

Plutonium assay and isotopic composition measurements in nuclear safeguards samples by inductively coupled plasma mass spectrometry

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SUPPLEMENTARY ONLINE MATERIAL

Quantification of uncertainty using GUM

A list of the components considered in the GUM uncertainty quantification is shown in **Sup. Table 1**; and will be hereafter referred to following the listed notation. Each uncertainty component has a corresponding sensitivity factor, which is calculated using a series of partial differential equations derived from Eq. 1. The solutions to the partial differential equations reported here are derived from Williams (2010). We follow their approach of partitioning the contribution of each isotope in an isotope ratio measurement to uncertainty, following Eq. 11 and 12:

$$U_A = \left(\frac{U_{A/B}}{(A/B)} \right) \sqrt{\frac{B^2 A \sqrt{A}}{B + A\sqrt{B}}} \quad (\text{SOM Equation 1})$$

$$U_B = \left(\frac{U_{A/B}}{(A/B)} \right) \sqrt{\frac{B^2 A}{B + A}} \quad (\text{SOM Equation 2})$$

where U_A and U_B are the uncertainties partitioned to isotope A and isotope B, respectively, $U_{A/B}$ is the measurement uncertainty of the ratio of isotope A to isotope B (usually calculated as the 2σ standard error of n cycles of measurement, and A and B are the measured signal intensities of isotope A and isotope B, respectively (units must be consistent). The calculated values of U_A and U_B are hereafter treated as the measurement uncertainty of isotope A and isotope B, respectively, and are utilized after calculation of the sensitivity factor of each uncertainty component. This approach allows for a cycle-by-cycle determination of uncertainty for Pu signal intensities.

Symbol	Uncertainty component description
$\delta K_{24x/239}$	Mass bias correction factor of $^{24x}\text{Pu}/^{239}\text{Pu}$
δG_{24x}	Gain correction factor for ion counter used to measure ^{24x}Pu
δi_{24x}	Measured intensity of ^{24x}Pu
δs_{24x}	Contribution of ^{24x}Pu from spike
δb_{24x}	Contribution of ^{24x}Pu from blank
δh_{24x}	Contribution of ^{24x}Pu from hydride
δG_{239}	Gain correction factor for ion counter used to measure ^{239}Pu
δi_{239}	Measured intensity of ^{239}Pu
δs_{239}	Contribution of ^{239}Pu from spike
δb_{239}	Contribution of ^{240}Pu from blank
δh_{239}	Contribution of ^{239}Pu from hydride

Supplementary Table 1. List of components considered in calculation of GUM-compliant uncertainty for Pu isotopic measurements. ^{24x}Pu denotes the Pu isotopes heavier than ^{239}Pu . This notation is used for SOM Equations 3-13.

Sensitivity factors (SF_x , where x is the component from Eq. 7 for which the sensitivity factor is being calculated) for the uncertainty components listed in **Sup. Table 1** are calculated using the following

(Eq. 13 through 23), the partial differential equation solutions, with respect to each variable, of the model equation (Eq. 7).

$$SF_{K_{A/B}} = \frac{\partial R_{A/B}}{\partial K_{A/B}} = \frac{G_A 1}{G_B n} \sum \frac{(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 3})$$

$$SF_{G_A} = \frac{\partial R_{A/B}}{\partial G_A} = \frac{K_{A/B} 1}{G_B n} \sum \frac{(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 4})$$

$$SF_{a_i} = \frac{\partial R_{A/B}}{\partial a_i} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{1}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 5})$$

$$SF_{a_b} = \frac{\partial R_{A/B}}{\partial a_b} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{-1}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 6})$$

$$SF_{a_s} = \frac{\partial R_{A/B}}{\partial a_s} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{-1}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 7})$$

$$SF_{a_h} = \frac{\partial R_{A/B}}{\partial a_h} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{-1}{(b_i - b_b - b_s - b_h)} \quad (\text{SOM Equation 8})$$

$$SF_{G_B} = \frac{\partial R_{A/B}}{\partial G_B} = K_{A/B} \frac{G_A 1}{n} \sum \frac{-(a_i - a_b - a_s - a_h)(b_i - b_b - b_s - b_h)}{[G_B(b_i - b_b - b_s - b_h)]^2} \quad (\text{SOM Equation 9})$$

$$SF_{b_i} = \frac{\partial R_{A/B}}{\partial b_i} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{-(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)^2} \quad (\text{SOM Equation 10})$$

