A new era of plutonium assay and isotope ratio measurements at ultra-low levels in IAEA safeguards environmental swipe samples by isotope dilution MC-ICP-MS using a ^{244}Pu spike

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Abstract

We present a new analytical method for accurately measuring femtogram amounts of Pu in environmental swipe samples using a high-purity ^{244}Pu spike and multi-collector inductively-coupled-plasma mass spectrometry. The method was validated by comparative measurements of samples that were previously analysed using a ^{242}Pu spike. The ^{244}Pu spike allows direct normalization of all Pu isotopes to both ^{244}Pu and ^{239}Pu, along with online monitoring of PbAr interferences, resulting in highly-sensitive and accurate Pu assay and isotope ratio measurements. Expanded uncertainties were typically $< 2.5\%$ for Pu amounts larger than 20 fg, and $< 1\%$ for Pu isotope ratios larger than 0.08. Detection thresholds (L_c) were well below 1 fg for all Pu isotopes.

Keywords Multi-collector inductively-coupled-plasma mass spectrometry · Isotope dilution mass spectrometry · ^{244}Pu · Plutonium · Femtogram amounts · Swipe samples

Introduction

The International Atomic Energy Agency's (IAEA) safeguards system provides independent verification that States are honoring their legal obligations to use nuclear material and facilities only for peaceful purposes. IAEA safeguards are a set of technical measures designed to detect the diversion of nuclear material as well as the misuse of nuclear material, facilities and/or technologies. The IAEA's verification role as the international safeguards inspectorate provides credible assurance to the international community that States are complying with their legal commitments [1]. Under Article III of the Treaty on the Non-Proliferation of Nuclear Weapons (NPT), each Non-Nuclear Weapon State (NNWS) is required to accept safeguards by concluding a Comprehensive Safeguards Agreement (CSA) with the IAEA, in accordance with the IAEA's Statute [2, 3]. Under the CSA, States are obliged to provide the IAEA with

information concerning both nuclear material that is subject to safeguards and the design of facilities that are relevant for safeguarding such material [3]. In the case of nuclear materials subject to safeguards, plutonium (Pu) is of particular interest as it is a direct-use material, which does not require further enrichment or transmutation before its use in nuclear weapons [4]. It is, therefore, of the utmost importance to collect information about the presence of Pu and its isotopic composition during safeguards inspections to mitigate the risk of diversion or misuse.

The presence of Pu and its isotopic composition can be determined through the IAEA's environmental sampling (ES) [5] program, in which inspectors collect dust samples on cotton swipes from the environment within a facility, which may contain minute traces of Pu, U and other actinides. Highly sensitive analytical techniques are then used to analyze the samples.

In environmental sampling, the so-called 'bulk analysis' method provides the highest level of sensitivity and can detect Pu at the femtogram (10^{-15} g) level in a swipe sample. In bulk analysis, the swipe is digested and analyzed as a whole, providing values for the amount of Pu and U present on the swipe as well as the average isotopic composition. Amount measurements of the swipe samples are typically performed by isotope-dilution mass spectrometry (IDMS),

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which is considered a primary measurement method when combined with the gravimetric preparation of the chosen spike [6, 7]. The Consultative Committee for Amount of Substance (CCQM) defines a primary method as follows: *"A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units"* [6, 7]. Due to its metrological qualities, IDMS analyses provide the most accurate results as long as certain pre-requisites are fulfilled, such as the quality of the reference material spike used and the measurement method for measuring isotope ratios.

The ideal spike reference material for ES analysis should have four main characteristics: It should be (1) the least abundant isotope in the sample; (2) extremely rare in nature and not be produced in quantities in the nuclear fuel cycle; (3) as stable as possible; and (4) have isotopic purity [8]. The last point is especially important for achieving detection limits in the femtogram to attogram range.

^{244}Pu, being the longest-lived Pu isotope with a half-life of 8.26×10^7 years [9], exhibits all these characteristics, and was, thus, identified as the ideal spike for low-level Pu assay measurements of Pu isotopes ranging from ^{239}Pu to ^{242}Pu [10, 11]. Until 2018, all commercially available ^{244}Pu spike certified reference materials (CRMs), NBL CRM 131 [12], IRMM-042a [13] and IRMM-042 [14], were lacking adequate purity for ^{244}Pu (isotopic abundance < 98%). The impurity of other Pu isotopes in the available CRMs additionally hindered its use for environmental swipe sample analysis. For example, the isotopic abundance of ^{242}Pu was larger than 1.3% in those CRMs.

Due to its higher purity, ^{242}Pu was commonly used as spike material (e.g. IRMM-085 [15]; isotopic abundance of ^{242}Pu > 99.9%) for Pu IDMS measurements. But since ^{242}Pu is produced in small quantities in nuclear reactors it may be present in field swipe samples, making reliable quantification challenging, especially in case of low total Pu amounts.

To overcome these limitations, the IAEA initiated a project in 1991 to produce a ^{244}Pu spike reference material with isotopic purity better than 99.99% [8, 10, 11, 16]. This was the beginning of an almost three-decade-long project involving international collaborations and negotiations. The US Department of Energy (DOE) agreed to provide a test portion of 0.5 g of the Pu source material 'FP-33' (~ 17% ^{244}Pu) to the IAEA for transferring it to the Russian Institute of Experimental Physics (VNIIEF). VNIIEF performed two rounds of electromagnetic separation to increase the isotopic purity of the source material – one in October 2012 and one in February 2014. The second separation round yielded 880 μg of highly-enriched ^{244}Pu with a purity of 99.983 ± 0.001 at% ^{244}Pu. The values reported by VNIEFF were confirmed by the US

DOE Lawrence Livermore National Laboratory (LLNL) in January 2015. The final purity was slightly below the target value of 99.99% [10]. The final product as well as other materials derived from the source material were delivered to LLNL in May 2015 to produce the ^{244}Pu spike CRM for ES analysis. The ^{244}Pu spike was characterized for its isotopic composition and Pu isotope amounts by LLNL, US DOE Los Alamos National Laboratory (LANL) and Commissariat à l'énergie atomique (CEA) in France [11]. The spike was prepared in collaboration with the US National Institute of Standards and Technology (NIST), and distributed to the IAEA Network of Analytical Laboratories (NWAL), marking an important milestone for ES Pu analysis.

Besides the choice of the spike reference material, the accuracy of IDMS measurements is determined by the measurement method. In recent years, the field of low-level U and Pu isotope ratio measurements has increasingly been dominated by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), primarily because of its higher sensitivity, especially for U, compared to thermal ionization mass spectrometry (TIMS) [17], and the possibility of performing automated measurements of small amounts of analyte. The configuration of detectors in the MC-ICP-MS collector block in the instrument in use by the IAEA, however, did not allow for the measurement of all Pu isotopes simultaneously with the ^{242}Pu spike in each measurement line. This meant that sequential measurements had to be normalized to the ^{242}Pu measurement, increasing the uncertainty as temporal fluctuations within the instrument were not cancelled out. With the new ^{244}Pu spike, the collector block could be modified to detect the ^{244}Pu spike in each measurement line, allowing the direct normalization to all Pu isotopes thereby reducing the uncertainty. The modified collector block necessitated a number of changes to the instrument set-up (e.g. zoom optics, center cup masses, measurement method files, measurement sequence) as well as in the data evaluation, uncertainty quantifications, interference corrections and use of certified reference materials (CRMs) for quality control.

This paper demonstrates the current performance of Pu assay and isotope ratio measurements in IAEA Safeguards environmental swipe samples using the ^{244}Pu spike for IDMS measurements and a modified MC-ICP-MS collector block arrangement. The newly-available ^{244}Pu spike has been in use at the IAEA's Environmental Sample Laboratory (ESL) for routine analysis since 2019. Here we show that the use of the ^{244}Pu spike has led to an improvement in measurement precision and accuracy of results for both Pu assay and isotope ratios as well as in improvements in detection limits and timeliness. Moreover, the paper will provide detailed insights into the experimental set-up.

Experimental

Materials

Reagents, certified reference materials and consumables

All materials and consumables that were used for chemical sample preparation of environmental swipe samples and for mass spectrometric measurements are listed as follows:

- Purified water (> 18 MΩ cm, Milli-Q® Advantage A10 Water Purification Systems, Merck Millipore, Darmstadt, Germany) for preparing acid dilutions, blanks and rinse solutions by diluting concentrated high-purity acids to the required concentrations [18];
- Concentrated high-purity nitric acid (69% (w/w) HNO_3), hydrofluoric acid (49% (w/w) HF), hydrochloric acid (35% (w/w) HCl), hydrogen peroxide (32% (w/w) H_2O_2) and hydrobromic acid (48% (w/w) HBr) (Baseline®, Seastar™, British Columbia, Canada) are used – either diluted or undiluted (i.e. HBr) – for sample digestion, U–Pu separation and Pu aliquot purification, and for diluting sample aliquots for ICP-MS measurements;
- Highly-enriched ^{244}Pu reference material [11, 19] ($n(^{244}$Pu)/n(Pu) greater than 0.99) with certified Pu amount and isotopic composition for plutonium isotope dilution measurements (IRMM-085 [15] was used for spiking (archive) samples with ^{242}Pu for comparison measurements);
- Uranium isotopic certified reference materials CRM 112-A [20] and IRMM-2025 [21] are used for the determination of MC-ICP-MS correction factors for mass bias, ion counter yield, peak tailing and hydride ions;
- Pu certified reference materials CRM 144 [22], IRMM-042a [13] and IRMM-047a [23] are measured as quality control standards for ^{239}Pu/^{244}Pu, ^{240}Pu/^{244}Pu, ^{241}Pu/^{244}Pu and ^{242}Pu/^{244}Pu isotope ratios, while CRM 137 [24], CRM 126-A [25], CRM 122 [26] and IRMM 047a [23] are used as quality control standards for ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, ^{242}Pu/^{239}Pu, and ^{244}Pu/^{239}Pu isotope ratios (the latter only in IRMM-047a [23]);
- Uranium ICP standard traceable to SRM from NIST $UO_2(NO_3)_2$ in HNO_3 2–3% 10 mg/l U Certipur® (Supelco®, Merck KGaA, Darmstadt, Germany) that is diluted to 1 ng g^{-1} is measured for daily MC-ICP-MS performance check and assessment of sensitivity;
- Lead ICP standard traceable to SRM from NIST $Pb(NO_3)_2$ in HNO_3 2–3% 1000 mg/l Pb Certipur® (Supelco®, Merck KGaA, Darmstadt, Germany) is measured for Pb interference correction;

