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LLNL-TR-856085

Characterization of actinide abundances and isotopic compositions by HR-ICP-MS. Part 2: Results from actinide doping studies

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October 18, 2023

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Characterization of actinide abundances and isotopic compositions by HR-ICP-MS. Part 2: Results from actinide doping studies

Security Level

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4th October, 2023

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Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344.

This work was supported by the National Nuclear Security Agency Office of Defense Nuclear Nonproliferation Research and Development.

1. Report Summary

Previously, we presented actinide isotopic and elemental data from fallout melt glass that was measured using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Direct comparison between these measurements and 'gold standard' data obtained by multi-collector ICP-MS showed broad overlap, indicating that HR-ICP-MS is a potentially valuable technique for producing actinide elemental and isotopic data on a relatively rapid timescale. To test the usefulness of this technique further, we doped varying amounts of uranium certified reference materials (CRMs) into a rhyolitic rock standard to establish the effects of uranium concentration and isotopic composition on the accuracy of uranium isotopic analyses by HR-ICP-MS. This also enabled us to quantify peak tailing effects from ^{238}U on the measurement of ^{239}Pu and ^{237}Np, which in turn allows us to constrain correction factors based on measured ^{237}Np/^{238}U and ^{239}Pu/^{238}U ratios. A second doping study involved the addition of a mixed actinide standard into three samples with different matrix compositions (termed soil, city, and seawater) to assess whether sample chemistry affects the accuracy and precision of these analyses. Results suggest that this is not the case. Systematic offsets were not observed in elemental or isotopic data derived from the three matrix samples. Results indicate that useful actinide isotopic data can be obtained from whole rock solutions by HR-ICP-MS. Our findings also have implications for solid sampling techniques such as laser ablation ICP-MS, which do not require sample dissolution.

2. Introduction

In Wimpenny and Brennecka (2022), it was demonstrated that elemental analyses of bulk rock samples by HR-ICP-MS can produce actinide isotopic data that broadly overlaps (to within 10-20%) with data produced by multi-collector (MC)-ICP-MS after spiking and purification. Thus, useful information about actinide isotope systematics can be obtained relatively rapidly from bulk rock solutions, without the need for time consuming chemical purifications or the use of an internal isotopic tracer. Depending on the sample purification scheme, this means isotopic data from a sample of interest can be obtained hours to days earlier than is typical while utilizing less personnel and/or infrastructure resources.

Although promising, the results of Wimpenny and Brennecka (2022) also posed several questions about the reliability of such analyses when faced with unknown samples. The measured uranium isotopic compositions of various historical fallout glass samples correlate well with MC-ICP-MS data, but consistent offsets in the HR-ICP-MS data of 10-20% were recorded for the ^{235}U/^{238}U and ^{234}U/^{238}U ratios. The accuracy of HR-ICP-MS data also suffered where actinide concentrations were very low. The influence of polyatomic species or peak tailing effects on ^{237}Np and ^{239}Pu are of particular concern, especially where ^{237}Np/^{238}U and ^{239}Pu/^{238}U ratios are relatively low. However, the relative size of tailing from the ^{238}U peak at m/z (mass to charge ratio) = 237 and m/z = 239 (i.e., the abundance sensitivity) is unconstrained, meaning that we cannot quantify ^{237}Np/^{238}U and ^{239}Pu/^{238}U ratios at which peak tailing becomes problematic and/or corrections cannot be made. Finally, the sample matrices encountered in historical fallout melt glass samples were mostly silicate based, meaning that the accuracy of analyses for samples with exotic chemical compositions (e.g., concrete, seawater, metal) have not been investigated.

In the current study, we attempt to address some of these questions by performing actinide doping experiments and comparing the calculated elemental and isotopic compositions with measured values obtained using the Thermo Scientific Element XR at Lawrence Livermore National Laboratory (LLNL). The first experiment involves the addition of varying amounts of New Brunswick Laboratory certified reference materials (NBL-CRM) U005a, U010, and U100 into dissolved aliquots of the USGS Rhyolite standard RGM-2. This has two purposes; first to assess whether the amount and/or isotopic composition of uranium influence the ability to accurately assess uranium isotope systematics by HR-ICP-MS. The second is to constrain the peak tailing effects of ^{238}U on ^{237}Np and ^{239}Pu, assuming that any plutonium and neptunium that is inherent to the CRMs is negligible. The second experiment involves the addition of a mixed U-Pu-Np-Am spike into dissolved aliquots of matrix standards that were prepared to mimic urban (city), desert/rural (soil) and marine (seawater) environments. The results of this experiment will not only enable us to further test the accuracy of plutonium, americium, and neptunium isotopic analyses, but also determine the extent to which sample matrix affects data accuracy and precision.

Ultimately, these results will provide more evidence to assess whether bulk rock analyses by ICP-MS are a viable technique to obtain robust actinide isotope data on a timeframe of hours to days.

Table 1 – Uranium isotopic concentrations in the uranium-doped RGM-2 solutions. Sample names reference the relative amounts of uranium deriving from RGM-2 and the doped uranium standard. For example, 1 to 10 contains 10 times more uranium from the doping standard.

	Total masses of U (ng)				U Concentration (ng/g)			
	^{234}U	^{235}U	^{236}U	^{238}U	^{234}U	^{235}U	^{236}U	^{238}U
RGM-2	0.0007	0.0949	0.0000	13.0871	0.00007	0.00949	0.00000	1.30871
U005-A, 1 to 1	0.0014	0.2007	0.0002	33.7381	0.00014	0.02007	0.00002	3.37381
U005-A, 1 to 2	0.0021	0.3054	0.0005	54.3020	0.00021	0.03054	0.00005	5.43020
U005-A, 1 to 5	0.0042	0.6177	0.0012	115.6807	0.00042	0.06177	0.00012	11.56807
U005-A, 1 to 10	0.0078	1.1425	0.0025	218.7717	0.00078	0.11425	0.00025	21.87717
U005-A	0.0007	0.1054	0.0002	20.6981	0.00007	0.01054	0.00002	2.06981
U010, 1 to 1	0.0014	0.2282	0.0009	26.1813	0.00014	0.02282	0.00009	2.61813
U010, 1 to 2	0.0022	0.3731	0.0019	40.7143	0.00022	0.03731	0.00019	4.07143
U010, 1 to 5	0.0044	0.7746	0.0046	80.2115	0.00044	0.07746	0.00046	8.02115
U010, 1 to 10	0.0080	1.4566	0.0093	147.4604	0.00080	0.14566	0.00093	14.74604
U010	0.0007	0.1365	0.0009	13.4658	0.00007	0.01365	0.00009	1.34658
U100, 1 to 1	0.0120	1.7908	0.0063	27.8356	0.00120	0.17908	0.00063	2.78356
U100, 1 to 2	0.0232	3.4801	0.0126	43.3529	0.00232	0.34801	0.00126	4.33529
U100, 1 to 5	0.0566	8.4994	0.0313	87.2862	0.00566	0.84994	0.00313	8.72862
U100, 1 to 10	0.1138	17.1113	0.0634	163.1254	0.01138	1.71113	0.00634	16.31254
U100	0.0114	1.7175	0.0064	15.1189	0.00114	0.17175	0.00064	1.51189

3. Methods

3.1. Sample preparation

Approximately 250mg of RGM-2 was weighed and dissolved using a combination of ultrapure concentrated HNO_3, HF, and HCl. Once fully digested, the sample was redissolved in ~11ml of 6M HCl, to a final dissolved concentration of ~21 mg/g. Based on a certified uranium concentration of 5.67 µg/g and assumed natural uranium isotopic composition (Richter et al., 2008), we calculated the concentrations of ^{234}U, ^{235}U, and ^{238}U in the sample stock solution (Table 1). We assume no ^{233}U or ^{236}U is present, as they are only produced in measurable quantities through anthropogenic means. The three uranium doping solutions (U005a, U010, and U100) were prepared from stock solutions at >20 µg/g and diluted to approximate uranium concentrations of ~100 ng/g. Final uranium concentrations were calculated by isotope dilution by spiking with a ^{233}U tracer and performing isotopic analyses using a Nu Plasma MC-ICP-MS (see Wimpenny and Brennecka 2022; Wimpenny et al. 2022 for details). Samples of RGM-2 were doped with the three uranium standard solutions at approximate uranium ratios of 1:1, 1:2, 1:5, and 1:10 between sample and spike. These samples were then equilibrated on a hot plate before being dried overnight. Dried samples were redissolved in 10ml of internal standard solution (2% HNO_3 + 0.005M HF, containing ~1 ng/g In, Re, and Bi) ready for analysis by HR-ICP-MS.

