Accurate Determination of Plutonium in Soil by Tandem Quadrupole ICP-MS with Different Sample Preparation Methods

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ABSTRACT: In this work, three commonly used digestion techniques, such as acid leaching with 8 M HNO₃, *aqua regia* and lithium metaborate fusion, were employed to extract Pu from different types of soil samples widely found across China, and to establish the influence of the major interference elements (U, Hg, Pb, Tl, and Bi) on the accurate measurement of Pu by tandem quadrupole ICP-MS. The three sample digestion techniques yielded good results for the analysis of Pu isotopes originating from global atmospheric fallout. The U and Pb contributions to $m/z=239$ (2.38 and 0.3 cps) in samples digested by the fusion method using AGMP-1M resin were higher than those digested by the acid leaching methods (0.55 cps for U and < 0.03 cps for Pb), which implies that additional purification with TEVA resin would be required for low-level Pu determination in soil samples. By taking advantage of tandem quadrupole ICP-MS in the NH₃/He mode, the count rates of Hg, Tl and Bi at $m/z=239$ (<0.01 cps) in the samples purified by using AGMP-1M resin and/or TEVA resin were found to be negligible for the different sample digestion methods.

INTRODUCTION

Plutonium (Pu) isotopes, especially ²³⁹Pu and ²⁴⁰Pu with half-lives of 24,110 years and 6561 years, respectively, are among the most important and dangerous transuranic nuclides in the environment due to their high radiotoxicity and long retention time in the environment. Pu is released to the environment mainly through atmospheric nuclear weapons testing, nuclear accidents and from nuclear fuel reprocessing plants. The ²⁴⁰Pu/²³⁹Pu atomic ratios carry an important signature to reflect the specific source of Pu because their ratios vary with different reactor types, weapon types, and weapon yield etc. The ²⁴⁰Pu/²³⁹Pu atomic ratio of global fallout is 0.180,^{1,2} which is lower than from the Chernobyl nuclear accident (0.386-0.408),³ the Fukushima nuclear accident (0.303-0.330)^{4,5} and the Pacific Proving Grounds (0.21-0.36),^{6,7} but is obviously higher than that from the Semipalatinsk nuclear test site (0.025-0.072).^{8,9} Thus, the accurate determination of ²³⁹Pu and ²⁴⁰Pu is critical for identification of their source term and their environmental studying, such as environmental risk assessment,¹⁰

their migration behavior related to nuclear activities and waste repository,¹¹ the evaluation of soil erosion,¹² and the chronology by identifying their accumulative peak.¹³

The mass spectrometry techniques, including accelerator mass spectrometry (AMS),¹⁴ inductively coupled plasma mass spectrometry (ICP-MS),^{15,16} thermal ionization mass spectrometry (TIMS)¹⁷ and resonance ionization mass spectrometry (RIMS),¹⁸ offer sufficient detection limits and enable the accurate determination of Pu isotopes in low-level environmental samples. However, the AMS, TIMS and RIMS techniques are limited for routine analysis of Pu because of their lower availability in the laboratory due to higher costs. Alternatively, ICP-MS has been widely applied for the determination of Pu in low-level environmental samples with the advantages of short analysis time, high sample throughput and analytical sensitivity, relatively easy operation as well as lower instrument cost.

Despite the remarkable advantages of ICP-MS, the accurate determination of Pu is still hampered by isobaric, polyatomic and molecular interferences. For the determination of ^{239}Pu and ^{240}Pu , possible interfering polyatomic ions in the mass-to-charge ratios (m/z) of the 239 and 240 region are usually formed in the plasma by a combination of interference elements (*e.g.*, Bi, Pb, Tl, Hg, U) in the sample solution and gaseous elements (*e.g.* H, O, S, Cl, and Ar).^{16,19-22} Moreover, the neighboring spectral interference of ^{238}U at $m/z=239$, whose concentration is usually several orders of magnitude higher than that of ^{239}Pu , is one of the major challenges for the accurate measurement of Pu isotopes in environmental samples. In this case, these interferences must be separated from Pu by chemical separation prior to ICP-MS measurement.