- Element 2 Tune Solution (Thermo Fisher Scientific Inc., MA, USA) that is diluted to 10 pg g^{-1} is used for tuning and calibration of a single collector ICP-MS as well as for interference correction;
- AG® MP-1 M ion exchange resin (analytical grade, 50–100 mesh, chloride form, BioRad Laboratories Inc., CA, USA) and UTEVA extraction chromatographic resin (particle size: 100–150 μm, Triskem—International, Bruz, France) for U–Pu separation; and
- PTFE filter membrane (pore size: 0.2 μm, Nalgene™, Thermo Fisher Scientific Inc., MA, USA) for filtering samples after wet digestion and before preparing the master solutions for each sample.

^{244}Pu spike preparation and amount verification

Unit X34 of the highly-enriched ^{244}Pu spike [11] was used for spiking samples for IDMS measurements. The ^{244}Pu spike was immobilized within a viscous film of dried phosphoric acid. In order to transfer the spike into a solution, 30 mL of 8 M HNO_3 were added gravimetrically to the 30 mL FEP Teflon bottle, which was the primary container of the spike, and left for two weeks. Then the solution (3.2 ng g^{-1}) was transferred into a new bottle, and further diluted with 3 M HNO_3 to a ^{244}Pu concentration of ca. 11 pg g^{-1} for spiking the samples. In addition, an aliquot of the 3.2 ng g^{-1} ^{244}Pu solution was spiked with IRMM-085 [15] for the verification of its ^{244}Pu amount by reverse IDMS measurements.

Samples and sample preparation

Environmental samples that are collected by IAEA inspectors typically comprise swipe samples, in which traces of nuclear material in particulate form are embedded in ambient dust in the environment of the facility being inspected. The most commonly used sampling medium is the 10 × 10 cm cotton cloth (Texwipe, Kernersville, North Carolina, USA) for wiping surfaces. Swipe samples were prepared according to the standard sample preparation procedure routinely used at the IAEA ESL and described in detail elsewhere [18, 27]. The samples were spiked with both a ^{244}Pu spike [11] and a ^{242}Pu spike [15] (IRMM-085) in order to compare the analytical performance of the method using a ^{244}Pu spike with the routine ^{242}Pu measurement procedure. For this purpose, samples were split into two aliquots for the two respective Pu spikes. Additionally, previously-analysed sample aliquots were retrieved from the ES archive and spiked with ^{244}Pu for comparison. Process and swipe blanks as well as internal quality control samples were analysed along with the samples to monitor quality control. Purified Pu aliquots were diluted to ca. 0.25 pg mL^{-1} with a 2% (w/w) HNO_3/0.2% (w/w) HF aqueous solution to meet the method's validated working range. Typical aliquot sizes were 2.2 mL for duplicate analyses.

Table 1 Neptune Plus™ MC-ICP-MS collector block configuration and measured Pu and U isotopes. An additional CDD ion counter (CDD6) was added between Faraday cup L3 and ion counter CDD5

Collector block configuration								Sub-configuration
Line	Element	L3	CDD6	CDD5	L4	IC1B*	L5**/IC2	IC3A*	
Pu-1	Pu		$^{206}Pb^{40}Ar$	^{244}Pu		^{241}Pu	^{240}Pu (IC2)	^{239}Pu	*239Pu@IC3A*
Pu-2	Pu		^{244}Pu	^{242}Pu		^{239}Pu	^{238}U (L5)	^{237}Np	*239Pu@IC1B*
U-1	U			$^{238}U^1H$	^{238}U	^{236}U	^{235}U (L5)	^{234}U	*U Main*
U-2	U			$^{238}U^1H$	^{238}U	^{236}U	^{235}U (IC2)	^{234}U	*U Main*
U-3	U	^{238}U	^{236}U	^{234}U					*238U@L3*

Line Pu-1 and Pu-2 are used for Pu sample analysis, and Line U-1 to U-3 are used for the "yield and mass bias measurement method"

*IC1B and IC3 ion counters are equipped with RPQ (Retarding Potential Quadrupole Lens) energy filters

**L5 was connected to a 10^{12} Ω amplifier

Instrumentation

Plutonium isotope ratio measurements were performed using a Neptune Plus™ multi-collector (MC)-ICP-MS (Thermo Scientific, Bremen, Germany) in the Clean Laboratory of the IAEA ESL in Seibersdorf, Austria. Samples were introduced into the mass spectrometer using an Aridus II™ desolvating nebulizer system and a PFA-100 C-flow nebulizer (both Cetac Technologies Inc., Omaha, NE, USA). Measurement sequences were automated using a SC-2 DX autosampler (Elemental Scientific Inc., Omaha, NE, USA).

The MC-ICP-MS instrument comprises a specially designed multi-ion-counting collector array for actinide measurements ("L5 ion counter package") and a Jet Interface, consisting of a high capacity interface pump and special cones for enhanced sensitivity. Because of the very low count rates, Pu isotope measurements require the use of ion counters for measuring all isotopes of interest, i.e. $^{239}Pu^+$, $^{240}Pu^+$, $^{241}Pu^+$, $^{242}Pu^+$, and $^{244}Pu^+$. In addition, the $^{238}U^+$ ion intensity must be also recorded in order to control the interference that is produced by $^{238}U^1H^+$ ions on m/z = 239. Because natural U can be present even in the purified Pu fractions at concentration levels that are significant with account to the high sensitivity of the MC-ICP-MS, the $^{238}U^+$ isotope must be recorded with a Faraday cup as ion counters might be saturated by the high $^{238}U^+$ ion intensity.

The original configuration of the "L5 ion counter package", which is described in detail elsewhere [18, 28, 29] and which was used in the past for Pu assay and isotopic composition measurements when using a ^{242}Pu spike [18], does not allow the measurement of all Pu isotopes of interest with ion counters, i.e. ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu, simultaneously with ^{244}Pu. A direct normalization to ^{244}Pu was only possible for ^{239}Pu, ^{240}Pu, ^{241}Pu, but not for ^{242}Pu, where ^{242}Pu was measured in a different measurement line than ^{244}Pu. The use of the original configuration would have introduced larger measurement uncertainties and inaccuracies due to

sequential peak-jumping measurements for normalizing ^{242}Pu and ^{244}Pu.

In order to overcome this limitation, the collector block was modified by adding a third compact discrete dynode [30] (CDD) ion counter (IC), i.e. CDD6, between the Faraday cup L3 and CDD5 (Table 1). This configuration change allows the simultaneous measurement of ^{239}Pu, ^{242}Pu, and ^{244}Pu in one measurement line, and of ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{244}Pu in another measurement line, which is important for accurate IDMS measurements, where the Pu isotopes are normalized to the ^{244}Pu spike isotope. The accuracy of IDMS measurements is further improved by online monitoring of $^{206}Pb^{40}Ar^+$ ions with CDD6 on m/z = 246, which allows the direct assessment of the contribution of PbAr$^+$ ions (originating from Pb in the sample and Ar from the plasma gas) on m/z = 244 and m/z = 242, and the direct calculation of respective interference correction factors assuming a natural isotopic composition of Pb.

Advantages that remained from the original configuration [18] are: (1) online monitoring of $^{238}U^+$ ions with the L5 Faraday cup for correcting the $^{238}U^1H^+$ interference on m/z = 239, (2) measurement of $^{239}Pu^+$ in both measurement lines, minimizing uncertainties in case of Pu isotope ratios, where the minor Pu isotopes are typically normalized to ^{239}Pu, and (3) measurement of $^{239}Pu^+$ with secondary electron multipliers (SEM IC1B and IC3A) that are equipped with Retarding Potential Quadrupole (RPQ) Lenses for improving ^{239}Pu abundance sensitivity.

Measurement procedure

Screening of purified Pu aliquots prior to MC-ICP-MS measurements

Sample aliquots as well as Pu CRMs were screened for their impurity content (from Li to Am) using a single-collector sector-field ICP-MS (Element 2™, Thermo Scientific, Bremen, Germany) prior to MC-ICP-MS measurements.

Pre-screening measurements after the last sample purification step confirmed adequately low levels of impurity elements including Na, Mg, Zr, Mo, Ba, Pb, W, Pt, Th, U, and rare earth elements (REE) that can potentially cause interferences on the measured Pu isotope masses of interest, during isotope ratio measurements. If impurity concentrations in the Pu fraction exceed specified limits (for instance, 2 ng g^{-1} for Pb and 10 ng g^{-1} for W) the fraction is repurified prior to analysis. In addition, screening measurements verify that Pu concentrations are within the validated working range of 0.2 to 0.3 pg mL^{-1} for the subsequent MC-ICP-MS measurements. For screening, diluted sample aliquots were measured at ultra-low concentration levels (0.01 pg mL^{-1} Pu) to avoid contaminating the high-efficiency sample introduction system (APEX HF, Elemental Scientific Inc., Omaha, NE, USA) with elevated levels of Pu and impurity elements, and to reduce memory effects on subsequent analyses.