Three samples with matrices relevant to real-world environments were prepared and termed soil, city, and seawater. The soil matrix sample was prepared by dissolving a subaliquot of SRM 2706 (New Jersey Soil) and redissolved in concentrated nitric acid. The final soil primary contained 56.6 mg of SRM 2706 per gram of solution. Similarly, the city matrix was prepared by dissolving SRM 635a (Portland Cement with slag) and diluted so 1 mL represented 24.5 mg of standard in 6N HCl. For the seawater matrix, non-acidified Ocean Scientific International Limited (OSIL) Atlantic Seawater was used directly. A mixed spike solution containing actinides in concentration ratios relevant to technical nuclear forensics (TNF) was produced at LLNL to test the accuracy of actinide isotopic analyses across different measurement platforms. The primary solution was diluted to concentrations of approximately 1 µg/g uranium, 10 ng/g plutonium, 1 ng/g neptunium, and 0.6 ng/g americium. The isotopic compositions of the mixed actinide solution were also chosen for TNF-relevance, using ~63% HEU, ~78% ^{39}Pu, ~pure ^{237}Np, and ~65% ^{241}Am. Details about the standards used to prepare the tracer, their isotopic compositions and the final composition of the tracer are provided in Table 2.

Table 2 – Actinide concentrations and isotopic compositions in the mixed actinide tracer. Plutonium and americium isotopic compositions were measured at LLNL using MC-ICP-MS. The uranium isotopic composition is the certified composition of U630. Uncertainties are given as 2σ.

	Standard	Conc. (ng/g)	Isotopic Composition		
U	CRM-U630	880.687	$^{234}U/^{235}U$ 0.0097698±0.0000124	$^{236}U/^{235}U$ 0.0151895±0.0000194	$^{238}U/^{235}U$ 0.55351±0.98
Np	Torres Np	0.815	$^{237}Np/^{236}Np$ N/A		
Pu	CRM-137a	8.235	$^{240}Pu/^{239}Pu$ 0.23771±0.00184	$^{241}Pu/^{239}Pu$ 0.005090±0.000128	$^{242}Pu/^{239}Pu$ 0.01507±0.00034
Am	IRMM-0243	0.557	$^{241}Am/^{243}Am$ 0.6472±0.0020		

3.2. Elemental analyses performed by HR-ICP-MS

All elemental analyses were performed using the Thermo Scientific Element XR HR-ICP-MS at LLNL. The instrument was configured with standard 'H' sample and skimmer cones, and samples were introduced to the plasma using a 100 µl/min glass nebulizer (Glass Expansion) and dual-cyclonic quartz spray chamber. In this configuration, the typical signal generated by a 1 ng/g solution of ^{115}In ranges between 1 and 2×10^{6} counts per second (cps). The Element XR has 3 detector modes spanning a dynamic range of >9 orders of magnitude, enabling trace and major elements to be measured at the same time. It also has a changeable entrance and exit slit system, which enables measurements to be performed at low, medium, or high-resolutions (m/Δm = 300, 4000, or 10,000 respectively). At higher resolution the entrance and exit slits narrow, meaning it is easier to resolve interferences such as polyatomic isobars from the isotope of interest. For example, high-resolution mode can be used to resolve ^{39}K from ^{38}Ar^{1}H and medium-resolution can be used to resolve ^{56}Fe from ^{40}Ar^{16}O.

Prior to sample analysis, the instrument is tuned to enhance sensitivity and lower oxide production to <10%. The peak shapes in medium and high-resolution are also refined to ensure optimal resolving power is achieved. In addition to a standard selection of major and trace elements, the method also includes a suite of actinide isotopes including ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu + ^{241}Am, ^{242}Pu, and ^{243}Am. All actinide isotopes are analyzed in low-resolution mode. A subset of isotopes including ^{235}U and ^{238}U are also analyzed in medium-resolution mode. Raw data is exported and reduced offline. Corrections are made for shifts in the intensity of the internal standard and instrument blank. The calibration standards contain uranium with a depleted ^{235}U content and unknown minor isotope abundances. They also contain no plutonium, americium, or neptunium. To convert intensities into concentrations we assume that ^{238}U is a good proxy for the behavior of the other actinides in the mass spectrometer. Thus, a calibration curve is created between the measured counts of ^{238}U and known ^{238}U concentrations in the standard solutions. The slope of the curve reflects the response of the detector to a solution with a known concentration. This slope, or calibration value, is then applied to all other actinide isotopes to obtain final concentrations. The uncertainty of the slope is propagated into the final uncertainties. Quality control checks are performed using USGS rock standards to assess the accuracy of major and trace element abundances, which typically agree with reference values to within 10%.

4. Results

4.1. Uranium doping into RGM-2 (Rhyolite)

Direct comparison between uranium isotopic compositions measured by HR-ICP-MS and calculated ratios are presented in Fig. 1. Uranium isotopic data was obtained at mass resolving powers (m/Δm) of 300, 4000, and 10000 (i.e., low, medium, and high-resolution) and clear differences exist between accuracy and precision of results obtained at these different resolutions. In general, uranium isotopic data obtained at low-resolution has the highest precision but measured ^{23x}U/^{238}U ratios are typically lower than calculated, particularly for the ^{235}U/^{238}U ratio (Fig. 1d, e, and f). High-resolution data are both highly imprecise and generally less accurate than data obtained at low and medium-resolution, probably as a consequence of the low counts rates when using such a narrow aperture slit. The most accurate isotopic data was obtained using medium-resolution with good agreement between measured and calculated ratios in almost all cases. This is consistent with results of Wimpenny and Brennecka (2022), in which isotopic data for historical fallout samples showed better agreement between HR-ICP-MS and MC-ICP-MS when measured under medium-resolution mode.

