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ARTICLE

Estimation of the Formation Rates of Polyatomic Species of Heavy Metals in Plutonium Analyses Using a Multicollector ICP-MS with a Desolvating Nebulizer

A.V. Mitroshkov, K.B. Olsen, M.L. Thomas

Pacific Northwest National Laboratory, PO Box 999, MSIN K3-62, Richland WA 99352, e-mail: alex.mitroshkov@pnnl.gov

The analyses of International Atomic Energy Agency (IAEA) and environmental samples for Pu isotopic content are conducted normally at very low concentrations of Pu—usually in the range of parts per trillion and even more often at the parts per quadrillion level. To analyze such low concentrations, the interferences in the analytical solution must be reduced as much as possible. Polyatomic interferences (PIs), formed by the heavy elements (HEs) from Hf to Bi, are known to create problems for Pu isotopic analyses, because even the relatively high resolution of a modern multicollector (MC) inductively coupled plasma-mass spectrometer (ICP-MS) is insufficient to separate Pu isotopes from such PIs in most cases. Desolvating nebulizers (DSNs) (e.g., APEX and AridusII) reduce significantly the formation of PIs compare to the use of wet plasma. The purpose of this work was to investigate the rate of PI formation produced by HMs when a high-resolution (HR) MC-ICP-MS with a DSN was used for Pu isotopic analyses and to estimate the influence of the HEs present in the sample on the results of the analyses. The NU Plasma HR MC and AridusII DSN were used in this investigation. This investigation was done for the interferences for all Pu isotopes normally analyzed by ICP-MS, including ^{244}Pu, with the exception of ^{238}Pu, which most of the time cannot be analyzed using a ICP-MS, because of the overwhelming presence of ^{238}U in the solutions. The PI formation rates were determined and reported. Selected IAEA samples were scanned for the presence of HEs and the influence of HEs on the results of Pu isotopic analyses was evaluated.

Introduction

When isotopic analyses of Pu are conducted using an inductively coupled plasma-mass spectrometer (ICP-MS), all of the metals that can possibly interfere with Pu analyses must be removed from the sample solution. The most common separation techniques using different ion-exchange resins—like Dowex AG1X4 and Dowex AG1X8 [1, 2], a combination of ion-exchange resin and UTEVA™ [3, 4], or TRU resin and Dowex AG 50W-X8 [5]—usually provide sufficiently purified Pu solutions, but some inconsistency is normally observed and the breakthrough of heavy elements (HEs) is not uncommon. The contamination of chemicals and labware used in the process of preparing samples is also possible. Therefore, it is important to evaluate quantitatively the possible errors of Pu analyses when HEs are present in the Pu fraction of the sample. In this work we have investigated the rate of formation of polyatomic interferences (PIs) produced by HEs when the solution of each HE at a concentration 200 ng/mil in 4% HCl was analyzed the same way as prepared solutions of Pu are normally analyzed.

The PIs were previously investigated using a quadrupole single-detector ICP-MS [2, 5], double-focusing sector field instrument [1] and multicollector (MC)-ICP-MS [7]. The investigations were done with [7, 2, 8, 9] and without [1, 6, 5] the use of a desolvating nebulizer (DSN), although the volume of work is clearly not sufficient to cover all aspect of PIs. In [7] only PIs produced by U (^{238}UH$^+$) and Pb were investigated. The

proportion of the formation of $^{238}UH^+$ to U was found to be in the range of
5.0×10^{-06} to 5.8×10^{-06}, which is close to what we observe on our MC-ICP-MS, which ranged from 4.8×10^{-06} to 6.0×10^{-06}. In [7] a magnetic sector MC-ICP-MS with a single Daly detector was used during the analysis. The authors also used a DSN (MCN6000), which explains why the values for the $^{238}UH^+$ formation rate are close to our values. When they were running 20 ng/ml of Pb, however, they did not observe the formation of PIs such as $^{207}PbOO^+$, $^{208}PbOO^+$, and $PbCl^+$. The conditions of the experiment probably rendered low formation rates and the concentration of 20 ng/ml was insufficient to register the PIs. The estimation of the PIs produced by Pb was done in [2] for ions 239, 240, and 242. In [8] the formation of PIs from Pt and Pb was observed, but the formation rates were not reported. During the analyses of Pu in the soils [4] the lanthanides were found to be the most likely source of PIs interfering with Pu determination. Later, lanthanide phosphates were demonstrated to constitute the potential source of these interferences.

The most comprehensive study investigating the formation of PIs produced by HEs was conducted by Pointurier et al. [1, 6, 9]. In the first part of their research, the formation rates were determined for wet plasma, and no DSN was used. The significant variations of the formation rates of molecular ions of HMs [1, 6] were observed depending on the ICP-MS setting.