MC-ICP-MS isotope ratio measurements and calibration

Prior to each measurement sequence, the MC-ICP-MS was optimized for highest sensitivity and signal stability. The sensitivity, defined as counts detected per introduced atom, was typically in the range of 1.5% to 2.5% for U and Pu isotopes, which are similar due to the relatively close ionization rates of these elements in the plasma, i.e. 6.19 eV for U, and 6.02 eV for Pu [31]. This level of sensitivity guaranteed that samples were analysed within the validated working range, which is necessary for achieving the required accuracy and detection limits. Signal stability was assessed by measuring the intensity of the $^{238}U^+$ signal from a 1 ng g^{-1} U concentration standard, and was typically below 1% RSD (integration time: 16.8 s, number of cycles/block: 9, number of blocks: 1).

Mass calibration – peak centering – was performed on m/z = 239 with ion counters IC1B and IC3A for Pu measurements, and on m/z = 238 with Faraday cups L4, L3, L5 and the centre cup for U measurements. Peak shapes were visually assessed for peak alignment and a flat top shape, which is a pre-condition at low mass resolution (m/Δm = 300) for monitoring the peak at its centre point.

Pu isotope ratios in samples and QC standards were measured in a multi-collection mode with the *239Pu@IC3A* (line Pu-1) and *239Pu@IC1B* (line Pu-2) sub-configurations described in Table 1. A typical measurement sequence (Table S1, Supplementary information) comprised the analysis of four samples, one process blank, and one swipe blank and one internal quality control (QC) swipe as well as the measurement of three QC standard solutions, which were primarily IRMM-047a [23], CRM 144 [22] and CRM 137a [24].

The same sub-configurations and measurement method (integration time: 16.8 s, idle time: 4 s, cycles/block: 9,

number of blocks: 1) were used for measuring a pure Pb elemental standard solution (1 ng g^{-1}) and CRM 112-A [20] (1 ng g^{-1}) for determining respective correction factors. Both solutions were measured three times within the measurement sequence. A low-enriched uranium isotope ratio CRM (IRMM-2025 [21], 0.2 ng g^{-1}) was used for the determination of yield and mass bias correction factor ß, using sub-configurations *U Main* (line U-1 and U-2) and *238U@L3* (line U-3) in Table 1. Yields of IC1B and IC3A as well as the mass bias correction factor ß were determined in line U-1, the yield of IC2 was determined in line U-1 and U-2, and the yields of CDD5 and CDD6 were determined in line U-3. The aspiration of U CRM solutions between Pu-containing samples had the positive effect of reducing Pu memory effects in the sample introduction system. Blank solutions (2% HNO_3/0.2% HF) were measured before each standard and sample solution to correct all measured isotope intensities for their instrument blank.

The applied mass bias correction was based on the assumption that U and Pu behave similar with respect to their mass fractionation factor. Similar assumptions were also made during the initial characterization measurements of Pu CRMs 136, 137, and 138 by the National Bureau of Standards [32], or by Taylor et al. [33], who used a ^{236}U-^{233}U double spike to correct for mass bias effects for Pu isotope ratio measurements. The authors are aware that this assumption is only an approximation as it was demonstrated that the fractionation factor is dependent on the element [34, 35]. Taylor et al.[33] reported that mass bias factors for U and Pu that were determined using equal atom standards were within 0.01% u^{-1}, equalling the maximum error for the $^{240}Pu/^{239}Pu$ ratio, and a 0.03% error for the $^{242}Pu/^{239}Pu$ ratio. For our measurements, such errors introduced by applying mass bias correction factors determined by a different element are not significant when compared to other uncertainty components, and are covered by the expanded measurement uncertainties. The measurement results are controlled by analysing Pu reference materials together with each set of field samples and plotted in respective QC charts, which confirm that the bias introduced by the applied mass bias correction is not significant. Pu ratios for the reference materials corrected by U derived mass fractionation factors were, as well as U ratios, consistently accurate and within our uncertainty limits.

Data processing

Correction of Pu isotope ratios and Pu amount calculation

Pu isotope ratios—$^{240, 241, 242, 244}Pu/^{239}Pu$ (for isotopic composition analysis where the Pu isotopes are normalized to the most abundant isotope ^{239}Pu) and $^{239, 240, 241, 242}Pu/^{244}Pu$ (for isotope dilution analyses where the Pu isotopes are

normalized to the spike isotope)—were calculated from blank-corrected raw signal intensities. The isotope ratios were further corrected for: (1) PbAr$^+$ ions interfering on m/z = 244 and m/z = 242; (2) interference of ^{238}U^{1}H$^+$ ions on m/z = 239; (3) ^{238}U$^+$ ions tailing into the Pu isotopes of interest; (4) signal contribution from other Pu isotopes present in ^{244}Pu spike; (5) ion counter yield; and (6) mass bias using the exponential mass bias correction law.

The mass bias correction factor ß was calculated from the ^{235}U/^{238}U isotope ratio (measured with two Faraday cups) using the exponential law. The U CRM IRMM-2025 was measured in a standard-sample bracketing scheme throughout the measurement sequence. The IC2 yield was calculated as the ratio of ^{235}U/^{238}U measured in IRMM-2025 in line U-1 (^{235}U on L5 Faraday cup) and line U-2 (^{235}U on IC2, see Table 1), whereas the yields of all other ion counters were calculated from the measured, mass bias-corrected, isotope ratios (^{234}U/^{238}U and ^{236}U/^{238}U) divided by their certified value.

Final Pu isotope ratios were calculated as mean ratios of the selected number of replicates after removing outliers.

Pu amounts for ^{239}Pu to ^{242}Pu were calculated according to Eq. (1).

$$m(^x\text{Pu}) = \left(\left(\frac{^x\text{Pu}}{^{244}\text{Pu}} \right)_{\text{blend}} - \left(\frac{^x\text{Pu}}{^{244}\text{Pu}} \right)_{\text{spike}} \right) \times m(^{244}\text{Pu, spike}) \times \frac{M(^x\text{Pu})}{M(^{244}\text{Pu, spike})} \times \frac{1}{f_{\text{Aliquot}}}$$

(1)

x = ^{239}Pu, ^{240}Pu, ^{241}Pu, or ^{242}Pu,

where $m(^x\text{Pu})$ is the amount of Pu isotope x in pg, $\left(\frac{^x\text{Pu}}{^{244}\text{Pu}}\right)_{\text{blend}}$ is the ^{x}Pu/^{244}Pu isotope ratio measured in the spiked sample aliquot, $\left(\frac{^x\text{Pu}}{^{244}\text{Pu}}\right)_{\text{spike}}$ is the certified ^{x}Pu/^{244}Pu isotope ratio, $m(^{244}\text{Pu, spike})$ is the amount of added ^{244}Pu spike in pg, $M(^x\text{Pu})$ and $M(^{244}\text{Pu, spike})$ are the atomic masses of the Pu isotope x, and ^{244}Pu, and f_{Aliquot} is the aliquot fraction.

The total Pu amount was calculated by summing up the amounts of all Pu isotopes.

The Report of Attribute Values [19] does not provide information regarding validity of reference values for opened units of the ^{244}Pu spike. Therefore, two spike aliquots were analysed in each sequence (see Table S1, supplementary information) and measured isotopic composition was plotted in respective QC charts. It was used to assess the stability of the working solutions during their routine use and the useful lifetime of opened items.

Interference correction strategies

High-quality chemical separation that effectively removes all interfering impurities is an important precondition for analysis. The purity of Pu fractions is controlled by screening prior to MC-ICP-MS measurements as described in Sect. "Screening of purified Pu aliquots prior to MC-ICP-MS measurements". If a Pu fraction cannot be re-purified due to complete sample consumption or due to any other reason, two different correction strategies are applied for samples containing elevated concentrations of concomitant elements (i.e., impurities).

Pb interference correction Typically, Pu fractions are sufficiently pure so that no interference correction is required at all. Nevertheless, as Pb is a ubiquitous element, which is present at low concentrations in reagents and glassware, the online assessment of the presence of PbAr$^+$ ions at m/z = 246 in the measured Pu fractions serves to detect accidental contamination of Pu fractions with Pb if such a contamination occurs at the final stage of sample preparation or during MC-ICPMS analysis. Then an interference correction for PbAr$^+$ ions at ^{242}Pu and ^{244}Pu masses can be applied when the analysis of the sample cannot be repeated otherwise.

A Pb single-element standard solution (1 ng g^{-1}) is routinely measured within the same measurement sequence as the unknown samples and QC samples using the same sub-configurations (Table 1, line Pu-1 and Pu-2). This allows calculating the ^{244}(PbAr)/^{246}(PbAr) and ^{242}(PbAr)/^{246}(PbAr) ratios measured in the Pb solution. These ^{242}(PbAr)/^{246}(PbAr) and ^{244}(PbAr)/^{246}(PbAr) interference correction factors are then multiplied with the counts that were measured on m/z = 246 in the sample. The resulting counts can be directly subtracted from the ^{242}Pu and ^{244}Pu isotopes that are interfered by PbAr$^+$ ions with the respective nominal masses.