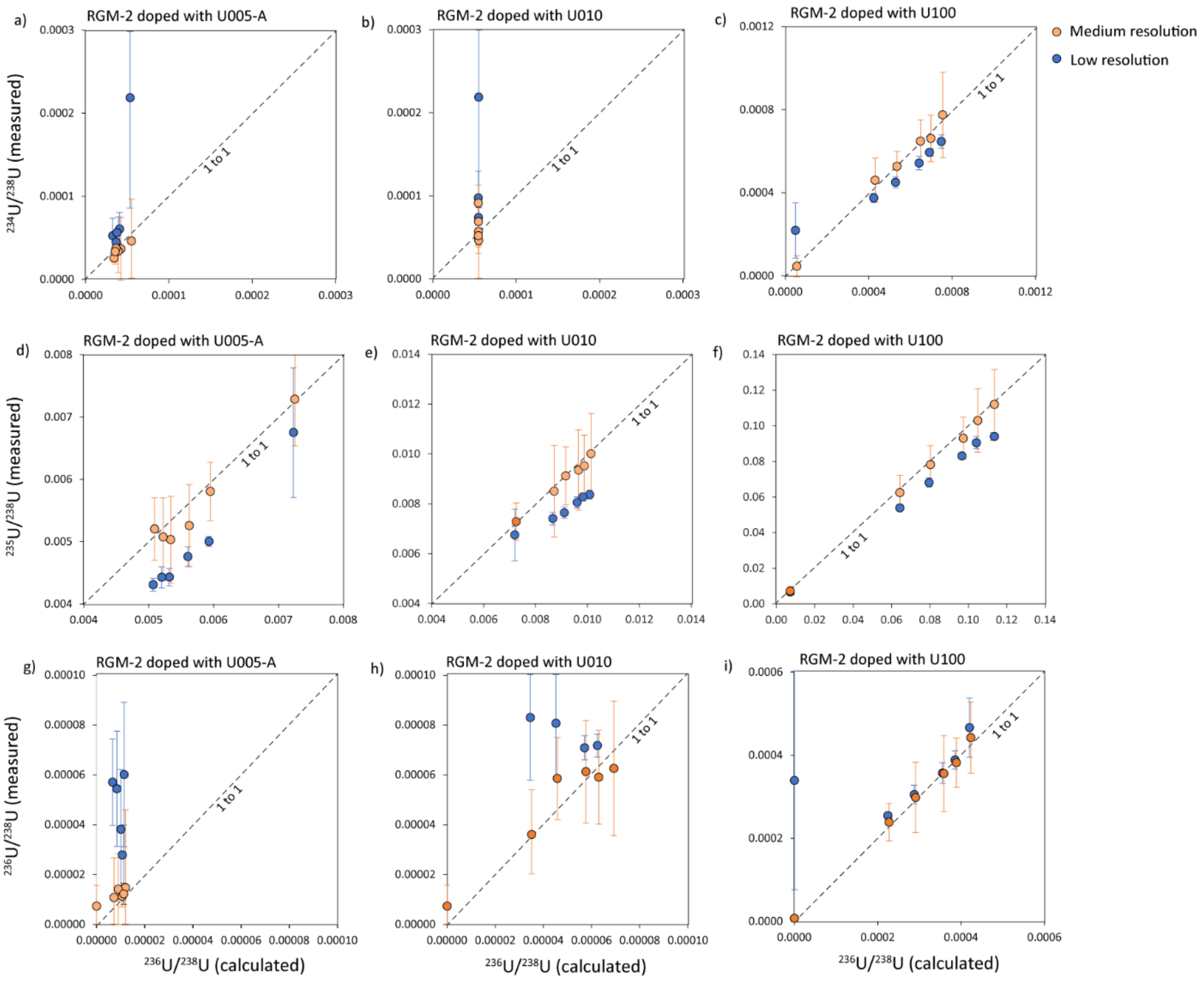

Fig. 1 – Uranium isotopic composition measured in RGM-2 samples doped with U005-A, U010, and U100. High resolution results are excluded All uncertainties are 2σ.

The effect of isotopic composition is also evident in the accuracy of isotopic data obtained by HR-ICP-MS. For the ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U ratios, the most accurate and precise data are obtained from samples doped with U100, and least accurate and precise data derived from samples doped with U005-A. This is likely to be a simple function of counting statistics; U100 has a higher abundance of ^{234}U, ^{235}U, and ^{236}U, hence will be less susceptible to interferences and minor isotopes will be counted at higher rates.

During the isotopic analysis of uranium by HR-ICP-MS we also monitored count rates of ^{239}Pu and ^{237}Np, to assess the effect of tailing from the ^{238}U peak at m/z = 237 and 239 (Fig. 2). As shown, clear correlations exist between the calculated ^{238}U concentration and measured concentrations at m/z = 237 and m/z = 239. Similar correlations between ^{238}U and m/z = 239 under low and medium resolving power are consistent with the signal at m/z = 239 being generated by peak tailing, rather than a polyatomic interference. Based on these correlations, we calculated the magnitude of ^{238}U tailing at m/z = 237 and 239 (i.e., abundance sensitivity) of approximately 6.7×10^{-6} and 2.5×10^{-5}, respectively. The fact that ^{238}U is the source of peak tailing, rather than other isotopes of uranium is logical, based on its relatively high abundance proximity to both m/z = 237 and 239. This is also supported by linear correlations between concentrations of ^{236}U and m/z = 237 (Fig. 2d) that differ depending on the ^{236}U/^{238}U ratio of the standard.

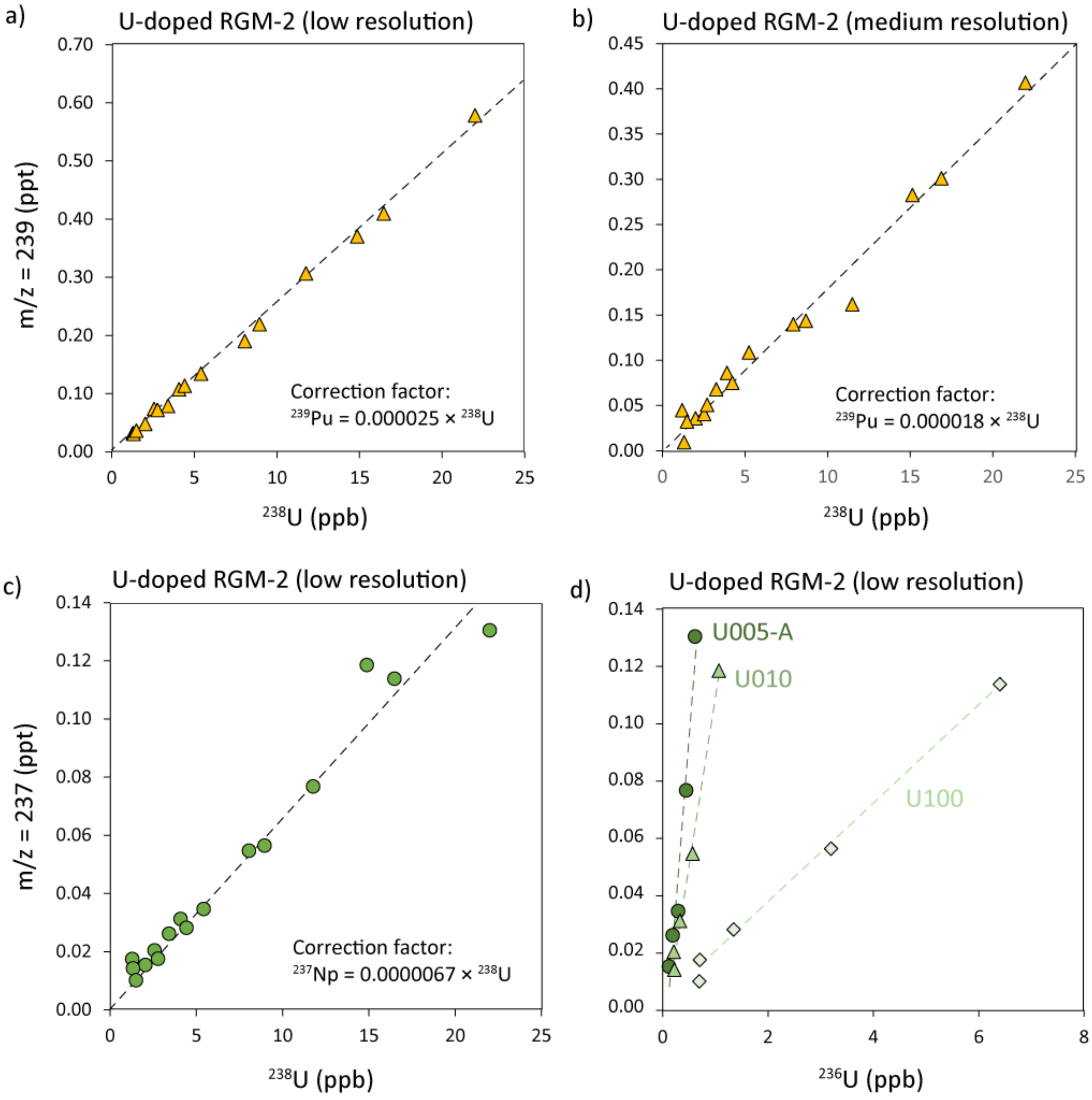

Fig. 2 – Apparent concentrations measured at m/z = 239 and m/z = 237 in RGM-2 samples doped with uranium. Relationships between uranium concentration and apparent concentrations of ^{239}Pu and ^{237}Np can be used to correct effects of peak tailing or hydride species from ^{238}U.

4.2. Mixed Actinide addition to soil, city, and seawater samples

4.2.1. Element concentrations

The composition of the mixed actinide spike is provided in Table 2. Between 0.04 and 1.1g of spike was added to the matrix sample aliquots, equating to a maximum of 1 µg of U, 9 ng of plutonium, 0.9 ng of neptunium, and 0.6 ng of americium. The matrix samples contained varying quantities of natural uranium, meaning that the proportion of uranium deriving from the spike varied from ~28% to ~100% of the total uranium. Due to relatively low uranium concentrations in seawater (~3ng/g, Owens et al., 2011), uranium derived from the spike accounted for 92-100%.

