples. Upgrades to instrumentation in recent years have made new tracers accessible, such as the $^{233}\text{U}/^{236}\text{U}$ isotopic ratio [Hain et al. 2020]. However, only actinides with negligible isobaric interference after chemical separation have been measured by AMS, because the electrostatic or magnetic filters used in AMS cannot distinguish atomic isobars. Advanced techniques for isobar separation in AMS based on the nuclear charge Z dependence of the energy loss in degrader/absorber foils [Kutschera et al. 1980], complex detector systems [Zoppi et al. 1994] and the mean charge state in gas-filled magnets [Knie et al. 1997] have been established for low-to-medium Z elements such as ^{10}Be , ^{26}Al , ^{32}Si , ^{53}Mn , ^{60}Fe , ^{93}Zr , and ^{99}Tc [Koll et al. 2019; Wallner et al. 2023]. Because the relative difference $\Delta Z/Z$ between neighboring isobars decreases with increasing Z , the particle velocity required for isobar separation must increase, eventually reaching technical or physical limitations. No existing AMS facility has been able to apply these isobar separation techniques to the high-mass range of the actinides. In a previous study, we introduced Anion Formation Isobar Analysis (AFIA) as a qualitative screening method to identify isobaric contaminants in samples containing U, Np, Pu, or Am [Wiederin et al. 2022]. This approach is based on the element-specific relative formation probabilities of the tetra- and pentafluoride molecular anions of these actinides in a Cs-sputter ion source. The data obtained in this previous study on an early Np prototype spike material showed no indication of isobaric interference at a mass of 236 u. However, a specific combination of ^{236}U and ^{236}Pu concentrations in the material could mimic the expected ^{236}Np formation ratio. Furthermore, the trace quantities of the materials analyzed to date, limited counting time, and the complex measurement scheme resulted in high statistical uncertainties, particularly for less efficiently formed anion species such as UF_4^- . Owing to these limitations, AFIA alone is not sufficiently reliable to characterize isobaric interference in ^{236}Np materials at the required trace levels or to address any of the other isobaric systems discussed above. Ion-Laser InterAction Mass Spectrometry (ILIAMS) [Forstner et al. 2015; Martschini et al. 2019b, 2017] uses a gas-filled radio frequency quadrupole (RFQ) ion cooler after the first magnetic filter to achieve ion residence times on the order of milliseconds. This comparatively long time allows the suppression of isobaric interference via selective photodetachment with high-power lasers, element-specific interactions with admixed gases, or even collisions with the inert He buffer gas. The gas reaction approach was pioneered by the Isobar Separator for Anions (ISA) system at the University of Ottawa [Alary et al. 2015] with a focus on

separating ^{36}S from ^{36}Cl . ILIAMS has already been employed for the measurement of ^{26}Al , ^{36}Cl , and ^{90}Sr [Martin Martschini et al. 2022] and other trace radionuclides.

Laser photodetachment is a non-resonant threshold process [Forstner et al. 2015], so that anions with detachment energies above the available photon energy are unaffected. When the photon energy exceeds the threshold, anion survival is mainly influenced by the photodetachment cross-section, interaction time, and effective photon flux. Under real experimental conditions, the ion behavior can become much more complex. A selection of potential factors responsible includes the presence of excited states with lower photodetachment threshold energies than ground state ions, space charge effects from macroscopic currents of other ion species injected alongside the ions of interest that can affect transmission and ion cooler residence times, or differences in laser beam tuning and overlap between laser and ion beam.

Selective laser photodetachment requires a suitable (molecular) anion system in which the detachment energy for the interfering isobar is below that of the isotope of interest and a laser with a photon energy that falls within this gap. Conversely, isobaric separation with reactive gases requires an anion system in which the added gas reacts with the interfering isobar, but not with the isotope of interest. Additionally, the respective anion system must be formed with reasonable efficiency for the isotope of interest and yield a stable ion source output. A lower formation efficiency of the interfering isobar would provide a first isobar separation step in the ion source. As actinides (An) in general do not form negative atomic ions efficiently, they are usually extracted in the form of monoxide anions (AnO^-) for AMS measurements [Middleton 1974]. In recent years, the use of fluoride molecular anions (AnF_mO_n^-) has been explored for the measurement of actinides [Zhao et al. 2010]. The large variety of fluoride and oxyfluoride molecular anions that can form, as well as the element-selective formation probabilities of these molecular anions [Wiederin et al. 2022; Zhao et al. 2022] significantly improve the odds of finding a suitable molecular anion system for isobar separation with ILIAMS. Both methods for isobaric separation by ILIAMS, that is, laser photodetachment and gas interactions, are based directly on the electronic configuration of the atomic or molecular anions involved and should therefore be well suited to high-Z elements such as actinides.

The present work explores the application of ILIAMS for isobar separation in the actinide group, with a focus on separating U from Np and Np from Pu to provide a reliable characterization method for ^{236g}Np -spike materials. To extend the ILIAMS portfolio to other relevant isobar systems described above, the separation of isobars at mass 241 u (Am/Pu) and 238 u (U/Pu) was also investigated.

A separation scheme for the U, Np, and Pu isobars was developed and applied to the characterization of prospective ^{236}Np -spike materials produced by ^7Li beam irradiation of ^{232}Th foils at the RIKEN Nishina Center. The results of these measurements suggest successful removal of both ^{236}U and ^{236}Pu during chemical purification.

5.3. Materials and methods

5.3.1. Instrumentation and measurement

All actinide AMS measurements and isobar suppression experiments were conducted at the University of Vienna (VERA). The actinide beamline and the corresponding procedure for actinide measurements were described in detail in a previous study [Steier et al. 2019]. The Faraday cups (FC) on the actinide beamline are equipped with Stanford Research Systems SR570 low-noise linear current amplifiers to measure $^{238}\text{U}^{3+}$ currents with a sensitivity of approximately 1 pA. Trace ions, such as $^{236}\text{U}^{3+}$, $^{236}\text{Np}^{3+}$, $^{237}\text{Np}^{3+}$, $^{242}\text{Pu}^{3+}$, and $^{243}\text{Am}^{3+}$, were detected in a Bragg-type gas-filled ionization chamber. Figure 5.3.1 shows a simplified schematic of the ILIAMS and actinide beamlines at the VERA AMS facility.

The ILIAMS setup is located on a dedicated low-energy beamline and is coupled to the AMS system in front of the low-energy injector magnet. It was used to investigate isobar suppression via laser photodetachment and chemical reactions in the buffer gas of AnO^- , AnO_2^- , AnF_4^- , and AnF_5^- , as well as a range of oxyfluorides AnF_mO_n^- with four or five ligands for the actinides (An) U, Np, Pu, and Am. A detailed description of the ILIAMS system has been reported previously [Forstner et al. 2015; Martschini et al. 2019b, 2017].

From the multiple-laser setup of ILIAMS, the 354.7 ± 0.1 nm (3.49 eV, AVIA-LX, Coherent Inc.) and 532.00 ± 0.03 nm (2.33 eV, Verdi V18, Coherent Inc.) were utilized in this study. A new laser system, a 637 ± 7 nm 15 W continuous-wave (CW) diode laser (model number LSR638CP-15W, Civillaser) was acquired to selectively suppress UF_4^- . Due to the lower beam quality of this laser (rectangular beam $6.4x \times 5.8$ mm, beam divergence 2.96×3.64 mrad) and the limited available space for the optical setup, only 0.6 W of laser power out of a total 15 W could be transmitted through the RFQ ion cooler, compared to the 6.5 W out of 12 W obtained for the permanently installed 532 nm laser. A tunable (~ 700 -970 nm) 1.5 W Ti:Sa laser [Kessler et al. 2008] from the Johannes Gutenberg University Mainz was available for a brief series of experiments involving oxide anions.

The composition of the buffer gas can be changed by mixing the desired gases, here typically He + 3 % O₂, in a pressurized vessel and connecting it to the buffer gas system of ILIAMS for a regulated flow. The gas pressure inside the ion cooler was regulated using a manual valve and measured at the gas entrance tube. Simulations conducted in a previous study indicated that the true pressure at the center of the ion cooler was four times lower than the measured value [Gaggl 2021]. All ion cooler gas pressure values reported here have already been corrected by this factor. Rapid switching between buffer gases is not possible; the flask must be manually filled, and several pumping steps are required to ensure a clean gas supply to the ion cooler.

To determine the suppression of a sufficiently prominent ion species, the intensity of

the corresponding molecular anion current can be measured in Faraday cups before and after the ion cooler. In the present study, this approach was only possible for uranium, for which $^{238}\text{UF}_m\text{O}_n^-$ ion currents in the pA to high nA range can be produced from the in-house natural uranium standard, Vienna-KkU [Steier et al. 2008], mixed with PbF_2 .

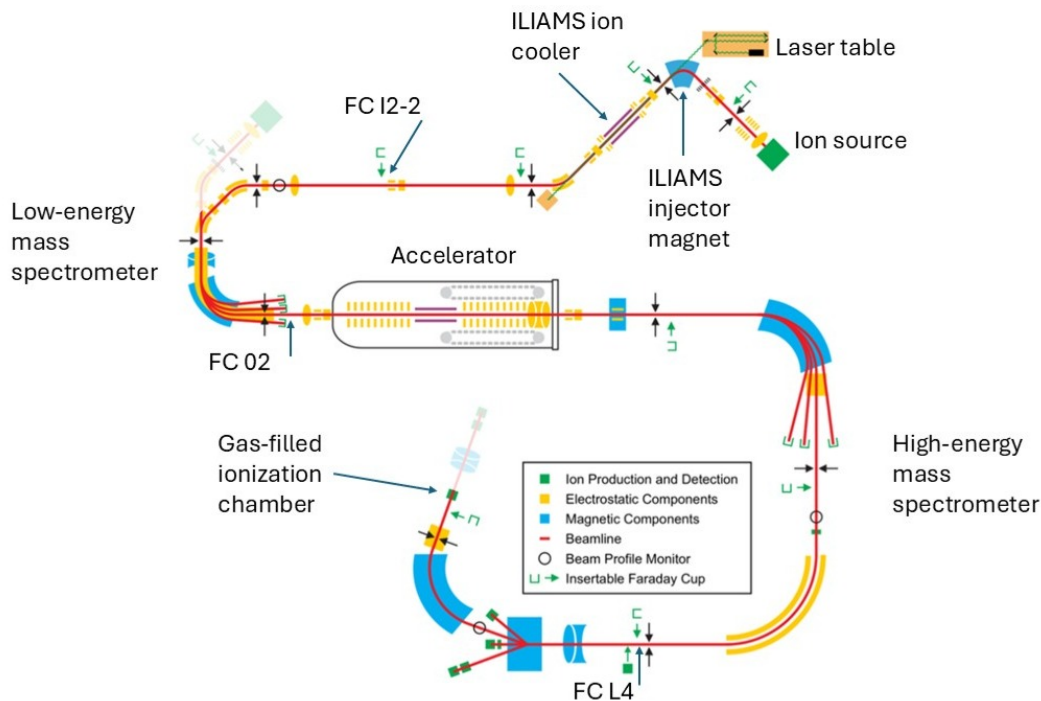


Figure 5.3.1.: Schematic of the VERA facility. The ILIAMS measurements described in this chapter were carried out from the dedicated ion source on the ILIAMS beamline. For investigating the transmission of macroscopic ion species with and without a laser, the ILIAMS injector magnet was scanned, and ion currents were measured at the Faraday cup FC I2-2. For identifying the formation of different anion species inside the ion cooler when injecting either $^{238}\text{UF}_4^-$ or $^{238}\text{UF}_5^-$, the injector magnet in the low-energy mass spectrometer was scanned and ion currents were measured in FC 02. For the calculation of anion survival fractions, trace ions were detected in the gas-filled ionization chamber, while macroscopic currents were measured in the FC I2-2 (ILIAMS beamline only) or FC L4.

Mass scans were performed to investigate the transmission of different molecular anion species with macroscopic currents through the ion cooler by scanning the magnetic field of the ILIAMS injector magnet and measuring the current in a Faraday cup behind the ion cooler (FC I2-2; see Figure 5.3.1). To investigate the formation of new anion species inside the ion cooler (e.g., $^{238}\text{UF}_4\text{O}^-$ from a $^{238}\text{UF}_4^-$ beam and O_2 in the buffer gas), the injector magnet of VERA's low-energy mass spectrometer was used for mass scans into a Faraday cup between the low-energy analyzing magnet and the accelerator (FC 02, see Figure 5.3.1). This type of investigation is only available for ion currents above 1 pA to ensure detection in a Faraday cup. The mass scale of the scans was calibrated using several prominent peaks, for example, $^{238}\text{UF}_5^-$ or $^{238}\text{UF}_2\text{O}_2^-$.

The measured effect of an anion suppression scheme might be limited by the sensitivity of the current amplifier. In addition, the various artificial Np, Pu, and Am isotopes could

only be used in trace quantities (typically 10^7 - 10^9 at/sample) for regulatory reasons and to avoid contamination of the VERA labs and AMS setup for future low-level environmental samples. When no macroscopic ion beam was available, the full actinide beamline at VERA had to be used for single-ion counting in a gas-filled ionization chamber. It is important to note that the measurements presented in the following were obtained using the ILIAMS injector and the full actinide beamline, resulting in the longest flight path from the source to the detector and the largest number of components available at VERA. The corresponding tuning with multiple pilot beams, such as $^{238}\text{UF}_5^-$, $^{238}\text{UF}_2\text{O}_2^-$, or $^{238}\text{UF}_4^-$ to ensure accurate setups for the neighboring trace ion species, proved very demanding and time-intensive, thereby constraining the available counting time for certain experiments.

5.3.2. Materials

The in-house uranium standard Vienna-KkU [Steier et al. 2008] or Vienna-KkU-D30 (diluted 1:30 by mass in Fe) mixed with PbF_2 (1:9 by mass) was used to provide $^{238}\text{UF}_{m,n}^-$ pilot beams for beam tuning or experiments with high uranium currents (up to ~ 200 nA at mass 333 u corresponding to $^{238}\text{UF}_5^-$ after the ILIAMS injector magnet).

Experiments involving trace amounts of U, Np, Pu, and/or Am were carried out using calibration samples with known concentrations of ^{236}U , ^{237}Np , ^{242}Pu , ^{243}Am , analogous to previous studies on anion formation [Kern et al. 2022; Wiederin et al. 2022]. The calibration samples were produced by mixing the desired amounts of radionuclide solutions with $300\text{ }\mu\text{g}$ of iron in dilute nitric acid and then dried in open FEP or PFA tubes. The dried mixture was then calcined in quartz crucibles at 800°C and mixed with PbF_2 using a 1:9 (sample: PbF_2) mass ratio. The other reagents involved in the preparation of the calibration samples were Rotipuran suprapure HNO_3 (Carl Roth GmbH & Co), ultrapure water produced by a Milli-Q system, and 99.997 % pure PbF_2 from Alfa Aesar. Dilutions in suprapure HNO_3 were prepared from the ^{237}Np single nuclide solution 7237 (Isotrak Calibrated Solutions Eckert&Ziegler) and IRMM-085 (^{242}Pu isotope standard solution, Institute for Reference Materials and Measurements) to allow 10^8 to 10^{10} atoms of these nuclides to be added to the calibration samples. An aliquot from a ^{243}Am single nuclide solution (Eckert&Ziegler) was available for a limited number of experiments at $\sim 10^8$ atoms per sample. For the ^{236}U spike solution, 99.973 % pure ^{236}U , provided by the IAEA, dissolved in HNO_3 was used.

The ^{236}Np -spike materials were produced at the RIKEN Nishina Center for Accelerator-Based Science in Saitama, Japan, by irradiating ^{232}Th using a ^7Li beam on the AVF cyclotron offline irradiation beamline. Stacks of ^{232}Th foils purchased from Goodfellow (99.5 % purity) were irradiated with 30-40 MeV ^7Li ions to investigate the excitation function of the $^{232}\text{Th}(^7\text{Li},\text{xn})^{239-x}\text{Np}$ reactions. The prototype spike material analyzed in the present study was produced by irradiating the foils twice for 24 h at $\sim 1\text{ }\mu\text{A}$ per irradiation. The irradiated foils were subsequently dissolved and chemically purified at

the University of Tsukuba (preliminary description in [Hayakawa et al. 2019]). For analysis of the isobaric composition of the prototype Np-spike, approximately $2 \cdot 10^8$ atoms of mass 236 were mixed with 300 μg of iron in dilute HNO_3 and prepared analogously to the calibration samples.

5.3.2.1. Data evaluation

Uncertainties in the counting results were either calculated from counting statistics or, if available, the empirical standard deviation of repeated measurements, whichever was larger. Unless otherwise stated, uncertainties are reported at the 1σ level. The anion survival fraction of anion species X, S_X , is a metric used to measure the effects of a laser or reactive gas on the corresponding anion beam. It is defined by dividing the rate $R_{\text{on}}(X)$ of detected ions of species X per second (current measurement or single-ion counting) with the laser or reactive gas in question, by those without $R_{\text{off}}(X)$, so that $S_X = \frac{R_{\text{on}}(X)}{R_{\text{off}}(X)}$. While the anion survival fraction quantifies the effect of a suppression scheme on one molecular anion species, the most relevant factor is the total separation of the two isobars in the same molecular anion system. The decontamination factor (DF) combines all relevant quantifiable mechanisms that suppress an unwanted isobar relative to the isotope of interest, and the instrumental decontamination factor excludes the contribution from chemical separation. In the context of this study, the relevant factors were primarily the anion survival fractions in the ion cooler and differences in the anion formation efficiency in the ion source.

Because of the time constants associated with changing the gas in the ion cooler, determining separate anion survival fractions was only possible for a selected number of buffer-gas experiments. Alternatively, the count rates were directly normalized to the number of spiked atoms in the initial samples (in units of 10^8 atoms). This approach accounts for the combined effects of the ion source and ion cooler on the suppression of the respective radionuclides for a given gas composition and/or pressure.

5.4. Results

5.1. Photodetachment experiments

Mass scans spanning the range from 305 u ($^{238}\text{UFO}_3^-$) to 333 u ($^{238}\text{UF}_5^-$) with and without the 355 nm laser were used to systematically investigate candidate (oxy-) fluoride molecular anion systems for U suppression. As the 355 nm laser has the highest photon energy currently available at ILIAMS, all other lasers can be ruled out for the suppression of all anion species, where no effect of the 355 nm laser on the respective ion current is observed. Figure 5.4.1 shows the result of these scans. Of all the fluoride and oxyfluoride molecular anions of uranium with four or five ligands, only the $^{238}\text{UF}_4^-$ and $^{238}\text{UF}_2\text{O}_3^-$ ion beams were significantly suppressed by the 355 nm laser. The tetrafluoride system was

identified as the best candidate anion system for the selective suppression of uranium isobars, as both low anion formation and suppression via the laser were reproducible across repeated measurements. In contrast, the formation of UF_2O_3^- depends on both fluorine and oxygen availability in the samples, making its output much more susceptible to small changes in the ion source. Furthermore, two unidentified background peaks at 323 u and 326 u further complicate the use of UF_2O_3^- . The minimum of the y-axis in Figure 5.4.1 (and Figure 5.4.5) was chosen so that low-level background from other molecular anions and electronic noise that does not affect the investigation of UF_mO_n^- suppression is not shown.

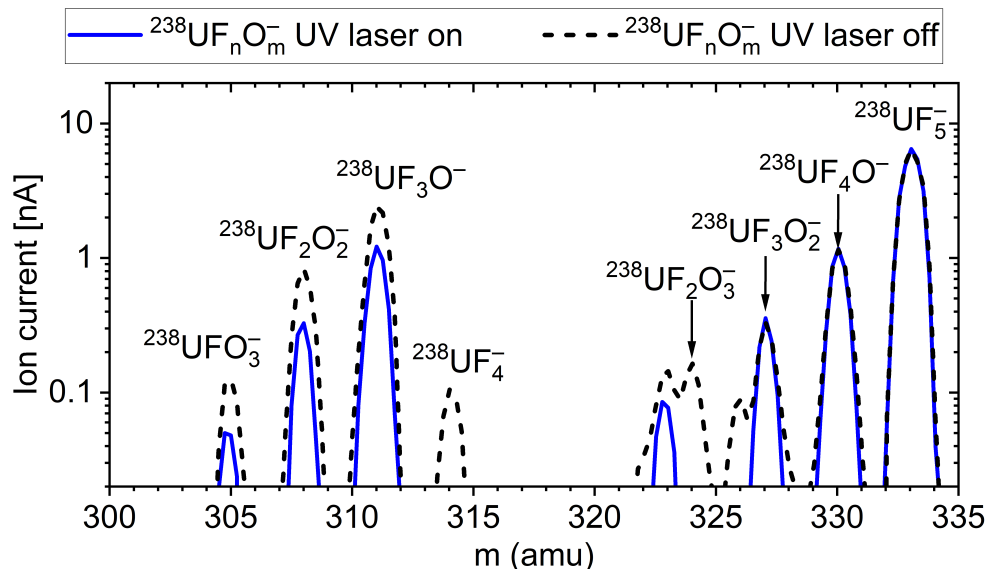


Figure 5.4.1.: Suppression of $^{238}\text{UF}_m\text{O}_n^-$ via laser photodetachment. The anion current transmitted through the ion cooler is shown as a function of mass selected by the ILIAMS injector magnet. The analyzed target was a Vienna-KkU-30 mixed with PbF_2 , and the magnet was scanned from 300 u to 335 u, covering the mass range of uranium (oxy-)fluorides with four and five ligands. Two scans, one with the 355 nm laser on (2 W transmitted laser power, solid blue line) and one with laser off (dashed black line), were performed to identify molecular anion systems suitable for laser photodetachment. A significant reduction in ion current has only been observed for masses 314 u ($^{238}\text{UF}_4^-$) and 324 u ($^{238}\text{UF}_2\text{O}_3^-$), even with this laser providing the highest photon energy (3.5 eV) available at ILIAMS. Non-labeled peaks cannot be assigned to U molecular anions.

Next, the stability of NpF_4^- , PuF_4^- , and AmF_4^- was investigated and compared with that of UF_4^- using the available lasers at VERA: 355 nm, 532 nm, and 637 nm. All lasers were tuned for maximum transmission through the ion cooler. The 355 nm laser delivered 1.8–2.0 W after the ion cooler in our experiments, while the 532 nm laser achieved 5.0–5.9 W and the 637 nm laser 0.5–0.6 W. The corresponding results for the anion survival fractions of the respective tetrafluoride ion species are shown in Figure 5.4.2. For $^{236}\text{U}_4^-$, a combination of low anion survival fraction and low formation rate would require impractically long counting times with the 532 nm and 355 nm lasers turned on. Instead, $^{238}\text{UF}_4^-$ was used to approximate the $^{236}\text{UF}_4^-$ behavior in these experiments. Such an approach may slightly increase the U anion survival fractions, as the anion residence time in the ion cooler has previously been shown to decrease with increasing injected

ion current [Martschini et al. 2017].

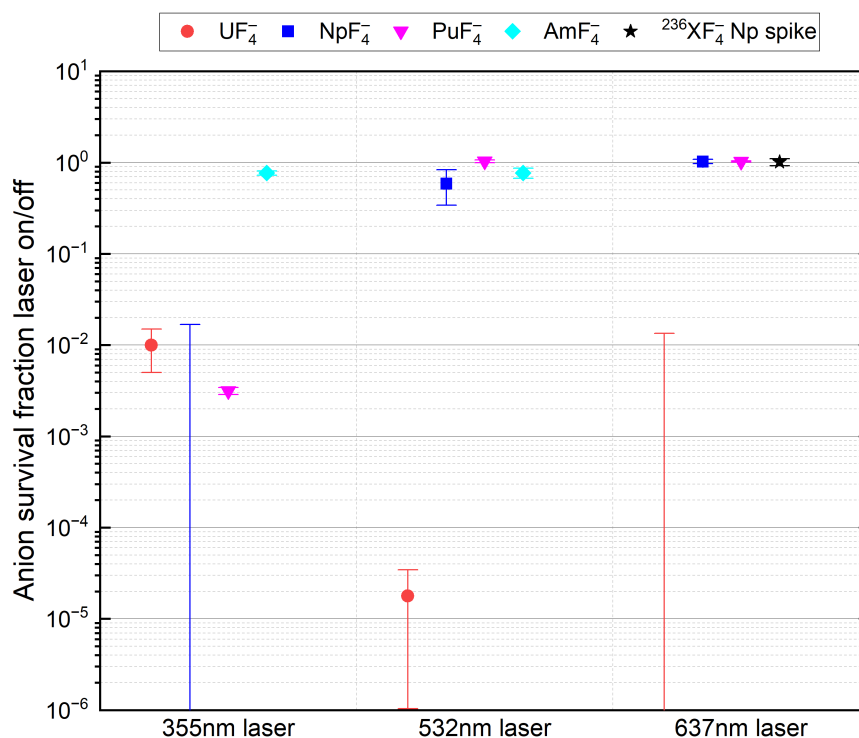


Figure 5.4.2.: The anion survival fractions for the tetrafluoride molecular anions of U, Np, Pu, and Am after the ion cooler are plotted for the 355 nm, 532 nm and 637 nm lasers. The 532 nm laser could provide a strong Np/U separation, but the anion survival fraction of NpF_4^- fluctuated in a range of 0.2 - 0.9. A lower but sufficient and reproducible separation of NpF_4^- and UF_4^- was observed for the 637 nm laser, which allowed a first application to a potential ^{236}Np -spike material (black star). The anion survival fraction for $^{236}\text{Xf}_4^-$ is indistinguishable from that of $^{237}\text{NpF}_4^-$, implying the absence of ^{236}U . While the 355 nm laser provides a promising separation for AmF_4^- and PuF_4^- , no separation was obtained for NpF_4^- and PuF_4^- with any available photon energy.

Overall, the results clearly show that the 355 nm laser is not suitable for separating U, Np, or Pu from each other, as $^{237}\text{NpF}_4^-$ and $^{242}\text{PuF}_4^-$ are suppressed along with $^{238}\text{U}_4^-$. In contrast, the 532 nm laser does not affect $^{242}\text{PuF}_4^-$ but suppresses $^{238}\text{UF}_4^-$ by 4-6 orders of magnitude. Variations in the absolute anion survival fraction for a given molecule when switching lasers are expected, as the photon flux in the ion cooler and the overlap of laser and ion beams change. With no apparent separation scheme for U, Np, and Pu, the 355 nm laser was not optimized for maximum U suppression. Furthermore, the photodetachment cross section might decline after reaching a maximum as has been shown e.g. in the H^- case [McLaughlin et al. 2017]. There is no systematic investigation for UF_4 – but it is possible that at 355 nm the photodetachment cross section is already declining. In combination with a much lower photon flux, these factors are likely the explanation for the higher anion survival fraction of $^{238}\text{UF}_4^-$ at 355 nm and, therefore, at a higher photon energy compared to the 532 nm laser.

For $^{237}\text{NpF}_4^-$, the anion survival fraction with the 532 nm laser exhibited significant variation over time. While it ranged from 0.8 to 0.9 in some experiments, it dropped to 0.235 ± 0.008 in others, with no obvious changes to the experimental setup or operational

parameters. As shown in Figure 5.4.3, the effect scales with the transmitted laser power and is reasonably reproducible within each beamtime for various targets and different sample matrices. The cause for the variation between different beamtimes has not been directly identified but may be the results of a small detachment cross section in combination with variations in effective photon fluence. While the total photon flux itself was almost constant across beamtimes, differences in the overlap between laser and ion beam as well as variations in space-charge-dependent average ion residence times inside the cooler can be significant [Martschini et al. 2017].

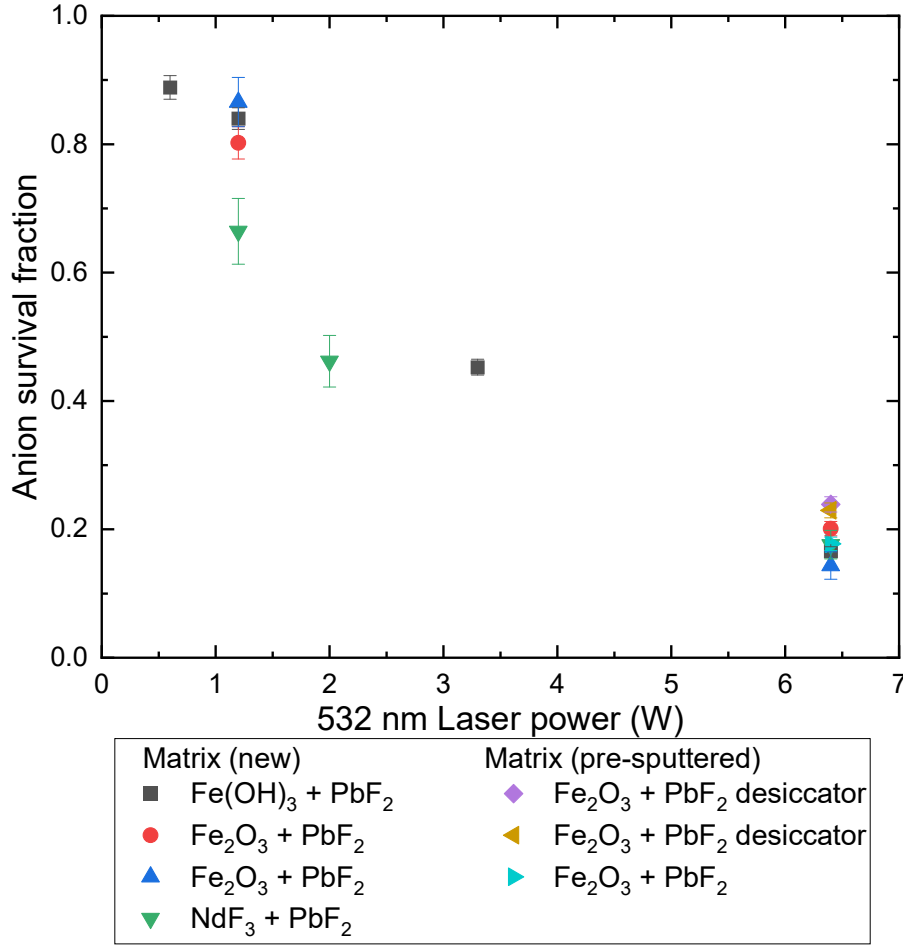


Figure 5.4.3.: NpF_4^- anion survival fractions as a function of 532 nm laser power for different matrices. A moderate suppression that increases with laser power can be seen for all investigated materials. These included samples dried or co-precipitated with iron, both with (Fe_2O_3) or without a calcination step ($\text{Fe}(\text{OH})_3$), mixed with PbF_2 1:9 by mass and a sample with the Np directly co-precipitated in NdF_3 . Fresh samples were also compared to pre-sputtered targets stored in air or a desiccator. If the oxygen content and humidity of the matrix is irrelevant to the observed effect, then it is likely that the effect is a direct photodetachment of NpF_4^- , not an indirect effect by a buildup of oxygen inside the cooler from other suppressed ion species.