General interference correction The general correction strategy is applied for interferences that cannot be directly monitored. Here, an impurity element X is added to a pure ^{244}Pu spike solution, which allows the determination of the count rate that is caused by the interference at the mass of the interfered Pu isotopes (e.g. ^{240}Pu). This spiked solution is analysed by MC-ICP-MS under the same measurement conditions as the samples and the pure ^{244}Pu spike solution. The count rate (i.e. counts from interference

X + counts of Pu isotope) that is measured in a ^{244}Pu spike solution is then normalized to the ^{244}Pu count rate. In addition, the same solution is measured with a single collector ICP-MS to determine the intensity ratio of the impurity isotope X to ^{244}Pu. The correction factor $K_{interference}$ is calculated according to Eq. (2).

$$K_{\text{interference}} = \frac{R_{\text{spiked,MC-ICP-MS}} - R_{\text{pure, MC-ICP-MS}}}{R_{\text{spiked},X,\text{ICP-MS}}} \quad (2)$$

where $R_{\text{spiked,MC-ICP-MS}}$ is the ion intensity ratio of (counts produced from interference X at m/z of Pu isotope of interest (e.g. m/z = 240) + counts of Pu isotope of interest at its m/z (e.g. ^{240}Pu))/(^{244}Pu counts) that is measured in a ^{244}Pu solution that was spiked with an impurity isotope X by MC-ICP-MS; $R_{\text{pure,MC-ICP-MS}}$ is the ion intensity ratio of (interfered Pu isotope (e.g. ^{240}Pu) counts)/(^{244}Pu counts) that is measured in a pure ^{244}Pu spike solution by MC-ICP-MS; $R_{\text{spiked},X,\text{ICP-MS}}$ is the ion intensity ratio of (counts of impurity isotope X)/(^{244}Pu counts) that is measured in a ^{244}Pu solution that was spiked with an impurity isotope X by single collector ICP-MS during pre-screening.

The Pu isotope ratio (e.g. ^{240}Pu/^{244}Pu) measured in the sample with MC-ICP-MS is then corrected as following (Eq. 3):

$$R_{sample,\text{int.corr.}} = R_{\text{sample,MC-ICP-MS,measured}} - \left(R_{\text{sample},X,\text{ICP-MS}} \times K_{\text{interference}} \right) \quad (3)$$

where $R_{\text{sample,int.corr.}}$ is the interference-corrected Pu isotope ratio (e.g. ^{240}Pu/^{244}Pu) of the sample; $R_{\text{sample,MC-ICP-MS,measured}}$ is the Pu isotope ratio (e.g. ^{240}Pu/^{244}Pu) measured in the sample by MC-ICP-MS; $R_{\text{sample},X,\text{ICP-MS}}$ is the ion intensity ratio of (counts of impurity isotope X)/(^{244}Pu) in the sample solution measured by ICP-MS during pre-screening; and $K_{\text{interference}}$ is the interference correction factor.

It was not necessary to implement these correction strategies because the concentrations of interfering elements were too low to produce any significant interferences on Pu isotopes, but they are nevertheless described here for providing the reader with a full overview of the established measurement method.

Uncertainty quantification

Expanded ($k = 2$) measurement uncertainties U were computed using an R [36] script following ISO/GUM [37] and Eurachem [38] guidelines. Sources of uncertainty that were included for Pu isotope ratio and amount measurements are given in Table 2.

Results and discussion

Prerequisites for accurate isotope ratio measurements—control of polyatomic interferences

The most critical elements that were identified to be causing significant interferences for Pu assay and isotope ratio measurements are Pb, W and U. Those elements can be present at problematically high concentrations even after chemical purification. Other elements that can lead to the formation of polyatomic interferences are Hg and Th, however, the concentrations of these elements in purified Pu aliquots is typically relatively low. Hg can also be present as a contamination in Ar plasma gas, producing ^{200}Hg^{40}Ar$^+$ and ^{202}Hg^{40}Ar$^+$ ions, which interfere with ^{240}Pu$^+$ and ^{242}Pu$^+$, respectively. The presence of HgAr$^+$ ions is monitored by blank measurements, which would show elevated blank levels on the isotope m/z ratios of interest in case of their presence.

Generally, if an element is present at an unusually high concentration (i.e. concentration that has not been observed before in purified sample aliquots and for which the effect is not known), another chemical purification step is performed to reduce its concentration, and thus the risk of introducing interferences for Pu isotope ratio measurements. However, if an additional purification step is not feasible due to time constraints, the presence of interferences is assessed by spiking pure ^{244}Pu solutions with exactly known concentrations of this particular element, typically using a single element standard for ICP-MS measurements. Analysis of a series of ^{244}Pu solutions that were spiked with different concentrations of a concomitant element helps to assess the concentration that is needed to produce detectable interferences. In general, the endpoint of such an analysis series in terms of the added concentration is the concentration that is observed in the purified aliquot. The interference contribution can be mathematically corrected by applying the general interference correction strategy described in the data processing section of this paper. For example, the most prominent interference candidate for applying this correction route in case of Pu isotope ratio measurements is W.

A thorough study of W and U polyatomic interferences (e.g. ^{186}W^{40}Ar^{14}N$^+$ on m/z = 240, ^{238}U^{1}H$^+$ on m/z = 239) on Pu isotope ratio measurements is described in detail in Eppich et al. [18]. Therefore, further discussions will solely focus on Pb interferences, which need to be carefully addressed when using a ^{244}Pu spike for IDMS measurements. As depicted in Fig. 1, PbAr$^+$ ion interferences are most pronounced for m/z = 244, 246, 247, and 248, the peaks of which (^{204}Pb^{40}Ar$^+$, ^{206}Pb^{40}Ar$^+$, ^{207}Pb^{40}Ar$^+$, ^{208}Pb^{40}Ar$^+$) reflect the isotopic abundance pattern of Pb. It is evident

Table 2 Sources of uncertainty for Pu isotope ratio and Pu assay measurements

Line	Sources of uncertainty	Uncertainty components
1	Pu isotope ratio measured in sample	Standard deviation of the mean of the measured isotope ratio (internal precision)
2	External reproducibility	Pooled estimate of the standard deviation of the measured isotope ratio. Standard deviations are obtained from the QC chart of respective CRM measurements*
3	Ion counter yields	Standard uncertainty of the yield correction factors
4	Non-linearity of ion counters	Standard uncertainty of the non-linearity correction factor
5	Blanks of Pu isotopes measured before samples	Standard uncertainty of the Pu isotope intensities measured in blank solutions before each sample
6	$^{238}U^+$ tail and $^{238}U^1H^+$ correction	Standard uncertainty of the tail and uranium hydride interference correction factor (3 individual measurements within the same measurement sequence)
7	Pu isotope ratio measured in the ^{244}Pu spike	Standard uncertainty of the measured isotope ratio in the ^{244}Pu spike
8	Blanks of Pu isotopes measured before spike	Standard uncertainty of the isotope intensities measured in blank before the ^{244}Pu spike
9	Mass of ^{244}Pu spike	Standard deviation of the ^{244}Pu mass that is added to sample
10	Mass of the sample aliquot	Standard deviation of the mass of the sample aliquot
11	Uncertainty associated with complete analytical procedure including sample preparation of swipes containing detectable Pu amounts	Pooled estimate of the standard deviation of the measured isotope ratio or amount. Standard deviations are obtained from the QC chart of internal QC swipes**
12	Uncertainty associated with preparation of swipe blanks, reflecting an uncertainty component at low Pu amounts	Pooled estimate of the standard deviation of the measured isotope ratio or amount of Pu isotope (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu), measured in swipe blanks**

Line 1–6: sources of uncertainty for Pu isotope ratio measurements;

Line 1, 3–10: Sources of uncertainty for Pu assay measurements

*Typically used CRMs: CRM137 [24] for isotope ratios $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$ (Pu isotope ratio measurements); IRMM047a [23] for isotope ratios $^{239}Pu/^{244}Pu$, and CRM144 [22] for $^{240}Pu/^{244}Pu$, $^{241}Pu/^{244}Pu$ and $^{242}Pu/^{244}Pu$ (Pu assay measurements)

**Uncertainties associated with sample preparation were excluded for QC standards (i.e. CRM137 [24], IRMM047a [23], and CRM144 [22]) that did not undergo chemical preparation as required for swipe samples (i.e. digestion, filtering, separation, and purification)

that Pb-containing samples need to be corrected for the contribution of $^{204}Pb^{40}Ar^+$ interference to $^{244}Pu^+$ counts so as to not introduce biases into the Pu amount results. Pb is a ubiquitous element, which is often present in swipe samples at critical concentrations levels of ca. 1 ng g^{-1}, even after sample purification.

The interference formation rate is highly dependent on the applied experimental conditions (Fig. 2), which was assessed by measuring a U solution (0.2. ng g^{-1}) that was spiked with 1 ng g^{-1} Pb single-element ICP-MS standard. $^{206}Pb^{40}Ar^+$ and $^{238}U^+$ ion signals were measured by applying the same measurement method that is used for Pu sample analysis, where $^{206}Pb^{40}Ar^+$ and $^{238}U^+$ are measured sequentially in line Pu-1 and line Pu-2 (Table 1), respectively. The interference rates varied significantly within the investigated gas flow rate ranges, whereupon the largest change was observed for changes in the sweep gas flow rate. The observed dependency of the interference formation on the gas flows, which need to be optimized daily, demonstrates the difficulty to control interference formation rates during routine optimization of the MC-ICP-MS. The optimization

of gas flows results in an uncontrolled change of interference rates and introduces a day-to-day variability of the corresponding correction factors. For example, variations (in terms of RSD) of Pb interference correction factors that were measured within 29 individual measurement sequences was 26% for $^{244}Pu/^{246}(PbAr)$.