Concentrations of uranium and plutonium measured by HR-ICP-MS are shown in Fig. 3 and 4 as a function of the calculated values. Data obtained in low and medium-resolution are compared. Based on the low accuracy and precision of high-resolution measurements derived from the uranium-doping experiments in Section 4.1., no high-resolution data was collected for this experiment. As shown, there is good agreement between measured and calculated concentrations of uranium and plutonium at both resolutions. In all cases the measured concentrations are ~10% higher than calculated, and the extent of this offset and associated uncertainties are unrelated to sample matrix composition. For uranium, there is slightly better agreement between measured and calculated concentrations at medium-resolution, whereas the accuracy of plutonium concentration measurements is slightly better at low-resolution.

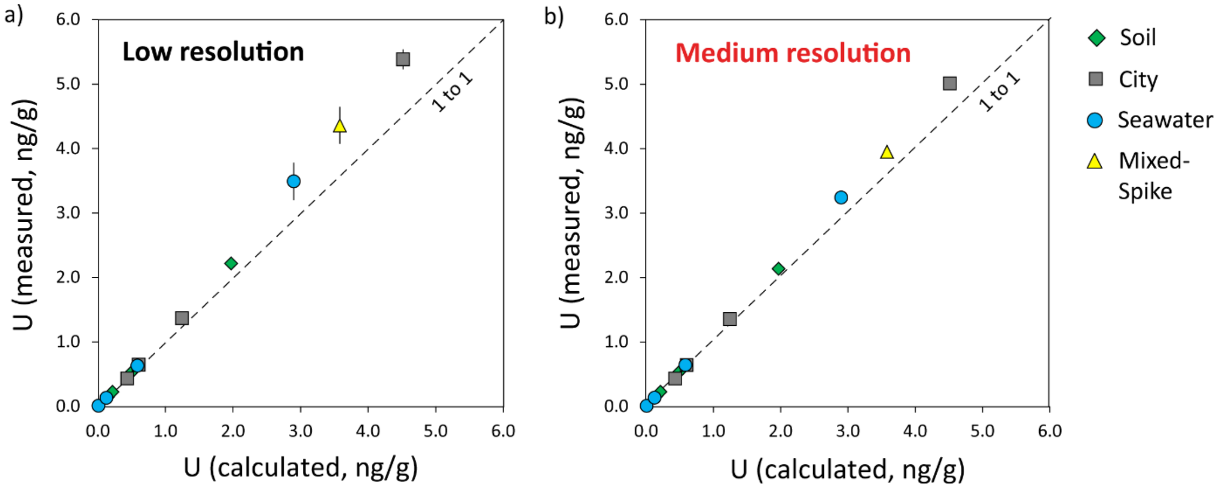

Fig. 3 – Comparison between measured and calculated uranium concentrations in the matrix samples and mixed actinide standards at (a) low and (b) medium-resolution. All uncertainties are 2σ.

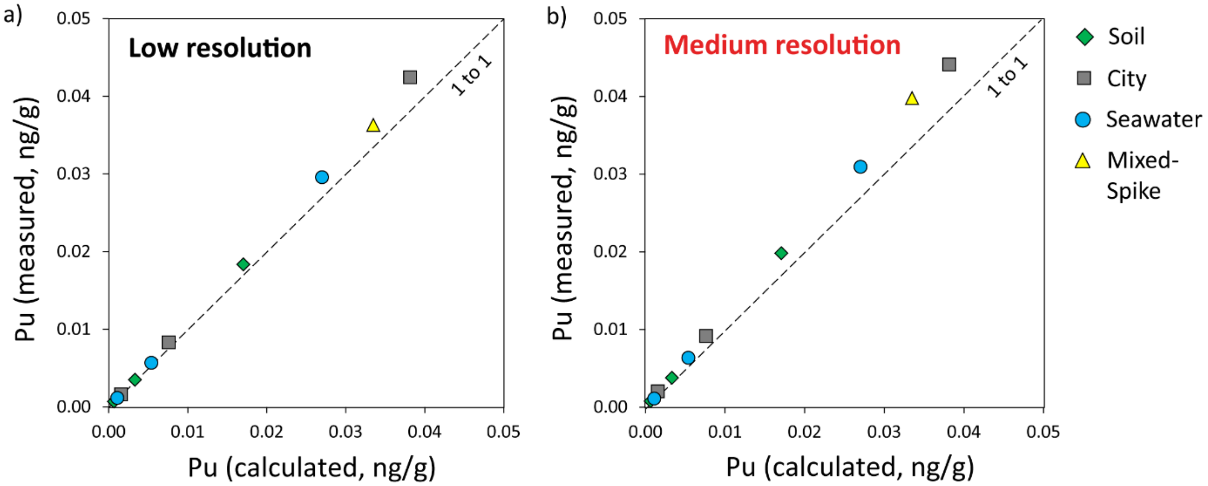

Fig. 4 - Comparison between measured and calculated plutonium concentrations in the matrix samples and mixed actinide standards at (a) low and (b) medium-resolution. All uncertainties are smaller than the symbols (2σ).

Similar to our observations from uranium and plutonium, the measured ^{237}Np concentrations are 10-20% higher than calculated values (Fig. 5a). Offsets between measured and calculated concentrations of ^{241}Am and ^{243}Am differ between the two isotopes (Fig. 5b and c). At m/z = 241 the HR-ICP-MS cannot distinguish between ^{241}Am and ^{241}Pu, requiring m/Δm of >10^6. Hence, the calculated concentrations at m/z = 241 include the abundances of both isotopes. Interestingly, the Element XR software allows separate collection of ^{241}Am and ^{241}Pu data, despite not having the resolving power to distinguish their masses. In this case, the measured ^{241}Am agrees well with calculated amounts of ^{241}Am and ^{241}Pu to within 5-10% (Fig. 5c), whereas the measured ^{241}Pu concentrations are 10-20% too low (Fig. 5d). The cause of this discrepancy is unclear and likely requires more robust understanding of the way the Element XR calibrates masses at high Z. Concentrations of ^{243}Am are ~60% higher than calculated values suggesting that an unidentified polyatomic interference is present at m/z = 243. Given the consistent offset between calculated and measured ^{243}Am, this is likely to derive from species inherent to the spike or, alternatively, the spike characterization is inaccurate.