A successful attempt in [9] was undertaken to solve the problem of some PIs by increasing the mass resolution of the mass spectrometer to 4000, yielding separation of PIs such as PbO_2^+, IrO_3^+, and $HgAr^+$ from Pu.

To compensate for the loss of sensitivity the APEX DSN was used. It is worth noting the authors did not find significant differences in the formation rates between the self-aspiration mode and the use of APEX. As one can see below, we have found that for many PIs the formation rates are much lower than those reported for wet plasma, especially for Hg, although for Pb and Ir the difference was not as drastic.

In our work we determined the formation rates of polyatomic species for dry plasma using an Aridus II DSN.

Experimental

Instrumentation

The research was performed using the NU Plasma High-Resolution (HR) MC-ICP-MS (NU Instruments, UK). The system has 11 Faraday cups and 3 ion counters (ICs) as detectors, which can operate simultaneously. To introduce the sample, an autosampler, ASX-112FR, and Aridus II DSN (both CETAC, Omaha, NE) were used. The analytical conditions were optimized for Pu analyses. A Quick Wash attachment was used for quick washout of Pu and HMs from the system after

every analytical run. Table 1 lists the instrument and acquisition settings for the HR MC-ICP-MS and DSN.

Table 1. Instruments and acquisition settings for the NU Plasma HR MC-ICP-MS (the optimal setting values change from day to day)

HR MC-ICP-MS Settings	
Forward power	1050−1300 W
Coolant gas	13−14 L/min
Auxiliary gas	1.2−1.4 L/min
Nebulizer pressure	35−39 psi
Resolution	400
Aridus II Desolvating Nebulizer Settings	
Sweep gas flow	4−6 L/min
Spray chamber	110°C
Desolvator	160°C
Solution introduction rate	150−200 µL/min.

Sample Preparation and Purification Procedure

To analyze Pu at the parts per quadrillion level, Pu must be separated from U and other interfering metals as much as possible. Although the most common method of isolating Pu uses ion-exchange resins [1, 3], alternative methods of Pu sample preparation are being developed; e.g., electrochemically modulated separation [11, 12], in which Pu is absorbed on the electrode and subsequently injected into the ICP-MS, or separation by ion chromatography [13−15]. Every such method has advantages and shortcomings, the latter including reproducibility and cross-contamination problems. A method of sample preparation similar to ours, based on separation on an AG1X4 ion-exchange resin, is described in detail in [16].

Most International Atomic Energy Agency (IAEA) samples are collected and delivered to the analytical lab on cotton swipes and sometimes on J-type (paper butterfly) swipes. The sample preparation includes the following steps:

- Place swipe in quartz crucible (lid on).
- Char at 350°C for 1 hour; ash at 750°C for 4.5 hour.
- Leach the ash residue with HNO_3 (7M)/HF (1M) acid solution.
- Adjust sample solution to 5-mL, of which 1 mL is archived.

The HNO_3, HCl, and HF acids are ultra-pure grade (Fisher Optima). All other reagents are reagent grade. The sample solutions are prepared with tracers for assay determination, and without tracers for isotope ratio measurement. Extraction resins, UTEVA® and TEVA ® (Eichrom Technologies, 100−150 µm), are manually packed into 2.5-mL plastic open columns (Environmental Express). Similar columns procured from Bio-Rad yielded lower analyte recoveries.

The swipes are transferred to quartz crucibles (Technical Glass Products) and ashed in a muffle furnace to decompose the swipe media. The residue is leached in 5-mL 7.5 M HNO_3–1 M HF solution; at least 20% is reserved for archive. A 1000-fold dilution is analyzed by Q-ICP-MS (ThermoElemental PQ Excel) to estimate the U and Pu content. An aliquot of the sample solution is spiked with ^{233}U (Oak Ridge National

Laboratory, Tennessee) and ^{244}Pu (National Bureau of Standards SRM-996). Another aliquot of the sample solution is used for non-spiked analysis.

Aliquots of the sample solutions are heated in Teflon vials (Savillex) with 2 mg of aluminum (to minimize absorption into the vial) and transposed to a chloride matrix with HCl. Hydroxylamine hydrochloride is used to reduce Pu to Pu III. The digest is dissolved in 6 M HCl and loaded onto a UTEVA® column. The column is eluted with 6 M HCl and the load and effluent solution are reserved. The UTEVA ®column is further eluted with 5 M HCl–0.05 M oxalic acid and 3 M HNO_3 to remove interfering species. The U is stripped from the column with 5% v/v HCl.