This high dependency of correction factors on experimental conditions demonstrates very well that an accurate interference correction requires the recording of interferences directly in the sample, exactly under the same measurement conditions as the isotopes of interest. The modified collector block arrangement (Table 1) allows the direct online monitoring of $^{206}Pb^{40}Ar^+$ ions with CDD6 on m/z = 246 during sample analysis, which was not feasible before modifying the collector block arrangement. Since the installation of an additional CDD detector allows the direct assessment of the presence of PbAr$^+$ ions in the sample, interference correction factors (i.e. $^{242}Pu/^{246}(PbAr)$ and $^{244}Pu/^{246}(PbAr)$) can be directly calculated and applied on m/z = 244 and m/z = 242,
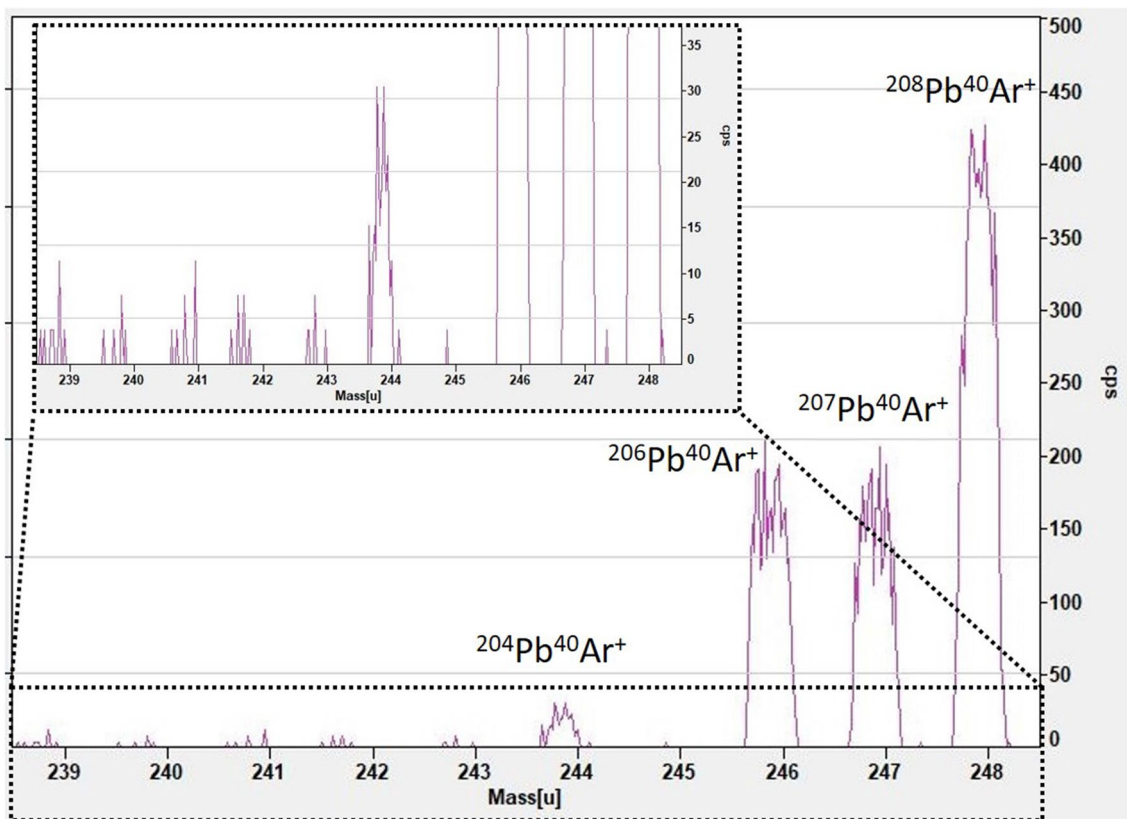
Fig. 1 Mass spectrum of a 1 ng g^{-1} Pb solution that was recorded on IC1C with the Neptune Plus™ in the mass range from m/z = 239 to 248
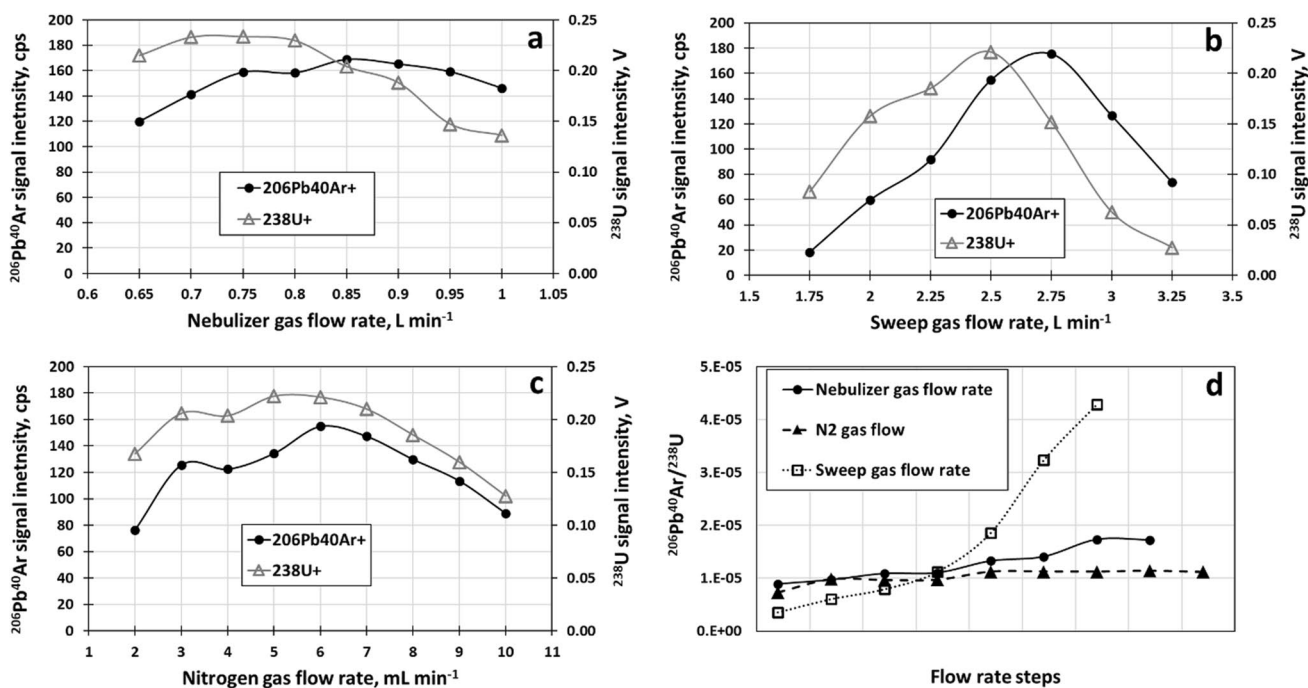

Fig. 2 Variability of ^{206}Pb^{40}Ar and ^{238}U signal intensities as function of **a** nebulizer gas flow, **b** sweep gas flow, and **c** nitrogen gas flow. **d** depicts the influence of changing gas flow rates on the ^{206}Pb^{40}Ar/^{238}U ratio. Measurements were performed with a U (0.2 ng g^{-1}) solution spiked with Pb (1 ng g.$^{-1}$)

which is one of the big advantages of the method presented here.

Analytical performance of Pu isotope ratio and amount measurements

Six archived field swipe samples (S1 to S6) with Pu amounts ranging from 88 fg to 397 pg were analysed and compared after splitting each sample into two fractions for spiking with both a 242Pu and a 244Pu spike. This allowed a direct comparison of the new "244Pu method" with the validated "242Pu method".[1] Applying the "242Pu method" for sample S2 resulted in slightly biased Pu isotope amount due to the non-detection of 242Pu when using a 242Pu spike, and is discussed separately below.

Figure 3 shows the relative differences between the two methods for the Pu isotope amounts (239Pu, 240Pu, 241Pu and 242Pu) along with their expanded uncertainties ($k = 2$) of the "244Pu method", and the uncertainty limits (the square root of the sum squares of the expanded ($k = 2$) uncertainties of both measurement methods). The same comparison is depicted in Fig. 4 for the measured Pu isotope ratios, and the data for both figures are summarized in the supplementary information (Table S2 and Table S3).

The individual Pu isotope amounts and isotope ratios determined with both methods were consistent with one another within their uncertainty limits. In most cases, the uncertainty limits were larger than the associated expanded uncertainties obtained with the "244Pu method", and in some cases by as much as a factor of 4 (e.g. 239Pu and total Pu in sample S3), indicating that the measurement uncertainties were improved using the new "244Pu method".

Compared to the "242Pu method", relative differences of 0.3% were observed for the total Pu amounts for samples containing less than 2 pg Pu (Table S2). Samples containing 13 pg and 396 pg Pu showed larger relative differences of 1.0% and 2.4%, respectively. Relative expanded uncertainties ($k = 2$) were typically lower than 2.5% for Pu isotope

amounts (239Pu, 240Pu, 241Pu) larger than 0.02 pg. As would be expected, larger relative expanded uncertainties ($k = 2$) were obtained for lower Pu amounts in the swipe, e.g. up to 17.1% for a 242Pu amount of 0.008 pg.

The swipe samples were analysed twice in two independent measurement runs and all duplicate Pu amount measurements were within corresponding expanded uncertainties ($k = 2$).

The main uncertainty contributions for the 239Pu and 240Pu amount measurements (Table 3) in samples containing Pu amounts in the tens to hundreds of pg (samples S1 and S3) were typically resulting from the uncertainty in the mass of the added 244Pu spike (ca. 80% for 239Pu, and 64% for 240Pu for sample S1), and from the uncertainty component that is associated with the complete analytical procedure (ca. 10% for 239Pu, and ca. 25% for 240Pu). Other, minor uncertainty contributions stem from the uncertainties of the measured isotope ratios and the ion counter yields.