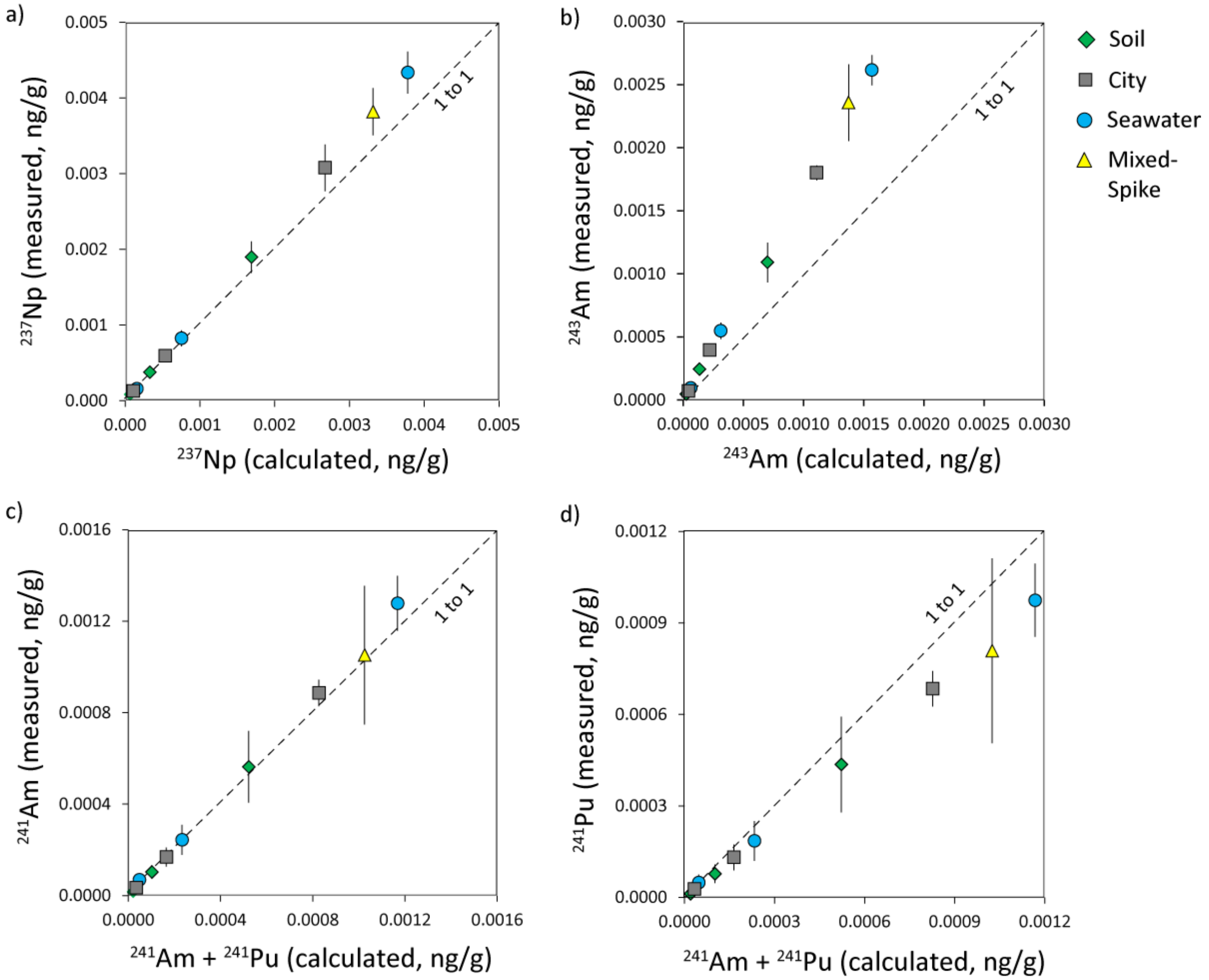

Fig. 5 – Comparison between measured and calculated concentrations of a) ^{237}Np, b) ^{243}Am, c) ^{241}Am and d) ^{241}Pu. In this case, the Element XR software has the option to collect data for ^{241}Am and ^{241}Pu separately, despite not being able to resolve the mass difference between isotopes. All uncertainties are 2σ.

4.2.2. Isotopic compositions

Measured isotopic compositions of uranium and plutonium are compared with calculated values in Fig. 6. Measured ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U ratios match well with calculated ratios at both low and medium-resolution. The accuracy of the uranium data is unaffected by differences in sample matrix. However, uranium isotope ratios from the seawater matrix are generally less precise than either the soil or city samples. For example, internal precision (2σ) of ^{235}U/^{238}U ratios in the soil and city samples range from 6 to 20%, whereas the precision ranges from 22 to 33% in the seawater samples. This may be a function of uranium concentration, given that the majority of uranium in the seawater samples derived from the mixed actinide spike.

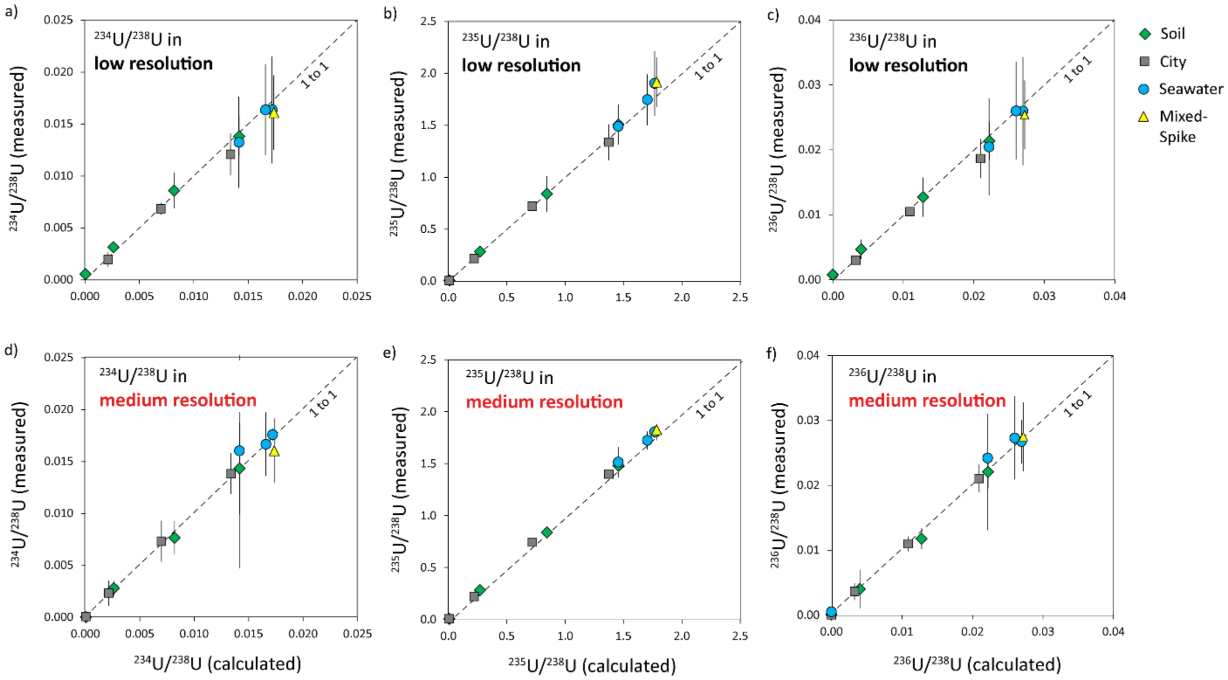

Fig. 6 – Comparison between measured and calculated uranium isotopic compositions in the three matrix samples. Measurements in low-resolution are shown in a-c and medium-resolution in d-f. All uncertainties are 2σ.

Given that the three matrix samples contained no plutonium, the plutonium isotope ratios of the variously doped matrix samples should all match the reference composition of NBL CRM 137 (Table 2), with the exception of ^{241}Pu/^{239}Pu, which is perturbed by the addition of ^{241}Am from the mixed actinide spike. As shown in Fig. 7, the ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios for each sample are within uncertainty of the reference values. Internal precision (2s) for the ^{240}Pu/^{239}Pu ratios range from 6.5 to 32% at low-resolution and 8.6 to 80% at medium-resolution. Internal precision for the ^{242}Pu/^{239}Pu ratios range from 11.7 to 96% at low-resolution and 18 to 267% in medium-resolution. For both isotope ratios, the precision correlates with the amount of spike added to the sample; samples with smaller spike additions have larger uncertainties and vice versa.

As the mixed actinide spike contained americium with a known ^{241}Am/^{243}Am ratio (0.647 ± 0.002) we also wanted to evaluate whether it is possible to obtain constraints on the americium isotopic composition by HR-ICP-MS. In this case, the measured ratio of masses at m/z = 241 and 243 is equal to (^{241}Am + ^{241}Pu)/^{243}Am, which we calculate as ~0.745, based on the amount of CRM 137 in the mixed actinide spike. However, as shown in Fig. 8, the measured (^{241}Am + ^{241}Pu)/^{243}Am ratios are systematically lower than this value, consistent with the offset between measured and calculated ^{243}Am concentrations shown in Fig. 5b. Uncertainties in the measured (^{241}Am + ^{241}Pu)/^{243}Am ratios ranged from 8 to 116% and, similar to results of plutonium isotopic analyses, samples with smaller spike additions have larger uncertainties.

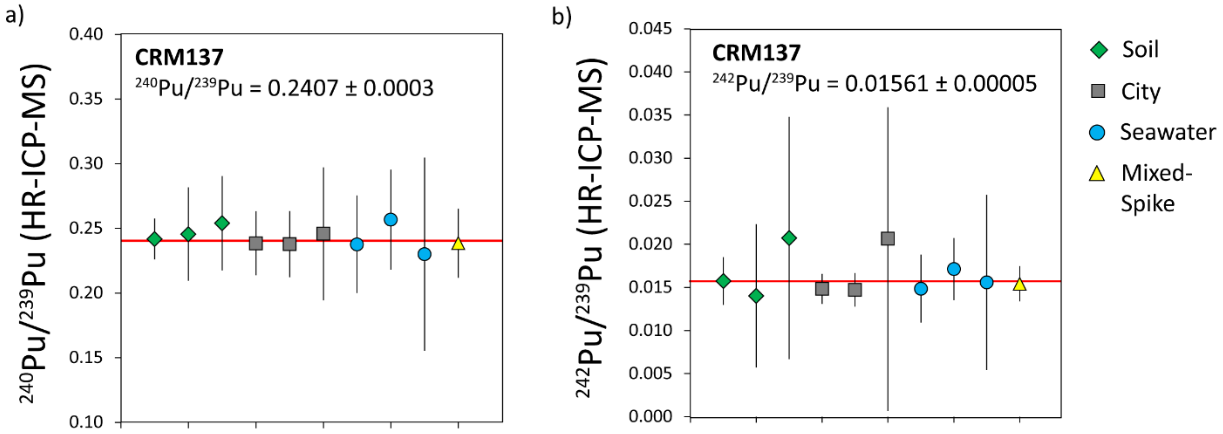

Fig. 7 – Measured a) ^{240}Pu/^{239}Pu and b) ^{242}Pu/^{239}Pu ratios in the matrix samples and mixed actinide spike. Red lines show reference values. All uncertainties are 2σ.