$$SF_{b_b} = \frac{\partial R_{A/B}}{\partial b_b} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)^2} \quad (\text{SOM Equation 11})$$

$$SF_{b_s} = \frac{\partial R_{A/B}}{\partial b_s} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)^2} \quad (\text{SOM Equation 12})$$

$$SF_{b_h} = \frac{\partial R_{A/B}}{\partial b_h} = K_{A/B} \frac{G_A 1}{G_B n} \sum \frac{(a_i - a_b - a_s - a_h)}{(b_i - b_b - b_s - b_h)^2} \quad (\text{SOM Equation 13})$$

where all variables are defined above. Note that the a_s and b_s are only applied in the case of the determination of Pu isotopic composition from spiked Pu fractions, and a_h and b_h are only applied for ^{239}Pu . Following GUM guidelines, the contribution to uncertainty for each component is calculated using Eq. 24:

$$U_x = (SF_x \times u_x)^2 \quad (\text{SOM Equation 14})$$

where U_x is the result of incorporating sensitivity factor and measured uncertainty for component x , SF_x is the calculated sensitivity factor for component x , and u_x is the measured uncertainty of component

x . In the case of a_i and b_i , u is U_A and U_B calculated using Eq. 10 and 11, respectively. u of $K_{A/B}$ is calculated as the propagated uncertainty of the measured $^{235}\text{U}/^{238}\text{U}$ of the bracketing standards (determined as the 2σ standard error of n measurement cycles) and certified uncertainty of the $^{235}\text{U}/^{238}\text{U}$ certified reference material (in this case, IRMM-025). u of G_A and G_B are calculated as the propagated uncertainty of the measured minor U isotope ratio of the bracketing standards (determined as the 2σ standard error of n measurement cycles) and certified uncertainty of the minor U isotope certified reference material. u of a_b and b_b is calculated as the 2σ standard error of n cycles of the acid blank (typically, $n = 10$) measured before each analysis. u of a_s and b_s is the certified uncertainty on the isotopic composition of the spike used for IDMS measurements.

From the calculated U_x for each uncertainty component, combined standard uncertainty is calculated following Eq. 25.

$$CSU = \sqrt{U_{sum}} \quad (\text{SOM Equation 15})$$

where CSU is the combined standard uncertainty of the isotope ratio measurement, and U_{sum} is the sum of all U_x . CSU is multiplied by a coverage factor k to produce an expanded uncertainty, which is the ultimate measure of uncertainty reported alongside isotope ratio measurements. In all cases here, $k = 2$. For Pu amounts calculated using isotope dilution (^{242}Pu as the numerator isotope, used for calculation of Pu isotope amounts), CSU is retained without expansion for the measured ratios. A list of the components considered in the GUM uncertainty quantification of Pu isotope amount are listed in **Supplementary Table 2**; these components will be hereafter referred to following this notation.

Symbol	Uncertainty component description
δR_{spike}	Certified Pu isotope ratio of spike
δR_{mix}	Measured Pu isotope ratio of spiked sample
δR_{sample}	Measured Pu isotope ratio of unspiked sample
δm_{sample}	fraction of sample used for determination of spiked Pu isotope ratio
$\delta n_{242added}$	Number of atoms of ^{242}Pu added from spike

Supplementary Table 2. List of uncertainty components considered in calculation of GUM-compliant uncertainty for Pu amount determination. This notation is used for SOM Eq. 16-20.

Sensitivity factors for the uncertainty components listed in **Sup. Table 2** are calculated using the following equations (Eq. 26-30). ^{239}Pu is used as the example isotope in the below equations, but these equations can be applied to any Pu isotope of interest, except for the spike isotope ^{242}Pu .

$$SF_{R_{spike}} = \frac{\partial n_{239_{sample}}}{\partial R_{spike}} = \frac{n_{242_{added}} R_{mix}}{m_{sample} R_{spike}^2 (R_{mix} - R_{sample})} \quad (\text{SOM Equation 16})$$

$$SF_{R_{sample}} = \frac{\partial n_{239_{sample}}}{\partial R_{sample}} = \frac{n_{242_{added}} (R_{spike} - R_{mix})}{m_{sample} R_{spike} (R_{sample} - R_{mix})^2} \quad (\text{SOM Equation 17})$$

$$SF_{R_{mix}} = \frac{\partial n_{239_{sample}}}{\partial R_{mix}} = \frac{n_{242_{added}} (R_{sample} - R_{spike})}{m_{sample} R_{spike} (R_{sample} - R_{mix})^2} \quad (\text{SOM Equation 18})$$