For sample S1 the uncertainty contributions from the measured 239Pu/244Pu and 240Pu/244Pu isotope ratios were as small as 0.9% and 2.6%, respectively. Overall, the contributions of the uncertainties of the measured isotope ratios were comparatively small for the analyzed samples, not at least due to the direct normalization to the denominator isotope 244Pu. This is important for improving precision for isotope ratio measurements, and thus, for allowing to propagate small standard errors in the uncertainty model. Hence, other contributions such as the mass of the added 244Pu spike became more pronounced. As one would expect, in the case of field samples with low Pu amounts (e.g. sample S4; 0.09 pg total Pu), increasing contributions for the Pu minor isotopes were observed from the uncertainty component associated with preparation of swipe blanks (> 65% for 240Pu, 241Pu and 242Pu, and 11% for the 239Pu amount) reflecting increased uncertainty at low Pu amounts.

For higher 241Pu amount measurements in sample S1, the main contribution, in addition to the uncertainty of the added spike amount, was the uncertainty of the measured 241Pu/244Pu isotope ratio.

As for the Pu isotope ratios, typical relative expanded uncertainties ($k = 2$) of less than 1% were observed for ratios greater than 0.08. Larger relative uncertainties were observed for smaller ratios as also depicted in Fig. 4. The main contributions originate from the measured 240Pu/239Pu and 241Pu/239Pu isotope ratios (> 90% for samples containing low Pu amounts such as in sample S4), followed by the respective ion counter yields. Since the isotope ratios are by far the main contributor, a direct normalization of the Pu isotopes (240Pu, 241Pu, and 242Pu) to 239Pu is of particular importance to obtain highly precise Pu isotope ratio measurement results, and thus low uncertainties.

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[1] The "242Pu method" has been in use at the IAEA ESL since 2013, and differs from the method described by Eppich et al. [18] in 2019. The published method [18] represented an experimental study for the determination of Pu assay and isotope ratios in swipe samples when using a 242Pu spike. However, that method has not been fully implemented for routine Pu analysis.
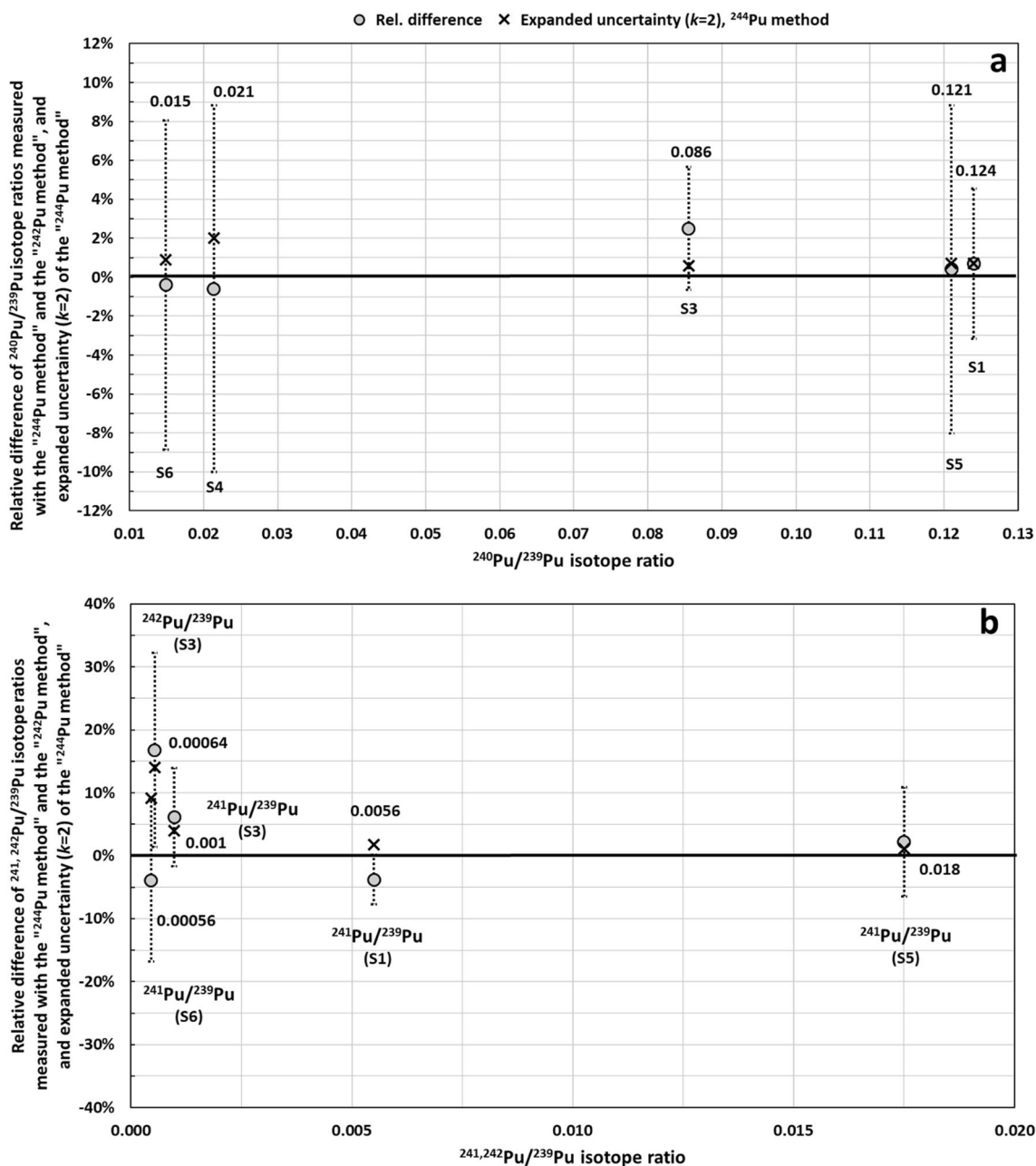
Fig. 4 Relative differences (grey circles) of $^{240}Pu/^{239}Pu$, $^{241}Pu/^{242}Pu$, and $^{242}Pu/^{239}Pu$ isotope ratios measured using both the "^{244}Pu method" and the "^{242}Pu method". $^{240}Pu/^{239}Pu$ isotope ratios are shown in (**a**), and $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ isotope ratios in (**b**). Error bars are the uncertainty limits calculated as square roots of the sum squares of the expanded uncertainties ($k=2$) of both methods. Expanded uncertainties ($k=2$) of the "^{244}Pu method" are shown as black crosses

Direct determination of ^{242}Pu in every sample and improvements in timeliness

An advantage of using the ^{244}Pu spike is that splitting samples into two Pu fractions for performing separate IDMS and isotope ratio measurements is not required. Sample splitting would only be required if the spike isotope could potentially be present in the field sample as is more likely for ^{242}Pu than

for ^{244}Pu, which is not produced in significant quantities in the nuclear fuel cycle. However, a pre-requisite for sample splitting was that the field sample contained high enough Pu amounts in order to ensure reliable mass spectrometric measurements in both fractions; to not only detect minute Pu amounts but to also accurately quantify them. The decision to split the sample depended on pre-screening analyses of a small aliquot (ca. 5%) of the un-spiked sample using

Table 3 Distribution of uncertainty contributions for Pu isotope amount and isotope ratio measurements based on the sources of uncertainty listed in Table 2. Sample S1 and S4 represent the samples containing the highest (S1: 396.8 pg) and the lowest (S4:0.088 pg) total Pu amounts in this study. Sources of uncertainty yielding contributions of less than 1.5% for all Pu isotope amounts or ratios are not shown. Main contributions are highlighted in bold

Sample ID	Pu isotope amount	^{x}Pu/^{244}Pu isotope ratio measured in sample (Line 1*), %	Ion counter yield for ^{x}Pu (Line 3*), %	Ion counter yield for ^{244}Pu (Line 3*), %	Mass of added ^{244}Pu spike (Line 9*), %	Mass of the sample aliquot (Line 10*), %	Uncertainty associated with preparation of swipe blanks, reflecting an uncertainty component at low Pu amounts (Line 11*), %	Uncertainty associated with complete analytical procedure including sample preparation of swipes containing detectable Pu amounts (Line 12*), %
S1	^{239}Pu	0.9	2.9	2.0	**79.9**	4.5	0.0	9.5
S4	^{239}Pu	5.7	2.4	2.3	**71.4**	0.0	10.8	7.1
S1	^{240}Pu	2.6	3.9	1.6	**63.9**	3.6	0.0	24.2
S4	^{240}Pu	16.2	0.1	0.2	5.7	0.0	**75.3**	1.8
S1	^{241}Pu	**46.1**	1.4	1.2	**47.9**	2.7	0.4	0.0
S4	^{241}Pu	3.9	0.0	0.0	0.0	0.0	**95.4**	0.0
S1	^{242}Pu	1.3	30.7	0.2	6.7	0.4	0.0	**60.5**
S4	^{242}Pu	27.1	2.4	0.0	0.0	0.0	**67.5**	0.4