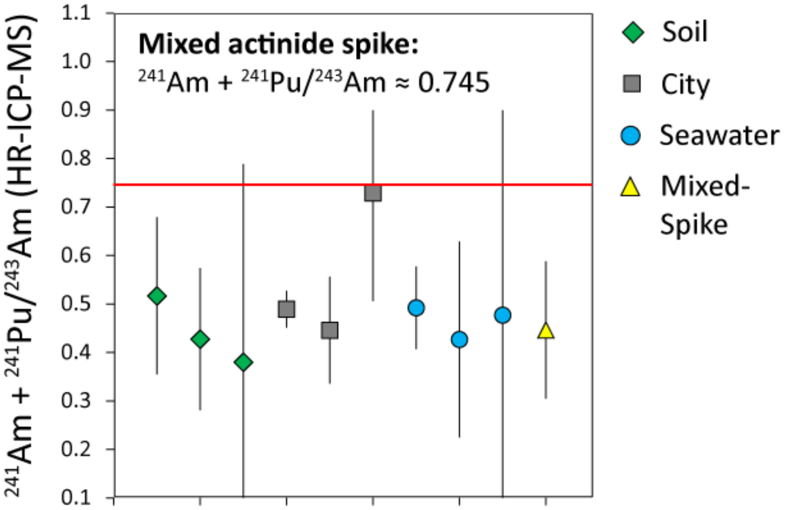

Fig. 8 – Measured (^{241}Am + ^{241}Pu)/^{243}Am ratios in the three matrix samples and mixed actinide spike. The reference value is 0.745. All uncertainties are 2σ.

5. Discussion

5.1. Uranium doping into RGM-2 (Rhyolite)

The doping of uranium reference materials into RGM-2 produced two key findings relevant to rapid isotopic analyses of actinides in bulk rock solutions. First, the accuracy and precision of uranium isotopic measurements by HR-ICP-MS are highly dependent on mass resolving power used on the Element XR. This is a tradeoff; at lower resolution ($m/\Delta m = 300$) the entrance and exit slits allow more ions to reach the detector and hence, higher signals are generated with lower statistical uncertainties. However, lower resolving power is more susceptible to polyatomic interferences that cannot be resolved from uranium species, such as those generated from platinum and lead (e.g., $^{196}Pt^{40}Ar^{+}$ on ^{235}U or $^{206}Pb^{16}O^{16}O^{+}$ on ^{238}U). It is notable that the measured $^{235}U/^{238}U$ ratios are consistently lower than calculated for the doped RGM-2 samples (Fig. 1) using the lowest resolution, suggesting an issue with unaccounted for interferences. In contrast, the results measured at medium-resolution ($m/\Delta m = 4000$) are far closer to the calculated ratios. This is consistent with the previous comparison between data generated from analysis of bulk rock solutions and purified uranium in Wimpenny and Brennecka (2022). This indicates that the cause of the offset $^{235}U/^{238}U$ ratios in low-resolution mode is an interference, potentially at $m/z = 238$. However, we again note that the measured $^{236}U/^{238}U$ ratios are consistent with calculated values. Thus, no simple interference is responsible, and it likely indicates that several polyatomic species are to blame for the offsets. It is also notable that there is a limit to the gains that can be achieved by measuring at higher resolving power. In high-resolution mode ($m/\Delta m = 10,000$) the data quality is severely compromised, both in terms of precision and accuracy. This is simply caused by a significant drop in counts at high-resolution, which dramatically increases uncertainties and, in turn, imparts a higher degree of scatter. Ultimately, these results echo the findings of the previous study; that the most accurate U isotope data are produced under medium resolving power using the Element XR.

The second key finding from the uranium doping study was the quantification of peak tailing effects and/or hydride generation from ^{238}U at $m/z = 237$ and 239. In other words, the extent to which measurements of ^{237}Np and ^{239}Pu are compromised by the presence of uranium in a bulk rock solution. In Fig. 2, we plot correlation lines between the measured concentration of uranium (in ng/g) and the count rates measured at $m/z = 237$ and 239. As shown, linear regressions can be fitted to each data array that equate to the apparent $^{237}Np/^{238}U$ and $^{239}Pu/^{238}U$ ratios generated by pure uranium solutions. Measurements at $m/z = 239$ were performed in both low and medium resolution modes but the correlation with uranium concentration persists even at higher mass resolving power. The slope of these correlation lines equate to the relative interference from ^{238}U at $m/z = 237$ and 239 (i.e., the abundance sensitivity), with respective values of 6.7×10^{-6} and 2.5×10^{-5}. Thus, for the Element XR to resolve ^{237}Np and ^{239}Pu from interferences generated by ^{238}U, the $^{237}Np/^{238}U$ and $^{239}Pu/^{238}U$ ratios in a sample must be greater than 6.7×10^{-6} and 2.5×10^{-5} respectively. To ensure interferences from ^{238}U contribute <10% of the final signal would require $^{237}Np/^{238}U$ and $^{239}Pu/^{238}U$ ratios of 6.7×10^{-5} and 2.5×10^{-4} respectively. These bounding limits are potted in Fig. 9. Although the combination of peak tailing effects and hydride generation at $m/z = 239$ outweigh peak tailing effects at $m/z = 237$, the ultimate significance is dependent on the expected $^{237}Np/^{238}U$ and $^{239}Pu/^{238}U$ ratios in a sample. In Fig. 9, the $^{237}Np/^{238}U$ and $^{239}Pu/^{238}U$ ratios of historical fallout samples are plotted that were measured as whole rock solutions by the Element XR at LLNL. As shown, most samples have $^{239}Pu/^{238}U$ ratios $>1\times10^{-3}$, meaning interferences from ^{238}U are unlikely to affect the elemental or isotopic analysis of plutonium. In contrast, ~50% of the samples have $^{237}Np/^{238}U$ ratios that fall below 6.7×10^{-4}, meaning peak tailing from ^{238}U is likely to be a significant component of the final ^{237}Np concentrations from bulk rock solutions. To improve ^{237}Np data one could use a data correction approach based on the known peak tailing effects on the Element XR. However, this would need to be tested on samples with known neptunium concentrations that have been purified and analyzed by MC-ICP-MS, a time-consuming and costly approach. Alternatively, the Element XR has an abundance sensitivity filter that would improve the amount of peak tailing. However, its use severely compromises measurements at lower mass ranges, making it useful only if actinides are targeted (i.e., not part of a standard multi-element run). Recent development of collision cell technology means other instrumentation, such as triple quadrupole ICP-MS or collision cell equipped MC-ICP-MS could be used to develop schemes to separate neptunium from uranium using collision cell gases. As yet, however, no such method has been documented in published literature. Finally, there is potential for techniques such as resonance ionization mass spectrometry (RIMS) to be used to detect neptunium in complex matrices; this is currently a work in progress for the R^3 team.

In Fig. 9, we plot the composition of the mixed actinide spike in ^{237}Np/^{238}U-^{239}Pu/^{238}U space. As shown, it has high enough ^{237}Np/^{238}U and ^{239}Pu/^{238}U ratios that interferences from ^{238}U should not pose a problem when characterizing ^{237}Np and ^{239}Pu abundances in the three matrix samples.