Due to this variability in Np suppression, the 532 nm laser was deemed unsuitable for the reliable characterization of a ^{236}Np -spike material. To prevent such partial Np suppression, a 637 nm laser was added to the ILIAMS setup. The measured anion survival fractions at 0.6 W transmitted 637 nm laser power were ~ 1 for $^{237}\text{NpF}_4^-$, ~ 0.1 ,

for the macroscopic $^{238}\text{UF}_4^-$ current, 0.0091 ± 0.0025 for $^{235}\text{UF}_4^-$ (for single ion counting on impurities in an Fe target), and <0.0135 with $^{236}\text{UF}_4^-$ (single ions injected, assuming one count if none was detected with the 637 nm laser on). The viability of $^{235}\text{UF}_4^-$ as a proxy for $^{236}\text{UF}_4^-$ is limited by the co-injection of macroscopic ion currents from other anion species of the same mass. Using a Vienna-KkU + PbF₂ target, ~ 1 nA of $^{238}\text{UF}_4^-$ was measured in a Faraday cup after the ion cooler without lasers, while on mass 311 u, several nA were registered on top of the expected ~ 7 pA $^{235}\text{UF}_4^-$. From the isotopic ratios and the formation rates for oxyfluoride beams in Figure 5.4.1, a large fraction of this ion current is likely $^{238}\text{UF}_3\text{O}^-$ which is not affected by the laser. By contrast, only ~ 30 pA of total ion current was injected alongside $^{236}\text{UF}_4^-$ on the calibration samples. For the 637 nm laser, with its comparatively small effective photon flux, these large differences in ion currents in the ion cooler significantly affect the suppression of different uranium anion species. Consequently, instead of the $^{238}\text{UF}_4^-$ proxy used for the other two lasers, an upper limit for $^{236}\text{UF}_4^-$ is included in Figure 5.4.2. It should be noted that the data on $^{236}\text{UF}_4^-$ was limited by counting time and usable ^{236}U concentrations and is not likely to be orders of magnitude below the ^{235}U and ^{238}U results. With these encouraging results for the calibration samples regarding U and Np separation, the 637 nm laser was also used to screen a ^{236g}Np -spike material produced by irradiation at RIKEN. The anion survival fraction of $^{236}\text{XF}_4^-$ for this material (black star in Figure 5.4.2) is (1.014 ± 0.091) and agreed well within 1σ with that of $^{237}\text{NpF}^{236}$ (1.027 ± 0.054) obtained for the calibration samples. This result indicates that the production of ^{236}Np and chemical separation of its isobar ^{236}U were successful. A more detailed analysis is provided in the Discussion section.

The $^{243}\text{AmF}_4^-$ count rate was only weakly attenuated by the 355 nm and 532 nm lasers, with anion survival fractions of 0.769 ± 0.040 and 0.770 ± 0.098 , respectively. Consequently, experiments at lower photon energies, that is, with the 637 nm laser, were not carried out. The signal reduction is very similar at both photon energies and fluxes; therefore, the direct laser photodetachment of AmF_4^- seems unlikely. Plausible hypotheses include an affected excited state in AmF_4^- or the suppression of other anions injected alongside AmF_4^- which could affect its average residence time and transmission. Comparing the 355 nm $^{242}\text{PuF}_4^-$ anion survival fraction of (0.00315 ± 0.00028) with the (relative) stability of $^{243}\text{AmF}_4^-$, an isobar separation scheme could be implemented to suppress ^{241}Pu or ^{241}Pu when measuring ^{241}Am or ^{242m}Am , respectively.

The effect of superimposing the 355 nm laser with pentafluoride anion beams of Np, Pu, or Am inside the ion cooler is shown in Figure 5.4.4. Count rates were normalized to the number of atoms of each radionuclide added per sample to highlight the differences in anion formation efficiency alongside the laser effect. The overall lower normalized count rates of AmF_5^- compared to PuF_5^- and NpF_5^- , even with the laser off, reflect a significantly lower anion formation efficiency. This effect is consistent with previously reported results [Wiederin et al. 2022; Zhao et al. 2022] and provides a suppression factor of 0.0466 ± 0.0075 relative to PuF_5^- in the ion source. With an anion survival fraction of

0.045 ± 0.032 for AmF_5^- , the 355 nm laser selectively suppressed AmF_5^- further whereas $^{242}\text{PuF}_5^-$ was almost unaffected at an anion survival fraction of 0.829 ± 0.083 . The combined effect of the ion source and ILIAMS resulted in an AmF_5^- decontamination factor of 0.0025 ± 0.0018 relative to PuF_5^- . The ion source output declined over time for all samples, with NpF_5^- (measured first) affected the worst. While there is no reliable way to correct for this drift given the few data points, the $^{237}\text{NpF}_5^-$ and $^{242}\text{PuF}_5^-$ data points both exhibit an exponential decline, and any deviation of the anion survival fractions from 1 is likely to be an artifact of the order of measurement. Dedicating valuable beamtime to repeat this experiment outside the scope of the funded project at a later date was not possible.

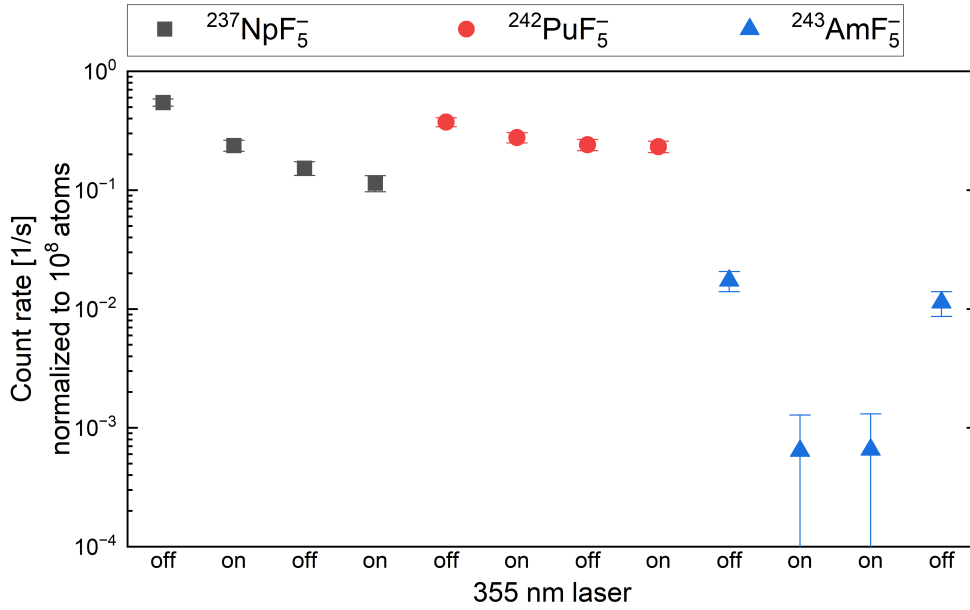


Figure 5.4.4.: The effects of a 355 nm laser (2 W transmitted) on NpF_5^- , PuF_5^- and AmF_5^- . count rates normalized to 10^8 atoms of each spike per sample with laser on and off are shown for individual measurements of 50 s (Np, Pu) or 300 s (Am) per point. All count rates decline from run to run due to an unstable ion source output, but the AmF_5^- is also affected by the 355 nm laser. In combination with the less efficient anion formation a total AmF_5^- decontamination factor of (0.0025 ± 0.0018) relative to PuF_5^- can be achieved. NpF_5^- and PuF_5^- show no relevant additional effect from the laser.

The data presented in Figure 5.4.2 clearly demonstrate that none of the lasers currently available at ILIAMS is suitable for the separation of NpF_4^- and PuF_4^- , as either both are suppressed (355 nm) or there is little to no suppression (532 nm, 637 nm). Switching to the pentafluoride system, that is, NpF_5^- and PuF_5^- , also does not provide a way to separate both elements via photodetachment. Both anion species were unaffected by the 355 nm laser, or the effect was below the uncertainty of the measurement, as shown in Figure 5.4.4. Consequently, any laser with lower photon energy will also be ineffective.

The 532 nm, 637 nm laser, and a Ti:Sa laser with a tunable wavelength of 700-970 nm were used to systematically investigate the selective suppression of mono- and dioxide-molecular anions of U, Np, and Pu, but no exploitable separation scheme could be

identified in the tested photon energy ranges and photon fluxes. The same applies to photodetachment experiments with several oxyfluoride systems, including AnF_2O_2^- , AnFO_3^- , AnF_2O_3^- , AnF_4O^- , and AnF_2O_3^- (An representing U, Np, or Pu) using 355 nm, 532 nm, and 637 nm lasers.

5.4.1. Selective gas reactions

The potential of using selective chemical reactions to suppress either the tetra- or pentafluoride anions of the relevant actinides was investigated by adding 3% O_2 to the He buffer gas of ILIAMS. This mixing ratio was chosen as a starting point based on previous experience with $^{182}\text{HfF}_5^-$ where a 30:1 He: O_2 ratio was identified as the optimal balance between effective chemical isobar suppression and minimizing collisional detachments during ion deceleration [Martschini et al. 2020]. No more advantageous mixing ratio has been identified for actinides to date. Analogous to the photodetachment experiments described above, uranium suppression was the easiest to investigate. With macroscopic beams available for $^{238}\text{UF}_4^-$ and $^{238}\text{UF}_5^-$, the transmitted ion currents as well as any major reaction products formed inside the ion cooler can be measured after the low-energy mass spectrometer of VERA in FC 02 (see Figure 5.3.1). While injecting the respective masses (314 u or 333 u) into the ion cooler, mass scans spanning 290 - 360 u were performed on the beam exiting it. This wide scan range was chosen to identify any oxygen pickup or fluorine detachment reactions for each injected beam. Figure 5.4.5 a) and b) compare the corresponding scans while injecting UF_5^- into the cooler, either filled just with the buffer gas He (a) or He + O_2 (3%) (b). The only peak in the mass spectrum in both cases is at 333 u, so oxygen in the buffer gas does not affect $^{238}\text{UF}_5^-$. In contrast, upon injection of $^{238}\text{UF}_4^-$, the reaction products $^{238}\text{UF}_3\text{O}_2^-$ and $^{238}\text{UF}_4\text{O}^-$ can be detected even with He buffer gas (see Figure 5.4.5 c). The involved oxygen could originate from gas impurities or the breakup of oxygen-containing molecules from other ion species simultaneously injected into the ILIAMS ion cooler. With 3% O_2 in the He buffer gas (see Figure 5.4.5 d), the $^{238}\text{UF}_4^-$ peak was effectively suppressed, while the formation of $^{238}\text{UF}_4\text{O}^-$ was enhanced. Because of the limited sensitivity of the current amplifiers and background from other anion species, only an upper limit in the range of 10^{-2} to 10^{-3} for the anion survival fraction of $^{238}\text{UF}_4^-$ could be derived from this experiment.

To achieve the dynamic range required to quantify the anion survival fraction for $^{238}\text{UF}_4^-$, the entire actinide beamline of VERA was used. With He buffer gas, the ion current was measured in FC L4. For measurements with He + O_2 (3%) buffer gas in the cooler, single-ion counting in the gas-filled ionization chamber was used instead (see Figure 5.3.1). With 5.0 Pa He inside the ion cooler, an $^{238}\text{U}^{3+}$ ion current of (2.85 ± 0.15) pA was registered for $^{238}\text{UF}_4^-$ extracted from a natural uranium target (Vienna-KkU + PbF_2). Conversely, with 5 Pa He + 3% O_2 , the same target only produced (1.83 ± 0.24) cps in the gas-filled ionization chamber. Based on these measurements, the anion survival fraction

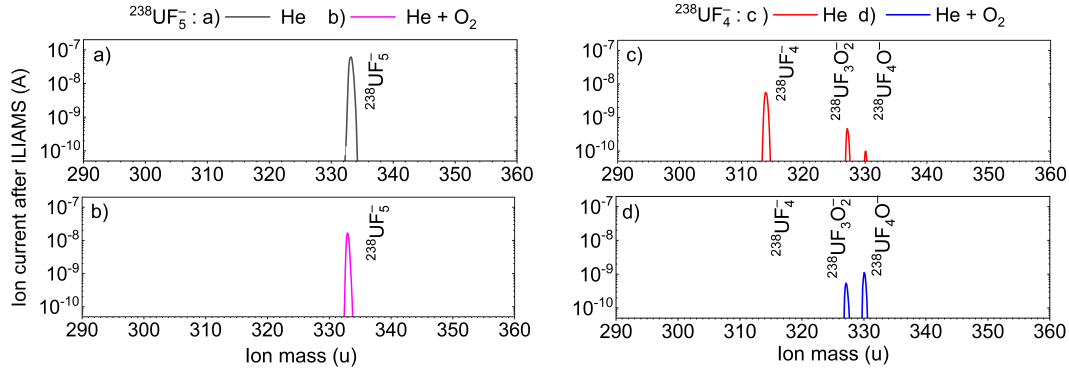


Figure 5.4.5.: The effects of a 355 nm laser (2 W transmitted) on NpF_5^- , PuF_5^- and AmF_5^- . count rates normalized to 10^8 atoms of each spike per sample with laser on and off are shown for individual measurements of 50 s (Np, Pu) or 300 s (Am) per point. All count rates decline from run to run due to an unstable ion source output, but the AmF_5^- is also affected by the 355 nm laser. In combination with the less efficient anion formation a total AmF_5^- decontamination factor of (0.0025 ± 0.0018) relative to PuF_5^- can be achieved. NpF_5^- and PuF_5^- show no relevant additional effect from the laser.

of $^{238}\text{UF}_4^-$ with admixed oxygen can be calculated as $(3.09 \pm 0.44) \cdot 10^{-7}$. Without a reactive gas in the ion cooler, the 532 nm laser strongly suppressed the $^{238}\text{UF}_4^-$ current, resulting in anion survival fractions of 10^{-4} - 10^{-6} (compare Figure 5.4.2). However, the suppression of $^{238}\text{UF}_4^-$ via the oxygen admixture is not enhanced by adding the 532 nm laser at 5.5 W transmitted laser power, as the resulting count rate of (1.59 ± 0.16) cps is compatible within one sigma with the (1.83 ± 0.24) cps without the laser (but 3 % O_2). The 532 nm laser had been observed to suppress $^{238}\text{UF}_4^-$ by 4-6 orders of magnitude in He (see Figure 5.4.2), and no plateau effect is expected for laser photo-detachment [Zhao et al. 2010]. With no additional suppression from the laser observed in the presence of reactive gases, it is therefore likely that $^{238}\text{UF}_4^-$ has already been fully suppressed by the gas reactions. The $^{238}\text{U}^{3+}$ counts that still reached the detector in this experiment could stem from a minute fraction of other U-containing molecular anions at mass 314 u, unaffected by both the 532 nm laser and the oxygen.

Figure 5.4.6 presents the count rates normalized to 10^8 atoms of ^{237}Np or ^{242}Pu added to the respective calibration sample as a function of gas pressure in the ion cooler with 3 % oxygen added to the He buffer gas. The $^{237}\text{Np}^{3+}$ count rates decrease gradually with increasing pressure of the He + O_2 (3 %) gas, reducing the $^{237}\text{Np}^{3+}$ count rate by at least two orders of magnitude for 10.0 Pa compared to the maximum at 3.1 Pa. The $^{242}\text{Pu}^{3+}$ count rate decreased by only 26 % over the same range, in agreement with the expected losses from increased scattering. For $^{237}\text{Np}^{3+}$, no counts could be detected above 7.5 Pa, resulting in upper limits by assuming one count. The difference in upper limits reported for 7.5 Pa and 10.0 Pa is due to differences in available counting time. The increase in uncertainties from 3.1 Pa to 5.0 Pa is driven by counting statistics, as fewer $^{237}\text{Np}^{3+}$ counts reach the detector. The observed behavior demonstrates that admixing O_2 into the ILIAMS buffer gas can be used to selectively suppress NpF_4^- by at least two to three orders of magnitude and UF_4^- even more, while PuF_4^- retains good ion cooler

transmission even at 10.0 Pa He O₂ (3 %).

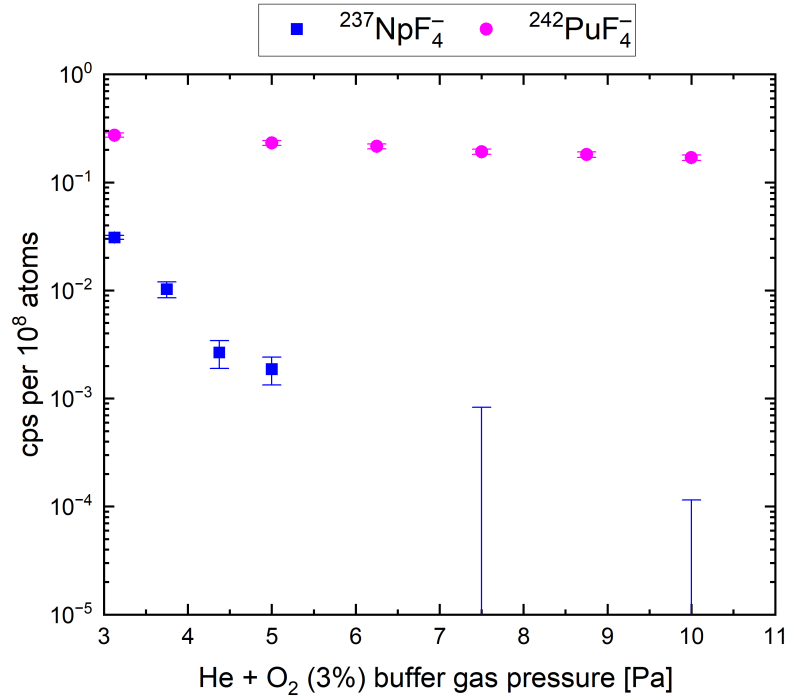


Figure 5.4.6.: Normalized count rates for both $^{237}\text{NpF}_4^-$ and $^{242}\text{PuF}_4^-$ for He+O₂ (3 %) buffer gas pressures ranging from 3.1 Pa to 10.0 Pa. Whereas the $^{242}\text{PuF}_4^-$ transmission is only marginally affected by increasing the pressure, $^{237}\text{NpF}_4^-$ is suppressed by at least two orders of magnitude. For the detected zero counts from NpF₄⁻ at 7.5 Pa and 10.0 Pa + O₂, the upper limits were calculated by assuming a single count, and the difference stems from a shorter counting time at 7.5 Pa.

The actual anion survival fractions for $^{237}\text{NpF}_4^-$ and $^{242}\text{PuF}_4^-$ on calibration samples were determined for one selected pressure (7.5 Pa He versus 7.5 Pa He + O₂ (3 %)) via the respective count rates shown in Table 5.4.1. Alongside these calibration samples, a $^{236}\text{XF}_4^-$ beam extracted from a prototype ^{236g}Np -spike material was also analyzed. When both ^{236}U and ^{236}Np were effectively removed from the ion beam with the He + O₂ buffer gas mix, ^{236}Pu could be measured directly with negligible isobaric interference. Neither $^{237}\text{NpF}_4^-$ nor $^{236}\text{XF}_4^-$ produced any $^{237}\text{Np}^{3+}$ or $^{236}\text{X}^{3+}$ counts with admixed O₂. The upper limits for the anion survival fractions, calculated by assuming one count in the total counting time t , are reported in Table 5.4.1. The He vs. He + 3 % O₂ anion survival fraction for PuF₄⁻ of (0.357 ± 0.017) shown in Table 5.4.1 indicates elevated collisional detachment of PuF₄⁻ on O₂, which could be partly mitigated by more thorough optimization of the ion injection energy and the guide electrode voltage for the different gas compositions. Any losses of $^{242}\text{PuF}_4^-$ anions by admixing O₂ were monitored alongside $^{236}\text{XF}_4^-$ in the same beamtime with reasonable precision; thus, the $^{242}\text{PuF}_4^-$ anion survival fraction can be used as a correction factor for ^{236}Pu in the calculation of the isobaric composition of ^{236}X . The number of ^{236}X atoms in this sample was provisionally estimated from the ratio of the count rates of ^{236}X (prototype Np-spike) and ^{237}Np

(calibration sample) multiplied by the number of ^{237}Np atoms added to the calibration sample at $(1.5 \pm 0.5) \cdot 10^8$ atoms. The ^{236}Np atom concentration of the prototype spike material must be determined more accurately in combination with other methods and will be published elsewhere.

	Calibration sample	Calibration sample	^{236g}Np -spike
Isotope	^{242}Pu	^{237}Np	^{236}X
Setup	$^{242}\text{PuF}_4^- \rightarrow ^{242}\text{Pu}^{3+}$	$^{237}\text{NpF}_4^- \rightarrow ^{237}\text{Np}^{3+}$	$^{236}\text{XF}_4^- \rightarrow ^{236}\text{X}^{3+}$
Count rate He [s^{-1}]	11.74 ± 0.37	9.27 ± 0.43	0.096 ± 0.007
Count rate He + O ₂ (3 %) [s^{-1}]	4.12 ± 0.15	<0.008	<0.0003
Anion survival fraction	0.357 ± 0.017	<0.00090	<0.0034
Atoms per sample [$\cdot 10^9$ at]	(4.809 ± 0.096) (added)	(1.433 ± 0.029) (added)	(0.15 ± 0.05) (estimated)

Table 5.4.1.: Count rates and anion survival fractions for $^{242}\text{PuF}_4^-$ and $^{237}\text{NpF}_4^-$ (calibration sample) and $^{236}\text{XF}_4^-$ (prototype Np-spike) with 7.5 Pa He vs He + O₂ (3%) buffer gas. With all potential isobaric interference suppressed by the admixture of O₂, not a single count of ^{236}Pu could be detected in 3005 seconds, ruling out relevant contamination of the prototype ^{236}Np spike by ^{236}Pu . Upper limits were calculated for the resulting anion survival fractions where no counts were registered ($^{237}\text{NpF}_4^-$ and $^{236}\text{XF}_4^-$ with admixed O₂), while all other uncertainties were derived from counting statistics. The number of ^{236}X atoms in the prototype Np spike sample was estimated from the ratio of the count rates with He of ^{236}X and ^{237}Np .

5.5. IV. Discussion

5.5.1. Characterization of the ^{236g}Np spike

The gas-suppression data for the prototype spike shown in Table 5.4.1 can be used to constrain the potential ^{236}Pu contribution to mass 236 (^{236}X) in this material. The ratio of the count rates on mass 236 for He and He + O₂ (assuming one instead of no counts in 3005 s), when corrected for the anion survival fraction of PuF_4^- , resulted in an upper limit of $<0.97\%$ ^{236}Pu on mass 236 in the $^{236}\text{XF}_4^-$ anion beam. Considering that PuF_4^- forms up to an order of magnitude more efficiently than NpF_4^- [Wiederin et al. 2022; Zhao et al. 2022], the actual limit for the ^{236}Pu content in the spike is even lower. Differences in anion formation efficiency are highly dependent on factors such as the conditions within the ion source, and can only be compared and evaluated within the same measurement [Wiederin et al. 2022]. Based on the calibration sample data for ^{237}Np and ^{242}Pu using only the He buffer gas shown in Table 5.4.1, the formation of PuF_4^- can be calculated to be 3.77 ± 0.24 times higher than that of NpF_4^- , which would result in an upper limit for the ^{236}Pu content of 0.26 %. With no registered counts in 3005 s, the present He $\pm$ O₂ ^{236}X anion survival fraction was only limited by the available counting time. Therefore,

the present limit for ^{236}Pu impurities is most likely to be improved further in the future, assuming the same quality of the produced material.

The anion survival fraction measured for ^{236}X for the prototype spike material ($S_{236\text{X}} = 1.014 \pm 0.091$) for the 637 nm laser was compatible with that of Np ($S_{\text{Np}} = 1.027 \pm 0.055$), whereas the anion survival rate of $^{236}\text{UF}_4^-$ was at least two orders of magnitude lower ($S_{236\text{U}} \leq 0.0135$). With ^{236}Pu already found to be negligible by the O_2 admixture measurement presented above, this result indicates that the prototype spike material predominantly consists of ^{236}Np . Quantifying a potentially small ^{236}U impurity is less straightforward than a direct and interference-free ^{236}Pu measurement. With a negligible Pu contribution and defining F_{U} as the uranium fraction of mass 236, the neptunium fraction can be expressed as $F_{\text{Np}} = 1 - F_{\text{U}}$. Using the anion survival fractions S_{Np} for Np and the upper limit for the anion survival fraction of U, $S_{\text{U,max}} = 0.0135$, the measured anion survival fraction for mass 236 of the spike material can be expressed as:

$$S_{236\text{X}} = (F_{\text{U}} \cdot S_{\text{U,max}}) + [(1 - F_{\text{U}}) \cdot S_{\text{Np}}]$$

Consequently, F_{U} can be calculated as

$$F_{\text{U}} = \frac{(S_{236\text{X}} - S_{\text{Np}})}{(S_{\text{U,max}} - S_{\text{Np}})}$$

This relation was used to estimate the maximum ^{236}U contribution, $F_{\text{U,max}}$ such that $S_{236\text{X}}$ is still consistent with the anion survival fraction of neptunium within 1σ uncertainty when using the conservative approach of replacing S_{Np} with the lower bound of its uncertainty interval, $S_{\text{Np,max}} = 1.082$. This results in a maximum ^{236}U contribution of 14.9 % to the detected $^{236}\text{X}^{3+}$ from the prototype spike material. This limit could be significantly improved by increasing the precision of the anion survival fraction data for the spike material, which will be possible once more material becomes available. We understood that this was a major limitation, but at this stage of the spike development, a compromise had to be struck between improving the characterization and ensuring enough material was left for validation and first applications. During the typical sample preparation for actinide measurements at VERA, U is separated from Np, whereas Pu (mostly) remains with Np [Hain et al. 2022]. Consequently, potential ^{236}U impurities introduced by the spike into the environmental sample are further chemically reduced in the final Np fraction, typically by a factor of 100 [Goodall et al. 1999; López-Lora et al. 2019b]; thus, it is small compared to the uncertainty of the AMS measurement. The uncertainty of the uranium content thus mainly results in an increased uncertainty of the ^{236}gNp concentration. The Pu contribution of $<0.26\%$ is already negligible even without further chemical separation.

5.5.2. Feasibility of the $^{238}\text{U}/^{238}\text{Pu}$ separation scheme for environmental samples

The U/Pu separation achieved with ILIAMS also brings ^{238}Pu analysis by AMS within reach. An admixture of 3% O_2 to the buffer gas reduces the anion survival fraction of UF_4^- on a Vienna KkU + PbF_2 uranium target to $(3.09 \pm 0.44) \cdot 10^{-7}$ while PuF_4^- is almost unaffected at (0.357 ± 0.017) . The anion formation probabilities provide an additional two orders of magnitude of UF_4^- suppression in the ion source relative to PuF_4^- [Wiederin et al. 2022; Zhao et al. 2022]. Therefore, an instrumental U decontamination factor of $<10^{-8}$ was achieved when the ion source and ILIAMS effects were combined. Although it is likely that the moderate PuF_4^- losses observed with O_2 could be reduced further, this would have to be the subject of dedicated experiments. In combination with basic chemical purification, this decontamination factor could be sufficient for AMS measurements of ^{238}Pu for some sample types. Peat, for example, generally has very low U concentrations in the ng/g range. A 25 g peat sample will contain roughly $6 \cdot 10^{13}$ atoms ^{238}U , and hence, would be a promising candidate matrix. With an estimated total UF_4^- decontamination factor of 10^{-8} to 10^{-9} , this would lead to a background limit of 10^5 - 10^6 atoms per sample before chemical U suppression, which typically further removes U by factor of 100 from the Pu fraction [Goodall et al. 1999; López-Lora et al. 2019b]. The total detection efficiency for $^{238}\text{UF}_5^-$ at VERA is below $3 \cdot 10^{-3}$ [Kern et al. 2022], and $^{238}\text{UF}_4^-$ forms another two orders of magnitude less efficiently whereas Pu forms tetra- and pentafluoride anions with comparable efficiency [Wiederin et al. 2022; Zhao et al. 2022]. Taken together, we estimated less than 1 count of ^{238}U would be expected during the measurement of ^{238}Pu in 25 g peat samples with ILIAMS, assuming complete consumption of the material.

In this section, the feasibility of determining ^{238}Pu concentrations in real environmental samples is discussed. These samples, including the reference materials IAEA-381 (Irish Sea water), IAEA-385 (Irish Sea sediment), and an Austrian peat bog sample were recently analyzed at VERA in a different context, with actinides, including ^{238}U and ^{239}Pu relevant here, extracted as oxide anions. Again, an instrumental U/Pu decontamination factor of 10^{-8} using ILIAMS ($\text{He} + \text{O}_2$ buffer gas) in the tetrafluoride anion system was assumed. The difference between the formation of monoxide and tetrafluoride anions of U and Pu is accounted for by the anion formation ratio in the decontamination factor. Table 5.5.1 contains the results of these estimates for the Pu fractions, after U was chemically separated.

The average $^{238}\text{U}^{3+}$ ion currents and $^{239}\text{Pu}^{3+}$ count rates from the previous measurement with no isobar separation scheme, $R_{\text{off}}(^{238}\text{U})$ and $R_{\text{off}}(^{239}\text{Pu})$, were used as a starting point to estimate the interfering ^{238}U count rate $R_{\text{on}}(^{238}\text{U})$ in an ILIAMS measurement of ^{238}Pu with the separation scheme applied. $R_{\text{off}}(^{238}\text{U})$ was multiplied by the uranium decontamination factor (ILIAMS + anion formation effects) of $<10^{-8}$, i.e., $R_{\text{on}}(^{238}\text{U}) = R_{\text{off}}(^{238}\text{U}) \cdot 10^{-8}$. The corresponding ^{238}Pu count rate, $R_{\text{on}}(^{238}\text{Pu})$, can be

calculated from the measured ^{239}Pu count rate for the respective sample and the expected $^{238}\text{Pu}/^{239}\text{Pu}$ atomic ratio. For the two reference materials, the atomic $^{238}\text{Pu}/^{239}\text{Pu}$ ratios were calculated from the certified massic activities [Povinec et al. 2002] and their respective half-lives. Then, the expected ^{238}Pu count rate for an ILIAMS with He + 3% O_2 buffer gas is:

$$R_{\text{on}}(^{238}\text{Pu}) = R_{\text{on}}(^{239}\text{Pu}) \cdot \frac{N(^{238}\text{Pu})}{N(^{239}\text{Pu})}$$

The expected interference from ^{238}U reported in Table 5.5.1 is the ratio $R_{\text{on}}(^{238}\text{U})/R_{\text{on}}(^{238}\text{Pu})$.

For the Austrian peat bog sample, a $^{239}\text{Pu}/^{238}\text{U}$ count rate ratio of $(2.03 \pm 0.21) \cdot 10^{-3}$ was measured in the Pu fraction after chemical separation of U [Hain et al. 2022]. There is no information on ^{238}Pu for this peat bog, but the measured $^{240}\text{Pu}/^{239}\text{Pu}$ ratio showed a clear global fallout signature of (0.1786 ± 0.0093) . A Polish peat bog sample influenced mainly by global fallout (A1 204, Wisla (S)) [Ketterer et al. 2004] was used as a proxy. For this sample, ^{238}Pu , $^{239+240}\text{Pu}$ activities, and the $^{239}\text{Pu}/^{240}\text{Pu}$ atom ratio are available so that, with the respective half-lives, the $^{238}\text{Pu}/^{239}\text{Pu}$ atom ratio and the expected ^{238}U interference could be calculated analogously to the reference materials. The anticipated ^{238}U interference for an ILIAMS ^{238}Pu measurement of the peat bog sample was calculated as $\sim 1\%$ of the inferred ^{238}Pu count rate. This would be considered acceptable, as it is below the typical uncertainty for actinide AMS measurements.

The $^{238}\text{Pu}/^{239}\text{Pu}$ ratio of the Chernobyl-influenced sample A0 224, Trzcianka (NE) from the same publication [Ketterer et al. 2004], was more than four times higher than that of A1 204. Therefore, the proposed approach is expected to yield even better accuracy and robustness for peat bog samples affected by the Chernobyl accident, assuming that the natural ^{238}U concentration in the matrix is comparable.