Sample ID	Pu isotope ratio	^{y}Pu/^{239}Pu isotope ratio measured in sample (Line 1*), %	External reproducibility (Line 2*), %	Ion counter yield for ^{239}Pu (Line 3*), %	Ion counter yield for ^{y}Pu (Line 3*), %	^{y}Pu blank measured before sample (Line 5*), %
S1	^{240}Pu/^{239}Pu	**35.9**	3.9	21.9	**36.5**	0.0
S4	^{240}Pu/^{239}Pu	**96.5**	0.2	1.2	0.7	1.4
S1	^{241}Pu/^{239}Pu	**93.1**	0.1	3.6	2.9	0.0
S4	^{241}Pu/^{239}Pu	**90.3**	0.0	0.0	0.2	9.5
S1	^{242}Pu/^{239}Pu	**70.7**	0.4	14.2	12.0	1.2
S4	^{242}Pu/^{239}Pu	**98.4**	0.0	0.4	0.0	1.2

*The line numbers in brackets are cross-referenced to Table 2

$x = {}^{239}$Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu for Pu isotope amount measurements

$y = {}^{240}$Pu, ^{241}Pu, and ^{242}Pu for Pu isotope ratio measurements

Table 4 Pu isotope amount results obtained with the "^{244}Pu method" and the "^{242}Pu method" for two swipe samples (S1 and S2) both containing 3 pg ^{242}Pu

Sample ID	Pu amount per swipe		Relative difference to ^{242}Pu analysis	Relative expanded uncertainties, $k=2$		Uncertainty limit[1]
				^{244}Pu method	^{242}Pu method	
S1	Total Pu, pg	396.8	2.4%	2.1%	0.9%	2.3%
	^{239}Pu, pg	348.3	1.5%	2.0%	1.0%	2.2%
	^{240}Pu, pg	43.4	2.2%	2.2%	3.8%	4.4%
	^{241}Pu, pg	2.0	-2.4%	2.6%	3.5%	4.4%
	^{242}Pu, pg	3.2	[2]	6.9%	n/a	n/a
S2	Total Pu, pg	50.1	21.3%	2.3%	1.8%	2.9%
	^{239}Pu, pg	33.4	13.8%	2.0%	2.1%	2.9%
	^{240}Pu, pg	11.8	15.1%	2.2%	4.1%	4.7%
	^{241}Pu, pg	1.9	9.2%	2.0%	3.8%	4.3%
	^{242}Pu, pg	3.1	[2]	6.9%	n/a	n/a

[1]Uncertainty limit was derived from the square root of the sum of the squares of the expanded uncertainties ($k=2$)

[2]Not measured with ^{242}Pu method

a single-collector ICP-MS instrument. It should be noted that pre-screening measurements only provide indicative information about the Pu content. Accurate Pu amounts can only be obtained after chemical separation and IDMS measurements.

Analyzing only a spiked fraction bore the risk of neglecting any potential presence of ^{242}Pu, and thus, of introducing biases in the amount measurements, the degree to which depends on both the ^{242}Pu amount and the total Pu amount in the sample.

As an example, one archived sample (S2) that was previously analyzed with the "^{242}Pu method" was re-analyzed with the "^{244}Pu method". When the sample was initially analyzed, it was not split for its Pu isotopic analysis in an un-spiked fraction. However, the sample contained 3 pg of ^{242}Pu, accounting for 6% of the total amount of Pu (50.1 pg) resulting in significantly biased Pu amount values as demonstrated in Table 4. For all Pu isotope amounts, relative differences between the two methods were much larger than the uncertainty limits ranging from 9 to 15%, and up to 21% for the total Pu amount. By comparison, the ^{242}Pu amount of 3.2 pg was also not determined in sample S1, yet since this sample contained ca. 8 times more total Pu (396.8 pg), the contribution of ^{242}Pu to the total amount was only 0.8%, resulting in less biased results for the other Pu isotopes (-2.4% to 1.5%) and the total Pu amount (2.4%). While the Pu amounts measured with both methods agreed within their expanded uncertainties, the total Pu amount showed a slight bias (uncertainty limit: 2.3%) as it did not account for the 3.2 pg of ^{242}Pu missed when measuring with the "^{242}Pu method".

Using the new "^{244}Pu method", ^{242}Pu is directly determined in each sample, without the need for analyzing an un-spiked fraction. Therefore, biases caused by a wrong decision with respect to sample splitting are avoided, ultimately improving the accuracy of reported analysis results for samples containing ^{242}Pu. In addition, measurement accuracy is improved by directly normalizing ^{242}Pu to the ^{244}Pu spike isotope, in contrast to calculating the Pu amounts from abundances determined from two separate fractions measured in two separate measurement runs.

Relative expanded uncertainties (k = 2) of 7% were observed for samples S1 and S2 containing ^{242}Pu isotope amounts of ca. 3 pg (Table 4). Larger expanded uncertainties were obtained for samples containing smaller amounts (see Table S3 Supplementary information). For example, for sample S5 (6 fg ^{242}Pu) the main contribution to the uncertainty budget originated from the uncertainty component associated with the complete analytical procedure, followed by the uncertainties of the measured isotope ratio (Fig. 5a). The main contributor for the sample with lower ^{242}Pu amounts originated from the uncertainty component that is associated with the preparation of swipe blanks, reflecting an uncertainty component at low Pu amounts, followed by the uncertainties of the measured isotope (Fig. 5b, Table 3).

In case of ^{242}Pu/^{239}Pu isotope ratios, the uncertainties of the measured ^{242}Pu/^{239}Pu isotope ratios were the main contributor to the uncertainty budget for all samples, followed by the ion counter yields for IC5 and IC1B that were used for measuring this isotope ratio, and the ^{242}Pu blank. The significant contributions of the uncertainties of the measured ^{242}Pu/^{239}Pu and ^{242}Pu/^{244}Pu isotope ratios highlight again the importance of precisely measuring the ratios as well as an appropriate interference correction of PbAr$^+$ interferences occurring on m/z = 242 and 244 as discussed in detail above.

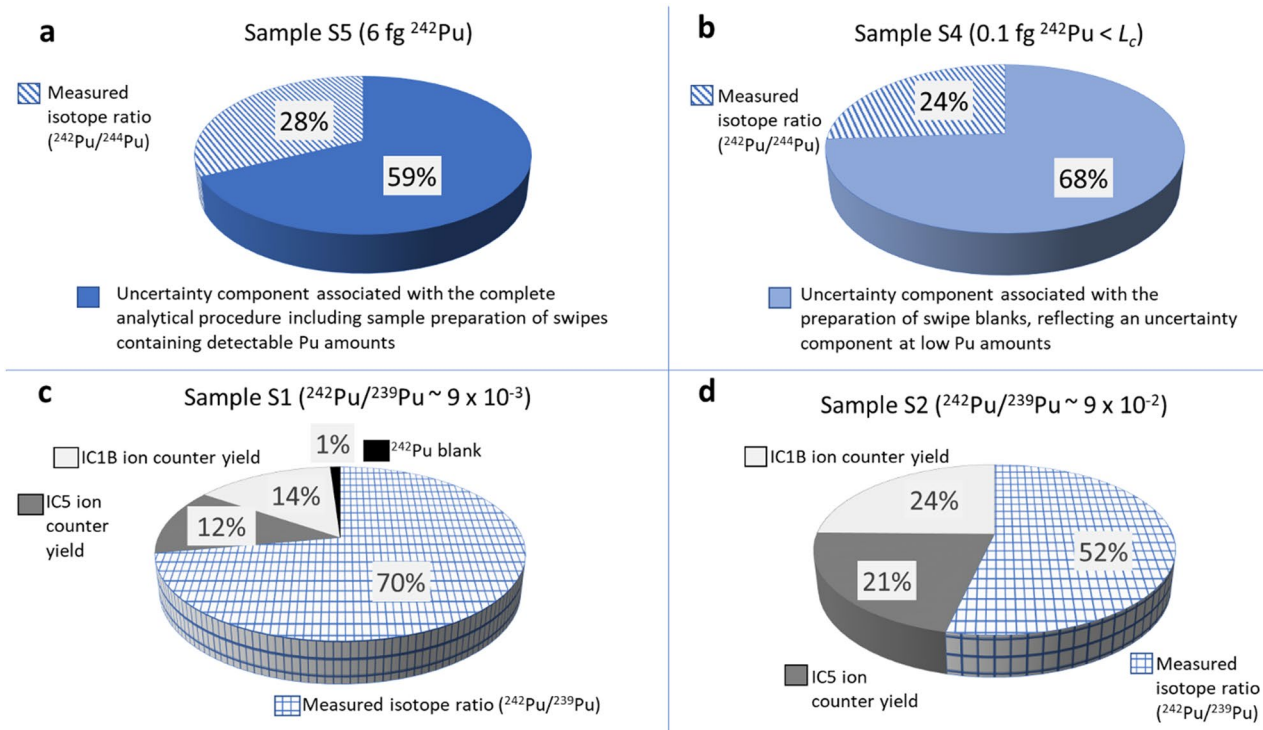The main contributions are depicted in Fig. 5c and d on the examples of samples S1 and S2. These samples were

Fig. 5 Main uncertainty contributions for ^{242}Pu amounts (**a** and **b**), and ^{242}Pu/^{239}Pu isotope ratio (**c** and **d**) measurements

selected to show the contributions for different ^{242}Pu/^{239}Pu ratio ranges; i.e. 10^{-3} and 10^{-2} range.

In addition to an improved accuracy for samples containing ^{242}Pu and an enhanced overall detection capability, the non-requirement of sample splitting resulted in a 50% improvement in timeliness for analysis and reporting of results.

Pu detection capabilities

Assessment of detection thresholds by means of swipe blank analysis

Reducing contamination risks and controlling the required level of cleanliness is crucial for the analysis and detection of extremely low abundant isotopes in environmental samples. Process blanks, procedural reagent blanks that also undergo the entire preparation and analysis process, along with swipe blanks are used for assessing the cleanliness level during sample preparation, and for monitoring potential cross-contamination from other samples, contaminated reagents, or from a contaminated laboratory environment.