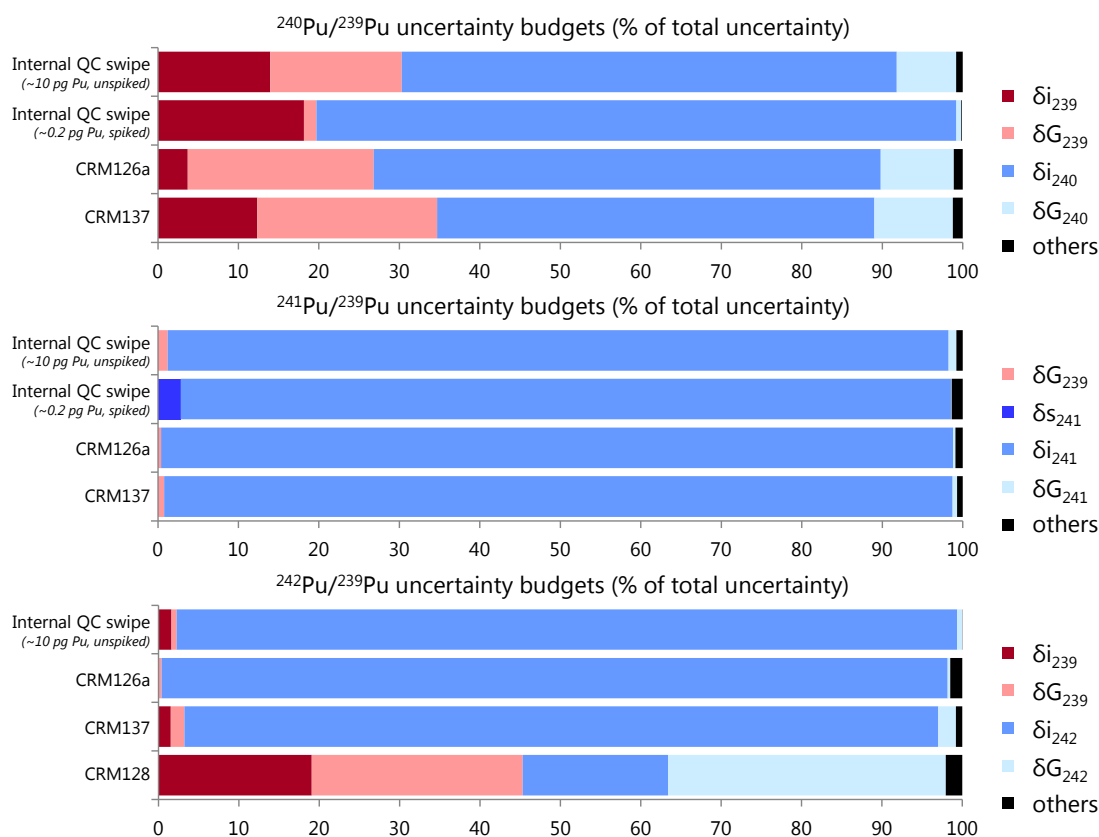
$$SF_{m_{sample}} = \frac{\partial n_{239_{sample}}}{\partial m_{sample}} = \frac{n_{242_{added}} (R_{spike} - R_{mix})}{m_{sample}^2 R_{spike} (R_{sample} - R_{mix})} \quad (\text{SOM Equation 19})$$

$$SF_{n_{242_{added}}} = \frac{\partial n_{239_{sample}}}{\partial n_{242_{added}}} = - \frac{R_{spike} - R_{mix}}{m_{sample} R_{spike} R_{sample} - m_{sample} R_{spike} R_{mix}} \quad (\text{SOM Equation 20})$$

Upon calculation of the sensitivity factors, U_x and CSU are calculated using Eq. 24-25. At this point, CSU is converted to an expanded uncertainty by multiplying by the coverage factor of $k = 2$. The individual Pu isotope amount uncertainties are then propagated to calculate a total Pu amount expanded uncertainty.