However, for seawater samples, the ^{238}U concentration is on the order of $3\text{ }\mu\text{g/kg}$ [Guidez et al. 2016]. Even for the IAEA-381 material with elevated concentrations of anthropogenic actinides, a ^{238}U interference of $\sim 25\%$ would significantly distort the ^{238}Pu result. This means that the suppression achieved by ILIAMS is not yet sufficient to analyze ^{238}Pu concentrations in ocean water. The IAEA-385 sediment sample is also expected to suffer from considerable interference, close to 30% .

A recent publication showed that there is room for significant improvements in the chemical separation of U and Pu. Using a TK200 resin, chemical U suppression by a factor of $1.81 \cdot 10^9$ has been reported [Peng et al. 2025] which would be an improvement of at least six orders of magnitude over the chemical U/Pu separation used to date at VERA. On the other hand, the U/Pu separation factor achievable with ILIAMS is two orders of magnitude higher than that reported for the C_2H_4 gas reaction cell in the same publication. Combining the new TK200 sample preparation with ILIAMS could achieve a total decontamination factor of at least 10^{-16} . In this case, the ^{238}Pu concentration

Sample	$^{239}\text{Pu}/^{238}\text{U}$ (measured)	$^{238}\text{Pu}/^{239}\text{Pu}$ (calculated)	Est. ^{238}U interference with ILIAMS
IAEA-381 100 mL	$(2.89 \pm 0.28) \cdot 10^{-5}$	$(3.02 \pm 0.30) \cdot 10^{-3}$ [50]	$\sim 25\%$
IAEA 385 1 g	$(9.413 \pm 0.045) \cdot 10^{-5}$	$(3.30 \pm 0.36) \cdot 10^{-4}$ [51]	$\sim 30\%$
Austrian peat bog 28.7 g	$(2.03 \pm 0.21) \cdot 10^{-3}$	$(6.64 \pm 0.76) \cdot 10^{-4}$ [52]	$< 1\%$

Table 5.5.1.: Estimates for the interference of $^{238}\text{U}^{3+}$ ions on $^{238}\text{Pu}^{3+}$ count rates. These estimates have been calculated from previously measured Pu samples ($^{239}\text{Pu}/^{238}\text{U}$ count rate ratios), $^{238}\text{Pu}/^{239}\text{Pu}$ atom ratios calculated from published data and an instrumental U decontamination factor of 10^{-8} relative to Pu, which combines the effects of 3 % O_2 gas in the ILIAMS ion cooler and the low formation rate of $^{238}\text{UF}_4^-$ in the ion source. For the two reference materials IAEA-381 and IAEA-385, measured ^{238}Pu data would still be significantly distorted by ^{238}U interference, and further improvements of either the instrumental or chemical U suppression would be required. The ^{238}U interference on the peat bog sample on the other hand would already be well below typical measurement uncertainties.

rather than the isobaric interference from ^{238}U would be the limiting factor. Overall, estimates of the expected ^{238}U interference in ^{238}Pu measurements using both ILIAMS and suitable chemical separation support the conclusion that measuring ^{238}Pu with AMS in environmental samples is well within reach. The overall sensitivity of the ILIAMS approach to ^{238}Pu is yet to be determined in dedicated experiments.

5.5.3. Feasibility of the $^{241}\text{Am}/^{241}\text{Pu}$ separation schemes for environmental samples

To demonstrate the potential for environmental applications of the Am/Pu isobar separation scheme with ILIAMS, the feasibility of measuring environmental ^{241}Pu emitted by the three most important sources (the Chernobyl and Fukushima accidents and nuclear weapons fallout) was investigated. As shown in Figure 5.4.4, the combined effects of the different anion formation rates and anion survival fractions with the 355 nm laser in the pentafluoride system yielded a ^{241}Am decontamination factor of (0.0025 ± 0.0018) relative to ^{241}Pu . This decontamination factor has been derived in Section 3.1 based on the anion survival fractions with the 355 nm laser and the difference in anion formation rate for PuF_5^- and AmF_5^- as shown in Figure 5.4.4. The expected ^{241}Am interference in a ^{241}Pu measurement is then a function of the $^{241}\text{Pu}/^{241}\text{Am}$ ratio in the measured sample, which in turn is predominantly a function of sample age, as ^{241}Pu ($t_{1/2} = 14.3$ yrs) decays into its longer-lived progeny nuclide ^{241}Am ($t_{1/2} = 432.6$ yrs). Reactor material builds up ^{241}Am prior to release, as ^{241}Pu is produced and decays during operation. By contrast, in nuclear weapons, it can be assumed that ^{241}Pu is predominantly produced during the explosion, and then the in-growth of ^{241}Am begins. In the following, an initial assessment of the feasibility of the proposed approach using the presented Am/Pu isobar

separation scheme for the measurement of ^{241}Pu is discussed on the basis of reported Chernobyl release data of 0.18 PBq ^{241}Pu and 0.00016 PBq ^{241}Am [Sich 1994]. Using this elevated ^{241}Am ratio as a starting point for all three source terms considered here is a conservative approach.

Figure 5.5.1 plots this expected isobaric ^{241}Am interference on ^{241}Pu measurements using the $^{241}\text{Pu}/^{241}\text{Am}$ ratios calculated over a range of 80 years and the decontamination factor for AmF_5^- relative to PuF_5^- using the 355 nm laser. After 14 years (which would in the year 2025 correspond to the age of the Fukushima reactor accident), the expected interference is $(0.25 \pm 0.18) \%$ of the mass 241 counts, while after 39 years (Chernobyl accident), it would be $(1.4 \pm 1.0) \%$. For the age range of global fallout from atmospheric nuclear weapons testing of 61-80 years (again in 2025), the large uncertainty of the decontamination factor impedes a clear evaluation. For the last atmospheric tests, the 1σ range for the expected ^{241}Am interference is 1.2 %- 7.5 %, while for the oldest tests, the respective range is 3.2 %- 19.7 %.

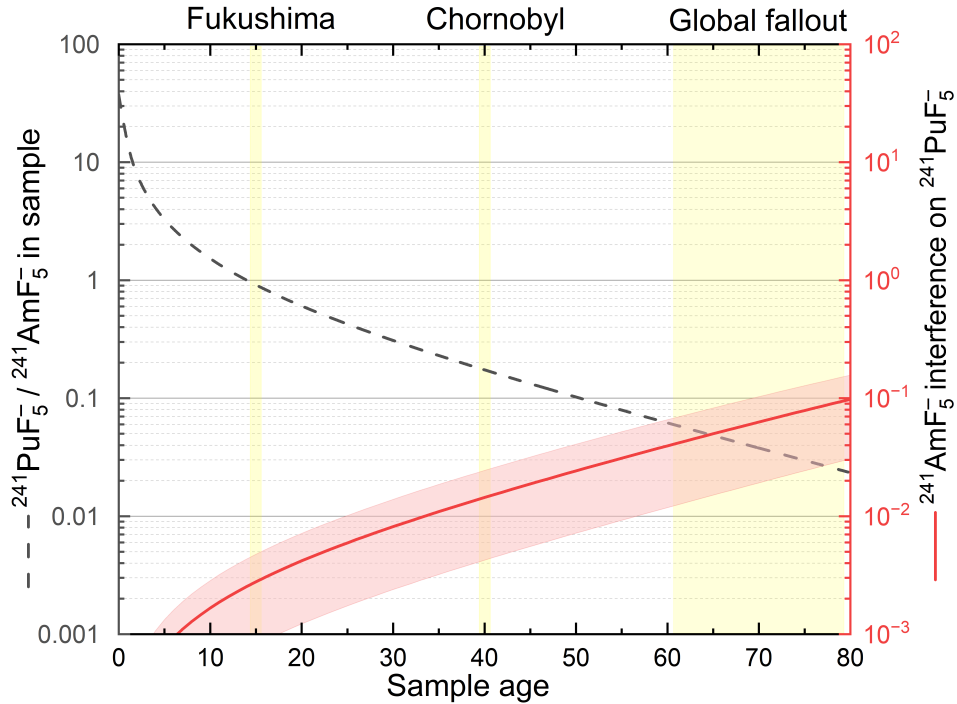


Figure 5.5.1.: The expected relative interference from the isobar ^{241}Am in ^{241}Pu measurements using the ILIAMS separation scheme as a function of sample age. The $^{241}\text{Pu}/^{241}\text{Am}$ atom ratio rapidly falls over time as ^{241}Pu ($t_{1/2}=14.3\text{ yrs}$) decays into ^{241}Am (dashed black line) using Chernobyl data as a starting point [Sich 1994]. Combining the suppression from the 355 nm laser and the lower anion formation rate, ^{241}Am to ^{241}Pu decontamination factor is (0.0025 ± 0.0018) . The solid red line shows the expected interference of ^{241}Am in the measurement of ^{241}Pu as a function of the changing isobaric composition over time. The uncertainty range was calculated from the upper and lower limits for the combined ^{241}Am suppression factor. The relevant ages for Fukushima, Chernobyl and Global fallout releases are indicated by yellow areas.

For both the Fukushima and Chernobyl age ranges, the ^{241}Am suppression achieved would already be sufficient for the reliable interpretation of the ratio for source term

identification. To accurately evaluate the expected ^{241}Am interference for older samples, such as those influenced by global fallout, the ^{241}Am decontamination factor must be quantified with higher precision.

In any case, for most environmental samples, counting statistics on ^{241}Pu will likely limit measurement sensitivity and efficiency because ^{241}Pu decays before significant interference from ^{241}Am has to be expected even with ILIAMS.

As shown in Figure 5.4.2, an inverse isobar separation scheme, whereby $^{241}\text{PuF}_4^-$ is suppressed relative to $^{241}\text{AmF}_4^-$, can be implemented in the tetrafluoride system using the same 355 nm laser that can be used to suppress AmF_5^- relative to PuF_5^- in the pentafluoride system. The anion survival fraction of AmF_4^- with this laser is (0.769 ± 0.040) whereas that of PuF_4^- is only $(3.15 \pm 0.28) \cdot 10^{-3}$. The formation of AmF_4^- is up to an order of magnitude more efficient than that of PuF_4^- [Wiederin et al. 2022; Zhao et al. 2022], further improving the decontamination factor of PuF_4^- relative to AmF_4^- . Because the same instrumentation was used and both tetra- and pentafluoride molecular anions of Am and Pu were produced from the same targets, these two isobar separation schemes could be implemented sequentially during the same beamtime. This means that an interference-free measurement of ^{241}Am using the tetrafluoride anion system, and the 355 nm laser could provide the data needed to calculate a correction factor for the ^{241}Am interference on ^{241}Pu data obtained in the pentafluoride system. At the very least, this approach could be used to identify samples for which the $^{241}\text{AmF}_5^-$ decontamination factor can be assumed to be sufficient if a quantitative correction proves elusive.

The anion survival fraction could act as an indicator for the $^{241}\text{Pu}/^{241}\text{Am}$ ratio in the sample. The variations in anion survival fractions and the low counting statistics for older samples are likely too large for exact dating; however, attributing a material to either Fukushima (low ^{241}Am , high anion survival fraction) or global fallout (almost no ^{241}Pu , low anion survival fraction) could be attainable. This strategy requires dedicated experiments, including evaluating the use of calibration samples for adjusting the baselines to experimental conditions similar to what is done in AFIA measurements [Wiederin et al. 2022].

5.5.4. Present limitations

In these first experiments, a limitation of the status of actinide isobar separation with ILIAMS is the comparably low attainable photon flux of the 637 nm test laser employed for investigating the UF_4^- suppression. As the anion survival rate in ILIAMS depends on the product of the cross section, photon flux, and interaction time, either more laser power or a photon energy closer to the 532 nm laser (but low enough to not affect NpF_4^-) where the detachment cross section might be higher could lead to a strong enhancement in suppression in the future. Longer measurements on several samples with a higher concentration of ^{236}U to obtain reasonable counting statistics would further improve the

upper limit for ^{236}U suppression, but this must be balanced with the risk of contaminating laboratories and the ion source, as well as cross-talk on low-concentration samples in the same measurement. The upper limit for the ^{236}U impurity was clearly dominated by the precision of the measured anion survival fraction of the spike material.

5.6. Conclusions

We succeeded in establishing separation schemes for actinide isobars by combining different operating modes of ILIAMS with AMS. A 637 nm laser was used to suppress UF_4^- by at least two orders of magnitude, while both NpF_4^- and PuF_4^- remained unaffected. Adding 3 % O_2 to the ILIAMS buffer gas can be used to suppress UF_4^- by 7 and NpF_4^- by two orders of magnitude, which allows the direct detection of the unaffected PuF_4^- .

These two isobar separation schemes have been applied to the characterization of a prototype ^{236}Np spike material produced from irradiated Th foils, demonstrating upper limits for isobaric contamination of $<0.26\%$ for ^{236}Pu and $<14.9\%$ for ^{236}U . The extreme scarcity of the prototype spike material limited the amount available for characterization; therefore, the large ^{236}U upper limit was dominated by counting statistics.

It can be assumed that these limits will be significantly improved if the spike material becomes more accessible. Based on the preliminary results from the present study, we can conclude that ^{236}X of the produced pilot spike material consists of $(92.5 \pm 7.5)\%$ ^{236g}Np . With no indication of isobaric interference in these measurements, the prototype Np spike material left over from the analysis with ILIAMS can now be used to normalize ^{237}Np data from a first set of environmental samples and reference materials. The next phase in the development of an isotopic Np spike would have to focus on improving the ^{236}Np yields to produce sufficient material for distribution in the scientific community, which, as a side effect, would also improve the isobaric characterization of mass 236 through reduced uncertainties.

The analytical tools presented in this study can also be applied to characterize ^{236}Np materials produced by alternative irradiation schemes, either previously implemented [Jerome et al. 2014] or entirely new. A promising strategy could be to combine a high-yield approach, such as the $^{238}\text{U}(\text{p},3\text{n})^{236g}\text{Np}$ reaction, which reaches a cross-section of $\sim 80\text{ mb}$ at 20 MeV proton energy [Ageev et al. 1987], with a technique for isotopic purification of ^{236g}Np and the analytical capabilities presented here for the characterization of the isobaric composition to achieve both the volume and the quality required for a wider adoption of such a material in the (A)MS community.

The additional separation schemes introduced here could enable or aid source-term identification based on $^{241}\text{Pu}/^{241}\text{Am}$ or $^{238}\text{Pu}/^{239}\text{Pu}$ isotope ratios using ILIAMS and AMS. Our estimates show that ^{238}Pu analysis in samples with low ^{238}U content, such as peat samples, could be performed with routine chemical U/Pu separation, whereas for samples with high ^{238}U concentrations, further optimization of the U decontamination factor

is still required. The selective suppression schemes for $^{241}\text{AmF}_5^-$ and $^{241}\text{PuF}_4^-$ could improve and simplify the analysis of ^{241}Pu or $^{241}\text{Pu}/^{241}\text{Pu}$ ratios as age-based emission source fingerprints.

The Pu and Am isobar separation schemes presented in this study can also have other applications. In recent years ^{242m}Am with a half-life of 141 years has gained some interest for the analysis of hot particles from the Chornobyl accident [Bosco et al. 2021]. While the secondary ion mass spectrometry with resonant laser ionization setup used for these ^{242m}Am measurements is a powerful analytical technique ideal for hot particles, it is less suited for environmental materials with a more dilute signal, such as the surrounding material in which such hot particles are embedded. An ILIAMS/AMS approach based on the $\text{AmF}_4^-/\text{PuF}_4^-$ separation scheme could be developed as a complementary method to measure the isotope of interest ^{242m}Am free from interference from ^{242}Pu .

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6. Characterization and first application of a new ^{236}Np spike for (A)MS measurements of ^{237}Np

6.1. Abstract

The anthropogenic radionuclide ^{237}Np has excellent potential as an environmental tracer, complementing more established anthropogenic actinide tracers such as $^{236}\text{U}/^{238}\text{U}$ or $^{239,240}\text{Pu}$. A major limitation in quantitatively measuring ^{237}Np concentrations by Accelerator Mass Spectrometry (AMS) has been the unavailability of sufficiently pure isotopic spike material for normalization of ^{237}Np counting results. A new ^{236}Np -spike material has been produced via the $^{232}\text{Th}(^7\text{Li},3\text{n})^{236}\text{Np}$ reaction, and its isotopic and isobaric composition has been characterized at the Vienna Environmental Research Accelerator (VERA). $(1.64 \pm 0.14) \cdot 10^9$ atoms ^{236}Np with a $^{236g}\text{Np}/^{237}\text{Np}$ ratio of 6.93 ± 0.27 have been produced. The ^{236}Np normalization has been validated using the IAEA-381 and IAEA-385 environmental reference materials, as well as a ^{237}Np dilution series in deep seawater. The ^{236}Np -normalized data reproduced the nominal values for the ^{237}Np concentrations within 1σ for the dilution series, whereas the complementary ^{242}Pu normalization was significantly below the nominal values ($2-17\sigma$) for all but one sample in the dilution series. First results from the analysis of environmental samples using the ^{236}Np -spike indicate a different vertical distribution of Pu and Np in peat, while seawater samples collected near the Fukushima Daiichi Nuclear Power Plant showed no influence of the ALPS-treated water releases on ^{237}Np concentrations. For the new Zurich sea water intercomparison sample (ZSW), a ^{237}Np concentration of $(9.50 \pm 1.2) \cdot 10^6$ at/kg can be reported. The new ^{236}Np -spike material has significantly outperformed the non-isotopic normalization. Remaining challenges due to limited availability and a considerable ^{237}Np co-production need to be addressed by scaling up production.

6.2. Introduction

Human nuclear activities have produced considerable amounts of ^{237}Np , a radionuclide with (2.144 ± 0.007) Ma half-life [Basunia 2006]. Nuclear weapons testing distributed about 1500 kg [Lindahl et al. 2005] with further releases mainly from reprocessing plants

or reactor accidents. Today, ^{237}Np is considered the second-most-abundant anthropogenic actinide in the environment, after ^{239}Pu [Kelley et al. 1999]. Nevertheless, the analysis of ^{237}Np has been largely neglected for decades [Thompson 1982], due to the analytical challenges involved at typical environmental concentrations. Accelerator Mass Spectrometry (AMS) would be ideally suited for this task, as it combines very high abundance sensitivity, efficient rejection of other matrix elements in bulk samples, and the ability to count individual ^{237}Np atoms free from molecular background or tailing from the primordial ^{238}U . However, as a relative detection method, AMS cannot directly determine absolute ^{237}Np concentrations from ^{237}Np count rates. Chemical yields, ionization efficiencies, ion-optical transmissions, and other factors may vary significantly between samples, beamtimes, or even within a measurement. Furthermore, the material of an AMS sample is generally not used up during a single measurement, and the sputtered fraction is poorly quantifiable. Consequently, there is no straightforward relation between radionuclide concentrations in a sample and the corresponding events in the AMS detector. The established solution to this problem of normalization in AMS is measuring relative to another, typically abundant (so either stable or primordial, e.g., ^{238}U for ^{236}U measurements), isotope of the same element. If no abundant isotope can be used, a known quantity of a different isotope of the same element – an isotopic spike – can be added to the sample and measured alongside the isotope of interest. Then, the number of atoms of the isotope of interest can be calculated from the measured isotopic ratio and the ratio of added-to-detected spike material. For Np, no stable isotope exists, and no sufficiently pure isotopic spike for mass spectrometry (MS) has been generally available [Jerome et al. 2017]. While ^{236}Np , which has a suitable half-life and no abundant isobar, is an obvious choice for an Np-spike. This isotope has been produced in the past (see [Jerome et al. 2017; Jerome et al. 2014] for an overview) but the resulting materials have typically exhibited high $^{237}\text{Np}/^{236}\text{Np}$ atom ratios such as ~ 4.5 in Efurd et al. 1991 [Efurd et al. 1991]. Because some of these experiments explicitly aimed to produce ^{236}Pu by irradiating ^{236}U , isobaric interference cannot be assumed negligible. A ^{236}Np material had been used for ICP-MS studies of Np in the 2000s [Kenna 2002, 2009]. After completion of the experimental work for the present study, a new ^{236}Np -spike material has been announced by the US Department of Energy [National Isotope Development Center 2025]. No characterization data detailing the concentrations of ^{236}Np , co-produced ^{237}Np , as well as isobaric and other contaminations have been published at the time of writing this paper.

The use of a non-isotopic spike, such as ^{242}Pu for ^{237}Np [Chen et al. 2002; Röllin et al. 2009], is generally less precise and less reliable than using a well-characterized isotopic spike, and data evaluation is also more complex. In this approach, correct normalization relies on chemical sample preparation without elemental fractionation between Np and Pu, and on correcting for ionization-yield or ion-optical transmission differences between the isotope of interest (^{237}Np) and the spike (^{242}Pu). The key to fulfilling the first requirement has been careful adjustment to the same oxidation state, so that Np and Pu

behave identically throughout the sample preparation [Qiao et al. 2010]. The reliability of the chemical sample-preparation procedure is then demonstrated using artificial samples or reference materials, assuming that all subsequent unknown environmental samples will behave analogously. Several publications over the last decade have significantly improved this approach for seawater samples [López Lora 2019; López-Lora et al. 2019a,b]. External $^{237}\text{Np}/^{242}\text{Pu}$ standards can provide a correction factor to account for Np/Pu fractionation during the AMS measurement, either in the ion source or due to differences in ion-optical transmission. For unknown samples, it is impossible to quantify, or even reliably identify, a normalization error using this approach. As a consequence, valuable data sets with unexpected results could be rejected due to suspected Np/Pu fractionation or, conversely, incorrect ^{237}Np data might be, or even have been published.

A new ^{236}Np material has been developed and produced in small-scale test runs using the $^{232}\text{Th}(^7\text{Li},3\text{n})^{236}\text{Np}$ nuclear reaction with the aim of minimizing ^{237}Np co-production [Hayakawa et al. 2019]. Several investigations have been completed or are ongoing regarding this and other reactions that occur simultaneously in the same irradiation experiments [Nagai et al. 2025; Nakajima et al. 2026; Teranishi et al. 2023]. In parallel, the analytical capabilities have been developed to address isobaric interference to be able to characterize mass 236 of the produced material, as presented in two recent works [Wiederin et al. 2022, 2026b] (Chapters 4 and 5). In the latest publication, the upper limit for ^{236}Pu interference on mass ^{236}X was determined to be less than 0.3 %, and the maximum potential ^{236}U fraction could be constrained to $(7.5\pm 7.5)\%$. The ^{236}U result is a conservative estimate of the maximum ^{236}U content that could have gone undetected due to uncertainties in the underlying count rates in the isobar measurement, and no indication of the actual presence of ^{236}U has been found. U is typically chemically removed from the Np/Pu fraction by a factor of 100 or more [Hain et al. 2022], so that the remaining uncertainty of the ^{236}U content of the prototype spike can be treated as a component of the uncertainty of the ^{236}Np concentration. Based on the isobar analysis results, mass 236 will therefore be referred to as ^{236}Np throughout this text unless explicitly stated otherwise.

The first aim of the present study was to characterize the prototype ^{236}Np -spike material with respect to its ^{236}Np concentration and ^{237}Np contamination. In a second step, the normalization of ^{237}Np data using the new prototype spike was validated against reference materials and a ^{237}Np dilution series. This approach enabled direct comparison of the new spike material against the complementary ^{242}Pu normalization methods and the identification of any limitations at the current stage of spike development. Finally, the new material has been used to quantify the ^{237}Np content in selected environmental samples across different environmental matrices.

6.3. Experimental

6.3.1. Materials

The materials involved in the production and purification of the ^{236g}Np -spike material are described elsewhere [Nakajima et al. 2026]. Multiple Th foils were irradiated once, and the two prototype spike materials, spike I and spike II, were produced by two irradiations of a single foil each. Consequently, in these two cases, material was left for use as prototype spikes after the characterization measurements, whereas the single-irradiated targets were consumed in analysis and method development. The total yield of the prototype Np-spike II (R4-12) after purification was estimated to be on the order of 10^9 atoms (at) ^{236g}Np based on previous irradiated targets in preliminary measurements [Nagai et al. 2025]. 4 M HNO_3 was used to produce 12.41 g of the prototype spike solution, with an intended ^{236g}Np concentration on the order of $1\text{--}2\cdot 10^8$ at/g. The ^{236}Np concentration was experimentally verified using a ^{237}Np isotope addition approach. The required samples were prepared in the same way as external Np/Pu standards as described in [Hain et al. 2022], using varying quantities of ^{237}Np and aliquots of the prototype spike II material via quantitative co-precipitation with 2 mg Fe from ml quantities of solution, followed by calcination.

Samples with known ^{237}Np concentrations are required to benchmark the normalization of ^{237}Np data using the new ^{236}Np -spike materials and to compare its performance to the non-isotopic ^{242}Pu approach. Suitable validation samples were prepared from small (150 ml and 500 ml) Pacific Ocean water samples (3000 m depth) that were spiked with $1\cdot 10^8$ to $7.5\cdot 10^8$ at ^{237}Np . Deep-sea water was selected as a representative environmental matrix to test the competitive analytical procedures, which might affect Np and Pu recoveries, while introducing a negligible ^{237}Np signal from the sample itself. The inherent ^{237}Np concentration in this Pacific Ocean water column below 2000 m depth has been determined to be $< 10^5$ atoms/kg by non-isotopic normalization using the ^{242}Pu -spike (unpublished) and therefore can be considered negligible, even for the validation sample with the lowest amount of $1\cdot 10^8$ atoms of ^{237}Np added. Nevertheless, an aliquot of 500 mL spiked only with $^{242,244}\text{Pu}$ was included in the measurement to monitor the ^{237}Np count rates and verify this assumption for the 3000 m sample. No ^{236}Np -spike was added to this sample, both to preserve the precious material and because the spike-derived ^{237}Np might have overwhelmed the expected signal of $< 10^5$ at ^{237}Np .

Another option for benchmarking the two normalization approaches is to use materials with published values for the ^{237}Np concentration. The elevated concentrations of the environmental reference materials IAEA-381 (Irish Sea water) and IAEA-385 (Irish Sea sediment) could be analyzed using complementary methods, thereby providing a certified reference value (IAEA-381) or information value (IAEA-385) for ^{237}Np [Mauring et al. 2019; Pham et al. 2008; Povinec et al. 2002]. Two large (~ 100 g) and two small (1.0 and 0.5 g) IAEA-381 and one sample of IAEA-385 (1 g) were used for this study. The different

sizes of the IAEA-381 samples provide an opportunity to test the performance of the ^{236g}Np normalization across varying amounts of ^{126}U in the initial sample material. With a half-life of 2.8 y and much less efficient production pathways than $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}$ in nuclear reactors or fallout, ^{236}Pu interference from the environmental samples is assumed to be negligible.

Finally, several unknown environmental samples were selected to showcase the application of the new ^{236}Np -spike. Peat is an interesting matrix for trace actinide analysis, with strongly reducing conditions that can influence oxidation states – and therefore particle reactivity and radionuclide retention [Quinto et al. 2013]. A plethora of organic molecules that can act as agents for colloid or complex formation, which could result in elemental fractionation, further complicates the use of non-isotopic normalization methods. ^{236}U has been found to be largely immobilized, while downward migration has been observed for ^{239}Pu [Quinto et al. 2013]. No published ^{237}Np data could be found, so the migration behavior of Np in such conditions is still unknown. In a previous measurement, a slice taken 5 – 15 cm below the surface from Pürgschachen Mire (47° 35' N, 14° 21' E) was analyzed [Wolf 2006]. However, there were inconsistencies in the ^{242}Pu -normalized results, raising doubts about the reliability of the results obtained with this approach. Two additional slices corresponding to depths of 17-20 cm and 20-23 cm below the surface were available for complementary analysis using the new prototype spike.

The aftermath of the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011 has resulted in a buildup of $1.3 \cdot 10^6$ t of cooling water containing various radionuclides. The Advanced Liquid Processing System (ALPS) drastically reduces the concentrations of most radionuclides before dilution and subsequent release of ALPS-treated water in batches of 7800 t into the Pacific Ocean [Mabon 2024]. However, some radionuclides, such as ^3H , cannot be retained by this method, while for some others, such as ^{99}Tc , the efficiency of the removal varies considerably [Maderich et al. 2024]. Two surface seawater samples were collected off the coast of Fukushima, one in the vicinity of the outlet for ALPS-treated water named FDNPP-1-km (sampling station SI-10, 37° 25.33' N, 141° 3.26' E) and one ~6 km south of the facility named FDNPP-6-km (sampling station OZ off, 37° 22.34' N, 141° 4.16' E). The seawater was collected on March 11th, 2024, during the ongoing fourth release of ALPS water from February 28th to March 17th, 2024 [Ministry for Foreign Affairs, Japan 2024]. The samples were filtered to remove suspended solids and larger organic material. Elevated concentrations of ^{237}Np at the FDNPP-1-km compared to the 6-km location, or at both sampling locations relative to suitable baseline samples, would indicate significant releases from the ALPS-treated water. The two FDNPP samples were divided into aliquots A (measured using ^{236}Np spike I) and B (^{236}Np spike II) and were measured in different beamtimes to assess the reproducibility of the normalization approaches and, if compatible, combine the two measurements for improved counting statistics.

The $^{236}\text{U}/^{236}\text{U}$ ratio in ZSW (Zurich Sea Water) has recently been determined in a large

intercomparison exercise, but no data on ^{237}Np have been made available to date [Christl et al. 2025]. A 10 L ZSW sample was provided by the ETH Zurich Ion Beam Physics Laboratory for a first ^{237}Np analysis using the new spike material. A list of all samples analyzed in the present study is provided in the SI (Sample and measurement data table SI-1).

The in-house uranium standards Vienna-KkU and Vienna-US8 were used for beam tuning and quality control for actinide measurements at VERA [Qiao et al. 2022; Steier et al. 2019; Steier et al. 2008]. ^{237}Np standards were prepared from the single-nuclide solution 7237 (Isotrak Calibrated Solutions, Eckert&Ziegler), and for Pu standards, IRMM-085 (^{242}Pu isotope standard solution, Institute for Reference Materials and Measurements) as well as a new ^{244}Pu solution from the US Department of Energy [Essex et al. 2020] were used, respectively. Dilutions in suprapure HNO_3 were prepared from these stock solutions. A solution produced from 99.973 % pure ^{236}U provided to VERA by the IAEA was also available. The use of non-isotopic normalization requires external standards in addition [Hain et al. 2022], targets with a well-defined $^{237}\text{Np}/^{242}\text{Pu}$ ratio that provide a correction factor for differences in ionization yields or ion optical transmission. These external standards were prepared by co-precipitation of weighed amounts of the respective radionuclide solutions with Fe. The precipitate was then washed, dried, and calcined at 800°C for several hours to produce ~ 2 mg of an iron oxide matrix suitable for AMS measurements.

Systematic normalization errors arising from matrix effects when using the ^{242}Pu -spike can be (partially) corrected if a suitable reference material is available that is affected in a similar way. The deviation of the measured value from the nominal value can serve as a correction factor for environmental samples with a similar matrix. This approach has been successfully applied in a recent air filter study [Wallner et al. 2026] and will be tested here using IAEA-385 for the two peat samples against the ^{236}Np and uncorrected ^{242}Pu normalization. While the sediment is not an ideal proxy for peat, there is no reference material for ^{237}Np in peat. Both materials are solid and were processed in the same batch, following the same procedure.