The reserved effluent from the UTEVA® column is heated in a Teflon vial with 2 mg Fe and transposed to a nitrate matrix with HNO_3. The digest is dissolved in 3 M HNO_3, treated with 0.6 M ferrous sulfamate and 3 M $NaNO_2$, and loaded onto a TEVA® column. The TEVA® column is eluted with 3 M HNO_3, 6 M HCl−0.15 M $NaNO_2$, and 9 M HCl to remove interfering species. The Pu is stripped from the column with 5% v/v HCl.

A reagent blank and swipe blank are also prepared in this manner. The isolated fractions of U and Pu are diluted to 4% v/v HCl with ultra-pure water and measured using a HR MC-ICP-MS.

Analytical Method

For the calibration of the system, Plutonium Standard CRM137, from New Brunswick Laboratory (Argonne, IL), at a concentration of 2.52 pg/ml was used. This standard is normally used for calibration of the system during Pu analyses to obtain the gains of ICs and mass bias correction factor. Individual solutions of Pb, Bi, Hf, W, Hg, Au, Re, Pt, and Tl at 200 ng/ml in 4% HCl (Ultra Scientific, RI USA) were used during the experiment. Because of the low concentration of Pu in the samples, only ICs and the three-cycle method were used for analyses of Pu and accordingly for the detection of polyatomic species.

1. PLUTONIUM ISOTOPIC RATIO ANALYSIS

Analyses of Pu isotopic ratio using a HR MC-ICP-MS involve three steps: 1) measurement of zeros, 2) calibration, which is the determination of IC gains and mass bias factor (MBiasF) and 3) sample run.

Each sample is divided into two fractions, which are analyzed separately: 1) the first run is done with no ^{244}Pu tracer added to the sample; 2) the second run for the same sample is done with the tracer-added solution. As a tracer, ^{244}Pu solution in appropriate concentrations (~2.5 pg/ml) is normally used.

Three methods of obtaining background values or zeros measurements are available for the NU HR MC-ICP-MS system: off-peak zeros, beam deflection zeros, and on-peak zeros. The procedure described here uses on-peak zeros.

For Pu analysis two different detector layouts are used: one for calibration and another for sample analyses. This is done because the concentration of the calibration standard is low and accurate gain values can be obtained only when each IC registers signal from ^{239}Pu in turn.

The following layout is used for **calibration:**

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
									239		237	236	
									241		239	238	
									242		240	239	

where IC0, IC1, and IC2 represent the three ICs, H1−H6 represent the higher Faraday cups relative to the axial faraday (Ax), and L1−L4 represent the Faraday cups on the lower side. Zeros are measured with an integration time of 20 s in each cycle from 5 to 10 measurements in one run.

The ^{239}Pu$^+$ beam is registered on all three ICs in turn in order to determine the relative responses of the ICs (gains). The gain of IC0 is considered to be 1.0. The gains of IC1 and IC2 are calculated as the ratios of the registered signal of ^{239}Pu on IC1 and IC2 to the signal of ^{239}Pu registered on IC0.

To determine the gains and mass bias correction factor any certified isotopic standard of Pu can be used; normally, a 2.52 pg/ml solution of CRM137 is used.

The mass bias correction factor is calculated according to the following formula:

$$MBiasF = (Log\ (True\_R/Obs\_R))/(Log\ (M240/M239))$$

where		
True_R	=	true ratio of ^{240}Pu/^{239}Pu in the standard;
Obs	=	observed ratio of ^{240}Pu/^{239}Pu - results of the measurement;
M240 and M239	=	atomic masses of ^{240}Pu and ^{239}Pu, accordingly.

The following layout is used for **sample analyses**:

H6	H5	H4	H3	H2	H1	Ax	L1	L2	IC0	L3	IC1	IC2	L4
									244		242	241	
									241		239	238	
									242		240	239	

The zeros must be measured again for the sample run in the layout, which is used for the sample run.

During the sample run the measured intensities of the beam, in volts, correspond to different isotopes of Pu, and the data for zeros, gains, and mass bias obtained previously are used for the calculation of isotopic ratios.

For example, the ratio ^{240}Pu/^{239}Pu is calculated for the third cycle as follows:

$^{240}Pu/^{239}Pu = ((^{240}Pu\_3/IC1)/(^{239}Pu\_3/IC2))*(M240/M239)^{MBiasF}$

The amount of ^{239}Pu isotope in the sample is calculated based on the ratio of $^{239}Pu/^{244}Pu$, which is produced during the run of the tracered samples. The total amount of the ^{244}Pu in the sample is registered during the sample preparation routine. The amounts of ^{240}Pu, ^{241}Pu, and ^{242}Pu in the sample are calculated based on the ratios $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$, which are determined during the non-tracered sample run. The ratios for these isotopes produced during the tracered sample run cannot be used, because the ^{244}Pu tracer contains low levels of other Pu isotopes as impurities and, although being relatively low, they can significantly change the isotopic ratios for low-concentration samples. If only tracered samples are available, then the known concentrations of minor Pu isotopes in ^{244}Pu should be stripped from the results. Although the results obtained for the tracered samples in many cases are acceptable, they are less accurate and have more significant errors than the isotopic ratios measured in non-tracered samples.