Assessment of results of GUM uncertainty quantification for Pu certified reference materials

Uncertainty budgets for measured $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$, and $^{242}\text{Pu}/^{239}\text{Pu}$ ratios in representative Pu solution certified reference materials and environmental swipe samples spiked with NBL CRM-947 (at ~ 0.32 and ~ 10.5 pg total Pu) are presented in **Sup. Fig. 1**. Uncertainty budgets are determined relative to the sum of U_x calculated using SOM Eq. 14 for each contributor to uncertainty listed in **Sup. Table 1**. Possible sources of uncertainty not listed in **Sup. Table 1** are ignored; this decision is justified on the basis of the accuracy and precision of replicate measurements of certified reference materials shown and discussed in detail in the main text. Uncertainty in $^{240}\text{Pu}/^{239}\text{Pu}$ ratios is dominated by the contribution from the intensity of ^{240}Pu , with minor but significant contributions from the intensity of ^{239}Pu and the calculated gain factors of the ion counters used to measure ^{239}Pu and ^{240}Pu . Uncertainty in $^{241}\text{Pu}/^{239}\text{Pu}$ ratios is dominated by the contribution from the intensity of ^{241}Pu , which makes up $>95\%$ of the total uncertainty budget in all cases. This is due to the typically low intensities of ^{241}Pu measured in Pu materials. Uncertainty in $^{242}\text{Pu}/^{239}\text{Pu}$ ratios is dominated by the contribution from the intensity of ^{242}Pu for the certified reference materials NBL CRM-137 and NBL CRM-126a, as well as the NBL CRM-947 used to spike blank environmental swipe samples used to assess the accuracy and precision of the total procedure. In the case of NBL CRM-128, this certified reference material contains a roughly sub-equal amount of both ^{239}Pu and ^{242}Pu ; therefore, the contribution of ^{242}Pu is much lower than that for the other certified reference materials that have $^{242}\text{Pu}/^{239}\text{Pu}$ ratios several orders of magnitude than the $^{242}\text{Pu}/^{239}\text{Pu}$ ratio of NBL CRM-128.



Supplementary Figure 1. Combined standard uncertainty budgets for Pu certified reference materials measured in this study. Included here are budgets for individual measurements that are typical for the total measurements performed in this study.

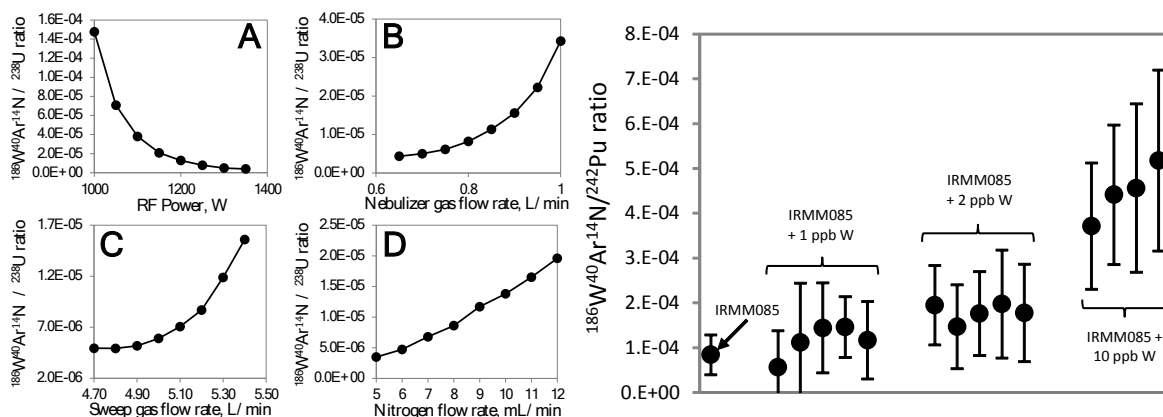
Polyatomic interference studies

The major types of interferences that can theoretically influence Pu isotope analysis by ICP-MS analyses include (i) direct isobaric interferences (e.g. ^{238}U interference on ^{238}Pu); (ii) polyatomic interferences (e.g. $^{204}\text{Pu}^{40}\text{Ar}$ interference on ^{244}Pu), and; (iii) doubly-charged ion interferences (e.g. $^{138}\text{Ba}^{++}$ interference on ^{69}Ga). Although in principle, some of the polyatomic interferences could be resolved by increasing instrumental mass resolution, an increase in mass resolution would cause a commensurate loss in sensitivity of Pu ion detection, and Pu abundances in environmental samples are too low to permit significant sensitivity loss. Therefore, chemical impurities must be removed to a sufficient degree as to decrease the contribution of each interference to negligible levels. If a particular impurity cannot be sufficiently removed, the contribution of this interference must be quantified, and a correction factor must be applied to correct the corresponding Pu isotope signal intensity.