Before chemical separation, Pu should be released from the solid sample matrices into the solution. The acid digestion and fusion methods have been widely applied to dissolve Pu from soil samples. Concentrated HNO_3 ,^{16,23} 8 M HNO_3 ²⁴⁻²⁶ or *aqua regia*^{15,27,28} have generally been employed for sample digestion with heating. However, the refractory Pu materials (*e.g.*, high-fired oxides) in some special samples affected directly by nuclear activities may not be fully dissolved by acid leaching, which would lead to underestimation of the analytical results. To avoid this problem, fusion methods, including alkali fusion and lithium metaborate fusion, have been developed for the complete dissolution of insoluble/refractory actinides.²⁹⁻³¹ Although the

fusion methods are the most effective methods for the digestion of solid samples containing refractory plutonium, a notable drawback is that all the interfering elements and sample matrices may also be decomposed and released into the solution, causing difficulty in the subsequent separation steps and leading to unreliable chemical recovery.³⁰ Thus, the interferences associated with different sample digestion techniques in the chemical separation steps need to be identified.

Although some reference materials,³²⁻³⁶ including IAEA-135, IAEA-300, IAEA-312, IAEA-367, IAEA-384, IAEA-385, IAEA-410, IAEA-412 and NIST-SRM-4353A, are commonly used for Pu analysis in environmental samples, these reference materials are stream sediments, rocky flat soil samples and soil samples collected from the marine coast and might not be the best representative of complicated environmental soil matrices, especially surface soils from inland regions. Thus, this work aims to (a) examine different sample digestion techniques and their influence on the Pu measurement in various types of soil samples widely found across China, and (b) to investigate the major interfering elements from different chemical separation steps, including acid leaching, pre-concentration of Pu by co-precipitation, purification by anion exchange chromatography and extraction chromatography, as well as tandem quadrupole ICP-MS measurement.

Fig. 1 Schematic diagram of the chemical procedure for separating plutonium by acid digestion and lithium metaborate fusion.

EXPERIMENTAL

Reagents, standards and samples. The radioisotope standard solutions of ^{242}Pu (NIST 4343I) were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). A stock solution of uranium standard (1 mg/mL in 2% HNO_3) was from SPEX CertiPrep (USA). Microporous anion exchange resin AGMP-1M (100–200 mesh of particle size) in chloride form and extraction chromatographic resin TEVA (100–150 μm of particle size) were from Bio-Rad Laboratories Inc. (USA) and TRISKEM International (France), respectively. High purity lithium metaborate (99.9%) and lithium iodide (99.0%) were purchased from the China Lithium Industrial Co., Ltd. (Shanghai, P.R. China). Other reagents, including HNO_3 , HCl , HF , NaOH , NH_4OH , $\text{Na}_2\text{S}_2\text{O}_8$ and NaNO_2 used in this work, were of analytical grade. All solutions were prepared using deionized water with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$, produced with a Milli-Q reference water purification system (USA).

Thirteen surface soil samples, including cultivated loessial soil, red earth, brown earth, fluvo-aquic soil, black soil, coastal solonchak and kastanozem, were collected in China (Table S1). After removal of the small stones and roots from the vegetation, all soil samples were air-dried, ground and sieved through a 200-mesh sieve.