The precision and accuracy of the method are very dependent on the concentration, and they are lower when the concentrations are low. For the CRM standard, which has the ratio of $^{240}Pu/^{239}Pu$ equal to 0.24086 (610 fg of ^{240}Pu per 1 ml), the precision determined as 2σ (relative standard deviation), is normally below 1%.

2. ELEMENTAL ANALYSIS

In the elemental analysis only the central Faraday cup (Ax) is used. In this mode the system quickly jumps from one isotopic peak of a certain element to the isotopic peak of another element. The scan rate is 1000 ms/amu and dwell time is 2 s. Unlike in isotopic analyses, where the MS has the ability to find precisely the center of the peak, the accurate centering of every peak every time is unavailable. Therefore, it is important to accurately calibrate the mass scale.

For this purpose two different standards are used: 1) the internal standard, containing eight elements: Bi, Ho, In, Lu, Rh, Sc, Tb, Y (High Purity Standards, SC, USA); in order to cover the low side of mass scale Be is also is added to this standard; and 2) the ICP-MS Standard, containing 68 elements (High Purity Standards, SC, USA). The internal standard provides a 9-point calibration, followed by the ICP-MS standard, which provides a 66-point calibration.

After the mass scale is calibrated, and the AridusII and MS are thoroughly washed, the blank sample (4% HCl) is run. After the blank sample is run, the background values, obtained during the zero run, are subtracted from the standard and from the sample values.

The blank cannot be run before the standard, because the precise mass range calibration is not available before the standard is run.

The concentration of the ICP-MS standard is 10 ng/ml, and it is used also as a quantification standard.

Results and Discussion

Determination of the Formation Rates

The formation rates for polyatomic species were calculated for each Pu isotope, except for ^{238}Pu, and for each element investigated: Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, and Bi (Table 2). It would be more accurate to calculate the rate of formation of certain PIs for every separate isotope of HM participating in PI production. For example, if only ^{204}Pb was participating in the production of PI interfering with ^{241}Pu, forming, for example, only $^{204}Pb^{37}Cl$, then we could calculate the rate of production of this PI relative to the number of ^{204}Pb atoms in the solution. There are, however, other PIs for ^{241}Pu can be formed from other isotopes of Pb, like $^{208}PbO_2H$ or $^{206}Pb^{35}Cl$. Therefore, because in most cases it is impossible to establish which isotope is participating in the formation of one or another polyatomic species, the formation rates were calculated by taking into account all of the atoms of all isotopes of specific metals. Positive identification of each PI was beyond the scope and capabilities of this research, but we included the formulas of the most likely formed PIs molecules in the table. The formulas in bold font are taken from [1]; those in italics were calculated using the ICP Interference Determination Utility (NU Instruments Ltd).

Also, we have found it convenient to have the rate of PIs formation expressed in terms of concentrations, showing what concentration of "Pu" or "False Pu" (in fg/ml) is formed relative to the concentration of certain HMs (expressed in ng/ml). Expressed in this way, the rate can be used when we perform elemental analyses of our sample solution and get the concentrations of HM in ng/ml. Then one can easily estimate quantitatively how much the presence of HMs affects the results for the concentration of a certain isotope of Pu.

The errors of the calculated formation rates were relatively high, because most of the measured responses were in the region of 10^{-10} to 10^{-8} V (0.01−2 cps). They ranged from 5-10% for the formation rates in the 10^{-8} V region and up to 30−40% for the rates in the 10^{-10} V region. High precision is not critical in this research, because, as mentioned before [6], these formation rates are changed by orders of magnitude depending on the sample content and analytical conditions of the experiments.

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Table 2. The rates of PIs formation.