The chemical procedures for preparing environmental samples largely followed the established protocol at VERA for actinide measurements in recent years [Hain et al. 2022]. This procedure aims to achieve high flexibility in extracting all major anthropogenic actinides (U, Pu, Np, Am) in parallel while keeping turnaround time and reagent use low, and assuming minimal user training. The central steps for water samples are a pre-concentration via co-precipitation of the actinides with Fe(III), a single UTEVA ion exchange column used to separate the sample into a U and a Np/Pu fraction, and a second Fe(III) co-precipitation, resulting in ~ 2 mg of iron oxide after calcination, containing the actinides of interest. All samples were spiked with ^{236}Np and ^{242}Pu at the beginning and ^{242}Pu just before the final Fe co-precipitation. The adoption of an Fe(II) coprecipitation for the initial pre-concentration of seawater samples has been shown to improve the reliability of the use of Pu as a non-isotopic spike for seawater samples [López-Lora et al.

2019b]. However, corresponding experiments with water samples available for analysis at VERA, which have been acidified with HNO_3 directly during the sampling cruise, resulted in non-quantitative recoveries of Np for Fe(II) co-precipitation in preliminary test runs. The ability to produce reliable results that do not depend on identifying and eliminating all potential, partially unknown, causes of elemental fractionation is a key advantage of using an isotopic spike and is a prerequisite for ^{237}Np measurements in more demanding sample matrices. Solid samples, such as the peat bog samples and the IAEA-385 sediment, were dried, ashed, and then, after the addition of the appropriate spikes, underwent a microwave digestion procedure in concentrated HNO_3 before the first Fe(III) co-precipitation. The remaining procedure was identical to that of seawater samples. Calibration samples containing ^{237}Np , ^{236}U , and ^{242}Pu were prepared as described in Wiederin et. al., 2022 for the investigation of isobaric interferences via the Anion Formation Isobar Analysis (AFIA) [Wiederin et al. 2022]. For the prototype spike II and the re-measurement of an IAEA-381 sample, residual material from sample holders used in the (oxide) AMS measurement was removed and mixed with PbF_2 (99.997% pure, Alfa Aesar) in a 1:9 (sample: PbF_2) mass ratio.

6.3.2. Instrumentation and data evaluation

The instrumentation for the irradiation of ^{232}Th has been described in recent publications on competing reactions in similar irradiation experiments [Nagai et al. 2025; Nakajima et al. 2026]. The actinide beamline of VERA, which was used for all AMS measurements, was described in detail in 2019 [Steier et al. 2019] and a schematic of VERA is included in Figure 3.3.1. The measurement technique and data evaluation for actinide AMS measurements at VERA have been described previously, both in general [Steier et al. 2019] and with additional descriptions on the use of non-isotopic spike materials [Hain et al. 2022]. We therefore limit ourselves to describing significant deviations from these established procedures.

For the characterization of the ^{236}Np concentration for the prototype spike II material, three sample types A (only ^{236}Np), B ($^{236}\text{Np} + 3 \cdot 10^8$ at ^{237}Np) and C ($^{236}\text{Np} + 6 \cdot 10^8$ at ^{237}Np) were available (see Table 1 in the Results section for exact values). Samples A1 and A2 were used to determine the $^{236}\text{Np}/^{237}\text{Np}$ ratio R_A of this material directly from the respective count rate ratios. The concentration of ^{236}Np (c_{236}) can then be calculated from the $^{236}\text{Np}/^{237}\text{Np}$ ratios R_A , R_B , and R_C , the masses m_{236} and m_{237} of the ^{236}Np and ^{237}Np -spike solutions added to each sample, and the concentration c_{237} of the ^{237}Np solution.

The ^{237}Np concentration $c_{0,237}$ in the ^{236}Np -spike material is given as $c_{0,237} = \frac{c_{236}}{R_A}$.

From expressing the isotope ratio in the sample i (either B or C) as

$$R_i = \frac{m_{i,236} \cdot c_{i,236}}{m_{i,237} \cdot c_{237} \cdot c_{0,237}} \text{ follows that } c_{i,236} = \frac{m_{i,237} \cdot R_i}{m_{i,236} \cdot \left(1 - \frac{R_i}{R_A}\right)} \cdot c_{237}$$

The final concentration c_{236} is then the arithmetic mean of the values calculated for samples B and C. However, c_{236} could still include contributions from the isobars ^{236}U or ^{236}Pu . The isobaric composition of mass 236 (^{236}X) in the prototype spike II material has been determined elsewhere [Wiederin et al. 2026b] (Chapter 5) to be $(92.5 \pm 7.5) \%$ ^{236}Np . To arrive at the final ^{236}Np concentration, c_{236} as calculated above must be corrected by this isobar factor and its associated uncertainty.

Co-produced ^{237}Np in the spike material contributes to the measured concentration of the respective sample, just like contaminations from other reagents, and is subtracted using process blanks. No blank correction was applied to the characterization of the prototype spike material, as any impurity of the material, regardless of origin, will add to the background introduced into the environmental samples and needs to be accounted for.

For validation samples, reference materials, and the environmental samples, a dual Pu-spike approach was used to estimate Pu chemistry yields. Then the ratio $(\frac{^{242}\text{Pu}}{^{244}\text{Pu}})_{\text{measured}}/(\frac{^{242}\text{Pu}}{^{244}\text{Pu}})_{\text{nominal}}$ can be used to estimate the chemical Pu yield. The standard deviation of the $^{237}\text{Np}/^{242}\text{Pu}$ relative detection efficiencies on individual external $^{237}\text{Np}/^{242}\text{Pu}$ standards in the measurement is used to monitor the uncertainty of the external standard correction and contributes to the final uncertainty of ^{242}Pu -normalized data.

The recently developed Anion Formation Isobar Analysis (AFIA) [Wiederin et al. 2022] was used to monitor isobaric interference by measuring the $\text{AnF}_4^-/\text{AnF}_5^-$ formation ratios, which serve as elemental fingerprints for the actinides (An) U, Np, and Pu. While the absolute values of the $\text{AnF}_4^-/\text{AnF}_5^-$ ratios may be affected by the pre-sputter history of the target material, the relevant information concerning the composition of mass 236 lies in the deviation of the $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ ratio from $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ for the same sample. Thus, the data were normalized by setting the $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ ratio to 1 for each target analyzed and applying the resulting normalization factor to the other formation ratios on the same target. With this approach, a significant deviation of the $^{237}\text{XF}_4^-/^{237}\text{XF}_5^-$ ratio from the normalized Np formation ratio ($=1$) would then be indicative of isobaric interference from ^{236}U ($<<1$) or ^{236}Pu ($>>1$).

6.4. Results and Discussion

6.4.1. ^{236g}Np spike characterization

The $^{236}\text{X}/^{237}\text{Np}$ ratios for materials produced in several irradiation experiments, including the two prospective spike materials and single-irradiation samples, are plotted in Fig. 6.4.1. Only the two prototype spikes I and II have undergone isobaric analysis, so the isobaric composition of most of these materials remains unknown and is therefore denoted as ^{236}X . For the prototype spike II, a $^{236}\text{Np}/^{237}\text{Np}$ ratio of 6.93 ± 0.27 was

measured, while for the earlier spike I material, this ratio was 3.72 ± 0.11 . These two materials were produced by multiple irradiations of a single foil each, which may have affected the ratio achieved, besides the desired increase in ^{236}Np production. The uncertainties of the $^{236}\text{X}/^{237}\text{Np}$ ratios for A1, A2 and B were calculated from the standard deviation of the count rates, while for uncertainty from the counting statistics was larger and therefore used instead. For the ^{236}Np spike II, the uncertainty is given by the sensitivity of the scale involved, whereas for the number of ^{237}Np atoms the uncertainty of the concentration of the spike solution was included in the calculation.

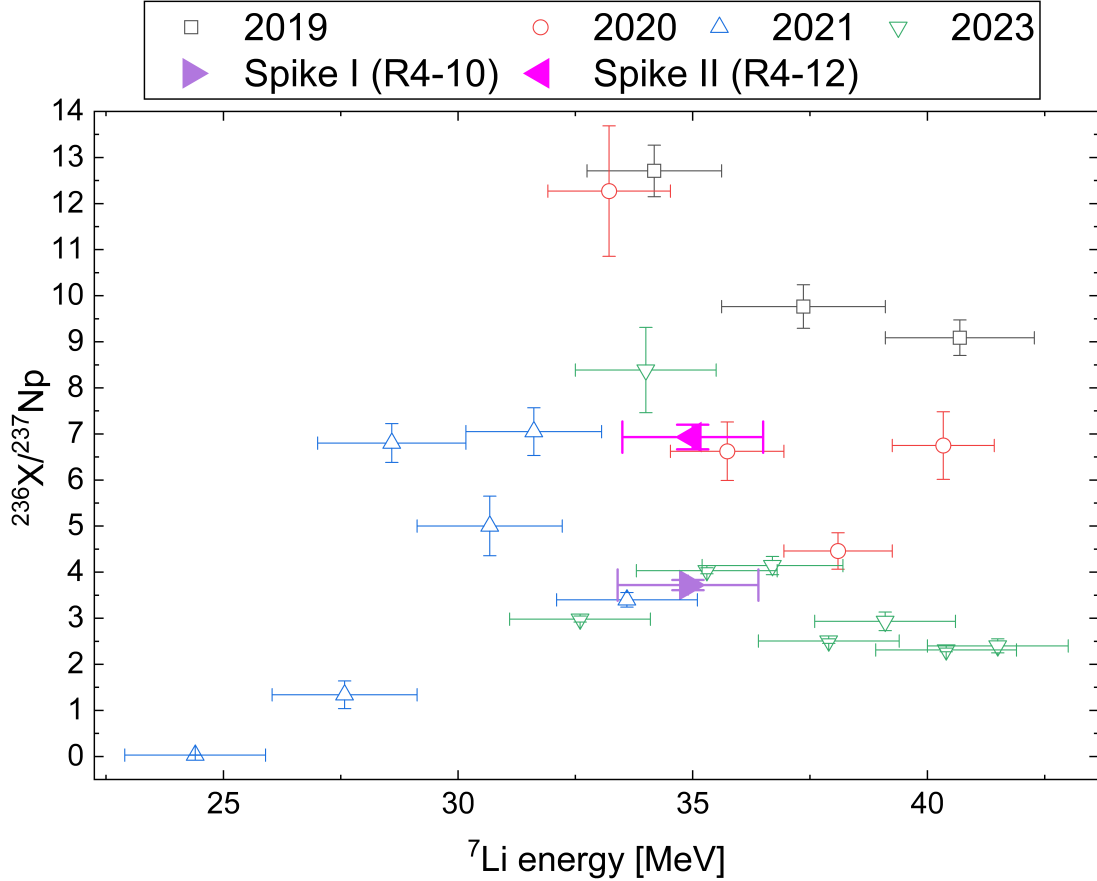


Figure 6.4.1.: $^{236}\text{X}/^{237}\text{Np}$ ratios for 23 samples from various irradiation experiments have been determined by AMS. Spike I and II have been irradiated twice, resulting in $^{236}\text{Np}/^{237}\text{Np}$ ratios of 3.72 ± 0.11 and 6.93 ± 0.27 , respectively.

Sample	$^{236}\text{X}/^{237}\text{Np}$	^{236}Np -spike II [g]	^{237}Np added [$\cdot 10^8$ at]
A1	6.95 ± 0.48	0.9838 ± 0.0098	
A2	6.92 ± 0.23	0.9901 ± 0.0099	
A_{avg}	6.93 ± 0.27	0.9869 ± 0.0098	
B	0.4128 ± 0.0071	0.9842 ± 0.0098	3.104 ± 0.031
C	0.219 ± 0.012	0.9770 ± 0.0098	6.221 ± 0.062

Table 6.4.1.: Samples A1 and A2 were used to determine the $^{236}\text{Np}/^{237}\text{Np}$ ratio of the prototype spike II. The $^{236}\text{Np}/^{237}\text{Np}$ ratios, the quantities of spike II solution, and the number of ^{237}Np added were used to calculate the ^{236}Np concentration of this material.

The data used to calculate the ^{236}Np concentration of spike II and the total amount produced and separated from the irradiation target R4-12 to produce this material are compiled in Table 6.4.1. The table includes both individual samples A1, A2, B, and C, as well as the arithmetic mean of the measured ratios and spike amounts for type A samples, A_{avg} . The isobar analysis results [Wiederin et al. 2026b] (Chapter 5) yielded an additional correction factor to the calculated ^{236}X concentration of $(1.429 \pm 0.042) \times 10^8$ at/g, resulting in a final ^{236g}Np concentration of $(1.32 \pm 0.12) \cdot 10^8$ at/g. For a total quantity of 12.41 g of spike solution, this corresponds to a produced and separated amount of $(1.64 \pm 0.14) \cdot 10^9$ at ^{236g}Np for spike II. The sum of all characterization measurements (including the isobar analysis) required $\sim 5.6 \cdot 10^8$ at ^{236}Np or $\sim 31\%$ of the material. For the older spike I (R4-10) material, a preliminary ICP-MS value of $(4.95 \pm 0.33) \cdot 10^8$ at/g for mass 236 was available, with material for 10-15 environmental samples remaining after characterization. See Appendix 10.3 for details.

6.4.2. Discussion of the spike characterization:

The cause of the large spread of $^{236}\text{X}/^{237}\text{Np}$ ratios for similar energies shown in Fig. 6.4.1 remains unknown. A reasonable hypothesis is that, for the early (2019 and 2020) batches, the chemical separation of U and Pu was insufficient, so that the measured $^{236}\text{X}/^{237}\text{Np}$ ratio may have been higher than the actual $^{236}\text{Np}/^{237}\text{Np}$ ratio due to the presence of ^{236}U or ^{236}Pu . The ratios declined significantly in 2021, coinciding with the implementation of an improved chemical purification procedure following the discovery of inconsistent Pu removal. Earlier samples were handled rapidly after irradiation, but this approach either required low overall activity and therefore lower ^{236}X production or used hot cells, which increased the risk of contamination from other highly activated materials previously handled there. Hot cells had resulted in high blank levels for both ^{237}Np and other actinides in preliminary tests. When the focus shifted from preliminary investigations to producing a usable quantity of ^{236}Np -spike material, a delayed processing scheme and, for the two prototype spike materials, a multiple-irradiation approach were implemented. While such an approach allows for the safe handling of the material in a cleaner environment than in the hot cells, a potential drawback is the in-growth of ^{237}Np from the decay of ^{237}U , which has a half-life of 6.752 days. The cross section of the $^{232}\text{Th}(^7\text{Li,pn})^{237}\text{U}$ reaction is 0.29-0.67 mb in the relevant energy range of 30-40 MeV [Zhao et al. 1999]. This cross-section is higher than the 0.25-0.39 mb measured recently for ^{236m}Np in the same energy range [Nakajima et al. 2026] and comparable to the <1 mb from a preliminary measurement of the ^{236g}Np cross-section [Hayakawa et al. 2019]. Dedicated experiments are planned to quantify the ^{237}Np contribution from ^{237}U via γ -spectroscopy on irradiated samples. Preliminary investigations using γ -spectrometry demonstrated the presence of ^{237}U but could not provide quantitative data on the $^{237}\text{U}/^{236g}\text{Np}$ ratio. While there is therefore the potential for future improvements, the $^{236g}\text{Np}/^{237}\text{Np}$ ratios achieved for the two prototype spikes are already sufficient for many applications.

6.4.3. Spike validation measurements

The results of the seawater validation sample measurements are shown in Fig. 6.4.2. The added quantities of ^{237}Np are plotted on the x-axis against the measured ^{237}Np results on the y-axis for each sample. Consequently, accurate normalization would place each data point on the 1:1 line within the measurement's precision. The ^{236}Np -normalized data agreed with the nominal values within 1σ for all samples. Using ^{242}Pu instead, only the $3\cdot 10^8$ at (1σ) and $2\cdot 10^8$ at (2σ) reasonably reproduced the nominal value, while all other ^{242}Pu normalized values deviated significantly (2.8 - 17.5σ). Furthermore, all ^{242}Pu -normalized results in Fig. 6.4.2 fall below the 1:1 line, indicating systematically lower chemical yields of Np than of Pu and therefore providing direct evidence of elemental fractionation, which led to normalization errors in the non-isotopic approach.

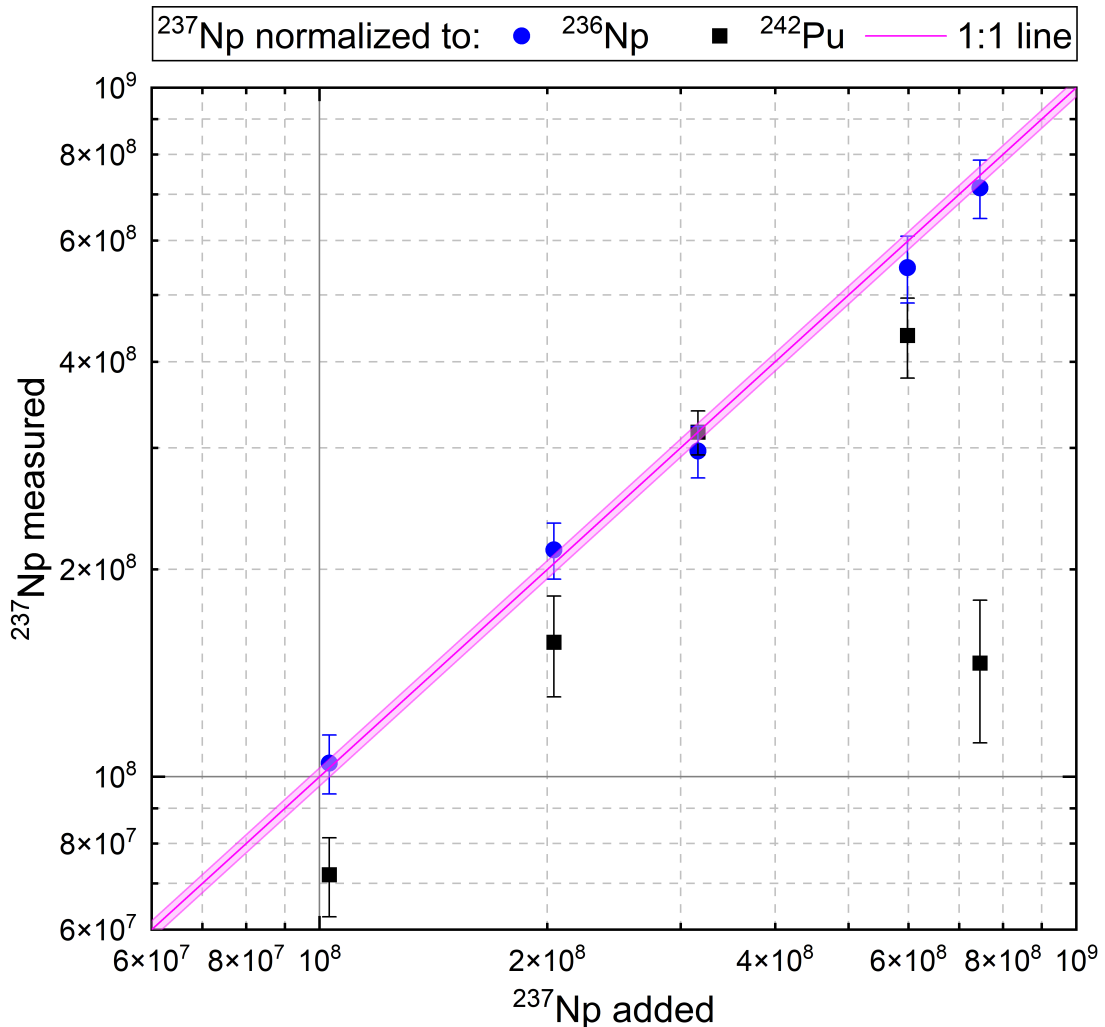


Figure 6.4.2.: Comparison between the measured and added numbers of ^{237}Np atoms for validation samples produced from deep-sea water by ^{237}Np -spike addition. When normalized to the ^{236}Np -spike (blue circles), all samples agree within 1σ with the 1:1 line, whereas this holds only for one sample when normalized to the non-isotopic ^{242}Pu -spike.

The underlying assumption of negligible inherent ^{237}Np could be confirmed using a sample with no added ^{237}Np . The ^{242}Pu normalized result for this sample was below

the process blank level, and the uncorrected ^{237}Np count rate was more than two orders of magnitude below that of the ^{237}Np spiked samples in the same measurement.

For the environmental reference materials literature values for the ^{237}Np concentration of $(0.0087 \pm 0.0005) \text{ Bq/kg}$ (IAEA-381) [Povinec et al. 2002] and $(0.0185 \pm 0.0027) \text{ Bq/kg}$ (IAEA-385) [Mauring et al. 2019] were used to evaluate the ^{237}Np normalization performance using ^{236}Np and ^{242}Pu -spikes. The normalized ^{237}Np data for both spikes are shown in Fig. 6.4.3, with concentrations converted to at/kg . The isotopic ^{236}Np -spike normalization reproduced the ^{237}Np information value of IAEA-385, while the ^{242}Pu normalization of the same sample led to an overestimation of the ^{237}Np concentration by 2σ . For the two small (0.5 g and 1.1 g) IAEA-381 samples, the isotopic ^{236}Np -spike normalized values agreed with the certified value within 1σ , but for both large (101 g and 99 g) IAEA-381 samples, the normalization was off by an order of magnitude. By contrast, the ^{242}Pu normalization reproduced the certified value for one out of two samples for both small and large IAEA-381 samples within 1σ , and three out of four total within 2σ . No effect correlating to the IAEA-381 sample size could be observed for the ^{242}Pu normalization.

6.4.4. Discussion of the spike validation measurements:

The isobar analysis correction factor introduced an additional uncertainty, which increased the overall uncertainties of the ^{236}Np normalized results considerably, and likely caused the 100% agreement within 1σ . However, without this component of uncertainty, still 60 % of ^{236}Np -normalized data would agree within 1σ and 100 % within 2σ . A linear fit of the ^{236}Np normalized data points is compatible with the 1:1 line at the 2σ level and scattering around the nominal line suggests the absence of any systematic deviation. These results therefore support the calculated ^{236g}Np concentrations for spike I and spike II and suggest that the true ^{236}U fraction of these materials may indeed be significantly lower than the upper limit of 15 % as conservatively estimated in [Wiederin et al. 2026b] (Chapter 5). While the ^{236}Np isotopic spike already outperformed the non-isotopic normalization, there is potential to significantly reduce overall uncertainties as soon as more ^{236g}Np -spike material will be available so that the isobar analysis correction factor can be determined more precisely.

The $^{242}\text{Pu}/^{244}\text{Pu}$ nominal and measured ratios were used to estimate the average Pu chemistry yield at $(74.1 \pm 7.6) \%$. The pronounced deviation towards lower values in the ^{242}Pu -normalized ^{237}Np results, combined with reasonable Pu yields, indicates significant fractionation of Np and Pu in these validation samples. While improvements to the sample preparation procedure could reduce the likelihood of such problems, elemental fractionation is an inherent risk in the non-isotopic spike approach. Furthermore, while the expected performance can be determined on samples with known ^{237}Np concentrations, for individual unknown samples, there is no reliable way to identify such issues without an isotopic spike. Consequently, unexpected results obtained in this way

will always face greater scrutiny, which could introduce a systematic confirmation bias into the analysis of environmental ^{237}Np or limit the investigations to a small subset of sample matrices.

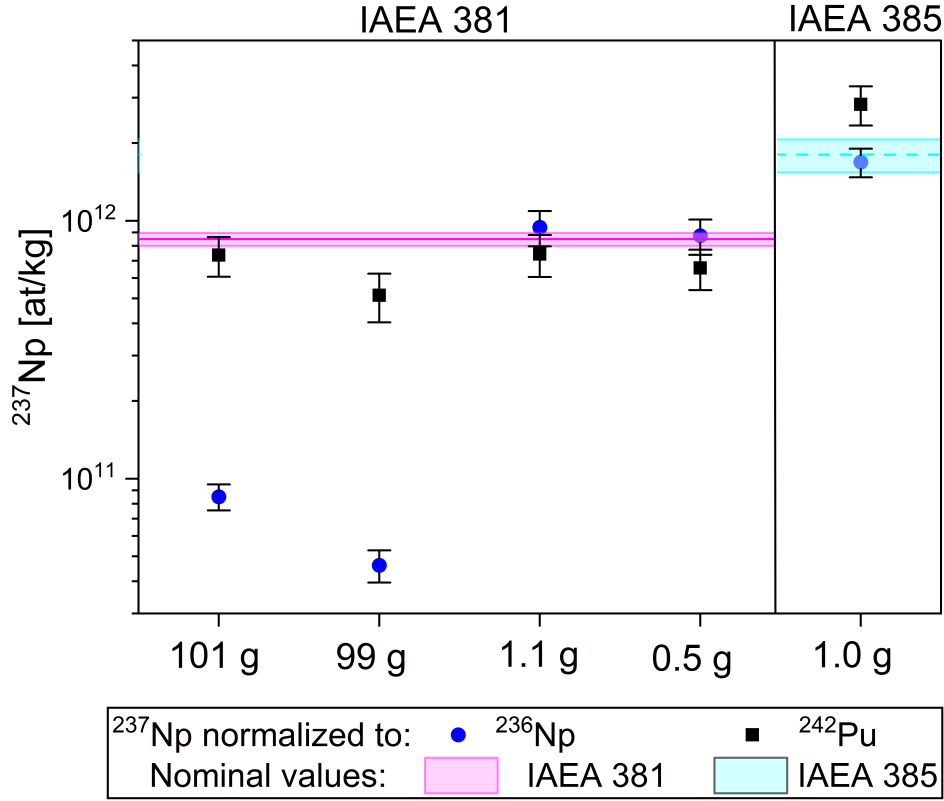


Figure 6.4.3.: Measured ^{237}Np concentrations are compared to nominal values for the environmental reference materials IAEA-381 (Irish Seawater) [Povinec et al. 2002] and IAEA-385 (Irish Sea Sediment) [Mauring et al. 2019; Pham et al. 2008] normalized to ^{236}Np (blue circles) and ^{242}Pu (black squares). The ^{236}Np normalization performed well for IAEA-385 and small samples of IAEA-381, but not for the large IAEA-381 samples due to ^{236}U interference (see main text). The ^{242}Pu normalization reproduced the IAEA-381 nominal ^{237}Np concentration (pink horizontal line) for 2 out of 4 samples and significantly overestimated it for IAEA-385 (turquoise horizontal line).

The quantity of spike-derived ^{237}Np added via the ^{236}Np -spike effectively sets a lower boundary for the detection limit (with reasonable precision) for the inherent ^{237}Np in a sample. Using a reduced quantity of the newer ^{236}Np spike II ($\sim 7 \cdot 10^6$ at ^{236}Np , as tested for the ZSW sample; see Fig. 5), the corresponding blank level of $> 1 \cdot 10^6$ at will limit reliable quantification to $> 2 \cdot 10^6$ ^{237}Np atoms (2x the minimum expected blank level) per sample using formal blank correction. The $\sim 1.5 \cdot 10^7$ at ^{237}Np added resulted in an average of ~ 2500 counts $^{236}\text{Np}^{3+}$ for samples with reasonable yields in the fraction of the measurement time devoted to the spike. A further reduction of the amount of ^{236}Np -spike used by at least a factor of 10 is still possible at the cost of increased uncertainty contribution from the spike counting statistics, an increased fraction of counting time required for the spike, and less robustness against lower Np yields. This low-spike approach would then enable measurements down to $\sim 2 \cdot 10^5$ at ^{237}Np .

At the other end, there is no reason to expect problems with the normalization of ^{237}Np data for samples containing 10^9 or 10^{10} atoms of ^{237}Np . For even higher concentrations, it would be advisable to measure dilute aliquots or use different techniques to avoid contaminating the AMS setup and laboratory.

For the two larger IAEA-381 samples, the ^{237}Np concentrations normalized using the ^{236}Np isotopic spike are significantly below the reference value. With a ^{236}U activity of $(1.92 \pm 0.06) \cdot 10^{-5}$ Bq/kg [Povinec et al. 2002], the ~ 100 g samples of IAEA-381 contained approximately $2 \cdot 10^9$ atoms of ^{236}U , two orders of magnitude more than the $\sim 1.5 \cdot 10^7$ at ^{236}Np added by the spike. Even assuming the usual chemical U suppression by two orders of magnitude, this would result in a ^{236}U content in the AMS target comparable to the spiked ^{236}Np . An insufficient removal of ^{236}U during chemical sample preparation could explain the low reproducibility of the nominal ^{237}Np concentration in these samples, as ^{236}U overlaps with the signal from the ^{236}Np -spike. To cause the observed deviation from the reference value, $\sim 90\%$ of the ^{236}X counts registered for the larger IAEA-381 samples would have to be ^{236}U instead of ^{236}Np .

For the IAEA-385 reference material, the initial publication only provided a very large range as an information value [Pham et al. 2008] which has been improved considerably to

(0.0185 ± 0.0027) Bq/kg in the updated reference sheet in 2019 [Mauring et al. 2019]. However, as this is still an information value, it was prudent to include ^{237}Np data from other publications on this material as well. In Qin et al 2024, a statistical value of 0.021 ± 0.002 Bq/kg $((2.05 \pm 0.20) \cdot 10^{12}$ at/kg) based on six ICP-MS data points [Qin et al. 2024] has been published for IAEA-385, which would represent a small revision of the ^{237}Np information value of (0.0185 ± 0.0027) Bq/kg $((1.80 \pm 0.26) \cdot 10^{12}$ at/kg). In the same publication, the authors reported their own measured result of (0.0176 ± 0.0009) Bq/kg $((1.71 \pm 0.09) \cdot 10^{12}$ at/kg) for ^{237}Np . The result obtained here, (0.0173 ± 0.0022) Bq/kg $((1.69 \pm 0.22) \times 10^{12}$ at/kg) using the isotopic ^{236}Np -spike, agrees with the IAEA information value and the measured Qin et al. result within 1σ and with the averaged ICP-MS value in the same publication within 2σ .

The ^{242}Pu normalization overestimated the ^{237}Np concentration significantly, whereas for most water samples (e.g., see Fig. 6.4.2 for the seawater validation samples), the ^{242}Pu approach tended to underestimate ^{237}Np . In a recent investigation into chemical yields using ^{236}Pu and ^{237}Np , the relative Np/Pu yields for IAEA-385 samples ranged from 1.4 to 1.7 [Wallner et al. 2026], which also indicates a more efficient Np recovery. For the IAEA-385 sample measured here, a comparison of the added nominal and the measured $^{242}\text{Pu}/^{244}\text{Pu}$ ratio has been used to estimate a Pu chemistry yield of $(65 \pm 5)\%$. Even if 100% Np recovery is assumed, the Pu losses up to the second co-precipitation (when ^{244}Pu is added) would not fully explain the overestimation for the ^{242}Pu normalization. Additional effects may arise from residual matrix elements that interfere with either Pu co-precipitation or PuO^- formation in the final samples, which are not accounted for by the external standard correction.

The ^{242}Pu normalized results for the small IAEA-381 samples showed a better accuracy than determined with the larger validation samples in the previous section (see Fig. 6.4.2). The amount of Fe(III) added for the initial co-precipitation was adjusted to the sample volume so that the concentration was identical for all samples, i.e., 15 mg/L. A notable difference in the preparation of these sample types was that the validation samples were left to settle overnight after the Fe(III) co-precipitation at pH 8.5, whereas the IAEA-381 samples were centrifuged after the precipitate had sufficient time to form. Lovett et. al. 1990, besides lower Fe concentrations, highlighted a lack of equilibration between analyte and tracer (e.g., complexation, differences in oxidation states or their distribution) or adsorption on surfaces as major sources of error in the analysis of plutonium [Lovett M. B. et al. 1990]. The longer settling time by itself should therefore be beneficial, but the opposite was observed here. Minor matrix differences between the Irish Sea at 20 m depth and the Pacific Ocean at 3000 m, or the longer time spent at pH 8.5 in a glass beaker with different volume-to-surface-area ratios, could have contributed to the observed increase in elemental Np/Pu fractionation for the validation samples.