Sample digestion and chemical separation. In this work, the three common sample digestion techniques of 8 M HNO_3 , *aqua regia* and lithium metaborate fusion were used to assess their influence on the chemical separation procedures and the Pu measurement by ICP-MS. The detailed analytical procedures are reported elsewhere.^{13,15,29} Fig. 1 shows the chemical procedure for separating Pu in a soil sample by acid digestion and lithium metaborate fusion. For acid digestion, 10 g of soil sample was first ashed at 450 °C overnight to decompose the organic matter prior to chemical separation. For the leaching method using 8 M HNO_3 , 200 mL of 8 M HNO_3 and 2 mBq of ^{242}Pu tracer were added to the soil sample, which was leached for 0.5 h at 150 °C and then for 3.5 h at 200 °C on a hot plate. For the leaching method using *aqua regia*, after spiking 2 mBq of ^{242}Pu , 10 g of soil sample was leached with 100 mL of *aqua regia* for 0.5 h at 150 °C and then for 2 h at 200 °C on a hot plate. For lithium metaborate fusion, the sample, consisting of lithium metaborate, lithium iodide and sodium persulfate with a mass ratio of 1:1:0.2:0.2, was mixed well in a 150-mL high-purity graphite crucible. After spiking 2 mBq of ^{242}Pu , the sample was first dried at 100 °C for 1 h, combusted at 650 °C for 1 h, and then fused at 1000 °C for 30 min in a muffle furnace. After cooling to room temperature, a glassy fusion button formed in the crucible, which was dissolved in approximately 200 mL of mixed acids (6 M HCl and 4 M HNO_3) at 150 °C on a hot plate in a 250-mL beaker. Then, 5 g of polyethyleneglycol-6000 (PEG-6000) was added to flocculate and remove the gelatinous silica precipitate while

stirring.

After sample dissolution, the Pu in the acid solution was separated from the sample matrix by co-precipitation with hydrous titanium oxide (HTiO , $\sim 60\text{ mg}$ of Ti^{4+}) using concentrated NH_4OH to neutralize the solution (pH 7–8). After centrifugation, the precipitate was washed with 6 M NaOH and deionized water. The precipitate was subsequently dissolved in a few milliliters of concentrated HNO_3 . Then, 1 mL of fresh 3 M NaNO_2 was added for valence adjustment of Pu prior to chromatographic separation.

For the separation of Pu using AGMP-1M anion exchange resin, the sample solution was prepared in 8 M HNO_3 medium and loaded to an AGMP-1M resin column (2 g of the resin packed in a plastic column of 8 mm in diameter and 110 mm in height). After successively rinsing the column with 60–100 mL of 8 M HNO_3 and 40 mL of concentrated HCl , Pu was eluted with 30 mL of 0.2 M HNO_3 +0.05 M HF . For purification of Pu with TEVA extraction chromatography resin, the sample solution was prepared in 8 M HNO_3 medium and loaded to a small TEVA resin column (0.2 g of the resin packed in a column of 2 mm in diameter and 50 mm in height). After rinsing the column with 20 mL of 8 M HNO_3 and 10 mL of concentrated HCl , Pu was eluted with 5–10 mL of 0.1 M HCl +0.05 M HF . The final eluate was carefully evaporated to near dryness on a hot plate, and the residue finally dissolved in 3.5 mL of 0.5 M HNO_3 for ICP-MS measurement.

ICP-MS measurement. An Agilent 8800 ICP-MS with an octopole collision/reaction cell situated between two quadrupole mass filters (Q1 and Q2)³⁷ was used to determine the Pu isotopes in the NH_3/He mode (the optimized instrumental parameters are given in Table S3). The contribution of U at $m/z=239$ by tailing of $^{238}\text{U}^+$ and $^{238}\text{U}^1\text{H}^+$ was estimated to be less than 5×10^{-5} . An aliquot of 3.5 mL in 0.5 M HNO_3 containing 1 $\mu\text{g/L}$ of ^{115}In (in the form of InCl_3) as the internal standard was measured. The estimated detection limits were 0.55 fg/mL (1.26 $\mu\text{Bq/mL}$) for ^{239}Pu and 0.09 fg/mL (0.76 $\mu\text{Bq/mL}$) for ^{240}Pu , respectively.¹⁵ No memory effects were observed in the consecutive measurement of samples with different Pu levels after washing with 0.5 M HNO_3 solution.

The major interfering elements (including Bi, Pb, Tl, Hg, U) of samples S-1, S-2 and S-3 and the procedural blanks were measured by tandem quadrupole ICP-MS with He collision gas in order to determine the decontamination factor in each of the chemical separation steps, including acid leaching, co-precipitation, and column chromatography using AGMP-1M resin and TEVA resin.