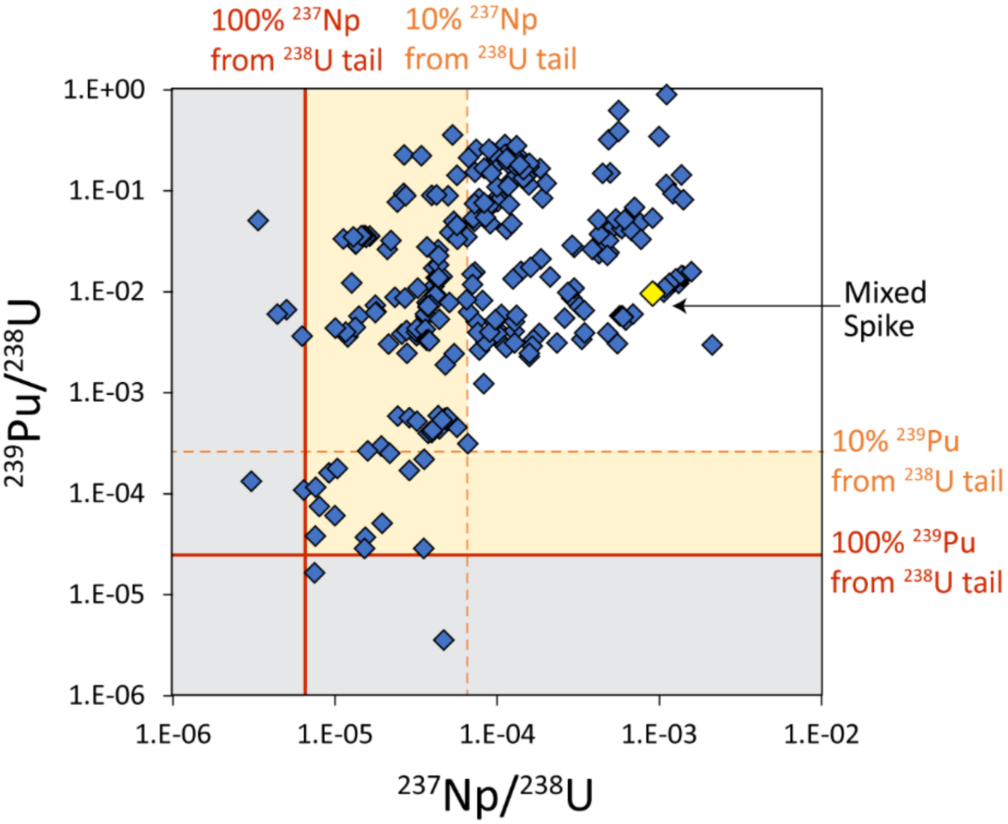

Fig. 9 – Measured ^{239}Pu/^{238}U and ^{237}Np/^{238}U ratios in historic fallout samples (blue) and the mixed actinide spike (yellow). Red and orange lines show the ratios at which 100% and 10% of the ^{239}Pu or ^{237}Np derives from ^{238}U tailing and/or hydride formation.

5.2. Spiked matrix samples

The addition of the mixed actinide spike to the three matrix samples (soil, city, and seawater) allows us to not only test the effect of sample matrix on actinide isotope measurements in bulk rock solutions, but also to investigate the accuracy and precision of plutonium, neptunium, and americium measurements in samples with known isotopic compositions. Based on the results presented in Fig. 4 to 7, there are no systematic differences in actinide concentration or isotopic composition data with respect to sample matrix.

Thus, based on the significant differences in bulk chemical composition between a soil, cement (city), and seawater, we infer that samples spanning this range of compositions should not present a problem if bulk actinide isotopic analyses are performed on unknown samples in the future. That being said, other compositions such as metal rich samples and more mafic rock types are not represented by these compositions, and further testing would need to be performed to validate that this technique could be used in a wider spectrum of post detonation samples. Furthermore, we recognize that a sample of fresh debris would contain much higher activity due to the presence of fission and activation products, and this level of activity may not be compatible with the ion counting detection system on ICP-MS instruments. Development of the analytical technique in conjunction with new rapid sample separation methods would be required to address this problem.

5.2.1. Concentration measurements

A comparison between measured and calculated uranium, plutonium, neptunium, and americium concentrations are provided in Fig. 3, 4, and 5. In general, the values agree to within 10-20%, but all measured concentrations are greater than calculated values. For uranium, the concentration in low-resolution is higher than that calculated in medium-resolution. Again, we infer that the low-resolution measurement is more prone to interferences, resulting in an artificially high final concentration. Measurement at medium-resolution improves the offset, consistent with the previous study (Wimpenny and Brennecka 2022) and observations from uranium doping into RGM-2. This highlights that uranium is best analyzed by the Element XR at higher mass resolving power, despite the compromise in signal intensity. Interestingly, measured plutonium and neptunium concentrations are slightly higher than calculated concentrations by ~10%. Based on their ratios to uranium (Fig. 8), interferences from uranium should be negligible. Although the presence of other polyatomics cannot be ruled out, we note that offsets are not linked to sample matrix, hence polyatomics from trace metals (e.g., REE's, lead) are unlikely to be responsible, as these metals are present at vastly different concentrations in the soil, city, and seawater samples. An alternative explanation is that these offsets represent small analytical problems during sample preparation and spiking (e.g., relating to weighing or spike homogenization). Repeat tests would help to verify this. However, given that the precision of trace element analyses are typically in the 5-10% range, such a small offset in the plutonium and neptunium concentration between measured and calculated values are not unexpected. Ultimately, these results verify the findings of the uranium-doping experiment in Section 4.1. (i.e., that ^{237}Np and ^{239}Pu concentration measurements are robust in bulk rock solutions with ^{237}Np/^{238}U and ^{239}Pu/^{238}U ratios above 6.7×10^{-5} and 2.5×10^{-4} respectively).

The americium data was less accurate than the other actinides. Americium is usually difficult to quantify without performing chemical purification because ^{241}Pu directly interferes with ^{241}Am. Because in this case the americium spike contains more ^{243}Am than ^{241}Am (Table 1), it should be possible to quantify ^{243}Am without accounting for direct isobars. However, the measured ^{243}Am content was ~60% higher than calculated, which indicates an interference at $m/z = 243$. The source of the interference cannot have been polyatomic species inherent to the matrix samples because no counts of ^{243}Am were recorded in the pure soil, city, and seawater samples. Peak tailing from large ion beams such as ^{238}U are unlikely to be a concern because ^{238}U is 5 mass units away from ^{243}Am and would be expected to affect plutonium masses and ^{241}Am to a greater extent than ^{243}Am, which is not observed. Other actinides are not present at sufficient abundance for either peak tailing effects or hydride generations to be problematic. For this reason, we infer that an unknown polyatomic species (e.g., oxide, nitride, argide) is generated at $m/z = 243$ by species in the mixed actinide spike, but currently the identity of this interfering species is unknown. Further testing would be necessary to identify and, potentially, correct for this in future studies. The measured mass-241 (^{241}Am) agreed well with calculated ^{241}Am + ^{241}Pu concentrations (Fig. 5c), consistent with previous results (Wimpenny and Brennecka 2022). However, restate here that americium is the most difficult of these elements to quantify in bulk rock solutions, and ^{241}Am can only be quantified if the plutonium isotopic data has been obtained for a sample. Thus, in the context of rapid actinide measurements, other techniques such as triple-quad ICP-MS or RIMS might be more successful quantifying ^{241}Am abundance on a timeframe of days.