6.4.5. Anion Formation Isobar Analysis (AFIA)

The AFIA technique is well-suited to test the hypothesis of ^{236}U interference in the 99 g IAEA-381 samples. Fig. 6.4.4 shows the measured $\text{AnF}_4^-/\text{AnF}_5^-$ anion formation ratios for calibration samples, the prototype ^{236}Np -spike, and the 99 g IAEA-381 sample, normalized to the $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ ratio measured in the respective sample. It has previously been demonstrated that this anion formation ratio serves as an elemental fingerprint [Wiederin et al. 2022] (Chapter 4). Data obtained from a previously sputtered spike II sample mixed with PbF_2 show good agreement of the ratio for ^{236}X and ^{237}Np , hence, confirming the isobaric characterization of ^{236}X in spike II as ^{236}Np and the validity of the normalization method for pre-sputtered samples. By contrast, the $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ anion formation ratio for the IAEA-381 99 g sample is almost an order of magnitude lower than expected for Np.

6.4.6. Discussion of the AFIA results:

The very low $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ ratio compared to $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ observed by AFIA for the IAEA-381 99 g sample implies that ^{236}X in this sample consists mostly of ^{236}U . An exact quantification of the $^{236}\text{Np}/^{236}\text{U}$ ratio is difficult, as the true $^{236}\text{UF}_4^-/^{236}\text{UF}_5^-$ formation ratio in this pre-sputtered sample could be offset from that measured on the calibration samples. However, assuming ^{236}X in this IAEA-381 sample is 95 % ^{236}U and 5 % ^{236}Np , would reproduce the measured $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$. Consequently, ~95 % of the ^{236}X count rate detected during the AMS measurement of this sample originates from environmental ^{236}U , not from the ^{236}Np -spike. Applying this isobaric composition determined with AFIA as a correction factor to the ^{236}X count rate (i.e. 5% of the ^{236}X

count rate) to obtain the actual ^{236}Np count rate for the IAEA-381 99 g sample, the resulting ^{237}Np concentration of $(9.4 \pm 1.5) \cdot 10^{-3} \text{ Bq/kg}$ would be compatible with the reference value of $(8.7 \pm 0.5) \cdot 10^{-3} \text{ Bq/kg}$.

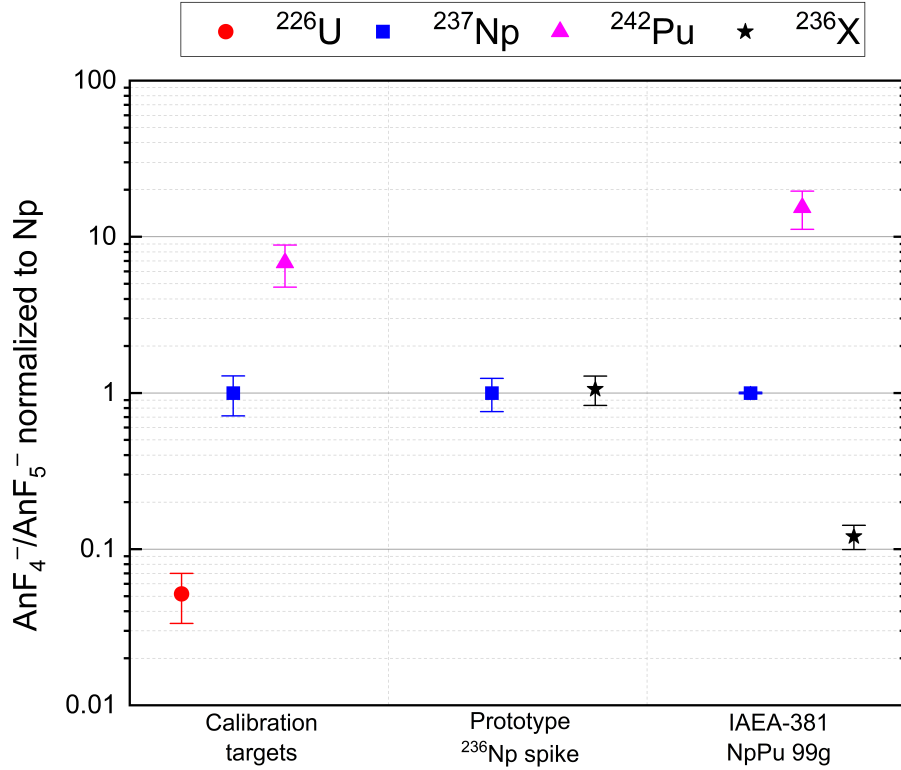


Figure 6.4.4.: $\text{AnF}_4^- / \text{AnF}_5^-$ anion formation ratios for U, Np, Pu and ^{236}X normalized to ^{237}Np for calibration samples using ^{236}U , ^{237}Np and ^{242}Pu (left), the ^{236}Np spike material I (middle), and the IAEA-381 sample (right). The lower anion formation ratio observed for ^{236}X on the IAEA-381-99g sample implies that ^{236}X on this sample is dominated by ^{236}U .

The average $^{238}\text{U}^{3+}$ currents measured for the Np/Pu and the U fraction of an IAEA-381 101 g sample are indeed similar and (the U fraction of IAEA-381-99 g processed in the same batch was not analyzed) fall within the range of $(1.20 \pm 0.25) \cdot 10^{-12} \text{ A}$ in both cases. Similar $^{238}\text{U}^{3+}$ ion currents imply that, rather than the typical two orders-of-magnitude separation, U was present in both fractions at comparable concentrations. In summary, the extremely high ^{236}U content in the sample, an insufficient removal of U from the Np/Pu fraction as well as the low quantity of ^{236}Np added ($\sim 1.5 \cdot 10^7$ at ^{236}Np vs. $\sim 2 \cdot 10^8$ at ^{242}Pu), have led to the ^{236}Np normalization error observed for the two large IAEA-381 samples. Consequently, for samples in which high ^{236}U concentrations are expected, particular attention must be paid to an efficient chemical U separation in the future to prevent interference with the ^{236}Np measurement and, consequently, with the ^{237}Np normalization. A simple monitoring scheme to identify potentially questionable samples with insufficient U suppression could be implemented by comparing the $^{238}\text{U}^{3+}$ currents on both the U and the Np/Pu fractions, in addition to the ^{236}U content in the U fraction.

6.4.7. Analysis of unknown environmental samples

The ^{237}Np concentration for the $(18.5 \pm 1.5 \text{ cm})$ depth peat sample from Pürschachen mire (PM) was measured at $(4.40 \pm 1.0) \cdot 10^{10} \text{ at/kg}$, and at $(21.5 \pm 1.5 \text{ cm})$ depth, it was $(1.47 \pm 0.33) \cdot 10^{11} \text{ at/kg}$ when normalized to ^{236}Np as shown in Fig. 5A. The calculated concentrations are roughly twice as high when normalized to ^{242}Pu . These samples were prepared alongside the IAEA-385 sample, using the same chemical protocol after drying and ashing the peat. If the deviation of the measured from the nominal value for the ^{237}Np concentration for the IAEA-385 sample (see Fig. 6.4.3) was used as a correction factor for the ^{242}Pu PM samples, as proposed by Wallner et. al., 2026 [Wallner et al. 2026]. The corrected concentrations agree with the ^{236}Np -spike-normalized data within 1σ . The uncertainties of the corrected data points also include the uncertainties of the measured IAEA-385 data and the corresponding information value. The ^{236}Np concentrations as well as the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios (cf. Fig 5B), increase significantly in the deeper sample, regardless of the normalization used. For PM $21.5 \pm 1.5 \text{ cm}$, the $^{237}\text{Np}/^{239}\text{Pu}$ ratio is compatible with the average northern hemisphere global fallout ratio [Kelley et al. 1999] of 0.48 ± 0.07 within 1σ (^{236}Np -spike and IAEA-385 corrected ^{242}Pu data). By contrast, the ratios obtained for the upper sample ($18.5 \pm 1.5 \text{ cm}$) are all clearly below the global fallout ratio, regardless of normalization. The ^{237}Np concentrations for three seawater samples from the Pacific Ocean (FDNPP-1-km and 6-km) and the Mediterranean Sea (ZSW) are shown in Fig. 6. From the FDNPP-1-km and 6-km samples, two aliquots (A and B) each were prepared independently and measured in different beamtimes. The ^{236}Np and ^{242}Pu normalized results agree only for two of five samples/aliquots. The ^{242}Np -normalized ^{237}Np concentrations for all aliquots from the two FDNPP samples all agree within 1.1σ .

By contrast, the ^{242}Pu -normalized data for the same samples showed significant differences between the A and B aliquots. The FDNPP-1-km-A aliquot was below the blank level when normalized to ^{242}Pu . Consequently, only an upper limit of $< 1.3 \cdot 10^6 \text{ at/kg}$ (uncorrected value + uncertainty) can be calculated in this case, which is an order of magnitude below the other data points calculated for the sample. This data point is therefore disregarded in subsequent calculations. With no significant deviation between the FDNPP-1-km and 6-km samples, the ^{237}Np concentrations were averaged over all aliquots for the two normalization methods, giving a mean value of $(1.44 \pm 0.18) \cdot 10^7 \text{ at/kg}$ for ^{236}Np normalization and $(1.53 \pm 0.53) \cdot 10^7 \text{ at/kg}$ for ^{242}Pu normalization. The corresponding uncertainties were calculated either from the individual uncertainties (^{236}Np -spike-normalized data) or from the standard deviation of the data points (^{242}Pu -normalized FDNPP-6-km-A and B and 1-km-B), whichever was larger. Both averages agree within 1σ . However, the uncertainty of the ^{242}Pu normalized concentrations is much higher due to increased scatter, even when discarding FDNPP-1km-A. For the ZSW sample, the ^{236}Np and ^{242}Pu normalized ^{237}Np concentrations differ by a factor of 3. Using the isotopic spike, a ^{237}Np concentration of $(9.5 \pm 1.2) \cdot 10^6 \text{ at/kg}$ was determined.

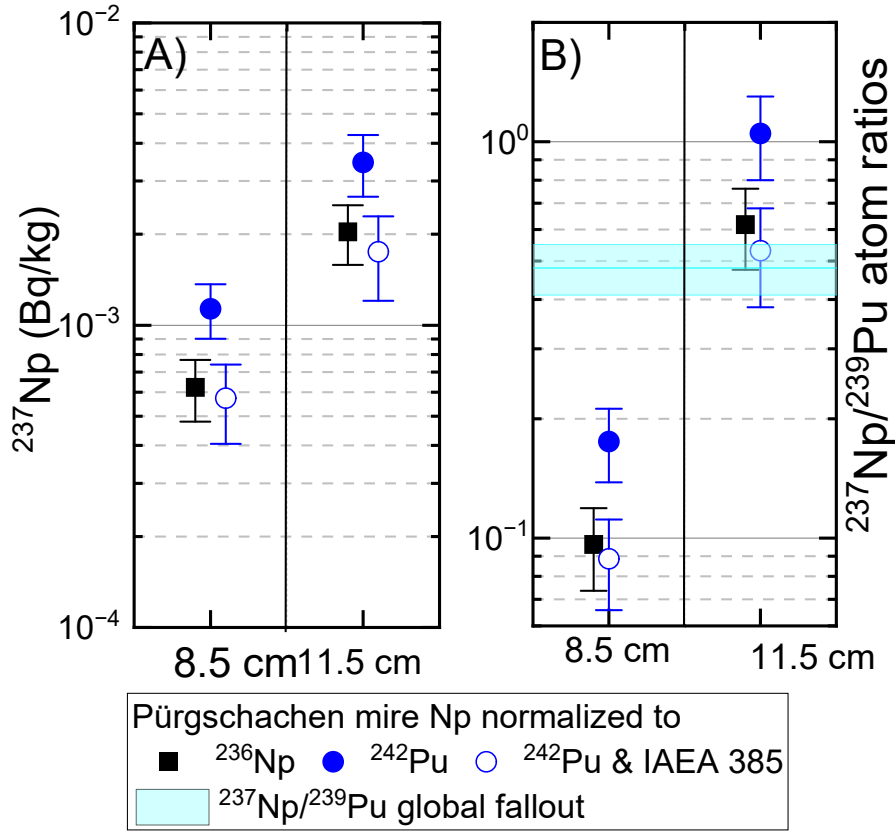


Figure 6.4.5.: ^{237}Np concentrations (A) and $^{237}\text{Np}/^{239}\text{Pu}$ ratios (B) obtained for the two Pürgschachen mire samples. Introducing a correction factor based on the ^{242}Pu -normalized IAEA-385 data results in good agreement (1σ) with the ^{236}Np normalization. The ^{237}Np concentration and the $^{237}\text{Np}/^{239}\text{Pu}$ ratio are significantly higher for the deeper sample, regardless of the normalization method. $^{237}\text{Np}/^{239}\text{Pu}$ in the 21.5 cm sample is compatible (1σ) with integrated northern hemisphere global fallout [Kelley et al. 1999] while the 18.5 cm sample is significantly lower.

6.4.8. Discussion of the environmental data sets:

The alignment of the isotopic spike-normalized data for the peat samples with the ^{242}Pu -normalized data when corrected using IAEA-385 to account for matrix effects, provides a consistent picture and highlights the reliability of the ^{236}Np -spike material. There is very limited data on ^{237}Np in peat samples available in the literature. However, a study of Finnish peat bog samples reported concentrations ranging from $(4.68 \pm 0.01) \cdot 10^{10}$ at/kg to $(3.76 \pm 0.08) \cdot 10^{11}$ at/kg [Salminen et al. 2009], which overlap with the ^{237}Np concentrations for the two peat samples shown in Fig. 5A. The increased ^{237}Np concentration for the deeper (21.5 ± 1.5) cm sample could either indicate that the deeper layer received a higher input from surface deposition at the time of formation, ^{237}Np has been washed out from the upper layers or ^{237}Np migrates vertically.

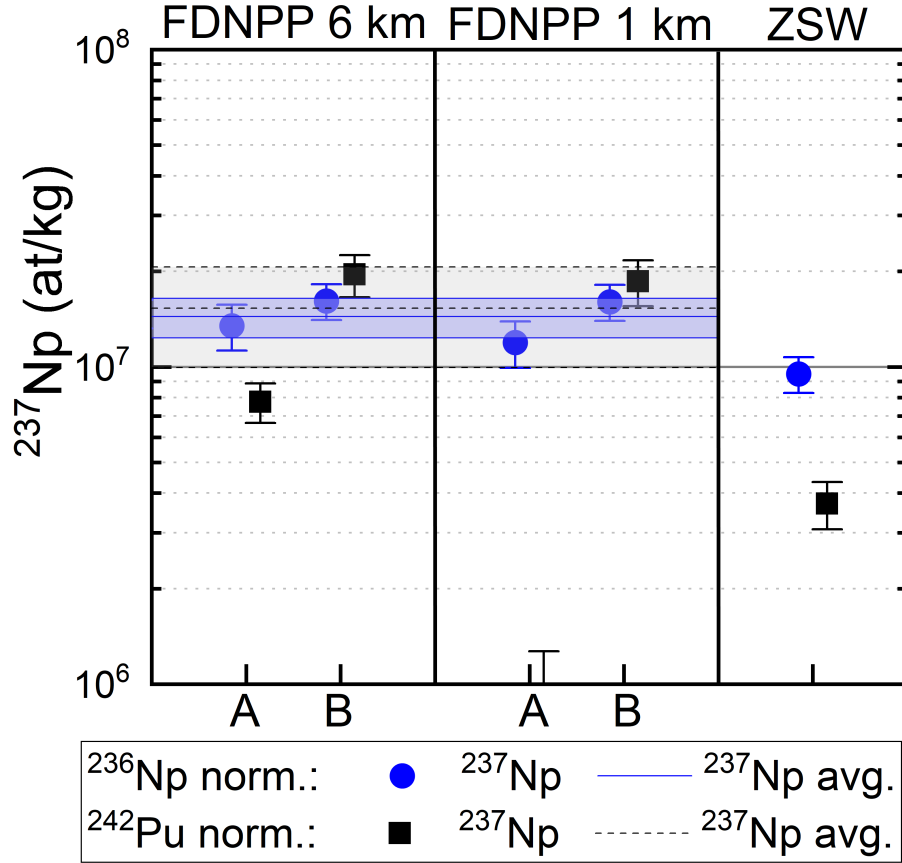


Figure 6.4.6.: ^{237}Np concentrations for the FDNPP-1-km and 6-km samples and the respective aliquots A and B measured in different beamtimes are compatible within 1σ when normalized to ^{236}Np . The ^{242}Pu normalized ^{237}Np data show larger scatter, and for FDNPP-1-km A, the non-isotopic spike normalization failed. The ^{242}Pu normalized Zurich Sea Water (ZSW) sample ^{237}Np concentration is a factor 3 below the ^{236}Np normalized value.

Whereas no peat depth profiles for ^{237}Np concentrations could be found in the literature, a study on soil samples found increased concentrations in deeper layers for ^{237}Np as opposed to other, less mobile actinides, which were found mainly in the top layers [Hursthouse et al. 1991] whereas Quinto et. al. already noted an increased mobility for $^{240,239}\text{Pu}$ compared to ^{236}U [Quinto et al. 2013]. For ^{239}Pu , the two peat samples showed a decline from $(5.02 \pm 0.24) \cdot 10^{12}$ at/kg ^{239}Pu in the upper sample to $(0.322 \pm 0.020) \cdot 10^{12}$ at/kg ^{239}Pu at 21.5 cm. In contrast, the Np activity increased, regardless of the normalization approach. The resulting change in the $^{237}\text{Np}/^{239}\text{Pu}$ ratios shown in Fig. 5B showcases that the Np deposition and/or behavior differ significantly from that of Pu in the Pürgschachen mire samples.

Given the comparable ^{237}Np concentrations measured at both the FDNPP-1-km and FDNPP-6-km stations, a release of significant quantities of Np from the treated water pipeline terminating near the FDNPP-1-km sampling location, at the time of sampling, seems unlikely. To assess whether the ^{237}Np concentrations at both FDNPP sites were elevated by the repeated ALPS water releases in general, a comparison of measured concentrations with representative baseline samples collected prior to the releases

was needed. Therefore, the averaged ^{237}Np concentration from ^{236}Np normalization of $(1.44 \pm 0.18) \cdot 10^7$ at/kg for both FDNPP stations and $(9.28 \pm 0.16) \cdot 10^6$ at/kg for the ZSW sample are compared to concentrations reported for ocean water in previous studies, as shown in Fig. 6.4.7.

To the best of our knowledge, no ^{237}Np data in this region immediately prior to the ALPS release, which was ongoing during sampling, has been published. The Zhang et al., 2020 ^{237}Np concentrations are the closest baseline samples and were measured by SF-ICP-MS and normalized to ^{242}Pu . The reported concentrations were $(9.5 \pm 1.1) \cdot 10^6$ at/kg for the average of the Tokyo Bay surface water (TBS) samples, and $(1.40 \pm 0.12) \times 10^7$ at/kg for sampling stations 30-60 km off the FDNPP (avg). [Zhang et al. 2023], so either 2σ below or indistinguishable from the FDNPP samples in the present study. The Hain et. al. and López-Lora et. al. ^{237}Np concentrations were analyzed by AMS using the non-isotopic ^{242}Pu normalization approach. For samples from two sampling stations 39 km (BD02, surface water) and 254 km (BD07, 50 m depth) east of FDNPP collected in 2012, ^{237}Np concentrations of $(3.0 \pm 0.3) \cdot 10^6$ at/kg and $(6.5 \pm 0.20) \cdot 10^5$ at/kg were reported [Hain 2016]. Surface water from the Pacific Ocean collected ~ 700 km west of the US coast (BD17) by the same sampling cruise, with a surface concentration of $(4.45 \pm 0.90) \cdot 10^5$ at/kg, can serve as a reference in the Pacific Ocean, with negligible direct influence from ALPS water, the FDNPP accident in 2011, and little contribution from the Pacific Proving Grounds. The FDNPP-avg ^{237}Np concentration is comparable to the Zhang data from 2020, but exceeded the other Pacific Ocean comparison samples by a factor of up to 31 (US coast). The difference is less pronounced (factor 5) for the sample collected 39 km off the Japanese coast where tropospheric fallout from the Pacific Proving Grounds is transported by the Kuroshio current. The ZSW sample is only slightly below the two ALPS influenced FDNPP-avg value at $(9.50 \pm 1.2) \cdot 10^6$ at/kg. In a different study, ^{237}Np concentrations in surface water samples ranged from $(1.60 \pm 0.09) \cdot 10^7$ at/kg (DYFAMED, Mediterranean Sea) to $(2.32 \pm 0.13) \cdot 10^7$ at/kg (St.43, Canada Basin) [López-Lora et al. 2021], which are all comparable to the Fukushima samples in the present study. Data on ^{237}Np concentrations from numerous surface water samples from the northern Benguela Upwelling System in the southern Atlantic is also available, with concentrations ranging from $(4.50 \pm 0.31) \times 10^6$ at/kg to $(8.49 \pm 0.62) \cdot 10^6$ at/kg [López-Lora et al. 2020]. By contrast, the IAEA-381 Irish Seawater reference material, which is heavily influenced by the Sellafield reprocessing plant [Povinec et al. 2002], is four orders of magnitude above the other seawater samples. Overall, the ^{237}Np concentrations at FDNPP-1-km and FDNPP-6-km samples fall within typical surface-water concentrations in the general environment as obtained from non-isotopic ^{242}Pu -normalized measurements. The ^{237}Np concentrations did not increase compared with samples taken in 2020 at distances of 30 – 60 km from the FDNPP. Consequently, no significant ^{237}Np source term from the ALPS-treated water in the spring 2024 release could be identified.

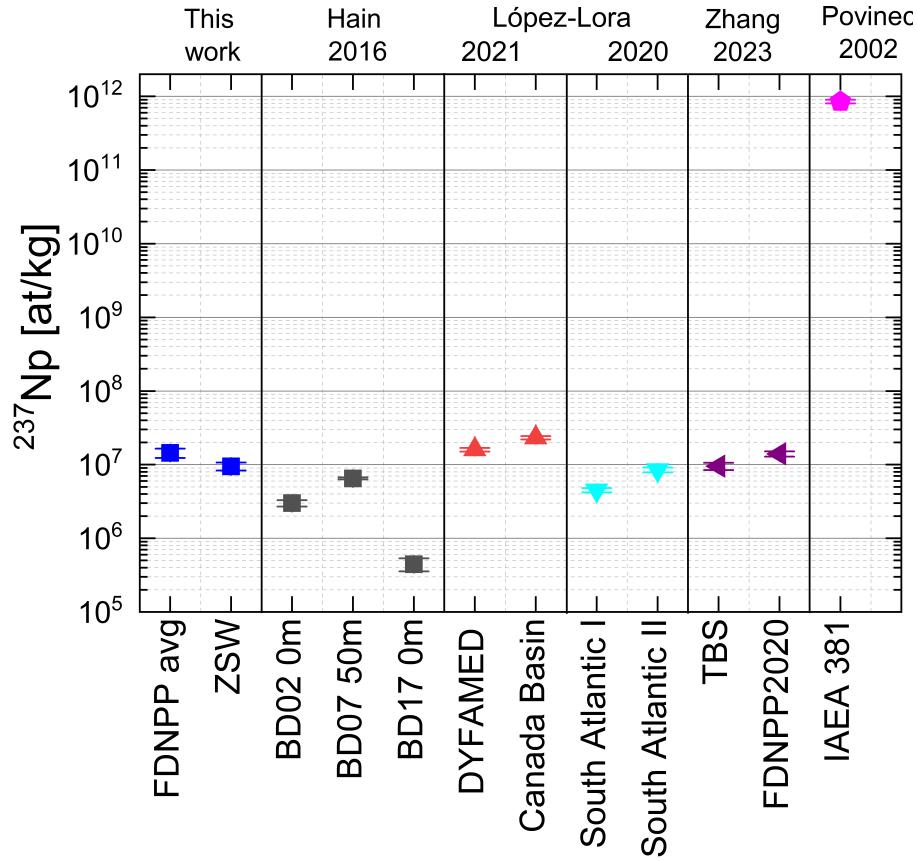


Figure 6.4.7.: The FDNPP-avg ^{237}Np concentration (averaged over both samples) is elevated compared to the other Pacific Ocean samples (BD02, BD07, BD17, Hain 2016 [Hain 2016]) and the Zürich Seawater (ZSW), but comparable to Tokyo Bay Seawater (TBS) and samples taken 30-60 km off FDNPP in 2020 [Zhang et al. 2023], as well as other ocean waters such as the Mediterranean DYFAMED station and the Canada Basin [López-Lora et al. 2021] or the northern Benguela upwelling system in the South Atlantic [López-Lora et al. 2020] but four orders of magnitude below the Sellafield influenced Irish Sea water IAEA-381 [Povinec et al. 2002].

6.4.9. Conclusions

We succeeded in completing the characterization of a new prototype ^{236}Np -spike material (spike II), combining the previous ILIAMS results [Wiederin et al. 2026b] (Chapter 5) of $<0.3\%$ ^{236}Pu and $(7.5 \pm 7.5)\%$ ^{236}U isobaric interference with AMS measurements to determine the $^{237}\text{Np}/^{236}\text{Np}$ ratio to be 6.93 ± 0.27 and the total number of produced and separated ^{236g}Np atoms as $(1.641 \pm 0.014) \cdot 10^9$. This approach, which combined AMS and ILIAMS and was conducted at a single facility, proved highly efficient and enabled the first full characterization of usable quantities of this new ^{236}Np prototype spike material. A total of $\sim 5.6 \cdot 10^8$ at ^{236}Np were consumed for characterization, so the prototype production run yielded sufficient material to normalize 73 environmental samples, assuming $\sim 1.5 \cdot 10^7$ at ^{236}Np spiked per sample [Zhang et al. 2023].

The isotopic spike normalization of ^{237}Np measurements was successfully validated using environmental reference materials and a ^{237}Np dilution series prepared from deep sea-

water samples. Benchmarked against the established ^{242}Pu normalization, the isotopic spike reproduced the nominal ^{237}Np content with higher accuracy, precision, and consistency for most samples. There are clear indications that elemental Pu/Np fractionation is the cause of the incorrect ^{242}Pu normalized results. Notable exceptions were two large IAEA-381 samples, in which isotopic ^{236}Np -spike normalization did not reproduce the nominal value. Using the new AFIA isobar analysis [Wiederin et al. 2022] (Chapter 4), this result could be attributed to significant ^{236}U interference arising from unsuccessful chemical separation of U from the Pu/Np fraction, an extremely high ^{236}U content in the original environmental sample, and the small ($\sim 10^7$ at) quantity of the prototype spike added.

The new prototype ^{236}Np -spike has been applied to selected environmental samples, indicating different behavior of Np and Pu in a peat bog and finding no evidence for a significant ^{237}Np source term from ALPS-treated water in seawater samples taken near the FDNPP. The ^{237}Np concentration of the Zurich sea water intercomparison sample, a proposed reference material for AMS collected from the Mediterranean Sea, was determined to be $(9.28 \pm 0.16) \sim 10^6$ at/kg using the new isotopic ^{236}Np -spike material. With only two data points for the peat bog, the apparent differences in Np and Pu behavior are noteworthy, but for a detailed investigation of Np migration in this matrix, complete depth profiles would be required. Such a data set could be used to either identify increased vertical Np migration compared to Pu if $^{237}\text{Np}/^{239}\text{Pu}$ ratios significantly above the global fallout ratios are found in deeper layers, whereas a depletion of the upper layers and an overall reduced ratio for the integrated column could indicate increased horizontal Np migration, e.g., through water exchange preferentially removing the conservative ^{237}Np . Based on the preliminary findings presented here and the demonstration of a robust normalization approach using the isotopic ^{236}Np -spike, further research on ^{237}Np distributions, full-depth profiles, and migration in peat bogs is now both warranted and feasible.

The current irradiation setup at the offline irradiation beamline of the RIKEN Nishina Azimuthally Varying Field (AVF) cyclotron is not suitable for large-scale production, as this is primarily a research facility with highly competitive beamtime applications. However, there is potential to improve the final ^{236}Np yield to the point that sufficient material for significant ^{237}Np investigations could be produced in the existing setup and transferred to external laboratories. The total quantity of the material produced could be increased by either combining multiple foils, presumably at the cost of a worse $^{236}\text{Np}/^{237}\text{Np}$ ratio; irradiating one foil more often or for a longer total time; or, ideally, irradiating multiple foils at the optimum energy and ^7Li flux for a longer total time. Abandoning the foil stack approach could also reduce thermal limitations and allow for higher ion fluence. Additional data on secondary reactions, such as the ^{237}U co-production, will be required to determine the ideal production scheme.

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7. Developments of analytical techniques for the determination of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios on air filters from Vienna, Austria

Highlights

- ^{237}Np and ^{239}Pu concentrations as well as $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios were determined in aerosol samples representing pure bomb test fallout.
- ^{237}Np and Pu isotopes (with ^{242}Pu as spike) were jointly separated from the matrix.
- By normalization of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios to external standards and to IAEA-385 reference material congruent results were found.

7.1. Abstract

Air filter samples collected in the 1960s and therefore representing pure weapons test fallout were investigated with respect to ^{237}Np and ^{239}Pu concentrations as well as $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios. ^{237}Np and the Pu isotopes (with ^{242}Pu as tracer for both elements) were jointly separated from the matrix using UTEVA resin and were then measured by accelerator mass spectrometry (AMS). Results were normalized to external standards to consider different Np and Pu outputs during the measurement. The resulting $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios were slightly higher than the $^{237}\text{Np}/^{239}\text{Pu}$ ratios of soil samples from literature. As the radiochemical yields of Np as well as of Pu, investigated by α -spectrometry of samples with added ^{237}Np and ^{236}Pu tracers, indicated chemical fractionation, the filter samples were for comparison also normalized to IAEA-385 reference samples which had been processed collaterally. When using the revised literature value for the $^{237}\text{Np}/^{239}\text{Pu}$ ratio of IAEA-385, accordance with the results obtained by normalization to the external standards was found.

7.2. Introduction

Environmental concentrations of ^{237}Np (half-life $2.14 \cdot 10^6$ yr) as well as the Pu isotopes ^{239}Pu ($2.411 \cdot 10^4$ yr) and ^{240}Pu (6563 yr) significantly increased since the onset of the

nuclear age in 1945. The main source of the transuranic radionuclides were the numerous nuclear bomb test explosions, where about 6500 TBq (2800 kg) of ^{239}Pu and 4300 TBq (500 kg) of ^{240}Pu were distributed globally [UN Scientific Committee on the Effects of Atomic Radiation 2000], while the estimated deposited activity of ^{237}Np was clearly lower with about 40 TBq (1500 kg) [Beasley et al. 1998a] which is mainly due to the longer half-life. Additional sources were nuclear accidents (e.g. Chornobyl) or releases from nuclear reprocessing plants (Sellafield, LaHague), which had a more regional or local impact. As ^{239}Pu and ^{240}Pu are α -emitters with very similar α -energies (5.157 MeV and 5.168 MeV, respectively), only sum activities have been measured by α -spectrometry in different samples with regard to radiation protection since the fallout onset (see e.g. [Harley 1980; Irlweck K 1981]), later on also the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios were investigated by thermal ionization mass spectrometry (TIMS) and by accelerator mass-spectrometry (AMS) as a fingerprint characteristic for the Pu origin (see e.g. [Fifield et al. 1996; Hrnccek et al. 2008; Irlweck et al. 1999; Lindahl et al. 2010; Oughton et al. 2001; Perkins et al. 1980; Strebin et al. 1977; Wallner et al. 2022]) and even $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios could be measured [Hain et al. 2017; Zheng et al. 2013].