The three most important interferences have been identified, which are polyatomic compounds of U, W, and Pb. The primary U polyatomic interference is $^{238}\text{U}^{1}\text{H}$ on ^{239}Pu . Tungsten has five stable isotopes, three of which can cause polyatomic interferences on Pu: (i) $^{183}\text{W}^{40}\text{Ar}^{16}\text{O}$ on ^{239}Pu ; (ii) $^{184}\text{W}^{40}\text{Ar}^{16}\text{O}$ on ^{240}Pu ; and, (iii) $^{186}\text{W}^{40}\text{Ar}^{16}\text{O}$ and $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$, on ^{242}Pu and ^{240}Pu , respectively. Lead produces one significant interference, $^{204}\text{Pb}^{40}\text{Ar}$ on ^{244}Pu . Because ^{244}Pu is below critical limit for all samples in this study, and no ^{244}Pu spike is applied here, treatment of the Pb interference will not be discussed further.

W polyatomic interferences

Here we investigate the influence of instrumental conditions on the production of the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ interference on ^{240}Pu . In order to assess the production of the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ interference, an ~ 0.1 ng/mL U + ~ 10 ng/mL W solution was analyzed using by MC-ICP-MS (W/U ratio ≈ 100); this solution contained no Pu. The following instrumental parameters were adjusted: (i) RF power (between 1000 and 1400 W); (ii) nebulizer gas flow rate (between 0.65 and 1.0 L Ar/min; (iii) the Aridus II sweep gas flow rate (between 4.70 and 5.40 L Ar/min; and, (iv) the Aridus II N_2 gas flow rate (between 5 and 12 mL Ar/min). The magnitude of the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ was determined as a mass 240/ ^{238}U intensity ratio. It was assumed that any increase in the signal of mass 240 originated from $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$.



Supplementary Figure 2. $^{186}\text{W}^{40}\text{Ar}^{14}\text{N} / ^{238}\text{U}$ ratio as a function of: A) RF power; B) nebulizer gas flow rate; C) sweep gas flow rate, and; D) nitrogen gas flow rate. Results of $^{240}\text{Pu} / ^{242}\text{Pu}$ measurements of IRMM085 spiked with W in concentrations of 1, 2, and 10 ppb.

The results of this investigation are shown in **Sup. Fig. 2**. We observed that the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ interference decreased with increasing RF power, and increased with increasing nebulizer gas flow rate, Aridus sweep gas flow rate, and Aridus nitrogen gas flow rate (**Sup. Fig. 2**). The decrease in the interference as a function of RF power increase can be explained as the increased destruction of the polyatomic compound with increasing plasma energy. An increase in RF power produces a more energetic plasma, with a higher rate of Ar collisions, increasing the rate of destruction of $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$. Increasing the gas flow rates causes the sample to move more rapidly through the plasma, as well as increases the amount of gas making its way to the plasma. Since $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ is composed partly of Ar and N ions, an increase in any of the Aridus II gas flow rates increases the production of this interference. And since $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ spends less time in the plasma at an increased gas flow rate, the rate of destruction decreases, as we observe here.

In order to determine the concentration of W necessary to observe the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ interference, a series of Pu standard reference materials spiked with different concentrations of W were analyzed. The Pu reference material IRMM-085 was used for this investigation, as it consists almost entirely of ^{242}Pu , with negligible amounts of the other Pu isotopes. The IRMM-085 standard was spiked with W in increments of 1 ng/mL, 2 ng/mL and 10 ng/mL, and was also analysed without W spike. The results of this investigation are shown in **Sup. Fig. 2**. Here we see that the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N} / ^{242}\text{Pu}$ ratio increases with increasing W concentration. However, at 1-2 ng/mL, the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N} / ^{242}\text{Pu}$ ratio remains within uncertainty of the unspiked IRMM-085 standard. At concentrations of 10 ng/mL, the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N} / ^{242}\text{Pu}$ ratio is outside of uncertainty of the unspiked IRMM-085, towards elevated $^{186}\text{W}^{40}\text{Ar}^{14}\text{N} / ^{242}\text{Pu}$ ratios of about 4×10^{-4} to 5×10^{-4} , albeit with magnified uncertainties relative to the unspiked IRMM-085.