	Hafnium	Form. Rate	"Pu"/Hf, fg/ng	Tantalum	Form. Rate	"Pu"/Ta, fg/ng
239	$^{177}Hf^{14}N^{16}O_3$; $^{176}Hf^{14}N^{16}O_3H$	3.9×10^{-10}	5.3×10^{-4}	$^{181}Ta^{40}Ar^{18}O$	3.1×10^{-10}	4.1×10^{-4}
240	$^{178}Hf^{14}N^{16}O_3$; $^{177}Hf^{14}N^{16}O_3H$	2.8×10^{-10}	3.8×10^{-4}	$^{181}Ta^{40}Ar^{19}F$	4.9×10^{-10}	6.5×10^{-4}
241	$^{179}Hf^{14}N^{16}O_3$; $^{178}Hf^{14}N^{16}O_3H$	8.9×10^{-11}	1.2×10^{-4}	$^{181}Ta^{37}Cl^{23}Na$	1.1×10^{-11}	1.4×10^{-5}
242	$^{180}Hf^{14}N^{16}O_3$; $^{179}Hf^{14}N^{16}O_3H$	4.4×10^{-12}	5.9×10^{-6}			
244	$^{174}Hf^{35}Cl_2$	4.4×10^{-10}	5.9×10^{-4}	$^{181}TaNO_3H$	8.2×10^{-12}	1.1×10^{-5}

	Tungsten	Form. Rate	"Pu"/W, fg/ng	Rhenium	Form. Rate	"Pu"/Re, fg/ng
239	$^{183}W^{40}Ar^{16}O$; $^{186}W^{40}Ar^{13}C$;	2.9×10^{-10}	3.8×10^{-4}	$^{181}Ta^{40}Ar^{18}O$	7.1×10^{-10}	9.1×10^{-4}
240	$^{184}W^{40}Ar^{16}O$; $^{186}W^{40}Ar^{14}N$	4.3×10^{-10}	5.5×10^{-4}	$^{181}Ta^{40}Ar^{19}F$	1.5×10^{-9}	1.9×10^{-3}
241	$^{186}W^{40}Ar^{15}N$	1.2×10^{-10}	1.6×10^{-4}	$^{181}Ta^{37}Cl^{23}Na$	1.1×10^{-10}	1.4×10^{-4}
242	$^{186}W^{40}Ar^{16}O$	7.2×10^{-11}	9.4×10^{-5}			
244	$^{182}W^{14}N^{16}O_3$	3.3×10^{-10}	4.2×10^{-4}	$^{181}TaNO_3H$		

	Osmium	Form. Rate	"Pu"/Os, fg/ng	Iridium	Form. Rate	"Pu"/Ir, fg/ng
239	$^{186}Os^{35}Cl^{18}O$; $^{184}Os^{37}Cl^{18}O$	2.3×10^{-8}	2.9×10^{-2}	$^{191}Ir^{16}O_3$; $^{193}Ir^{14}N^{16}O_2$	3.3×10^{-8}	4.1×10^{-2}
240	$^{188}Os^{40}Ar^{12}C$; $^{188}Os^{36}Ar^{16}O$	4.7×10^{-6}	5.9×10^{1}	$^{191}Ir^{16}O_3{}^{1}H$; $^{193}Ir^{14}N^{16}O_2{}^{1}H$	2.3×10^{-9}	3.0×10^{-3}
241	$^{189}Os^{40}Ar^{12}C$; $^{192}Os^{37}Cl^{12}C$	1.7×10^{-8}	2.1×10^{-2}	$^{193}Ir^{16}O_3$;	6.0×10^{-8}	7.4×10^{-2}
242	$^{190}Os^{40}Ar^{12}C$; $^{186}Os^{40}Ar^{16}O$	3.0×10^{-8}	3.8×10^{-2}	$^{193}Ir^{16}O_3{}^{1}H$;	1.7×10^{-8}	2.1×10^{-2}
244	$^{192}Os^{40}Ar^{12}C$; $^{188}Os^{40}Ar^{16}O$	3.3×10^{-10}	4.2×10^{-4}	$^{193}Ir^{35}Cl^{16}O$; $^{191}Ir^{37}Cl^{16}O$	3.5×10^{-8}	4.3×10^{-2}

	Platinum	Form. Rate	"Pu"/Pt, fg/ng	Gold	Form. Rate	"Pu"/Au, fg/ng
239	$^{198}Pt^{40}Ar^{1}H$	3.1×10^{-11}	3.9×10^{-5}	$^{197}Au^{40}Ar^{2}H$	1.2×10^{-10}	1.4×10^{-4}
240	$^{194}Pt^{14}N^{16}O_2$	5.7×10^{-11}	7.0×10^{-5}		0	0
241	$^{195}Pt^{14}N^{16}O_2$; $^{194}Pt^{14}N^{16}O_2{}^{1}H$	1.5×10^{-10}	1.8×10^{-4}		0	0
242	$^{195}Pt^{14}N^{16}O_2{}^{1}H$; $^{196}Pt^{14}N^{16}O_2$; $^{194}Pt^{16}O_3$	1.2×10^{-10}	1.5×10^{-4}		0	0
244	$^{198}Pt^{14}N^{16}O_2$; $^{198}Pt^{16}O_3$; $^{195}Pt^{16}O_3{}^{1}H$	7.4×10^{-11}	9.0×10^{-5}	$^{197}AuNO_2H$;	3.2×10^{-11}	3.9×10^{-5}