Environmental ^{237}Np studies, however, have been scarce until now, one of the reasons being that it cannot be measured by decay counting because of its low specific activity in the environment. Being the second most abundant anthropogenic actinide in the environment after ^{239}Pu concerning the deposited mass, again mass spectrometry is the method of choice. However, the scarcity of a convenient isotopic yield tracer hinders the determination of the Np detection efficiency including the chemical yield in mass spectrometric measurements. The beta and gamma emitting ^{239}Np produced by neutron activation of ^{238}U or “milked” from a ^{243}Am tracer can be used for monitoring the chemical recovery during sample preparation [Mietelski et al. 2016], but its short half-life of 2.35 days is an obstacle for mass-spectrometric measurements [Hain et al. 2015][Shi et al. 2015]. ^{235}Np (half-life 396 d) is also omitted due to isobaric interferences (when using ICP-MS or AMS) and its rather short half-life [Qiao et al. 2010]. The isotope ^{236g}Np (half-life $1.53 \cdot 10^5$ yr) used by [Kenna 2002, 2009] would be a better candidate, but its availability is very limited and production and subsequent purification are very elaborate [Jerome et al. 2014; Nakajima et al. 2026; Wiederin et al. 2022]. Most recently, a limited amount has been made commercially available by the US Department of Energy’s (DOE) Isotope Program [National Isotope Development Center 2025]. Therefore, until the ^{236g}Np becomes more readily available, the short-term method of choice has been to separate ^{237}Np together with the Pu isotopes from the sample matrix, and to use ^{236}Pu (half-life 2.85 yr) or ^{242}Pu (half-life $3.76 \cdot 10^5$ yr) as non-isotopic tracer also for ^{237}Np [Chen et al. 2002; Dai et al. 2014; Huang et al. 2024; López Lora 2019; López-Lora et al. 2019a; Matteson et al. 2015; Maxwell et al. 2010b; Qiao et al. 2010, 2011; Röllin et al. 2009]. This method, however, comes with the disadvantage of possible elemental fractionation during the sample preparation process as well as during the measurement. In particular, the formation of negative ions as required for AMS, is strongly

element-dependent [Fifield 2008] and therefore requires correction/normalization using representative external standards [López Lora 2019].

A few years ago, we started to re-investigate air filter samples originally collected in the early 1960s in Vienna, Austria. Directly after collection, short-lived fission products like $^{141}\text{Ce}+^{144}\text{Ce}$, ^{103}Ru and $^{95}\text{Zr}+^{95}\text{Nb}$ had been measured by gamma spectrometry [Schönfeld et al. 1960], later $^{239+240}\text{Pu}$ concentrations were determined [Irlweck K 1981]. A part of the left-over filters was investigated recently relating to $^{240}\text{Pu}/^{239}\text{Pu}$, $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ atom ratios, using the unsurpassed low detection limits of accelerator mass spectrometry (AMS) [Wallner et al. 2022]. The measurement of the “neglected actinide” ^{237}Np , as it was called by Thompson (1982), in these samples representing pristine global weapons testing fallout is the challenge of our recent work. Due to sampling near ground level only a small contribution of resuspended matter might be present. Also, post-depositional migration is excluded, so that the samples reveal snapshots of the aerial fallout concentrations within 3-months periods of the years 1964 to 1966 (unfortunately samples from 1961-1963 were not available).

With only a ^{242}Pu -spike available for the two Pu isotopes and ^{237}Np , not only the AMS recovery rates of ^{237}Np and the Pu isotopes must be well known, but also the conformity between Np and Pu during the chemical separation must be verified. The relative AMS detection efficiencies can be estimated from the above mentioned “external standards”, i.e. samples with a known $^{237}\text{Np}/^{239}\text{Pu}$ ratio containing defined amounts of ^{237}Np and ^{242}Pu solutions dried or co-precipitated with $\text{Fe}(\text{OH})_3$ followed by calcination. Chemical conformity of Np and Pu during the separation procedure first was checked by α -spectrometry with double-spiked (^{237}Np and ^{242}Pu) filter samples. Later we used the reference material IAEA-385 for the correction of possible chemical fractionation during the chemical separation procedure and potential matrix effects. Also, different Np and Pu ion outputs from the AMS ion source, as well as differences in ion transmission throughout the entire AMS setup, could be revised simultaneously.

7.3. Materials and Methods

As the pursued data should represent the mean value of a 3 months’ period to be directly comparable with our previous research [Wallner et al. 2022], quarters were cut off from 40 out of 90 sequenced filters and ashed at 450 °C overnight. The respective ash masses were 50-60 mg and represent the aerosol mass present in 1500 m³ of air. Complete dissolution of the ashes was achieved by microwave digestion (30 min heating up, then 30 min at 220 °C) using 7 mL inverse aqua regia (HNO_3 conc./ HCl conc. = 3/1) and 1 mL of concentrated hydrofluoric acid. After cooling down, the microwave step was repeated after adding 0.4 mg boric acid for destruction of the redundant HF. The resulting solutions were twice evaporated to dry with 7.2 M HNO_3 and the residues were dissolved in 15 mL 7.2 M HNO_3 . No losses of Pu and Np were found at this stage by

processing spiked samples. 10 % of these solutions (corresponding to 150 m^3 of air, or 5-6 mg aerosol mass) were then processed as respective samples.

For the microwave and leaching (see below) procedures as well as for the AMS sample preparation, HCl 30% Suprapur (MerckTM) and HNO₃ ROTIPURANTM Supra (Carl Roth GmbH + Co) were used. All other chemicals were of normal p.a. grade.

For preparing an AMS sample containing Np as well as Pu, we followed a procedure already in use at VERA [Hain et al. 2022; Maxwell et al. 2010a]: to a 1.5 mL aliquot of the sample solution a weighted amount of a ^{242}Pu -spike (IRMM-085) was added at least 72 hours before starting the sample preparation. Then 15 mL of Milli-Q water, 0.75 mL of a pre-nuclear FeCl₃ solution (concentration of the Fe carrier: 2 mg/mL) and NH₃ (25 %) were added until Fe(OH)₃ precipitation started (maximum pH 8.5). Afterwards, the precipitate is centrifuged, washed, and dissolved in 12 mL 3 M HNO₃ – 0.5 M Al(NO₃)₃. By subsequently adding 0.5 mL of 1.5 M sulfamic acid, 1.25 mL of 1.5 M ascorbic acid, and after 3 min waiting 240 mg NaNO₂ in small portions, the oxidation states of Np as well as of Pu were adjusted to 4+ [Maxwell et al. 2010b]. After that the solution should be stirred for at least 15 min to get rid of gases still present in the samples, which would not allow a smooth sample flow through the column in the following step. Np and Pu are both separated from matrix elements and other radionuclides by using a small column (2 mL) containing UTEVA resin conditioned with 3 M HNO₃. To elute Np and Pu from the column, 20 mL of 2 M HNO₃ – 0.1 M oxalic acid were used. This solution is then heated up to 220°C in a microwave (1 hour heating up, then 1 hour at 220°C) to destroy the oxalates. This is necessary as oxalates compete with the formation of the Fe(OH)₃ precipitate and therefore might reduce the recovery of Np from the subsequent co-precipitation with Fe(OH)₃. The precipitate is centrifuged and dried at 90°C for 20 hours before being calcinated for 4 hours at 800°C. The calcined samples (Np and Pu in Fe₂O₃) were pressed into Al sample holders for AMS measurement.

Usually, 3 samples are processed simultaneously together with a blank (1.5 mL of 7.2 M HNO₃, spiked with ^{242}Pu). To correct for differences in the ionization yields of Np and Pu from the Cs sputter ion source, weighted amounts of the ^{242}Pu -spike (IRMM-085) and of a ^{237}Np solution (diluted from: Eckert & Ziegler 6237, 370 Bq) were coprecipitated with Fe(OH)₃ and calcined as external standards. For some of the experiments external standards were prepared without Fe(OH)₃ coprecipitation for comparison: the ^{242}Pu -spike and the ^{237}Np solution were added to a pre-nuclear FeCl₃ solution (containing 1 mg Fe), which was then dried at 90°C before calcination (satisfying agreement between coprecipitated and dried only external standards was found).

The reproducibility of the synchronous Np and Pu separation was tested by α -spectrometry of corresponding samples (i.e. 1.5 mL aliquots of the aerosol sample solution) after addition of known amounts of ^{236}Pu and ^{237}Np spike solutions (25 and 35 mBq of AN-Pu236-1-2019 and AN-Np237-1-2019, respectively). Due to the small sample mass, the interfering ^{230}Th activity ($E_\alpha = 4.69\text{ MeV}$) was much smaller than the added ^{237}Np activity ($E_\alpha = 4.79\text{ MeV}$). After elution from the column, ^{237}Np and

^{236}Pu were measured using an ion-implanted surface-barrier detector (BU-019-450-500, OrtecTM) after microprecipitation with neodymium fluoride [Hindman 1983; Joshi 1985].

For validation/normalization of our procedure also samples of the IAEA-385 reference material (natural and artificial radionuclides in sediment from the Irish Sea [Mauring et al. 2019]) were prepared. In the absence of reference materials for radionuclides in air filters, we consider the sediment to represent the best available proxy for mineral dust that forms the matrix of the aerosol samples (this assumption was verified within the scope of this work – see below). In this case, 2 g of sediment were dried at 105°C for 24 hours and subsequently leached in 50 mL of boiling inverse aqua regia (HNO_3 conc./ HCl conc. = 3/1) for 3 hours. After filtering off the remaining sediment and repeated evaporation of the leachate to dry with 7.2 M HNO_3 , the residue was taken up in 50 mL of 7.2 M HNO_3 . From this solution, ^{242}Pu -spiked aliquots corresponding to sample masses of 0.1, 0.25 and 0.5 g were processed.

However, using IAEA-385 sediment samples as reference encompasses a problem: only the sum activity of ^{239}Pu and ^{240}Pu is given as certified value of (2.98 ± 0.26) mBq/g, whereas the ^{239}Pu and ^{237}Np activities are denominated as information values only, with (1.92 ± 0.07) and (0.0185 ± 0.0027) mBq/g, respectively [Mauring et al. 2019]. From these values a $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio of 0.86 ± 0.13 can be calculated. In the meantime, measured values of the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios were published (e.g. by [Goldstein et al. 2021; Huang et al. 2023; Zheng et al. 2022]) with an average atom ratio of 1.014 ± 0.016 derived by [Qin et al. 2024] in a comprehensive survey of reference materials.

To check for possible matrix effects, different amounts of the IAEA-385 reference material, i.e. 0.1, 0.25 and 0.5 g, were double-spiked with ^{236}Pu and ^{237}Np and measured by α -spectrometry. Obtained ^{237}Np and ^{236}Pu yields were compared to the respective yields of double-spiked filter samples.

7.3.1. AMS measurement

The AMS measurements were performed at the Vienna Environmental Research Accelerator (VERA) of the University of Vienna. The current configuration of the setup and the routine procedure for actinide measurements have been described previously [Steier et al. 2019]. In short, monoxide actinide anions (NpO^- , PuO^-) are extracted from a Cs-sputter ion source mass selected for injection into the tandem accelerator using the low-energy mass spectrometer consisting of a 45° electrostatic analyzer and a 90° injector magnet. The accelerator is operated at a terminal voltage of ~ 1.65 MV and He is used as stripper gas to disintegrate all molecules by charge exchange processes leading to a positive charge state distribution. The subsequent high-energy mass spectrometer, consisting of a 90° electrostatic analyzer and two 90° magnets, selects the desired mass in the 3^+ charge state. Macroscopic ion currents – mainly $^{238}\text{UO}^-$ or $^{238}\text{U}^{3+}$ used for beam tuning and quality control – are measured in Faraday cups, while trace ions can

be measured via single ion counting in a gas filled ionization chamber (Bragg type detector). The second high-energy magnet suppresses the background from multiple scatter events as well as tailing from neighboring masses, so that with a sufficiently high stripper gas pressure for the suppression of $^{238}\text{UH}^{3+}$, $^{239}\text{X}^{3+}/^{238}\text{U}^{3+}$ ratios below 10^{-14} can be achieved [Steier et al. 2019]. A similar performance can be expected for $^{237}\text{Np}^{3+}/^{238}\text{U}^{3+}$.

For each sample, the trace isotopes ^{239}Pu , ^{240}Pu , and ^{237}Np were measured alongside the spike isotope ^{242}Pu . For each run, the $^{239}\text{Pu}/^{242}\text{Pu}$ or $^{237}\text{Np}/^{239}\text{Pu}$ ratio was then calculated, averaged over all runs and then multiplied by the nominal number of ^{242}Pu -spike atoms to obtain the absolute number of ^{239}Pu or ^{237}Np in the sample. Process blanks are measured alongside all samples, and a blank correction is performed by subtracting the number of atoms calculated for the blank from each corresponding sample. The deviation of the measured $^{237}\text{Np}/^{242}\text{Pu}$ ratio from the nominal ratio of the external standard is used as a correction factor to compensate for differences in anion formation efficiency or ion optical transmission. This correction factor is applied to the $^{237}\text{Np}/^{242}\text{Pu}$ ratio in each run before averaging, in order to take variations in the ion source output into account. Furthermore, the three samples from the reference material IAEA-385 were also analyzed alongside the filter samples for comparison. The same IAEA-385 AMS targets were also used in an independent measurement to verify the reproducibility of the results.

Uncertainties are calculated either from the statistical uncertainties of the counting results for the individual runs or the standard deviation of all averaged runs, whichever is larger, using Gaussian error propagation. For samples with less than 10 registered events per run, the total number of detected counts is divided by the total counting time to calculate the average count rate. Uncertainties are given at the σ confidence interval unless stated otherwise.

7.4. Results and discussion

Before preparing the AMS sample set, a corresponding filter sample set was double-spiked with higher amounts of ^{237}Np and ^{236}Pu for α -measurements to check the conformity of the Np and Pu separation. The chemical yields of ^{237}Np and ^{236}Pu were only slightly different with $(83.0 \pm 2.7) \%$ and $(79.9 \pm 2.2) \%$, respectively, resulting in a fractionation factor of $\text{Np-yield}/\text{Pu-yield} = 1.04 \pm 0.07$ (see Fig. 7.4.1), the uncertainty being the standard deviation of the average value from 10 samples. This means that fractionation can be considered negligible in this case.

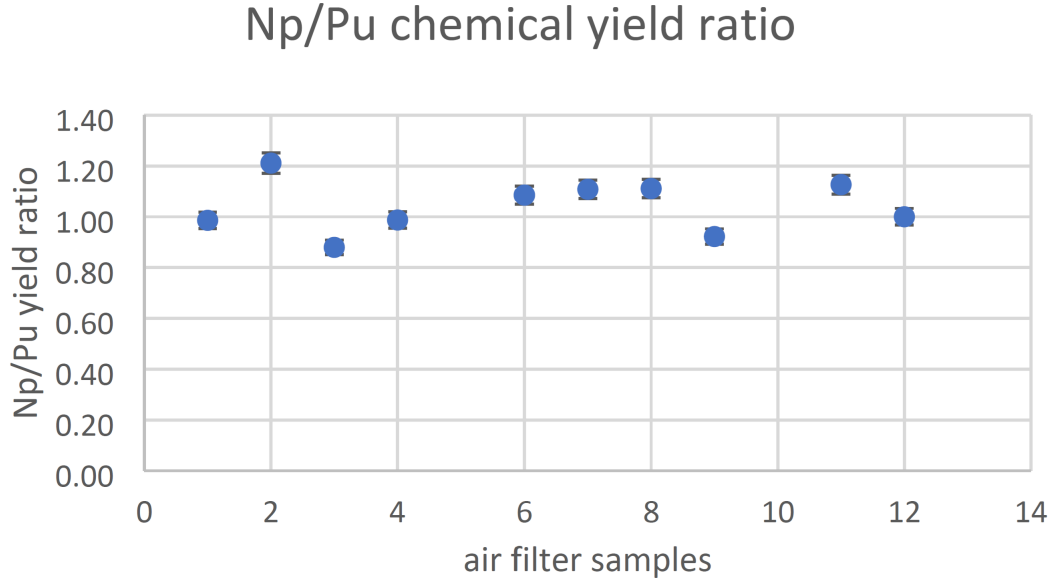


Figure 7.4.1.: Np/Pu chemical yield ratios of filter samples spiked with known amounts of ^{237}Np and ^{239}Pu and measured by α -spectrometry.

The AMS measurement results of 10 filter samples from the years 1964-66 are presented in Tab. 7.4.1. The $(^{239}+^{240})\text{Pu}$ activity concentrations as well as the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of the filter samples agree very well with our previous measurements from 2022 [Wallner et al. 2022] and again indicate the homogeneity and therefore also comparability of our samples made up of different filter quarters selected from filters collected within three month periods. Tab. 7.4.2 shows ^{239}Pu and ^{237}Np concentrations in atoms per sample and Fig. 7.4.2 reveals clearly the concordant trend of these radionuclides over three successive years. A contribution to the uncertainty of the final concentration that is similar to the measurement uncertainty comes from the collected air volume, which is only known to an accuracy of 10 %. The radionuclide concentrations and the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios are blank corrected as well as corrected for different Np and Pu output from the AMS machine via the external standards. These ratios show a higher scatter as well as higher uncertainties compared to the isotopic $^{240}\text{Pu}/^{239}\text{Pu}$ ratios (see Tab. 7.4.1) and are in the range of 0.46 ± 0.07 to 0.69 ± 0.06 , clearly higher than expected from the ratios given by [Beasley et al. 1998b] (0.45 for the northern hemisphere) and [Kelley et al. 1999] (0.45 to 0.53 for middle and northern Europe). It has to be noted that blank levels for ^{237}Np are substantially higher than for the Pu isotopes. Especially for sample 1965-Q4, the blank correction accounts for 30 % of the measured value (Fig. 7.4.3). This leads to correspondingly increased uncertainties so that this value has less influence on the weighted average for the overall $^{237}\text{Np}/^{239}\text{Pu}$ ratio of global fallout derived from these data.

Sample	$^{239+240}\text{Pu}$ activity conc. (mBq/100 m ³)		$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	
	this work	Wallner et al. (2022)	this work	Wallner et al. (2022)
1964 Q1	1.04 ± 0.14	1.05 ± 0.11	0.234 ± 0.009	0.221 ± 0.009
Q2	3.12 ± 0.33	3.29 ± 0.35	0.209 ± 0.023	0.208 ± 0.020
Q3	1.79 ± 0.18	1.71 ± 0.17	0.195 ± 0.006	0.196 ± 0.008
Q4	0.28 ± 0.03	0.26 ± 0.03	0.195 ± 0.009	0.188 ± 0.008
1965 Q1	0.39 ± 0.05	0.37 ± 0.04	0.195 ± 0.026	0.190 ± 0.006
Q2	0.74 ± 0.08	0.76 ± 0.08	0.177 ± 0.008	0.199 ± 0.007
Q3	0.42 ± 0.05	0.44 ± 0.04	0.176 ± 0.009	0.184 ± 0.005
Q4	0.50 ± 0.05	0.09 ± 0.01	0.152 ± 0.007	0.184 ± 0.005
1966 Q2	0.41 ± 0.05	n.m.	0.169 ± 0.005	0.164 ± 0.007
Q3	0.18 ± 0.03	0.13 ± 0.01	0.165 ± 0.008	0.182 ± 0.007

Table 7.4.1.: AMS results normalized to external standards: Calculated $^{239+240}\text{Pu}$ activity concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of filter samples in comparison with previous measurements.

Sample	^{239}Pu atoms ·10 ⁸ /sample	Normalized to ext. standard		Norm. to IAEA-385 reference	
		^{237}Np atoms ·10 ⁸ /sample	$^{237}\text{Np}/^{239}\text{Pu}$ atom ratio	^{237}Np atoms ·10 ⁸ /sample	$^{237}\text{Np}/^{239}\text{Pu}$ atom ratio
1964 Q1	9.83 ± 0.71	6.81 ± 0.30	0.694 ± 0.059	6.64 ± 0.31	0.676 ± 0.060
Q2	30.2 ± 2.70	18.2 ± 0.65	0.593 ± 0.063	17.9 ± 0.70	0.583 ± 0.063
Q3	18.2 ± 1.57	12.3 ± 0.54	0.653 ± 0.072	11.9 ± 0.92	0.632 ± 0.080
Q4	2.74 ± 0.16	1.56 ± 0.40	0.572 ± 0.049	1.56 ± 0.06	0.571 ± 0.052
1965 Q1	3.80 ± 0.22	2.23 ± 0.12	0.586 ± 0.053	2.27 ± 0.74	0.598 ± 0.048
Q2	7.41 ± 0.44	4.81 ± 0.35	0.637 ± 0.074	4.74 ± 0.36	0.628 ± 0.074
Q3	4.32 ± 0.23	2.27 ± 0.11	0.527 ± 0.047	2.33 ± 0.10	0.542 ± 0.047
Q4	0.78 ± 0.06	0.35 ± 0.03	0.456 ± 0.069	0.33 ± 0.03	0.426 ± 0.066
1966 Q2	4.24 ± 0.22	2.94 ± 0.12	0.693 ± 0.054	2.86 ± 0.16	0.673 ± 0.058
Q3	1.81 ± 0.27	1.09 ± 0.05	0.560 ± 0.079	1.04 ± 0.06	0.535 ± 0.077

Table 7.4.2.: AMS results for atom concentrations and atom ratios: ^{237}Np and $^{237}\text{Np}/^{239}\text{Pu}$ normalized to external standards and normalized to IAEA-385 reference samples.

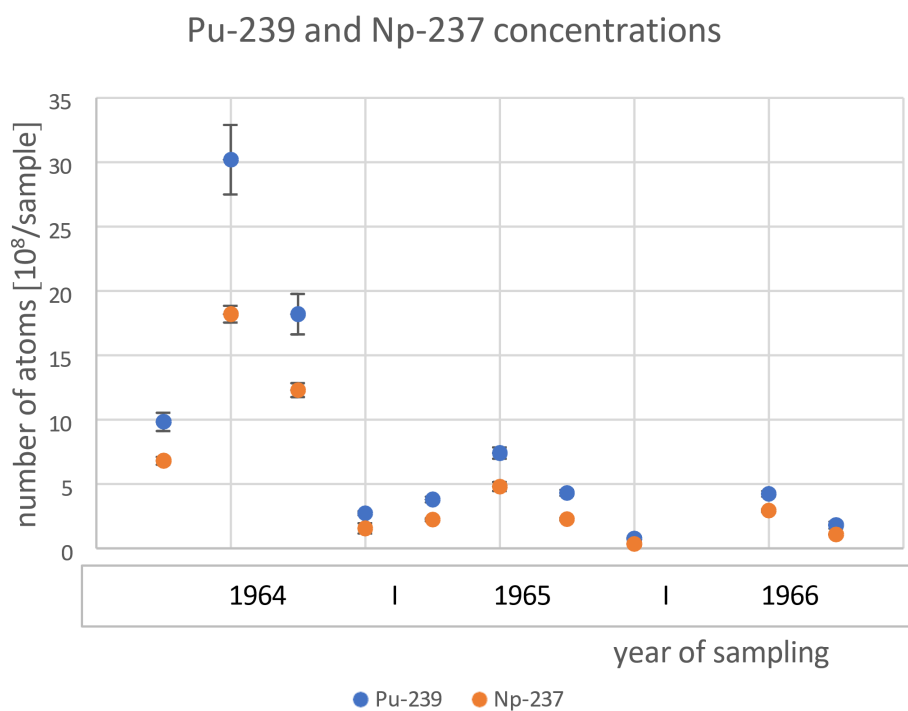


Figure 7.4.2.: AMS results normalized to external standards: ^{239}Pu and ^{237}Np atom concentrations.

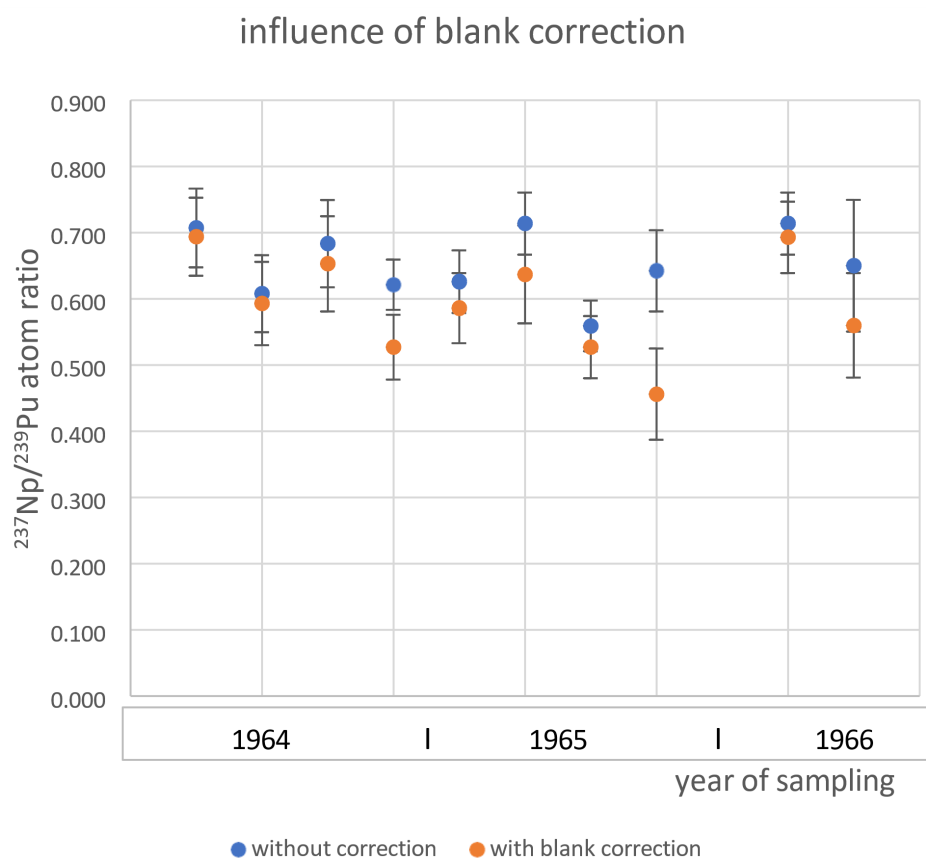


Figure 7.4.3.: $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios normalized to external standards without and with blank correction

The three IAEA-385 reference samples, processed and measured together with the filter samples for quality control, were initially also normalized to the external standards to obtain values for the ^{237}Np concentration and $^{237}\text{Np}/^{239}\text{Pu}$ ratios for comparison with the literature values (see Tab. 7.4.3). The measured ^{239}Pu atom concentrations of all three reference samples are a bit lower (within 1σ), while the ^{237}Np values of the 0.1 g and 0.5 g samples are slightly higher (again within 1σ) than the respective information values. The 0.25 g reference sample failed due to severe loss of ^{237}Np (this implies that at least three reference samples per measurement must be produced for quality control). The average $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio of the 0.1 g and 0.5 g reference samples was 1.09 ± 0.12 from the two independent measurements. This value is 26% higher than the value calculated from the information values in the IAEA reference sheet, but it is in very good agreement with the average measured value of 1.014 ± 0.016 already published by [Qin et al. 2024]. Our work therefore supports a higher ^{237}Np concentration of the IAEA-385 reference material.

When comparing filter and reference samples we must bear in mind that we compare different sample matrices (aerosols vs. sediment) and different sample masses (5-6 mg aerosol mass vs. at least 100 mg sediment mass), which can influence the chemical yields of Np and Pu as well as their respective ionization yields. The chemical yield investigation required repeated parallel sample preparations of two filter and two 0.1 g IAEA-385 sediment samples for α -spectrometry, all of them double-spiked with known activities of ^{236}Pu and ^{237}Np . Table 7.4.4 shows the $^{237}\text{Np}/^{236}\text{Pu}$ yield ratios found in these experiments: the ratios of filter and sediment samples agree within the measurement uncertainties ($\pm 3\%$) for all sample sets, which means that the IAEA-385 sediment reference sample is a reasonably good proxy for the mineral dust collected on air filters. Although different sample matrices are investigated, this probably can be attributed to the fact that not only the aerosol masses, but also the sediment masses are rather small. The results of different sets, however, are diverging by 15%. Yet really striking is the fact that the chemical yield ratios in this measurement series show variable chemical fractionation with Np yields 40-60% higher than Pu yields, in contradiction to the first investigation with a fractionation factor of only 1.04 ± 0.07 (see Fig. 7.4.1). The normalization of ^{237}Np to a non-isotopic Pu-spike is extremely sensitive to small variations in the chemical conditions during the preconcentration and separation steps [Hain et al. 2022; Qiao et al. 2010]. Most likely the oxidation state adjustment is the critical step: when the reaction time after the NaNO_2 addition varies, Np and Pu yields show large differences [Qiao et al. 2010]. The AMS filter samples were stirred for 15 min after adding NaNO_2 and before transferring them to the UTEVA columns, because shorter stirring times as applied with the first set used for Np and Pu yield determination had caused practical problems on the columns: nitrous fumes still dissolved in the sample solution effused and so dispersed the resin and/or made it floating on top of the sample solution. When investigating the sets comprising 2 filter and 2 0.1 g IAEA-385 samples, the stirring times varied and were even longer. When using cartridges instead of open

columns it should be possible to adjust shorter and repeatable stirring times and so to minimize this problem. To completely eliminate this problem an isotopic Np-spike would be necessary.

Based on the results of the radiometric experiments that the IAEA-385 reference material is a good proxy for the aerosol matrix, a complementary data evaluation was carried out using the literature values of IAEA-385 for normalization. The comparison with the results obtained by normalization to the external standards allows to investigate potential fractionation effects during chemical sample preparation as well as in the ion source caused by matrix effects during ion formation. For the normalization, we used the 0.1 g and the 0.5 g samples which did not show obvious Np losses during sample preparation and the literature value from [Qin et al. 2024] of 1.014 ± 0.016 for the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio (see Tab. 7.4.2), as also an independent AMS measurement of the IAEA-385 reference samples gave a value higher than derived from the information value (see discussion above). Both the ^{237}Np concentrations as well as the $^{237}\text{Np}/^{239}\text{Pu}$ ratios were in excellent agreement (within one sigma) with the results determined by normalization to the external standards (Fig. 7.4.4), which indicates negligible elemental fractionation between Pu and Np by the applied preparation and measurement procedures.