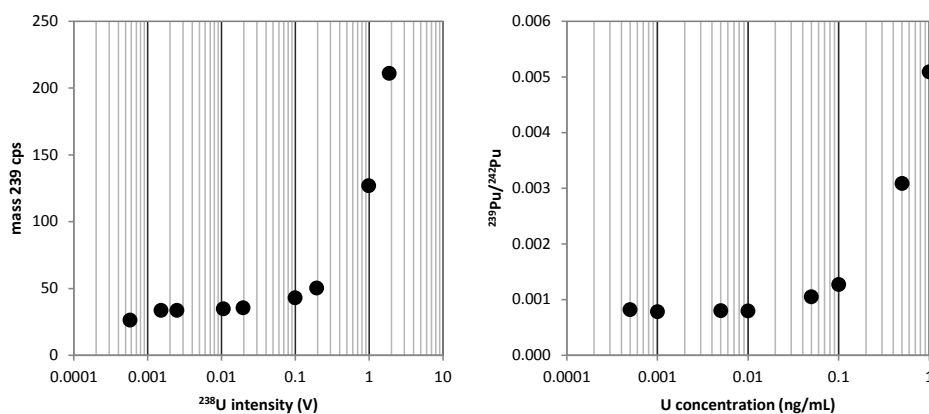
Based on these findings, we conclude that a W impurity concentration of ≤ 1 ng/mL is a good benchmark to decide whether a Pu sample has been sufficiently purified of W for accurate measurements of ^{240}Pu . This equates to a W/Pu ratio of less than 5,000 for sufficiently purified Pu samples. In some cases, it can be difficult to sufficiently separate W from Pu using ion exchange chromatography, particularly in samples with low Pu abundances. In cases where W cannot be sufficiently separated from Pu prior to

analysis, care must be taken to assess the contribution of $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ on ^{240}Pu , considering that the production of this interference can vary as a function of instrumental RF power and sample introduction system gas flow rates. In order to determine a correction factor for the $^{186}\text{W}^{40}\text{Ar}^{14}\text{N}$ interference on ^{240}Pu , solutions of IRMM-085 (or similar Pu standard with negligible ^{240}Pu) with 1-10 ng W/mL can be analysed alongside samples. The samples themselves should be screened prior to analysis, in order to determine if the W/Pu ratio is above or below 5,000. If this ratio is higher than 5,000, a correction factor should be applied to the ^{240}Pu intensity, using the measured mass 240/ ^{242}Pu ratios of IRMM-085 aliquots spiked with W and analysed alongside samples.

U polyatomic interferences

It is critical to monitor polyatomic interferences in order to obtain precise and accurate Pu isotopic ratios, especially for samples with low total Pu amounts. Most elemental interferences are removed in the chemical purification process prior to analysis by MC-ICP-MS, but not all elements are efficiently separated from Pu. The chemical behaviour of Pu in solution is complex; Pu can adopt several valence states, and can complex with several different anions, necessitating good control over laboratory conditions during chemical separation. The effects of W interferences on Pu are addressed in SG-RP-12665, and are not further considered here. No corrections for W are made in this study, as all solutions have been chemically purified and screened to ensure that W concentrations are negligible. Below we address the effect of the $^{238}\text{U}^{1}\text{H}$ interference on ^{239}Pu .

To determine the concentration of U required to produce a detectable $^{238}\text{U}^{1}\text{H}$ interference on ^{239}Pu , a series of analyses were performed using mixed Pu/U solutions. Each solution consisted of ~ 0.2 pg/mL ^{242}Pu made using the monoisotopic Pu standard IRMM-085 (note that this standard contains trace ^{239}Pu). The concentration of U in each solution was made to vary, prepared using the U isotopic standard NBL CRM-112a at concentrations from 0.0005 to 1 ng/mL. IRMM-085 was also analysed without the addition of uranium. The results of these measurements are shown in **Sup. Fig. 3**; the demonstrate that additional signal beyond that of what is generated by the trace ^{239}Pu in IRMM-085 become detectable at a U concentration of 0.05 ng/mL, equivalent to a U/Pu ratio of ~ 250 . The signal intensity of ^{238}U analysed at this concentration produces a Faraday detector signal intensity of 0.099 V. Because solutions were analyzed at concentrations of 0.01 and 0.05 ng/mL, the $^{238}\text{U}^{1}\text{H}$ interference must appear somewhere between the two, at a U/Pu ratio somewhere between 50 and 250. Uranium concentrations of all Pu samples and standards in this study are monitored using the methods described above. Since no samples or standards measured here contain U at elevated concentrations requiring a correction for the $^{238}\text{U}^{1}\text{H}$ interference, the $^{238}\text{U}^{1}\text{H}$ correction is negligible in all cases.



Supplementary Figure 3. Charts demonstrating the relationship between ^{238}U intensity (U concentration) and the intensity measured on mass 239 (due to the $^{238}\text{U}^{1}\text{H}$ polyatomic interference). The measurement of the standard containing negligible U is not plotted in Panel B.