The acid solutions of the samples S-1, S-2 and S-3 digested by lithium metaborate fusion were used for the determination of main composition. It is noted that PEG-6000 wasn't added to those acid solutions. The main chemical composition, including the determination of Th, Hg, Zn, Fe, U, Pb, Bi, Tl, Ca, and Mg, was obtained by ICP-MS (X-series II, Thermo Scientific, USA). The results are shown in Table S2.

Fig. 2 Comparison of concentrations and atomic ratios of plutonium isotopes by different digestion techniques in various types of samples. The horizontal dashed line indicates the average global fallout $^{240}\text{Pu}/^{239}\text{Pu}$ ratio.

RESULTS AND DISCUSSION

Influence of the three digestion techniques on Pu measurement. The measurement results for the concentrations and atomic ratios of ^{239}Pu and ^{240}Pu in 13 surface soil samples widely found across China by three digestion techniques are shown in Fig. 2. Due to the limited experimental sample size, we reported on twelve, nine and nine out of thirteen samples for *aqua regia*, 8M HNO_3 and lithium metaborate fusion, respectively. It can be seen that the relative errors of samples measured by three different digestion methods were calculated to be less than 5%, indicating a good consistence between the analytical results for the Pu isotope concentrations and the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios for the various kinds of soil samples. The average $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios for surface soil samples ranged from 0.15 to 0.24, which were consistent with the typical global fallout value of 0.180 ± 0.014 in the Northern Hemisphere ($71\text{--}30^\circ\text{N}$)¹ within the statistical margin of error, indicating a predominant global atmospheric fallout source. This observation confirms that all three sample digestion techniques were suitable for the analysis of Pu isotopes originating from global atmospheric fallout.

Elimination of U interference. In general, the isobaric interferences by $^{238}\text{UH}^+$ and $^{238}\text{UH}_2^+$ at masses 239 and 240 and the spectral interference by the tailing of $^{238}\text{U}^+$ at mass 239 are the major challenges for the accurate measurement of Pu isotopes by ICP-MS.^{15, 21, 27} In this case, the separation of the Pu isotopes from U should be carefully checked prior to instrumental measurement. As it is known, the concentrations of Ca, Mg and Fe in IAEA

reference materials, which were stream sediment or soil samples collected from the marine coast, are two orders of magnitude higher than those in the soil samples (Table S2). Those reference materials were easily digested and might not be the best representative of complicated surface soils from inland regions. In the absence of appropriate reference materials of environmental soil samples for Pu isotopes, three representative samples of surface soils widely found across Northern China, including loessial soil sample (S-1), red soil (sample S-2) and brown earth (sample S-3), were recommended for comparison in the current work. The characteristics of the ^{238}U concentration in the samples S-1, S-2 and S-3 in each chemistry processing step for the different digestion techniques are compared in Fig. 3, and the results of the dissolution efficiencies and decontamination factors are presented in Table 1.

The total ^{238}U concentrations of samples S-1, S-2 and S-3 are, respectively, $1.46 \pm 0.05 \mu\text{g/g}$, $1.94 \pm 0.06 \mu\text{g/g}$ and $1.49 \pm 0.05 \mu\text{g/g}$ (Table S2). As shown in Fig. 2, the average concentrations of ^{238}U in the acid leaching step by 8 M HNO_3 and *aqua regia* after blank subtraction were 767 ng/g and 705 ng/g in S-1, 1100 ng/g and 1072 ng/g in S-2, and 815 ng/g and 757 ng/g in S-3, respectively. Meanwhile, the average concentrations of ^{238}U fused by lithium metaborate were 1459 ng/g in S-1, 1937 ng/g in S-2 and 1490 ng/g in S-3, which were 1.7–2.1 times as high as those by acid digestion. This suggests that only 48%–57% of uranium in the sample could be leached out by acid digestion, and the rest would remain in the sample residue (Table 1).

Fig. 3 Comparison of three digestion techniques (8 M HNO₃, *aqua regia* and lithium metaborate fusion) on the ²³⁸U concentrations in different chemistry processing steps for soil samples. The tandem quadrupole ICP-MS analyses were conducted in the He mode with a measurement uncertainty of <5%.