Swipe blanks consist of pure cotton swipes, identical to those used by inspectors to collect environmental samples, that undergo exactly the same chemical sample preparation and mass spectrometric measurements along with the actual field samples that were taken at nuclear facilities.

As swipe samples are made of natural cotton fibres they always contain a few nanograms of natural uranium that had been absorbed by plants from the soil and water [27, 41]. In principle, swipe samples might also contain extremely small quantities of Pu from the global fallout. Along with that the residue impurities that originate from swipe matrix and from reagents might produce isobaric interferences, and thus, contribute to the background count rate on Pu isotope masses in swipe blanks. In the further discussion we define the "background equivalent Pu amount" as the amount of a Pu isotope that would produce a net signal equal to the background count rate that is acquired in a swipe blank (after subtracting the instrumental background of MC-ICP-MS). The background equivalent amount of Pu accounts for integral effect of isobaric interferences that originate from sample matrix and reagents and from a potential presence of ultra-trace amounts of Pu originating from the environment.

Analysing swipe blanks allows an assessment of the background signal measured on the masses corresponding to the Pu isotopes for determining the detection threshold, which is a critical decision criterion for the positive detection of an analyte. In general, the detection threshold L_c [39] depends on the variance of the respective background signal. Here, the detection thresholds for the individual Pu isotope amounts (i.e. ^{239}Pu, ^{240}Pu, ^{241}Pu, or ^{242}Pu) were calculated as three times the standard deviation of the background signal recorded on the masses corresponding to the respective Pu

Table 5 Detection threshold L_c values calculated from swipe blanks that were measured with different Pu-IDMS methods using a ^{244}Pu and a ^{242}Pu spike, respectively

L_c	n swipe blank analyses	^{239}Pu, fg	^{240}Pu, fg	^{241}Pu, fg	^{242}Pu, fg
^{242}Pu method[a]	47	0.43	0.10	0.08	[b]
Eppich et al. [18]	7 [c]	0.58	0.07	0.13	[b]
^{244}Pu method	45	0.08	0.05	0.04	0.05

[a]The "^{242}Pu method" refers to the validated method that was employed in the past for Pu assay measurements using a ^{242}Pu spike

[b]Excluded as a ^{242}Pu spike was used for IDMS

[c]Eppich et al. [18] combined in his experimental study 3 process and 4 swipe blanks to calculate the L_c

isotopes plus the mean of these measurements. The 45 swipe blanks were analysed over the course of one year.

Table 5 compares L_c values that were calculated from 45 swipe blank measurements using a ^{242}Pu and a ^{244}Pu spike, respectively. The L_c values using the ^{244}Pu spike were ca. 2 (for ^{240}Pu, ^{241}Pu) to 5 times (for ^{239}Pu) lower compared to those using a ^{242}Pu spike. Similar L_c values were reported by Eppich et al.[18], in which a ^{242}Pu spike was also used. Here, the L_c values for all Pu isotope amounts and the total Pu amount were well below 1 fg, with the L_c for total Pu being improved by ca. 4 times to below 0.2 fg. The main reason for the improved L_c values is the purity of the ^{244}Pu spike, e.g., the abundance of ^{239}Pu in the used ^{242}Pu spike [15] was about 72 times higher than in the ^{244}Pu spike [19].

As the samples are usually split into several sub-samples (aliquots) for the analysis of different analytes, the detection limits for Pu isotopes in the whole sample are calculated by normalizing the L_c stated in Table 5 to the analyzed aliquot fraction $f_{Aliquot}$ of the swipe that is used for Pu analysis.

Figure 6 demonstrates the average background equivalent Pu amounts measured in 45 swipe blank samples over the course of one year. Background equivalent amounts were 0.05 fg, 0.02 fg, 0.008 fg, and 0.02 fg for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu, which reflects either a presence of small residue Pu amounts in blank swipe samples or an effect of interferences that were not completely corrected for. Nevertheless, these residue effects were extremely small. Thus, the values in Fig. 6 are given for the whole swipe samples. The maximum background equivalent Pu isotope amount that was observed in one swipe sample was 0.124 fg ^{239}Pu. Pu background equivalent amounts for all isotopes measured in 31 process blanks were below 0.4 fg/sample.

These low values indicate good control of the chemical sample preparation with respect to cross-contamination in the laboratory as well as minimized sample carryover in the mass spectrometer's sample introduction system.

Additional considerations for improvements in overall Pu detectability

Another important factor for achieving sufficiently low detection thresholds as reported here, is the selected aliquot concentration that is subject to the MC-ICP-MS measurement. An aliquot concentration of ca. 0.25 pg mL^{-1} has been chosen to avoid contaminating the high-efficiency sample introduction system with high Pu amounts, which can reduce memory effects in the system. In addition, 0.2% (w/w) HF has been added to the 2% (w/w) HNO$_3$ matrix as it forms stronger complexes [40] with Pu, which has helped to effectively wash Pu out of the sample introduction system further reducing memory effects and keeping blank levels low. The same HNO$_3$/HF matrix has also been used as rinse solution, with which the sample introduction system has been cleaned after each sample and standard analysis. Boulyga et al. [27]

Fig. 6 Background equivalent amounts of Pu isotopes measured in swipe blank samples using the ^{244}Pu method ($n=45$). The values are given for the whole swipe samples. No uncertainties are depicted. Data are sorted from smallest to largest values for each Pu isotope separately
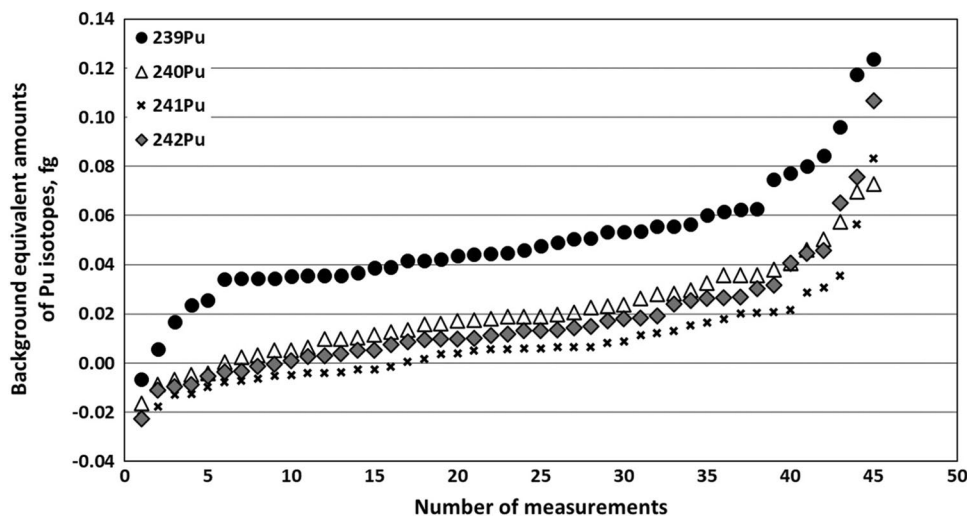
applied the same rinse solution for U isotope ratio measurements, and showed that lower expanded uncertainties were observed for all measured enrichments, and that the blank contribution to the whole uncertainty budget was significantly reduced. In addition, U CRM solutions (which were used as calibration standards) have been aspirated between Pu containing samples, which additionally helps to maintain low Pu blank levels in the sample introduction system.

Another aspect that has to be considered when talking about overall Pu detectability is the effect of analysing only a single spiked fraction when using a [244]Pu spike, as opposed to (potentially) analysing two fractions in case of a [242]Pu spike, as discussed above. If only one fraction needs to be analyzed for obtaining both assay and isotope ratio data, 100% of the aliquot (or all available analyte ions) is available for analysis, enhancing the likelihood of detecting Pu in samples having low Pu amounts. For example, in the case of the swipe blanks, having the possibility of analysing 100% of the aliquot has a positive effect on counting statistics, and thus on the precision of the apparent measured isotope ratio, and ultimately on the precision of the determined L_c values.

Conclusions

The implementation of a high-purity [244]Pu spike CRM from LLNL enables a new era in Pu assay and isotope ratio measurements, improving analytical figures of merit for samples containing ultra-low Pu amounts in the femtogram to picogram range typical for IAEA environmental swipe samples.

The availability of this spike required the installation of an additional detector in the multi-collector array of the MC-ICP-MS instrument to allow the simultaneous measurement of the spike isotope [244]Pu and of the most abundant isotope [239]Pu together with the other Pu isotopes, achieving higher accuracy for both assay (direct normalization to [244]Pu) and isotope ratio measurements (direct normalization to [239]Pu). Another advantage of the new collector block design is the on-line monitoring of PbAr interferences that are critical for accurate Pu isotope ratio measurements in samples with elevated Pb concentrations.

In addition, the use of this high-purity [244]Pu spike material allows the direct determination of all Pu isotopes, including [242]Pu, in the same sample fraction, making sample splitting unnecessary as was the case when using a [242]Pu spike. The analysis of only one sample fraction results in improved accuracy (i.e. detection of [242]Pu in all samples, in addition to the normalization of all Pu isotopes to the denominator isotope, and direct interference correction), timeliness (i.e. reduced sample preparation and measurement time for only one Pu fraction), and overall Pu detection. The Pu detection capability in the swipe is further improved by the sufficiently low Pu isotope detection thresholds (less than 1 fg for all

Pu isotopes) that can only be achieved due to the absence of other Pu isotopes in the spike material. Achieving detection thresholds in the femtogram range and reporting results with high level of accuracy as demonstrated in this paper are crucial for high quality ES analysis.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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