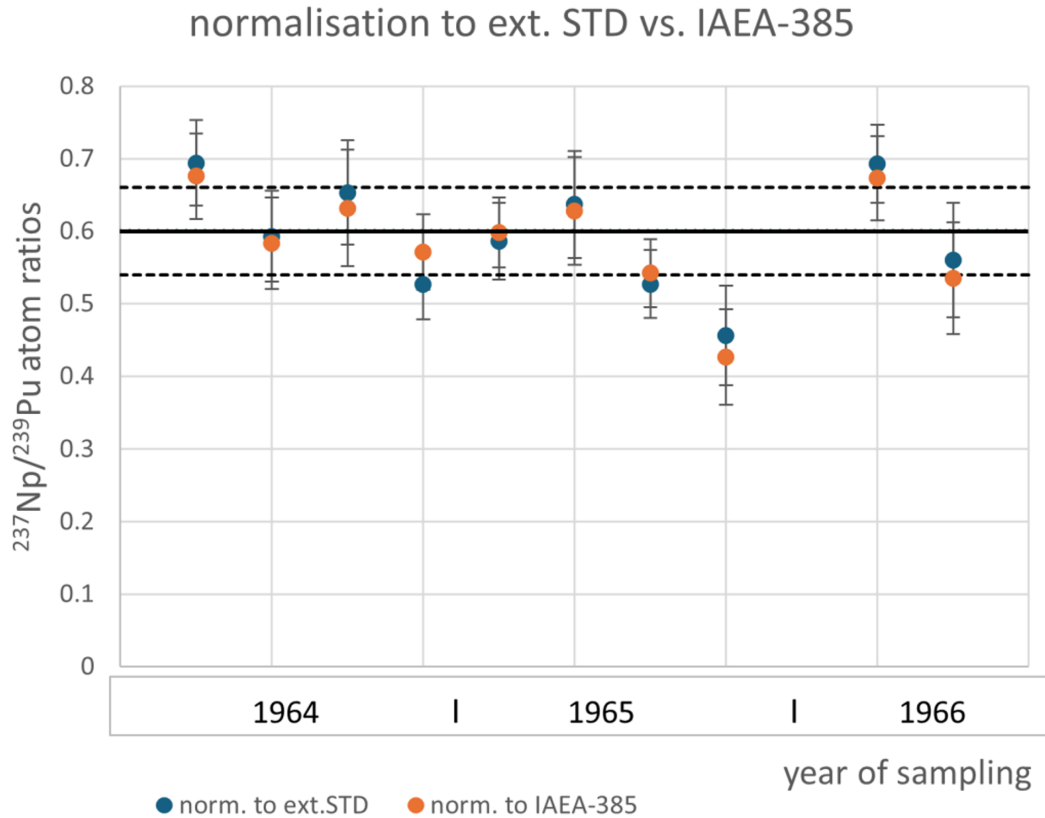


Figure 7.4.4.: $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios normalized to external standards (blue) and to IAEA-385 reference (orange). The dashed lines indicate the average of all results (full line) $\pm 1 \sigma$ uncertainty.

IAEA-385	$(^{239}+^{240})\text{Pu}$ activity conc.(mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	^{239}Pu atoms $\cdot 10^8 /$ g	^{237}Np atoms $\cdot 10^8 / \text{g}$	$^{237}\text{Np}/^{239}\text{Pu}$ atom ratio
0.1 g	2.88 ± 0.18	0.172 ± 0.013	19.3 ± 1.1	20.8 ± 2.1	1.04 ± 0.13
0.25 g	2.63 ± 0.24	0.188 ± 0.018	17.1 ± 1.5	6.9 ± 0.8	0.40 ± 0.06
0.5 g	2.57 ± 0.42	0.190 ± 0.034	16.6 ± 2.5	20.8 ± 1.6	1.13 ± 0.19
certified value	2.98 ± 0.26				
information val. /calcu- lated val.			21.0 ± 0.8	18.1 ± 2.6	0.86 ± 0.13
Qin et al. (2024)					1.014 ± 0.016

Table 7.4.3.: Results of IAEA-385 reference samples (normalized to external standards).

Sample	yield Np	yield Pu	yield Np / yield Pu	average
IAEA-385 0.1g-a	0.87 ± 0.02	0.58 ± 0.01	1.50 ± 0.04	
IAEA-385 0.1g-b	1.02 ± 0.02	0.60 ± 0.01	1.70 ± 0.05	1.60 ± 0.04
1964 Q3-a	0.83 ± 0.02	0.52 ± 0.01	1.60 ± 0.04	
1964 Q4-a	0.95 ± 0.02	0.60 ± 0.01	1.58 ± 0.04	1.59 ± 0.04
IAEA-385 0.1g-c	0.98 ± 0.02	0.67 ± 0.02	1.46 ± 0.04	
IAEA-385 0.1g-d	0.82 ± 0.02	0.55 ± 0.01	1.49 ± 0.04	1.48 ± 0.04
1964 Q3-b	0.94 ± 0.02	0.65 ± 0.01	1.45 ± 0.04	
1964 Q4-b	0.86 ± 0.02	0.61 ± 0.01	1.41 ± 0.04	1.43 ± 0.04
IAEA-385 0.1g-e	0.96 ± 0.02	0.67 ± 0.02	1.43 ± 0.04	
IAEA-385 0.1g-f	1.01 ± 0.02	0.71 ± 0.02	1.42 ± 0.04	1.43 ± 0.04
1966 Q3-a	0.99 ± 0.02	0.74 ± 0.02	1.34 ± 0.04	
1964 Q1-a	0.74 ± 0.02	0.54 ± 0.01	1.37 ± 0.04	1.36 ± 0.04
IAEA-385 0.1g-g	0.98 ± 0.02	0.65 ± 0.01	1.51 ± 0.04	
IAEA-385 0.1g-h	0.86 ± 0.02	0.56 ± 0.01	1.54 ± 0.04	1.53 ± 0.04
1966 Q3-b	0.69 ± 0.02	0.48 ± 0.01	1.44 ± 0.04	
1964 Q1-b	0.63 ± 0.01	0.43 ± 0.01	1.47 ± 0.04	1.46 ± 0.04

Table 7.4.4.: Chemical yields of Np and Pu: comparison of IAEA-385 and filter samples double-spiked with ^{237}Np and ^{236}Pu and measured by α -spectrometry.

From the individual results for the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios within the investigated time span between the beginning of 1964 and the end of 1966, we can derive an overall $^{237}\text{Np}/^{239}\text{Pu}$ signature for global fallout by calculating the weighted average value using their inverse relative 1σ -uncertainties as weights. The $^{237}\text{Np}/^{239}\text{Pu}$ average for the results obtained by normalization to external standards was 0.61 ± 0.06 , while those normalized to the IAEA-385 reference material (assuming that the compiled Q_{in} value is correct) give a weighted average of 0.60 ± 0.06 . While both values are in excellent agreement, in our opinion 0.60 ± 0.06 is the preferred value as it is – contrary to the values normalized to external standards – also corrected for chemical fractionation and not only for different ion output during the AMS measurement (although in this case this is a rather theoretical decision). The value of the present study is a bit higher than the values given by [Kelley et al. 1999] for middle and northern Europe (0.45 to 0.53) but show reasonable agreement within the given uncertainty, i.e. 1.2σ , with results from Ispra (Italy), Munich (Germany), Wantage (UK) and Roskilde (Denmark) (0.52-0.53), the sampling stations nearest to Austria. It has to be noted that the investigated sample batch does not cover the most active phase of nuclear testing as corresponding filter samples were no longer available. [Kelley et al. 1999] already pointed out that the production of ^{237}Np could be much more device dependent than the ^{239}Pu production. As the weapons design strongly changed from fission to fusion devices and from US to UdSSR design during the phase of atmospheric testing, it seems likely that the difference in the $^{237}\text{Np}/^{239}\text{Pu}$ global fallout ratio originates from different time spans covered in the different studies.

7.5. Conclusions and outlook

Ten air filter samples collected in Vienna in the years 1964 – 1966 and representing pure weapons test fallout were investigated with respect to ^{237}Np and ^{239}Pu concentrations and $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios. ^{237}Np and the Pu isotopes (with ^{242}Pu as tracer for both elements) were jointly separated from the sample matrix and then measured by AMS. The found ^{237}Np concentrations followed the time trend of ^{239}Pu at lower concentration, and the average $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio (derived by normalization to the IAEA-385 reference sample) of 0.60 ± 0.06 was only slightly higher than the values given by [Kelley et al. 1999] for middle and northern Europe (0.45 to 0.53).

Even though in the present study no matrix effects could be observed, the radiometric experiments indicate a strong dependence on the prepared batch and hence on the chemical (redox) conditions, as for the presented approach it must be ensured that Np and Pu are in the same oxidation state, i.e. +IV. It should also be pointed out that our conclusion that there was no fractionation is based on the assumption that the Q_{in} value for IAEA-385 is accurate. This is supported by our independent measurement of the reference samples using normalization to external standards, but the critical dependence on this value demonstrates the urgent need for more reference materials certified also

for ^{237}Np for method validation and quality control. The developed approach yielded promising results for the analysis of air filters, but it requires parallel measurements of additional reference materials and standards, hence limiting the number of free positions on the AMS sample wheel for unknown samples. While this approach therefore seems well suited to analyzing further selected air filters from the period of maximum atmospheric testing to finally characterize the $^{237}\text{Np}/^{239}\text{Pu}$ signature of global fallout, it is too time-consuming for monitoring environmental ^{237}Np concentrations. For this purpose and to obtain results with higher accuracy and precision, an isotopic spike for Np would be still essential to be less dependent on exact reiteration of the separation protocol. Beyond that it would be particularly important for the correct determination of the ^{237}Np concentration in reference materials which are then used for quality control.

Part III.

Synthesis

8. Discussion

8.1. Overview of the outcome

The overall goal of the thesis, the development of the methodology for characterizing a new isotopic ^{236}Np -spike for ^{237}Np measurements, has been achieved. Two new and independent methods for the analysis of the isobaric composition of ^{236}X in the spike material have been developed and applied, demonstrating the successful production and separation of ^{236}Np in Chapters 4 and 5. Then, ^{236}Np was quantified along with co-produced (or in-grown) ^{237}Np using AMS measurements in Chapter 6. The final prototype spike material (spike II) has a $^{236}\text{Np}/^{237}\text{Np}$ ratio of 6.93 ± 0.27 and a total of $(1.64 \pm 0.14) \cdot 10^9$ atoms ^{236}Np have been produced and separated. Isobaric interference from ^{236}Pu has been determined to be less than 0.3 %, and the ^{236}Np fraction is $(92.5 \pm 7.5) \%$ of ^{236}X , with the uncertainty dominated by the limited sensitivity of the ^{236}U analysis.

After the full characterization, small quantities of two prototype spike materials, sufficient for the normalization of 15 (spike I) and 73 (spike II) environmental samples respectively, have been available for first applications. Using these ^{236}Np -spikes on environmental reference materials, validation samples and environmental samples were analyzed. A non-isotopic ^{242}Pu -spike was also added to provide a direct comparison of the normalization performance for ^{237}Np measurements by AMS.

Overall, the ^{236}Np normalization clearly outperformed the non-isotopic approach, providing both a better accuracy and reliability on a ^{237}Np dilution series in deep sea water: As shown in Figure 6.4.2, for individual validation samples the average relative uncertainty of the isotopic spike normalized data at 12 % was lower than the 16 % achieved for the non-isotopic normalization. These uncertainties were calculated either from counting statistics and error propagation or the standard deviation of repeated measurements, whichever was larger. However, out of five validation samples, only one ^{242}Pu normalized ^{237}Np value agreed within 1σ with the added number of ^{237}Np , while the other four deviated by 2σ - 16σ . By contrast, all 5 isotopic spike normalization results agreed with the added ^{237}Np . So while normalizing to the isotopic spike only moderately improved the precision of the results, the gains in accuracy were significant. As discussed in Chapters 5 6 the conservative approach used in the calculations may have overestimated the uncertainty of the ^{236}U fraction and, consequently have inflated the uncertainty of the ^{236}Np normalized ^{237}Np data. Ignoring the uncertainty contribution of the isobar

analysis, the average relative uncertainty of the ^{236}Np normalized data drops to 7.8 %, with three out of five samples within 1σ and the remaining two within 2σ .

The environmental reference materials revealed a potential limitation of the ^{236}Np isotopic spike approach, as an exceptionally high ^{236}U content in large IAEA-381 samples interfered with the measurement of the ^{236}Np -spike, resulting in incorrect normalization. The AFIA method introduced in Chapter 4 was used to confirm and quantify the ^{236}U interference suspected in the AMS measurement in Chapter 6. The ^{236}Np -spike clearly demands a more robust U/Np separation than the single UTEVA column approach that relied on the instrumental suppression of background from $^{238}\text{U}^{3+}$ at VERA for ^{237}Np and ^{239}Pu measurements, particularly for samples where ^{236}U above the quantity of ^{236}Np -spike added have to be expected. Once larger quantities of the ^{236}Np -spike material become available, potential ^{236}U interference can be minimized by simply increasing the amount of spike added per sample. As demonstrated in chapter 4, extracting the actinides in the tetrafluoride system would provide another order of magnitude of separation, as NpF_4^- forms more efficiently than UF_4^- .

Data on ^{237}Np in urban dust collected in air filters during the years of nuclear weapons testing, an Austrian peat bog and seawater samples was produced in Chapters 6 and 7 using isotopic and non-isotopic normalization methods.

For sea water collected close to Fukushima during an ongoing release of the Advanced Liquid Processing System (ALPS) treated water, the measured ^{237}Np concentration of $(1.44 \pm 0.21) \cdot 10^7$ at/kg was consistent with other surface ocean water samples from previous studies, and no evidence for a significant ^{237}Np source term from the ALPS treated water could be found. For the Zurich sea water intercomparison sample, a first ^{237}Np concentration of $(9.5 \pm 1.2) \cdot 10^6$ at/kg can be reported. A key result for the peat samples is the increase of the $^{237}\text{Np}/^{239}\text{Pu}$ ratio from the shallower to the deeper sample. As this increase might indicate differences in the behavior of these two radionuclides in peat, a thorough investigation of Np/Pu ratios in this type of environment could be an ideal next application of the ^{236}Np prototype spike material. In the air filter samples, a $^{237}\text{Np}/^{239}\text{Pu}$ ratio of 0.60 ± 0.06 could be measured in materials influenced only by the global fallout, which is slightly above the 0.45-0.53 reported for central and northern Europe previously [Kelley et al. 1999].

The the following sections highlight the links between the manuscripts and complement the experiment-specific discussions in the individual manuscripts to place the findings in a broader context in this field of research to be able to also give a perspective for the future.

8.2. Anion Formation Isobar Analysis

The method development for isobar analysis of ^{236}X quickly became a major focus of the research. Two very different solutions to the problem of the isobaric analysis of

mass ^{236}X , based on AFIA (Chapter 4) and ILIAMS (Chapter 5) have been successfully developed and applied within the scope of this thesis. These methods represent the first isobar analysis and separation capabilities for actinides ever achieved in AMS, and both have distinct advantages and limitations. Besides the analysis of irradiated materials, the AFIA method also succeeded in identifying and quantifying ^{236}U interference with the ^{236}Np -spike normalization of an IAEA-381 reference material sample in Chapter 6. The method is useful as a qualitative analysis tool to detect significant isobaric interference, but quantitative results are difficult to obtain or impossible for small interferences. The anion formation ratios as discussed in Chapter 4 shift over time, most likely linked to the availability of fluorine, but there is also some scatter between targets introducing uncertainty on top of the often unfavorable counting statistics. Changing formation ratios over time and a more rapid depletion of samples mixed with PbF_2 compared to oxide actinide samples limit the available counting time per sample, and the very basis for the method - the element specific relative formation probabilities for AnF_4^- and AnF_5^- requires the measurement of anion species that are produced very inefficiently, such as UF_4^- or AmF_5^- .

A significant improvement to this method that was developed after the publication of [Wiederin et al. 2022] is the normalization to the $^{237}\text{NpF}_4^-/^{237}\text{NpF}_5^-$ ratio within each sample introduced in Chapter 6. This specific formation ratio is set to 1, and all other ratios measured for the same sample are corrected with the same factor, so that deviations from 1 for $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ indicate isobaric interference from either ^{236}U ($\ll 1$) or ^{236}Pu ($\gg 1$). This approach has the advantage of eliminating potential offsets of the formation ratios on calibration samples and the samples that are to be analyzed. As shown in Chapter 4, these formation ratios shift over time, so that the ion source conditions and sputter time for calibration samples and the samples to be analyzed have to be carefully matched, and for pre-sputtered samples significant deviations in the observed formation ratios are to be expected as has also been observed in [Zhao et al. 2022]. This internal calibration approach automatically accounts for all these factors, which is crucial for the analysis of pre-sputtered materials.

The prototype ^{236}Np -spike has been analyzed by AFIA alongside the IAEA-381 sample in Chapter 6, and the $^{236}\text{XF}_4^-/^{236}\text{XF}_5^-$ result is compatible with ^{236}Np and therefore support the ILIAMS results presented in Chapter 5. However, the AFIA result could not improve the precision of the isobaric analysis of the prototype spike material (spike II) further due to the involved uncertainties. The upper limit for the maximum U fraction of ^{236}X that would not have been detected in the AFIA measurement was 22 %, and therefore higher than the 15% achieved in the ILIAMS measurement.

Low counting statistics on the $^{236}\text{UF}_4^-/^{236}\text{UF}_5^-$ formation ratio for the external calibration sample and the conversion between external calibration sample and the sample to be analyzed were major components of the overall uncertainty of the AFIA result

Significant improvements of the precision of the formation ratios, and therefore the sensitivity of the AFIA method could therefore likely be achieved, if the expected U

formation ratio would be measured directly on the same sample to be analyzed, instead of the reliance on a calibration sample. For most uranium samples, this could be achieved simply by including a measurement of $^{238}\text{UF}_4^- / ^{238}\text{UF}_5^-$. Depending on the uranium content of the sample, the resulting ion current may fall into the gap between what is reliably measurable with Faraday cups ($>1\text{ pA}$) and the practical maximum counts per second that can be handled by the ionization chamber ($<10^5\text{ cps}$) for at least one of the two currents. If that is the case, suitably attenuating both beams equally could be a solution and VERA has recently received upgraded attenuators. The installation of a new detector for this count rate range ($10^4\text{-}10^7\text{ cps}$) such as micro-channel-plate (MCP) detectors would be an even better solution, if funding can be obtained.

Then, the counting statistics on $^{236}\text{XF}_4^- / ^{236}\text{XF}_5^-$ would likely become the limiting factor for the AFIA sensitivity, which could be significantly improved by using more of the spike material for the analysis. The changes to the original methodology discussed here were developed during the data evaluation and interpretation of the AFIA measurement presented in 6, and experimental verification of the achievable uncertainties with an optimized experimental design will have to wait until a new spike material batch is produced. However reducing one major component of the uncertainty and eliminating another can only be beneficial, so that future use of AFIA for the analysis of ^{236}X should generally move from the original calibration sample approach to this new internal normalization approach for each sample wherever possible.

The AFIA method remains vulnerable to a specific combination of U and Pu which would result in the same formation ratio as Np. In the case of the calibration sample shown in Figure 6.4.4, a false Np signature would result from an U:Pu ratio of $\sim 6:1$. The developed AFIA method is therefore neither sensitive nor reliable enough for a characterization of a new Np-spike material by itself. Despite these limitations, AFIA represented the first isobar analysis capability for this high mass range in AMS.

Furthermore, thanks to the isobar separation achieved in principle by AFIA, an additional suppression of either Pu or U instead of both by complementary techniques such as ILIAMS would be sufficient for the Np spike characterization: Constraining at least one of the two isobars would remove the potential ambiguity of the AFIA measurement through excluding the problematic $^{236}\text{U}/^{236}\text{Pu}$ ratio. In this way, AFIA has significantly reduced the demands on the ILIAMS method development: In general, for two interfering isobars, a direct separation via laser photodetachment is impossible if the stability of the target isotope falls between those of two other isobars in the system. General trends for anion formation observed in both [Zhao et al. 2022] and [Wiederin et al. 2022] (Chapter 4) that correlate with the proton number, such as preferential formation of pentafluoride anions for U and tetrafluoride anions from Am onward, with Np and Pu in between, made such an outcome likely for U, Np and Pu. However, through developing a combination of direct and indirect measurements, this challenging situation could be overcome and characterizing both ^{236}U and ^{236}Pu interferences became possible with ILIAMS in the tetrafluoride system, as elaborated in Chapter 5.

AFIA then provides an independent second method to test the ILIAMS results, which can be implemented at any other AMS system capable of measuring actinides. In contrast, ILIAMS was until very recently a unique instrumentation, which naturally limits the possibilities for external verification and reproduction of results. Very recently, a new setup at the University of Cologne has been introduced, e.g., in [Marchhart et al. 2025] that would be capable of reproducing the ILIAMS results directly. Furthermore, combining this type of anion formation fingerprinting method and the suppression of one isobar via ILIAMS provides a higher degree of flexibility and could help expanding the reach of ILIAMS to other multi-isobar systems.

Whereas the AFIA method itself focused on AnF_4^- and AnF_5^- , the investigation showed that a variety of AnF_mO_n^- molecular anion species are formed with reasonable efficiency compared to the most prominent anion species for each actinide in this range. The multitude of (oxy)fluoride anion species formed for Np and Pu in the ion source poses an obstacle to increasing ionization efficiency using fluoride beams. This broad distribution of formed anions for Np and Pu has also been noted by another study using a different AMS ion source [Zhao et al. 2022]. A similar improvement of the ionization yield over the extraction as AnO^- as reported for UF_5^- [Kern et al. 2022] may therefore be difficult to obtain for Np. As noted in Section 8.1, measuring environmental ^{237}Np samples with the ^{236}Np isotopic spike in the tetrafluoride system would have the benefit of an additional suppression of ^{236}U from the sample. Dedicated experiments would be necessary to determine the abundance sensitivity of such an approach due to this complex (oxy-)fluoride anion formation for Np. On the other hand, this observed anion formation variety provides a large selection of candidate systems for isobar separation experiments. The very low formation rate of UF_4^- compared to NpF_4^- and PuF_4^- marked this anion system as a promising candidate for the selective suppression of U via laser-photodetachment or gas reactions in ILIAMS. In this regard, and through building up experience with operating the ion source for a comparatively stable output of various AnF_mO_n^- anions, the AFIA studies also acted as preparatory work for the following ILIAMS investigations.

8.3. Ion-Laser InterAction Mass Spectrometry for actinides

The ILIAMS investigations (see Chapter 5) confirmed the suitability of the tetra-fluoride system for selective U suppression suggested by the AFIA measurements. Both isobar separation schemes developed for the isobaric analysis of ^{236}X materials are based on the tetra-fluoride system. However, as was to be expected, no molecular anion system could be found where both U and Pu can be suppressed without affecting Np. Instead, two different isobar separation schemes - one based on the 637 nm laser and one on the admixture of O_2 to the ILIAMS buffer gas can be used to suppress either only UF_4^- , or UF_4^- and NpF_4^- , respectively. Whereas the latter allows for the direct measurement of the ^{236}Pu content of the samples, the analysis of the ^{236}U content is indirect: If only

UF_4^- is affected by the laser, then the effect the laser has on the overall $^{236}\text{X}^{3+}$ count rate when injecting $^{236}\text{XF}_4^-$ into the ion cooler is a measure for the relative proportion of ^{236}U in ^{236}X . This indirect approach results in much larger uncertainties than the direct ^{236}Pu measurement. Consequently the upper limit for the U fraction of ^{236}X is also significantly higher at 15% compared to that of ^{236}Pu . It should be noted, that there was no indication for the actual presence of ^{236}U in the data. Instead the upper limit was defined very conservatively as the largest fraction of U that could evade detection with this method.

A systematic investigation was conducted to identify a direct measurement scheme for ^{236}U , striving for a performance similar to that achieved for ^{236}Pu . This investigation included the fluoride-, oxyfluoride and oxide molecular anion systems AnF_1O_3^- , AnF_2O_2^- , AnF_3O^- , AnF_4^- , AnF_2O_3^- , AnF_3O_2^- , AnF_4O^- , AnF_5^- , AnO^- and AnO_2^- ($\text{An} \in \{\text{U}, \text{Np}, \text{Pu}\}$) and the available lasers at ILIAMS (355 nm, 532 nm, 637 nm and for the oxides also a tunable 700-970 nm Ti:Sa laser). However, no other exploitable isobar separation scheme for analyzing ^{236}X could be found. While there are certainly other molecular systems that incorporate these actinides that potentially could form anion beams in a Cs- sputter ion source, the range investigated has covered most systems known to form actinide anion beams with reasonable efficiency as described e. g. in [Zhao et al. 2022].

The cause for the variability of the suppression of $^{237}\text{NpF}_4^-$ by the 532 nm laser remains an open question. In some measurements the anion survival fraction of $^{237}\text{NpF}_4^-$ was above 80%, in others around 10 % at 5.5-6.5 W transmitted laser power. Data documented in in Figure 5.4.3 shows that the effect scales with laser power. Several hypotheses were formulated and investigated to explain this effect, which are discussed in the following:

Since oxygen admixture can be used to suppress NpF_4^- (see Figure 5.4.6), a hypothesis was that samples with a higher oxygen content may result in the injection of more oxygen via other ion species injected alongside the anion of interest. If these anions are then broken up in the ion cooler, the resulting oxygen concentration along the beam axis might be responsible for the NpF_4^- suppression. Consequently, if the hypothesis was true, then a sample matrix with a lower oxygen availability should also have been affected less by the 532 nm laser. Such a material was produced via co-precipitation of Np with NdF_3 instead of iron-hydroxide and mixed with PbF_2 . However, as shown in Figure 5.4.3 this $\text{NdF}_3+\text{PbF}_2$ sample exhibited lower anion survival fractions than samples consisting of iron oxide or iron hydroxide at similar laser power settings. Furthermore, variable suppression of NpF_4^- was observed for all tested sample matrices: $(\text{Fe}(\text{OH})_3+\text{PbF}_2)$, $(\text{Fe}_2\text{O}_3+\text{PbF}_2)$ or $\text{NdF}_3+\text{PbF}_2$, new or pre-sputtered, stored in air or argon. Therefore, the effect does not correlate with oxygen availability, rendering the whole oxygen injection hypothesis unlikely.

A small effect from the laser, e.g., a very low cross-section, with the photon energy barely exceeding the required detachment energy, could explain the anion survival fractions for NpF_4^- in individual beamtimes, but it is unclear what mechanism could then have caused

the large variability observed, with anion survival fractions for NpF_4^- varying from 0.1 - 0.9.

Other potential explanations for this variable suppression may lie in the ion cooler and the confinement itself. The voltage applied to the guiding electrodes and the buffer gas pressure are the primary parameters that can be used to influence the average residence time of ions inside the RFQ. Experiments performed in November 2023 investigated the anion survival fractions at only 0.025 mbar He buffer gas inside the RFQ, compared to the usual pressures of 0.06 - 0.09 mbar. The 532 nm laser provided ~ 6 W transmitted laser power for these experiments. At this low pressure, the anion survival fraction for $^{237}\text{NpF}_4^-$ was 0.83 (3.64 ± 0.12 cps laser on, 4.37 ± 0.24 cps laser off), while the anion survival fraction of $^{238}\text{UF}_4^-$ increased from $<10^{-4}$ (0.06 mbar He and 532 nm laser, see Figure 5.4.2) to >0.1 . So with a very low buffer gas pressure the NpF_4^- anion survival fraction with the 532 nm laser was large, but still below 1, whereas the U data shows an insufficient isobar suppression likely due to a short average residence time. Therefore, measuring at low buffer gas pressures is not a solution to the variable NpF_4^- suppression.

Another hypothesis was, that small deformations in the guide electrodes could have created potential wells inside the RFQ volume that trap ions. With sufficiently high ion currents (laser off) the accumulated space charge from trapped ions would eventually fill the well, so that subsequent ions can pass. Such traps should increase in depth (and therefore be able to confine more ions) with higher guide electrode voltages, and trapped ions might produce delayed counts after escaping the well.

In one of the experiments, the total current passing the ion cooler alongside the trace amounts of $^{237}\text{NpF}_4^-$ dropped by 94 % (from 50 pA to < 2 pA) when turning the 532 nm laser on. The respective $^{237}\text{Np}^{3+}$ count rates also dropped by ~ 90 % (from ~ 100 cps to ~ 10 cps) when turning on the laser. These results indicate, that the total current transmitted through ILIAMS and the NpF_4^- transmissions are affected similarly, which may be consistent with transport losses or trapping effects for low total ion currents. Adjusting the guide electrode voltage to different settings did not eliminate the NpF_4^- losses. Rapidly reducing the guide electrode voltage (e.g. from 100 V to 40 V) should have resulted in the release of trapped ions, and conversely a decreased count rate would have been expected when increasing the voltage. However no significant effects on the count rate could be observed after these voltage changes. Finally: a delayed count rate after stopping beam injection into ILIAMS with or without simultaneous guide electrode voltage changes could be an indication for the presence of potential well traps inside the guiding field, but again such an effect could not be observed: all count rates immediately dropped to 0 when the ion beam was stopped via the insertion of a Faraday cup in front of the ion cooler. Some less straightforward effect based on changes to the space-charge distribution through the neutralization of almost all of the co-injected ion currents could still play a role. Unfortunately, the limited diagnostic options available at ILIAMS have been exhausted. Should actinide measurements be attempted at some point in the future on a next generation of ion coolers such as the design presented in [Marchhart et al. 2025]

it would be worthwhile to revisit this question of the NpF_4^- losses with the 532 nm laser. For the ILIAMS setup, the purchase and installation of a new 637 nm laser proved the best option, sidestepping this issue and completing the isobar analysis scheme for the ^{236}Np -spike, but at the cost of a significantly reduced UF_4^- suppression.

8.4. AMS - oxides

A significant fraction of Chapter 7 is aimed at optimizing the chemical separation and normalization procedure to minimize Np/Pu fractionation, and then verifying the success of these efforts in various test measurements. For the isotopic spike normalization, it has been demonstrated in Chapter 6 that variations in chemical yields between Np and Pu matter only insofar as very low yields eventually have an effect on the uncertainties via counting statistics. Based on the ^{236}Np -spike count rates, the chemical Np yield of the FDNPP-1-km A sample shown in Figure 6.4.6 can be estimated as $\sim 5 - 10\%$ of that of the other samples in the same batch, and still, the isotopic spike normalization produced a result compatible with the second aliquot of that material, and a relative uncertainty of 21 %. A general availability of an isotopic Np-spike would therefore allow shifting the focus of ^{237}Np related research from extensively optimizing every step in the chemical sample preparation, to finding the most interesting and important samples, and increasing sample throughput to fully develop the potential of ^{237}Np as an environmental tracer.

However, in the absence of a large scale ^{236}Np production in the near future, a significant fraction of ^{237}Np samples will continue to be measured using non-isotopic normalization. Therefore, work on optimizing the non-isotopic spike normalization and adapting it to other sample matrices is certainly still justified. Furthermore, optimized chemical separation procedures developed to enable the non-isotopic normalization can and should continue to be used after an isotopic Np-spike has become widely available to improve counting statistics.

The non-isotopic normalization in Chapter 7 introduced using a chemically similar reference material to provide a (partial) correction factor for Np/Pu fractionation due to matrix effects. For this purpose, an IAEA-385 sample was processed and measured alongside the air filter samples and used as an external standard for normalization. An similar approach was used in Chapter 7 for the normalization of peat samples: the deviation of the ^{237}Np concentration on IAEA-385 from the nominal value when normalized to ^{242}Pu was used as a correction factor for the ^{237}Np concentration in the peat samples. These corrected ^{237}Np concentrations were then compatible with the results of the isotopic spike normalization as shown in Figure 6.4.5. This successful second application of this type of combined normalization in Chapter 6 suggests, that similar strategies should be tested for on all ^{237}Np measurements using a non-isotopic spike normalization. It has to be noted though, that this approach can only correct for systematic losses that affect

all samples of the same or a similar matrix. Variations of the Np/Pu yield ratios in individual samples would still evade correction by this approach. A dual normalization (non isotopic spike + reference material correction) can likely improve the accuracy of the obtained results by eliminating some potential normalization errors, but this gain comes at the cost of decreased precision, since additional quantities with relevant uncertainties are included in the calculation.

Furthermore, there is already a need for more Np reference materials suitable for AMS in terms of concentration and with a variety of matrices, which would become even more urgent with this combined normalization, where matching the reference matrix to the sample matrix is crucial.