	Mercury	Form. Rate	"Pu"/Hg, fg/ng	Thallium	Form. Rate	"Pu"/Tl, fg/ng
239	$^{199}Hg^{40}Ar$; $^{201}Hg^{38}Ar$	1.8×10^{-9}	2.1×10^{-3}	$^{203}Tl^{36}Ar$;	7.7×10^{-9}	9.0×10^{-3}
240	$^{200}Hg^{40}Ar$; $^{202}Hg^{38}Ar$	1.7×10^{-9}	2.0×10^{-3}	$^{203}Tl^{37}Cl$; $^{205}Tl^{35}Cl$	1.2×10^{-8}	1.5×10^{-2}
241	$^{201}Hg^{40}Ar$; $^{204}Hg^{37}Cl$	1.9×10^{-9}	2.1×10^{-3}	$^{205}Tl^{36}Ar$;	2.6×10^{-8}	3.1×10^{-2}
242	$^{202}Hg^{40}Ar$	2.3×10^{-9}	2.7×10^{-3}	$^{205}Tl^{37}Cl$	2.3×10^{-9}	2.7×10^{-3}
244	$^{204}Hg^{40}Ar$; $^{198}HgNO_2$	3.4×10^{-10}	4.1×10^{-4}	$^{203}Tl^{40}Ar^{1}H$	5.2×10^{-10}	6.1×10^{-4}

	Lead	Form. Rate	"Pu"/Pb, fg/ng	Bismuth	Form. Rate	"Pu"/Bi, fg/ng
239	$^{208}PbNOH$; $^{207}PbO_2$; $^{204}Pb^{35}Cl$	3.8×10^{-10}	4.4×10^{-4}	$^{209}Bi^{14}N^{16}O$	3.0×10^{-10}	3.3×10^{-4}
240	$^{207}PbO_2H$; $^{208}PbO_2$; $^{204}Pb^{36}Ar$	3.1×10^{-8}	3.5×10^{-2}	$^{209}Bi^{14}N^{16}OH$	3.3×10^{-8}	3.7×10^{-2}
241	$^{208}PbO_2H$; $^{206}Pb^{35}Cl$; $^{204}Pb^{37}Cl$	6.2×10^{-9}	7.2×10^{-3}	$^{209}Bi^{16}O_2$	4.2×10^{-9}	4.8×10^{-3}
242	$^{207}Pb^{35}Cl$; $^{206}Pb^{36}Ar$	1.3×10^{-8}	1.5×10^{-2}	$^{209}Bi^{16}O_2H$	2.5×10^{-10}	2.9×10^{-4}
244	$^{207}Pb^{37}Cl$; $^{204}Pb^{40}Ar$; $^{208}Pb^{36}Ar$	1.7×10^{-7}	2.0×10^{-1}	$^{209}Bi^{35}Cl$	6.3×10^{-9}	7.2×10^{-3}

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As one can see, most of the formation rates are in the region of 10^{-09} and below. In most of the IAEA samples it is unlikely to have concentrations of HMs that are high enough to have a noticeable effect on the Pu measurement. The most serious concerns are the rates in the region of 10^{-8} and higher. The highest production rates observed are for Os ("^{240}Pu"), which is 4.69×10^{-6}, and for Pb ("^{244}Pu"), which is 1.71×10^{-7}. Os is a very rare element and does not occur in high concentrations in Pu samples.

Pb is much more common, but ^{244}Pu usually presents in the samples as a tracer in relatively high concentrations (in the pg/ml region). As such, Pb does not have much effect on ^{244}Pu at such concentration levels. However, in our method, where we analyze tracered and non-tracered fractions, we also can analyze the ratio ^{239}Pu/^{244}Pu in non-tracered fractions and in this case Pb can have some effect on the results. The presence of ^{244}Pu is relatively rare in the samples normally analyzed for the IAEA. It appears that if false ^{244}Pu is present in the blanks, there is a high probability that they are contaminated with Pb.

It is not a simple task to compare the formation rates reported previously [1, 6] with our data. First of all, they were obtained under different analytical conditions, most notably, in the absence of a DSN. Second, they were calculated for separate HE isotopes and single PIs, although, as can be seen in Table 2, there are numerous combinations of isotopes of HEs participating in the formation of PIs and multiple variants of PI molecules formation. More likely, some of them were left out of the scope of our table.