5.2.2. Actinide isotope measurements

Uranium in each sample is a two-component mixture between natural uranium and U630 in the mixed actinide spike. Thus, the final isotopic composition reflects the amount of uranium in the matrix sample and the amount of spike added to each fraction. There is excellent agreement between measured and calculated uranium isotope ratios for the three matrix materials regardless of using low or medium-resolution (Fig. 6). This was far more successful than results of uranium doping into RGM-2, probably because in this case, the samples were doped with depleted uranium (U005-A) or low enriched uranium (U010 and U100) that did not contain significantly higher ^{234}U and ^{236}U contents. Thus, whereas the spread in ^{23x}U/^{238}U ratios in the RGM-2 doping experiments was relatively minor (see Fig. 1) and difficult to resolve using HR-ICP-MS, the spread of isotopic compositions after doping varying amounts of U630 into natural uranium is orders of magnitude greater, resulting in better defined linear arrays between measured and calculated ratios. In this case, there is no improvement in the accuracy of uranium isotopic data obtained in medium-resolution mode, contrary to data from the uranium doping study and previously obtained data from historic testing (Wimpenny et al., 2022). This probably reflects the isotopic composition of uranium in the mixed actinide spike (i.e., ~60% ^{235}U), which means isotopic analysis of ^{234}U, ^{235}U, and ^{236}U are less susceptible to polyatomic interferences and measurements in low and medium-resolution produce equivalent results. Although no systematic differences in accuracy exists between the three matrix samples, the seawater samples have consistently higher uncertainties for all uranium isotopic data. This could reflect a greater degree of instability during measurement of the high salt matrix by the ICP-MS, although more testing would be required to verify this. Ultimately, data from the three matrix samples demonstrate that accurate ^{235}U/^{238}U ratios can be obtained for samples with varying sample matrices with precision of ~10% (2σ), increasing to 20-30% for lower abundance isotopes.

Plutonium isotopic data from the three matrix samples are more straightforward to interpret given that their plutonium derived solely from the mixed actinide spike. The fact that measured ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios fall within uncertainty of the certified ratio for CRM137 indicates that polyatomic species generated by matrix elements, including uranium, are relatively unimportant when analytical precision is at the 10-20% level. In this case, the ^{239}Pu/^{238}U ratio of the mixed spike is relatively high, ~0.01 (Fig. 9), so artifacts from ^{238}U interferences are unimportant. Given that ^{239}Pu/^{238}U ratios in historic debris samples can be less than 0.0001 (Fig. 9), this will not always be the case. The accuracy of the plutonium isotope ratios was similar in low and medium resolutions, but uncertainties were larger in medium-resolution due to lower count rates. For this reason, we recommend that future attempts to measure plutonium isotope ratios by HR-ICP-MS use low-resolution.

Americium isotope ratios were also measured by HR-ICP-MS. Similar to plutonium, the matrix samples contained no americium, so all samples were expected to return the same (^{241}Am + ^{241}Pu) /^{243}Am ratio of 0.745. The fact that the samples and pure mixed spike gave systematically lower (^{241}Am + ^{241}Pu) /^{243}Am ratios (~0.45) indicates that an interference was present at m/z = 243. This is consistent with measured ^{243}Am concentrations being ~60% higher than calculated, whereas measurements at m/z = 241 were consistent with calculated ^{241}Am + ^{241}Pu (Fig. 4c). These data indicate that, at present, the analysis of whole rock solutions by HR-ICP-MS cannot obtain robust elemental or isotopic data for Am. Even if the interference on ^{243}Am could be identified and corrected for, the final ^{241}Am abundance can only be quantified if the plutonium isotopic distribution is known, which requires separation of americium from plutonium by ion exchange chromatography.

6. Conclusions

The results presented here and in the previous report (Wimpenny and Brennecka 2022) demonstrate that useful information about actinide abundances and isotopic compositions can be provided for post-detonation samples by analyzing whole rock solutions. Sample matrices tested here do not noticeably reduce the accuracy or precision of the measurements made by HR-ICP-MS, indicating that samples incorporating material from an urban (city), desert/rural (soil), and marine (seawater) environments should not pose a problem to this type of chemical analysis. More exotic matrices have been found in fallout samples from near surface nuclear tests, (e.g., metal rich samples, Wimpenny et al., 2022) but whether these would pose a problem for bulk rock analyses by ICP-MS cannot be ascertained without further testing. Based on the results of the current study, we predict that the analysis of whole rock solutions by HR-ICP-MS would generate useful elemental and isotopic data for actinides for the majority of matrices encountered in post-detonation samples. In situations where fresh debris is encountered, with appreciable activity from fission and activation products, it would likely be beneficial to process the sample to separate actinides from the rest of the sample matrix. Thus, further work to combine bulk rock analyses with rapid separation techniques would be required to validate this method for use in forensics investigations.

The analysis of uranium concentration and isotopic composition was previously shown to be offset from known values when samples were analyzed in low-resolution mode (Wimpenny and Brennecka 2022). Here, we show that use of the Element XR's medium-resolution slits enable us to negate polyatomic interferences present at low-resolution, resulting in improved accuracy of uranium elemental and isotopic data. Precision associated with ^{235}U/^{238}U ratios are relatively poor (5-20%) compared to MC-ICP-MS measurements on purified uranium solutions (<1%), however, lower precision data may still be useful if data can be turned around rapidly. Plutonium analyses are less prone to analytical artifacts, particularly those generated from the major and trace elements inherent to the matrix samples. This is demonstrated by accurate ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios in the three matrix samples at all spiking levels. That being said, polyatomic interferences and/or peak tailing effects from ^{238}U can cause problems where the ^{239}Pu/^{238}U ratio is $< 2.5\times10^{-4}$, so we recommend that ^{239}Pu/^{238}U ratios be assessed in all unknowns when evaluating plutonium isotopic data. One of the most impressive results of the whole rock solution analyses is that ^{237}Np can be quantified accurately at a fraction of the time required to process and analyze ^{237}Np by MC-ICP-MS. Current neptunium analytical protocols require spiking with a short-lived ^{239}Np tracer to establish yield of ^{237}Np through column chemistry. This is not only time consuming to prepare, but requires final solutions be counted and yields determined prior to isotopic analysis. Neptunium separation from plutonium is also challenging as neptunium must be in the correct oxidation state for the separation to be successful. Results of whole rock solution analyses show that ^{237}Np concentrations in the matrix samples match within ~20% of calculated values. One caveat to the ^{237}Np analyses is that the mixed actinide spike has a ^{237}Np/^{238}U ratio that is relatively high (~0.001). At lower ^{237}Np/^{238}U ratios of 6.7×10^{-5} and below the peak tailing from ^{238}U would contribute >10% of the ^{237}Np signal. As shown in Fig. 9, a significant proportion of historic fallout samples analyzed in Wimpenny et al., (2022b) have ^{237}Np/^{238}U ratios below 6.7×10^{-5} and hence their measured ^{237}Np contents are likely to have been perturbed by tailing from the neighboring ^{238}U peak. Similar to inferences from plutonium, we recommend that the ^{237}Np/^{238}U ratio be quantified in all unknown samples and future work may be needed to assess whether robust corrections can be applied based on quantification of the peak tailing effect at m/z = 237. Americium is the least straightforward element to quantify given that ^{241}Am cannot be distinguished from ^{241}Pu, and concentrations of ^{243}Am are affected by a hitherto unidentified interference that is present in the mixed actinide spike. Measured concentrations of ^{241}Am and ^{241}Pu at m/z = 241 accurately reproduce calculated values but calculation of the final ^{241}Am concentration would require knowledge of the plutonium isotopic distribution that can only be achieved by measuring purified plutonium. Thus, determining the americium content and isotopic composition of any unknown by mass spectrometry is unlikely to be feasible over a timeframe of days.

The future of this technique for nuclear forensics studies is likely to be dependent on the acceptable accuracy and precision of silver standard data and the time required to process a sample (including sample dissolution), analyze it, and reduce the data. Sample dissolution is the key obstacle to obtaining rapid actinide isotopic data from samples with complex matrices, but this is outside of the scope of this report. Instead, there are ways to optimize the current analytical process if fast turnaround is required. First, samples are usually aliquoted for analysis by weight, which is the most accurate technique as it compensates for sample density and variations in pipetting volume. However, accurate weighing is time consuming and relative uncertainties introduced by preparing samples volumetrically are likely to be far smaller than analytical uncertainties. Second, sample analysis time could be reduced by excluding many of the low mass isotopes and focusing on the actinide mass range. Current major and trace element analyses take 8-10 minutes per sample due to the range of elements analyzed and performing analyses in low, medium, and high-resolutions. Sixty to eighty percent of the analytical time could be reduced by down selecting the species of interest and excluding high-resolution analyses, which provide no improvement over data obtained in medium-resolution. Last, data collected by the Element XR is currently reduced by hand using Excel spreadsheets, which can take hours. A custom data reduction program in R/Python/Matlab could potentially speed up the data reduction process and ensure that samples are all reduced using a standard method, fully propagating uncertainties and helping to reduce user errors.

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