8.5. Spike production

The irradiation experiments were not directly part of this thesis, which focused on the analysis of the resulting materials. However, the way the irradiations and subsequent chemical purification are performed has a significant impact on the the availability and quality of new Np-spike materials. In the following, an investigation into a potential source of ^{237}Np in the spike materials is discussed, whereas several ideas that could potentially increase the ^{236g}Np yield, based on both the analysis of resulting materials and my participation on one of the irradiation experiments, are presented out in the outlook (Chapter 9).

^{237}Np can be produced directly in the nuclear reaction $^{232}\text{Th}(^7\text{Li},2\text{n})^{237}\text{Np}$ during the irradiation of Th foils, in parallel to the corresponding 3n reaction that produces ^{236}Np . If this is the dominant source of ^{237}Np in the prospective spike materials, then the only options for improving the $^{236}\text{Np}/^{237}\text{Np}$ ratios achieved are choosing the optimal irradiation energy range or implementing some form of isotope enrichment.

^{237}U has also been shown to be formed in this type of irradiation [Zhao et al. 1999] and would decay into ^{237}Np with a half-life of (6.752 ± 0.002) days. If this in-growth after the irradiation contributes significantly to the overall ^{237}Np content of the irradiated materials, appropriate steps could be taken to reduce it, and consequently improve the achieved $^{236}\text{Np}/^{237}\text{Np}$ ratio of prospective ^{236}Np -spike materials. The observation of lower $^{236}\text{Np}/^{237}\text{Np}$ ratios since the implementation of a multiple irradiation approach and delayed chemical processing as discussed in Chapter 6 could be an indication for in-grown ^{237}Np .

A first step towards investigating the role of ^{237}U in the Np-spike production was experimentally verifying its presence in irradiated Th samples. For this purpose, a Th target produced via electrodeposition was separated one day after irradiation and measured as described in [Nakajima et al. 2026]. ^{237}U can be identified via prominent γ - emissions at 208.0 keV (34.5 % emission probability) and 59.5 keV (21.2 % emission probability) [Valdovinos et al. 2023]. However, due to large background count rates on the irradiated

sample, multiple chemical separation steps were necessary to identify peaks in the spectrum at these energies. In this first test, no chemical yield tracers were used so that no quantitative data could be generated. To confirm the attribution of these two peaks in the γ -spectrum to ^{237}U , the samples were then measured multiple times over a period of 40 days, and the background-subtracted count rates for the selected peak areas were plotted over time of both peaks as shown in Fig. 8.5.1. The data for each emission line was fitted with exponential functions of the form $N(t) = N_0 \cdot e^{B \cdot t}$. The parameter B then corresponded to decay constants (with t expressed in days) ranging from -0.094 to -0.104. The resulting half-life was calculated from the parameters B of each fit, with a conservative estimate of the uncertainties for both emission lines at 7.0 ± 0.5 days, which is compatible with the half-life of ^{237}U of 6.752 days.

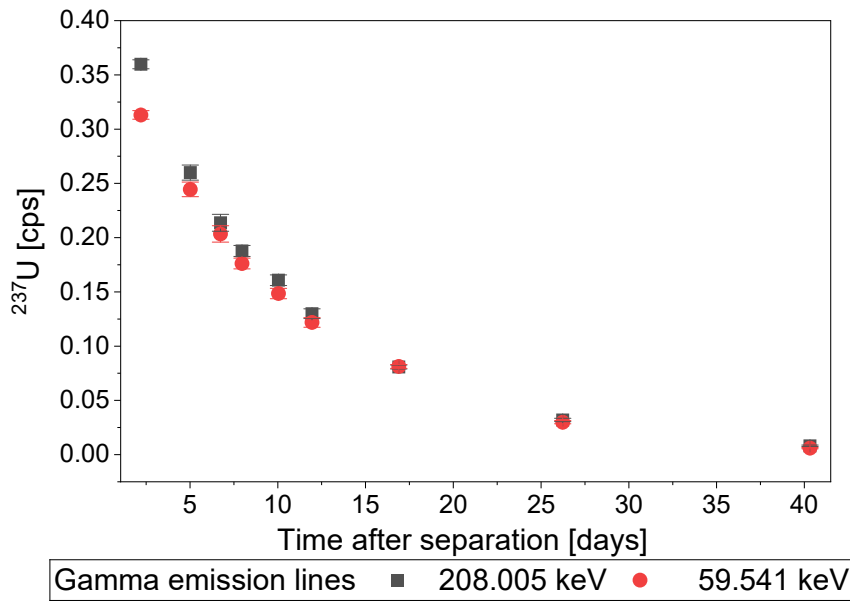


Figure 8.5.1.: Evolution of count rates for two γ -peaks corresponding to the 208.0 keV and 59.5 keV emission lines associated with the decay of ^{237}U . Both peaks decay with a half-life of 7.0 ± 0.5 days which is compatible with ^{237}U .

The spectrum shows a high density of emission lines, indicating the production of a multitude of radionuclide via various reactions caused by the irradiation. The nuclides ^{86m}Y , ^{177m}Lu , ^{190m}Re , ^{195m}Hg , and ^{242m}Am (excluding short-lived radionuclides) have γ -lines in an energy range that would overlap with the 208.0 keV peak. ^{86m}Y with a half-life of 47 minutes would have mostly decayed by the time of the measurement and the 1076 keV peak that would correspond to the daughter ^{86}Y was insignificant compared to the 208 keV peak. For ^{177m}Lu , ^{190m}Re , ^{195m}Hg , and ^{242m}Am , other prominent emission lines were missing in the spectrum, which excludes a significant contribution to the 208.0 keV peak. Overall, peaks corresponding to prominent γ -emissions of ^{237}U were identified, they decay with a half-life compatible with that of ^{237}U within 1σ , and other radionuclides that could have interfered with the measurement could be excluded via the absence of their other emission lines, leading to the unambiguous identification of

^{237}U in the irradiated Th sample. The raw data for this preliminary experiment has been made available via the PHAIDRA repository Wiederin [2026b].

A full and quantitative investigation is being carried out as of the time of the completion of this thesis by the Japanese project partners. Should quantitative results via γ -spectroscopy prove elusive, AMS could be a viable option for quantifying the ^{237}U decay contribution to ^{237}Np in the spike material. For this purpose, U would have to be separated from Np as soon as possible after the irradiation of a small irradiated sample. The ion fluence and sample mass would have to be sufficiently small to allow rapid handling the material. After waiting for several half-lives of ^{237}U , Np should again be separated from the initial U fraction, before measure both resulting Np fractions with AMS. Then the ^{237}Np in-growth could be determined from the Np separated from the initial U fraction, and it's influence quantified by comparison to both ^{236}Np and ^{237}Np in the initial Np fraction.

9. Outlook

Isobaric interference from ^{236}U on mass 236 can be quantified via the effect of the 637 nm laser on $^{236}\text{XF}_4^-$, but the sensitivity of this indirect approach is limited by the uncertainties of the involved anion survival fractions. This uncertainty in turn is a major component of the overall uncertainty of the prototype ^{236}Np -spike, and consequently of all ^{237}Np measurements normalized using this material. Improving the uncertainty of the ^{236}U quantification would therefore be highly advantageous, and could be achieved by further lowering the anion survival fraction of UF_4^- , improving the counting statistics of the ^{236}X and the calibration ^{236}U and ^{237}Np count rates, or ideally both.

The probability for photodetachment depends exponentially on the photon flux (see Equation 3.4.1), so the anion survival fraction of UF_4^- could be significantly reduced by implementing a red laser with power output and beam geometry comparable to the available 532 nm laser, i.e., increasing the transmitted laser power from 0.6 W to 5-6 W. Additional improvements may be possible with a wavelength that has a higher photodetachment cross-section for UF_4^- . An optimal wavelength would likely fall between 532 nm, where NpF_4^- was also affected and 637 nm where the suppression of UF_4^- is small.

Improving the involved ^{236}U , ^{237}Np and ^{236}X counting statistics would require more material and/or longer counting time. Realistically, more spike material would only be available for the characterization, if the production yield for ^{236}Np could be significantly increased - as will be discussed below. An improved determination of the $^{236}\text{UF}_4^-$ and $^{237}\text{NpF}_4^-$ anion survival fractions could however be achieved by increasing the amount of material used for the calibration samples (readily available), and the counting time dedicated to the calibration samples. The measurement of the ^{236}U count rate with the laser on is likely to be the main limiting factor, since the combination of low anion formation of $^{236}\text{UF}_4^-$ and the suppression by the laser has so far only enabled the determination of upper limits. A significant improvement of the uncertainty of the $^{236}\text{UF}_4^-$ anion survival fraction, may require multiple calibration samples and many hours of combined counting time. By contrast, the accuracy and precision of the ^{236}Pu measurement is already excellent, and further improvements would have little effect on the overall results.

The experiments regarding the separation of other isobar systems in the actinide range go beyond the scope of the original research question, and were investigated to test and expand the limits of isobar separation for actinides on the ILIAMS instrumentation. These experiments were driven by personal curiosity, using reagents already available at

VERA and were performed whenever there was beamtime available after the completion of the main experiments. The results on other isobar systems presented in Chapter 5 have to be regarded as a first explorative study. The achieved instrumental decontamination factors suggest that isobaric interference on ^{241}Am or ^{238}Pu measurements would already be sufficiently suppressed to enable several environmental applications. However, a lot of work remains to turn the anion survival fractions achieved on calibration samples or uranium standards into reliable measurements on real samples produced from complex environmental matrices. A crucial point will be achieving the abundance sensitivities required for the respective environmental applications. Here the large variety of fluoride and oxyfluoride Pu anions formed from iron oxide samples mixed with PbF_2 or FeF_3 as shown in Chapter 4 or [Zhao et al. 2022] may prove to be an obstacle. For the heavier actinides Am, Cm, Bk, Cf and Es, there are several isobar systems involving long lived radionuclides that could be investigated for suitable separation schemes using ILIAMS. The identification of relevant applications would certainly accelerate such time consuming investigations.

The characterization of the spike materials shown in Chapters 5 and 6 demonstrated, that the production and separation of ^{236}Np was successful, and spike material for limited applications is now available. However, further improvements of both the $^{236}\text{Np}/^{237}\text{Np}$ ratio of the final material, and the total quantity of ^{236}Np produced would be highly desirable.

Should the full investigation determine that the quantity of ^{237}U produced significantly contributes to the production of ^{237}Np , then a rapid first U separation step would be required, and both multiple irradiations of individual foils, and delayed processing after the decay of short lived fission products would have to be abandoned. If the highest $^{236}\text{X}/^{237}\text{Np}$ ratios measured to date in the range of 13 - 14 could be achieved again by removing ^{237}U as early as possible, the ^{237}Np added to each sample via the ^{236}Np -spike - and with it the detection limit for ^{237}Np using this spike for normalization - could be halved. If the high $^{236}\text{X}/^{237}\text{Np}$ ratios in these early experiments cannot be achieved again, then this would point to an isobaric contribution from ^{236}U or ^{236}Pu to ^{236}X , and an insufficient chemical separation in the early experiments.

The overall production capacity of ^{236}Np in the presently used configuration is rather limited, and alternative facilities or even different reactions should be considered to scale up the production by 2-3 orders of magnitude now that the methodology for the characterization of the resulting materials has been developed. However, there are still options to optimize the current irradiation setup and procedure to increase the spike production. The baseline for the options discussed in the following is the production, separation and characterization of the spike II material, which was sufficient for the measurement of 73 environmental samples, assuming $1.5 \cdot 10^7$ atoms ^{236}Np -spiked per sample.

As a first step, there are still minor efficiency gains possible in the characterization: For the calculation of the ^{236}Np concentration and the measurement of the $^{236}\text{Np}/^{237}\text{Np}$

ratio, two samples, one without and one with added ^{237}Np would have sufficed. Considering that the large uncertainty of the isobaric composition as determined in Chapter 5 the amount of spike II solution used per remaining (oxide) characterization sample - and the corresponding counting statistics - could also have been further reduced. Assuming the elimination of two samples, and reducing the amount used for the others two by 50 % would have freed up sufficient material for 25 - 30 environmental samples.

With the end of the joint project, there are no immediate plans for further irradiations at RIKEN. However, in the following, some estimates are given on what could be achieved based on the techniques already established, with the hope that they could serve as the starting point for new beamtime applications at RIKEN or another suitable facility. With one or two additional (identical) irradiation runs and the reduced number of characterization samples, the fully characterized material would have sufficed for up to 140 or 200 samples, respectively. Furthermore, as discussed in Chapter 6 in the context of the effect of spike derived ^{237}Np , the quantity of spike used per environmental sample could be reduced further, assuming ^{236}U in the Np fraction is low enough. In the case of the ZSW sample, $7.5 \cdot 10^6$ at ^{236}Np have been used successfully. Extrapolating from the registered ^{236}Np counting results, even a reduction to $1.5 \cdot 10^6$ at spiked has been calculated to be feasible in Chapter 6, assuming reasonable chemical Np yields and at the cost of dedicating considerable counting time (3000 s - 5000 s) on the spike. Combining the reduced spike amounts, the reduced number of characterization samples and a total of four instead of two irradiation runs, 400 samples (at $7.5 \cdot 10^6$ at per sample) could be measured. While the material would still be extremely scarce, if distributed to the most active AMS groups in environmental actinide analysis and their users, such quantities could already provide a significant boost to global ^{237}Np data.

For even higher yields, the foil-stack approach mandated by a parallel investigation of reaction cross-sections would have to be abandoned. Then, a single foil could be irradiated at a higher intensity for longer periods without risking fused foil stacks due to cooling limitations. This would allow increasing the intensity of the ^7Li current from $1 \mu\text{A}$ to the maximum of $3 \mu\text{A}$ reported for the AVF in [Suda et al. 2016], thus potentially tripling the production rate. A suitable carrier material for the foil to aid structural integrity, thermal management and ion beam energy adjustment would have to be used. The central requirement for such a carrier would be a simple, sufficient, and reliable removal of the carrier during the initial chemical purification steps without negative effects on the Np yields. The resulting initial activities would again pose the dilemma of radiation protection requirements and contamination risks in clean labs versus the risk of significant ^{237}Np contamination in hot cells that have been used to process other high activity materials, as has been discussed in Section 6.4.2. The initial hot-cell approach was abandoned in preliminary experiments due to high ^{237}Np levels in process blanks. A dedicated spike production project aiming for distributable quantities of the ^{236}Np -spike would require sufficient resources to manage and mitigate these cross contamination risks. Extensive cleanup- and refurbishing efforts of a cell, with the

success of both individual measures and the overall effort monitored on series of process blanks, would likely be required.

With sufficient ^{236}Np -spike material for the normalization of at least 60 additional samples still available at VERA, our understanding of the distribution and mobility of ^{237}Np in various environmental compartments could be significantly improved by using this material. I would propose a twofold strategy for selecting samples: on the one hand verifying existing data sets, especially wherever reasonable doubts remain concerning the non-isotopic normalization results. Even a few isotopically normalized data points in a depth profile can support a larger ^{242}Pu normalized data set. On the other hand, the ^{236}Np -spike should be used on sample matrices that have so far been neglected concerning ^{237}Np , such as peat bogs which are recognized as an important archive for other, surface deposited radionuclides.

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10. Appendix

10.1. Appendix A - Abbreviations

AMS	Accelerator Mass Spectrometry
AVF Ring Cyclotron	Azimuthally Varying Field Ring Cyclotron
FDNPP	Fukushima Daiichi Nuclear Power Plant
GF	Global Fallout
IAEA	International Atomic Energy Association
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IRMM	Institute for Reference Materials and Measurements
NAA	Neutron Activation Analysis
PUREX	Plutonium Uranium Reduction Extraction
RFQ	Radio Frequency Quadrupole
RIKEN	Rikagaku Kenkyūsho - Institute of Physical and Chemical Research
SF-ICP-MS	(Sector Field) Inductively Coupled Plasma Mass Spectrometry
SNICS	Source of Negative Ions by Cesium Sputtering
TOF	Time Of Flight
VERA	Vienna Environmental Research Accelerator

Table 10.1.1.: List of abbreviations

10.2. Appendix B- Signed statement of contribution

Erklärung zum Eigenbeitrag für Dissertationen aus dem Gebiet Physik des Curriculums für das Doktoratsstudium der Naturwissenschaften sowie der technischen Wissenschaften aus dem Bereich der Naturwissenschaften

Statement of own contribution for dissertations of the field Physics of the Doctoral programme in Natural Sciences and Technical Sciences in the field of Natural Sciences

Diese Erklärung versteht sich als Ergänzung zu den [Formvorschriften](#) und dem [Leitfaden für die Verwendung von Publikationen in wissenschaftlichen Arbeiten](#) der Universität Wien.

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Angaben zur Person Personal Data			
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Dissertationsprojekt Thesis Project	
Studienkennzahl lt. Studienblatt: <i>Degree programme code according to the student record sheet:</i>	A 796 605 411
Thema des Dissertationsvorhabens: <i>Topic of the dissertation project:</i>	Characterization methods for the application of a new isotopic Np spike material

Liste der Publikationen (inklusive pre-prints), die aus der Dissertation hervorgegangen sind:

List of publications (including pre-prints) resulting from the dissertation:

1. **A. Wiederin**, M. Kern, K. Hain, M. Martschini, A. Sakaguchi, P. Steier, A. Yokoyama, R. Golser, „Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu and Am in accelerator mass spectrometry measurements at VERA”, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Volume 528, 2022, Pages 40-44, ISSN 0168-583X, <https://doi.org/10.1016/j.nimb.2022.07.011>
2. **A. Wiederin**, M. Martschini, A. Sakaguchi, P. Steier, K. Hain, „Separation of Actinide Isobars via Laser Photodetachment and the characterization of a new isotopic Np spike”, submitted at JPhysG, currently in peer review
3. **A. Wiederin**, M. Martschini, A. Sakaguchi, P. Steier, K. Hain, "First applications of a new isotopic Np spike“, Measurements completed, manuscript sent to co-authors for internal review and feedback before submission (planned: JAAS)
4. G. Wallner, P. Rohrbach, L.J. Krammer, **A. Wiederin**, P. Steier, K. Hain, “Developments of analytical techniques for the determination of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios on air filters from Vienna, Austria”, submitted to the Journal of Environmental Radioactivity, currently in peer review.

The abstracts for all published, submitted or drafted manuscripts are attached at the end of this file.

Erklärung des Eigenbeitrags aufgeschlüsselt ad personam Dissertant*in (nicht als Teamleistung) – falls Publikationen aus der Dissertation hervorgegangen sind, bitte auf die spezifische Publikation Bezug nehmen:

Declaration of own contribution ad personam Doctoral candidate (not as team contribution) - if publications resulted from the dissertation, please refer to the specific publication:

1. This method was my original idea. I designed and performed all experiments for developing the idea into a working method as well as the first applications and prepared all samples. I have conducted all measurements independently as the person responsible for the respective beamtimes at the VERA Accelerator Mass Spectrometry facility, but I received help dealing with technical problems and defects at the accelerator. I developed and performed the data analysis, wrote the draft for the manuscript and collected and implemented feedback from all co-authors, before handling the submission and peer review process as the corresponding author. I was supported by my supervisor and co-authors with supervision and feedback throughout this process.
2. I was responsible for method development, sample preparation, beam tuning, performing all measurements, data evaluation and interpretation, as well as drafting the manuscript, implementing feedback by co-authors, and handling article submission and review as the corresponding author. I also participated in the production of the analyzed ^{236}Np spike material at the RIKEN Nishina AVF cyclotron together with the Coauthor A. Sakaguchi. Several experiments for this paper were performed together with M. Martschini, but I performed most experiments independently and all as the person responsible for the beamtime. I was supported

by my supervisor K. Hain and co-authors, particularly M. Martschini, with supervision and feedback throughout this process, and received help with technical problems and defects at the accelerator when they occurred.

3. The selection of samples, sample preparation for most samples, beam tuning, measurements on the accelerator, data evaluation and interpretation, as well as writing the first draft and implementing feedback from co-authors and reviewers, were among my responsibilities for this paper. I also personally collected seawater samples off the coast of Fukushima, designed the experimental approach for completing spike characterization myself with AMS and isotope addition series measurements, rather than relying on external ICP-MS data, and handled communication with the Japanese partner group to coordinate on open questions such as the ^{237}U co-production before and during drafting the manuscript. Some environmental samples were prepared under my supervision by a laboratory technician.
4. For this final paper, I am a co-author and was responsible for some steps in sample preparation, the production of external standards and tuning targets, test measurements with AMS and corresponding data evaluation, and drafting of the corresponding parts and review of the whole manuscript, and contributed to the planning of the experiments and interpretation of the data. Furthermore, I contributed to ongoing discussions on the iterative planning of experiments and to multiple rounds of internal review of the manuscript leading up to the submission.

Besteht der Wunsch einer optionalen Stellungnahme der Studienprogrammleitung, ob der dargelegte ausgewiesene Eigenbeitrag und die Kohärenz der Publikationen nicht gegen das Verfassen einer kumulativen Dissertation im Fachbereich Physik sprechen?

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Ja. / Yes.

☐

Nein. / No.

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Die dargelegte Erklärung zum Eigenbeitrag und die Kohärenz der Publikationen spricht nicht gegen das Verfassen einer kumulativen Dissertation im Fachgebiet Physik. <i>The provided statement of own contribution and the coherence of the publications is not in contradiction with a cumulative dissertation in the field of Physics.</i>		☐ Ja. / Yes. ☐ Nein. / No.	
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Appendix: Abstracts for publications

1)

Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu and Am in accelerator mass spectrometry measurements at VERA

A. Wiederin ^{a b}  , M. Kern ^{a b}, K. Hain ^a, M. Martschini ^a, A. Sakaguchi ^c, P. Steier ^a, A. Yokoyama ^d, R. Golser ^a

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Abstract

Fluoride molecular anions have emerged as a potential alternative to oxides for the analysis of actinides in AMS. Research at the Vienna Environmental Research Accelerator (VERA) has focused on mixing samples prepared in an Fe₂O₃ matrix with PbF₂ for in situ fluoridation during the sputter process. The relative formation probabilities for a range of (oxy-)fluoride molecular anions of uranium, neptunium, plutonium, and americium have been found to be characteristic for each of the actinides investigated. These data can help to identify isobaric interference for the mentioned actinides. A first application is monitoring of the ²³⁶U co-production with ²³⁶Np during Th irradiation. Extracting these actinides in the form of tetrafluoride anions allows the suppression of U by an order of magnitude relative to Np.

2)

Isobar separation of actinides in mass spectrometry by the combination of laser photodetachment with ion-gas interactions

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Abstract

Isobaric interference is a major limitation of mass spectrometric measurements of trace radionuclides. For Accelerator Mass Spectrometry (AMS), isobaric separation is only available up to the mass range of fission products. The present work explores the potential of Ion-Laser InterAction Mass Spectrometry (ILIAMS) for trace analysis of anthropogenic actinides with isobaric interference. Such capabilities are crucial for characterizing a highly sought-after isotopic spike material for ²³⁷Np measurements and for accessing additional anthropogenic actinides with AMS, which could serve as environmental tracers, emission source signatures, or for determining the age of nuclear materials. ILIAMS is a novel low-energy isobar separation technique that combines a gas-filled ion cooler with reactive gases or high-power lasers to suppress isobars selectively. In this study, we demonstrate that UF₄⁻ can be selectively suppressed by two orders of magnitude using a 637 nm laser without affecting NpF₄⁻. Initial results indicate the potential for the selective suppression of AmF₅⁻ to measure PuF₅⁻ or, in reverse, the suppression of PuF₄⁻ to measure AmF₄⁻ using a 355 nm laser. The admixture of O₂ with the buffer gas of the ion cooler can be used to suppress UF₄⁻ by up to seven and NpF₄⁻ by up to three orders of magnitude against PuF₄⁻. The first application of these separation schemes for the characterization of a prototype ²³⁶Np spike demonstrated the successful chemical removal of the co-produced isobars ²³⁶U and ²³⁶Pu, and similar measurements can now be performed for other prospective Np spike materials. The isobar separation schemes developed here can also enable the measurement of ²⁴¹Pu without chemically removing ²⁴¹Am or ^{242m}Am in the presence of ²⁴²Pu. Even measuring ²³⁸Pu using AMS has become feasible for suitable sample matrices, despite the presence of the primordial isobar ²³⁸U. These are important isotopic signatures for attributing environmental contamination to potential sources of emissions.

3)

Characterization and first application of a new ^{236}Np spike for (A)MS measurements of ^{237}Np

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Background: The anthropogenic radionuclide ^{237}Np has excellent potential as an environmental tracer, complementing more established anthropogenic actinide tracers such as $^{236}\text{U}/^{238}\text{U}$ or $^{239,240}\text{Pu}$. The main limitation to measuring ^{237}Np quantitatively by accelerator mass spectrometry has been the lack of an isotopic Np spike, while legacy ^{236}Np materials have suffered from very high levels of ^{237}Np contamination. **Purpose:** A new ^{236}Np material has been produced via the $^{232}\text{Th}(^7\text{Li},3\text{n})^{236}\text{Np}$. In the present work, this prototype Np spike is characterized and applied for the first time to the normalization of environmental samples, and the results are compared with those from the non-isotopic normalization approach using Pu isotopes. **Methods:** The Vienna Environmental Research Accelerator (VERA) Accelerator Mass Spectrometry facility was used to determine the ^{236}Np concentration and $^{236}\text{Np}/^{237}\text{Np}$ ratio of the new prototype spike. A ^{237}Np dilution series in deep-sea water, environmental reference materials, as well as a selection of unknown environmental samples, were prepared using both the prototype ^{236}Np spike material as well as two Pu isotopes and measured at VERA. Anion Formation Isobar Analysis was used to investigate ^{236}U interference on large IAEA-381 samples. **Results:** The total amount of ^{236}Np in the prototype spike characterized at VERA has been determined as $(1.64 \pm 0.14) \times 10^9$ atoms with a $^{236}\text{Np}/^{237}\text{Np}$ ratio of 6.93 ± 0.27 . Benchmarked against ^{242}Pu normalization on a ^{237}Np dilution series in deep seawater, the new spike material provided more accurate and reliable results. Dual Pu spikes (^{242}Pu before and ^{244}Pu after chemistry) used to estimate the chemical Pu yields revealed significant Np/Pu fractionation for several samples. **Conclusions:** The characterization of a new Prototype ^{236}Np spike material has been completed, and its use for the normalization of environmental ^{237}Np data has been validated. Although the low quantity of ^{236}Np produced, the co-produced ^{237}Np and potential ^{236}U interference from heavily contaminated samples can impose limitations on the use of this new spike material, it has been demonstrated to outperform the non-isotopic normalization approach significantly.

4)

Developments of analytical techniques for the determination of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios on air filters from Vienna, Austria

G. Wallner, P. Rohrbach, L.J. Krammer, A. Wiederin, P. Steier, K. Hain

Keywords: $^{237}\text{Np}/^{239}\text{Pu}$, aerosols, bomb test fallout, AMS

Highlights:

^{237}Np and ^{239}Pu concentrations as well as $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios were determined in aerosol samples representing pure bomb test fallout.

^{237}Np and Pu isotopes (with ^{242}Pu as spike) were jointly separated from the matrix.

By normalization of $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios to external standards and to IAEA-385 reference material congruent results were found.

Abstract

Air filter samples collected in the 1960s and therefore representing pure weapons test fallout were investigated with respect to ^{237}Np and ^{239}Pu concentrations as well as $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios. ^{237}Np and the Pu isotopes (with ^{242}Pu as tracer for both elements) were jointly separated from the matrix using UTEVA resin and were then measured by accelerator mass spectrometry (AMS). Results were normalized to external standards to consider different Np and Pu outputs during the measurement. As the radiochemical yields of Np as well as of Pu, investigated by α -spectrometry of samples with added ^{237}Np and ^{236}Pu tracers, indicated chemical fractionation, the filter samples were re-measured together with IAEA-385 reference samples which had been processed collaterally. The resulting $^{237}\text{Np}/^{239}\text{Pu}$ atom ratios estimated by normalization to the IAEA-385 reference samples were in satisfying agreement with $^{237}\text{Np}/^{239}\text{Pu}$ ratios of soil samples from the literature.

10.3. Appendix C - SI for 6 - Chemical separation of ^{236}Np

Np-236 measurements by ICP-MS for spike material I

The Np fraction obtained by separation and purification using TK-400 resin was left to stand for approximately three months in order to allow sufficient decay of $^{236\text{m}}\text{Np}$. Thereafter, the solution was evaporated to dryness and subsequently dissolved in 3 mL of 3 M HNO_3 . In order to reduce neptunium to the tetravalent state, 125 μg of ferric iron (Fe^{3+}) and 279 mg of ascorbic acid were added, and the solution was allowed to stand for 25 minutes. Following this reaction period, the solution was loaded onto the column. The original Np fraction vessel was then thoroughly rinsed with 2 mL of 0.072 M ascorbic acid in 3 M HNO_3 , and the rinse solution was likewise loaded onto the column. To remove plutonium, an additional 4 mL of 0.072 M ascorbic acid in 3 M HNO_3 was passed through the column. Subsequently, 18 mL of 3 M HNO_3 was applied to the column in order to remove residual ascorbic acid. Finally, neptunium was eluted by passing 0.2 M oxalic acid in 2.5 M HNO_3 through the column in 1 mL aliquots, to a total volume of 4 mL. This Np fraction eluted from the UTEVA® resin was collected in a PFA vial with a screw cap (PFA standard vial, 7 mL, rounded inner bottom; Savillex) and evaporated to dryness. Subsequently, 0.5 mL of 3 M HNO_3 and 0.5 mL of H_2O_2 were added, the vial was tightly sealed, and the solution was heated for 15 minutes to decompose the oxalic acid. Thereafter, 0.3 mL of 3 M HNO_3 and 2–3 drops of HClO_4 were added, and the solution was evaporated to dryness until no white fumes were observed, in order to remove residual organic compounds originating from the resin and/or oxalic acid. After evaporation to dryness, 1 mL of 3 M HNO_3 was added to the PFA vial, which was sealed and heated for 15 minutes. The solution was then transferred to a polypropylene (PP) container (self-standing flat-bottom tube, 5 mL; Sarstedt). The PFA vial was subsequently rinsed twice with 1 mL of ultrapure water, and the rinses were combined in the same PP container, yielding a final solution volume of 3 mL for mass spectrometric analysis. The chemical separation scheme was shown as figure S1. The $^{236\text{g}}\text{Np}$ was quantified by sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS) at the National Institutes for Quantum Science and Technology (QST), Japan, and by inductively coupled plasma QQQ mass spectrometry (ICP-QQQ-MS) at the University of Tsukuba. As for the ICP-QQQ-MS, MS/MS mode was employed, and Np isotopes were measured as on mass mode.

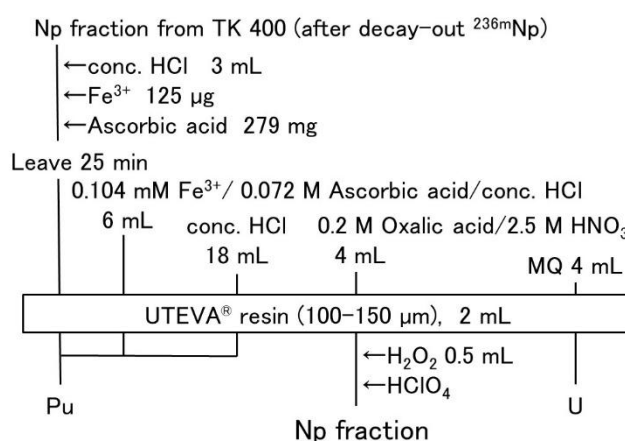


Figure S1 Chemical separation scheme for long-lived Np isotope measurements.