It was found in [6] that for PIs at mass 239 the highest rates were observed for $ArHg^+$, IrO_3^+, and PbO_2^+. To be able to compare our results with those previously reported, we have to recalculate them, based on the assumption that they are produced by one isotope of a HE. If we recalculate our formation rates in Table 2, suggesting that there is only ^{199}Hg^{40}Ar and no ^{201}Hg^{38}Ar (which is relatively low anyway), and also that we have only ^{191}Ir^{16}O$_3$, there is no ^{193}Ir^{14}N^{16}O$_2$, and there is only ^{207}PbO$_2$ and no ^{204}Pb^{35}Cl and ^{208}PbNOH, then we come to Table 3 for comparison.

Scanning IAEA Samples for HMs and Calculation of PIs.

Several IAEA samples were scanned for the presence of HEs. In all of the samples most HEs were present in concentrations below or close to the detection limit, which varies for different metals from 3 to 10 pg/ml. Rhenium and bismuth were present in concentrations higher than other HEs and for them PIs were calculated based on their concentrations and formation rates

listed in Table 2. The results of those calculations are reported in Table 4 and Table 5.

Table 3. Comparison of formation rates.

	239, Formation Rate		
	^{199}Hg^{40}Ar	^{191}Ir^{16}O$_3$	^{207}Pb^{16}O$_2$
This research	1.1×10^{-8}	8.9×10^{-8}	1.7×10^{-9}
Pointurier at al [1]	6.0×10^{-6}	3.1×10^{-6}	2.2×10^{-8}
Pointurier at al [6]	$8.0 \times 1^{-6} - 7.0 \times 10^{-5}$	$1.0 \times 10^{-7} - 6.0 \times 10^{-6}$	$1.0 \times 10^{-9} - 5.0 \times 10^{-7}$
Magara et al [17]			3.0×10^{-8}

Notes: In [6] the data are taken from the chart with multiple points.
In [1] the rate for PbO$_2$ is given as for ^{208}Pb^{16}O$_2$, which is an obvious misprint.
The ion 239 is produced by ^{207}Pb^{16}O$_2$.

The instrumental detection limit for all Pu isotopes, determined as three times the standard error during the measurement of the blanks, varies from day to day, depending on the condition of the instrument, and generally was between 1.0×10^{-2} and 2.0×10^{-2} fg/ml. As can be seen in Table 5, only in one sample (23129-19-03) there was the PI in concentration close to the detection limit for ^{240}Pu and ^{241}Pu.

Conclusions

Our experiments demonstrate that the implementation of a DSN significantly reduces the formation of molecular ions of HEs interfering with the measurements of Pu. Although some of the formation rates derived from this research are not far from previously reported data, especially for Pb [1, 6, 17], in general they are significantly lower (by 2 to 3 orders of magnitude) for some elements, especially for Hg. One of the reason for lower formation rates in "dry plasma" might be relatively low abundance of ions H^+ and OH^- compare to "wet plasma".

The scanning of selected IAEA samples shows that the concentrations of HEs are, for the most part, far from being able to affect the Pu isotopic ratios measurements.

It appears that the sample preparation method used in our laboratory is sufficiently effective in removing HEs from the Pu fraction of the sample. Nevertheless, unlike the authors of [18] we think it is not enough just to suggest that the preparation method is 100% sufficient to remove all HEs from the samples. Breakthrough of HEs can happen in every sample preparation technique, so conducting elemental analyses of samples is necessary on a regular basis.

The measured formation rates of PIs allows for estimation of the contribution of PIs in the resulting Pu measurements and

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Table 4. Calculated PIs, caused by the presence of rhenium, in selected IAEA samples.

Sample	"239Pu", fg/mL		"240Pu", fg/mL	"241Pu", fg/mL	"242Pu", fg/mL	"244Pu", fg/mL
	Re, ng/ml	Re PI	Re PI	Re PI	Re PI	Re PI
Prep. Blank-1	9.4×10^{-2}	8.6×10^{-5}	1.8×10^{-4}	1.3×10^{-5}	NA	NA
Prep. Blank-2	1.0×10^{-1}	9.2×10^{-5}	1.9×10^{-4}	1.4×10^{-5}	NA	NA
Swipe Blank-1	6.0×10^{-2}	5.4×10^{-5}	1.1×10^{-4}	8.4×10^{-6}	NA	NA
Swipe Blank-2	2.1×10^{-2}	1.9×10^{-5}	3.9×10^{-5}	2.9×10^{-6}	NA	NA
23074-21-02	1.5×10^{-2}	1.3×10^{-5}	2.7×10^{-5}	2.0×10^{-6}	NA	NA
23084-15-02	$<5.0 \times 10^{-3}$	NA	NA	NA	NA	NA
23084-16-02	$<5.0 \times 10^{-3}$	NA	NA	NA	NA	NA
23087-19-02	$<5.0 \times 10^{-3}$	NA	NA	NA	NA	NA
23088-13-02	$<5.0 \times 10^{-3}$	NA	NA	NA	NA	NA
20057-02-04	1.4×10^{-1}	1.3×10^{-4}	2.6×10^{-4}	1.9×10^{-5}	NA	NA
20057-07-04	1.9×10^{-2}	1.7×10^{-5}	3.6×10^{-5}	2.7×10^{-6}	NA	NA
23129-19-03	2.3×10^{-1}	2.1×10^{-4}	4.3×10^{-4}	3.2×10^{-5}	NA	NA
23129-18-03	$<5.0 \times 10^{-3}$	NA	NA	NA	NA	NA

Table 5. Calculated PIs, caused by the presence of bismuth, in selected IAEA samples.

Sample	"239Pu", fg/mL		"240Pu", fg/mL	"241Pu", fg/mL	"242Pu", fg/mL	"244Pu", fg/mL
	Bi, ng/ml	Bi PI	Bi PI	Bi PI	Bi PI	Bi PI
Prep. Blank-1	7.7×10^{-2}	2.6×10^{-5}	2.9×10^{-3}	2.9×10^{-3}	2.2×10^{-5}	5.5×10^{-4}
Prep. Blank-2	6.3×10^{-2}	2.1×10^{-5}	2.4×10^{-3}	2.4×10^{-3}	1.8×10^{-5}	4.5×10^{-4}
Swipe Blank-1	2.6×10^{-2}	8.5×10^{-6}	9.5×10^{-4}	9.5×10^{-4}	7.3×10^{-6}	1.8×10^{-4}
Swipe Blank-2	4.0×10^{-2}	1.3×10^{-5}	1.5×10^{-3}	1.5×10^{-3}	1.1×10^{-5}	2.9×10^{-4}
23074-21-02	7.5×10^{-3}	2.5×10^{-6}	2.8×10^{-4}	2.8×10^{-4}	2.1×10^{-6}	5.4×10^{-5}
23084-15-02	ND	NA	NA	NA	NA	NA
23084-16-02	ND	NA	NA	NA	NA	NA
23087-19-02	ND	NA	NA	NA	NA	NA
23088-13-02	2.4×10^{-2}	8.0×10^{-6}	9.0×10^{-4}	9.0×10^{-4}	6.8×10^{-6}	1.7×10^{-4}
20057-02-04	2.2×10^{-1}	7.3×10^{-5}	8.2×10^{-3}	8.2×10^{-3}	6.3×10^{-5}	1.6×10^{-3}
20057-07-04	1.9×10^{-1}	6.4×10^{-5}	7.2×10^{-3}	7.2×10^{-3}	5.5×10^{-5}	1.4×10^{-4}
23129-19-03	5.7×10^{-1}	1.9×10^{-4}	2.1×10^{-2}	2.1×10^{-2}	1.6×10^{-4}	4.1×10^{-3}
23129-18-03	3.2×10^{-1}	NA	NA	NA	NA	NA

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potentially for correction of results, when the concentrations of HE are determined. Such an approach was used in [1].

Although we think that such approach is acceptable, we consider it somewhat impractical and the same author in [6] to some degree agrees with that assessment.

In [9] it was suggested that the higher resolution of a MS (up to 4000) can be used to separate ^{239}Pu from PIs such as PbO_2^+, IrO_3^+, and $HgAr^+$. We do not find it practical to use higher resolution to limit the impact of PI on Pu measurements, because 1) three above-mentioned PIs are not only PIs for ^{239}Pu; 2) there are many other PIs for minor isotopes of Pu, such as ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu; and 3) it is impossible to separate all Pu isotopes from all possible PIs just increasing the resolution 4-5 times. Furthermore, increasing the resolution means loss of sensitivity, which cannot be afforded, because the concentration of minor isotopes of Pu, such as ^{241}Pu and ^{242}Pu is very often close to the instrument detection limit. As mentioned before, the PI formation rates are subject to change depending on the current condition of the plasma and sample introduction system of the instrument, therefore the corrections of the results made after the analyses, based on previously measured rates, can lead to more significant errors than the errors introduced by PIs. Nevertheless, the knowledge of the rates and of the HE presence in the samples, gives better understanding of the analytical problems encountered in the process of Pu analyses and might lead to making the necessary corrections of the method overall and in the sample preparation, in particular.

Acknowledgements

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