Table 1. Comparison for Dissolution Efficiencies and Decontamination Factors of ²³⁸U in Soil Samples by Different Digestion Techniques

Sample	Digestion technique	Dissolution efficiency	Decontamination factor		
			Precipitation	AGMP-1M	TEVA
S-1	8 M HNO ₃	52.6%	1.60	476	27.4
	<i>Aqua regia</i>	48.3%	1.16	369	27.8
	Lithium metaborate fusion	100%	7.63	68.6	33.6
S-2	8 M HNO ₃	56.8%	1.43	404	107
	<i>Aqua regia</i>	55.3%	1.33	609	68.1
	Lithium metaborate fusion	100%	9.35	31.2	74.8
S-3	8 M HNO ₃	54.7%	1.77	480	36.5
	<i>Aqua regia</i>	50.8%	1.19	386	85.7
	Lithium metaborate fusion	100%	9.11	41.7	49.3

The concentrations of ²³⁸U digested by 8M HNO₃ and *aqua regia* were 13%-38% less (decontamination factor of 1.16-1.77) in the co-precipitation step, possibly due to the formation of some soluble uranium complexes that would not co-precipitate with HTiO in the alkali solution (Fig. S1). Interestingly, the ²³⁸U decontamination factor was 8.70 for lithium metaborate fusion, indicating that up to 90% of U could be removed in this step. Except for the partial loss in the alkali solution, a fair amount of U loss (>50%) has likely occurred in the PEG-6000 step. PEG and its derivatives have been employed as nonionic surfactants for the solvent extraction of uranium.³⁸ Tests were conducted to check the extraction of U by PEG-6000 in simple matrices, such as for deionized water and 2 g of soil sample, where U was obviously not extracted. However, for the analysis of 10 g of soil sample, the matrix would be more complicated and contained notable amounts

of inorganic salts and silicates. Thus, more than 50% of U might be extracted by PEG-6000, which would then be removed by the precipitation of gelatinous silica in the flocculation step. In contrast, the extractability of Pu was measured to be only < 3.4%.

In the AGMP-1M separation step, the concentrations of ²³⁸U in the samples treated by 8M HNO₃ were 1.00 ng/g for sample S-1, 1.90 ng/g for sample S-2 and 0.96 ng/g for sample S-3, which were close to those of 1.65 ng/g, 1.33 ng/g and 1.64 ng/g for the corresponding samples digested by *aqua regia*, but approximately 3 times lower than those of 2.79 ng/g, 6.65 ng/g, 3.92 ng/g for the samples digested by lithium metaborate fusion. Compared to the fusion method, a large fraction of the residues still remained insoluble when the soil samples were leached with acids (73.7%-79.2% by 8M HNO₃ and 75.8-81.7% by *aqua regia*, respectively).

This suggested that only <30% of sample composition was transferred to the acid leaching solution. Thus, the low decontamination efficiency of ^{238}U in this step by lithium metaborate fusion could be attributed to the relatively high content of matrix,³⁸ as the soil samples were completely dissolved with the addition of a large number of salts.

In this work, low decontamination factors of ^{238}U by using a single anion exchange resin column were observed (7.11×10^2 for 8M HNO_3 , 5.65×10^2 for *aqua regia* and 3.98×10^2 for lithium metaborate fusion), which were about 10-100 times lower than the reported values using the extraction chromatography (TEVA) resin for 10 g of soil sample.⁴⁰ This indicates that an additional extraction chromatography step for the purification of Pu isotopes may be required in the analysis of low-level Pu samples. The chemical yield of Pu for 10 g of soil with a single TEVA resin column was found to be less than half of the yield obtained using a single anion exchange separation. Hence, the AGMP-1M resin was chosen for the primary separation stage of Pu separation from the sample matrix components, followed by further purification of Pu by extraction chromatography with TEVA resin. For different soil samples digested by acid leaching, the average concentrations of ^{238}U in the TEVA eluates were around 0.03 ng/g, which were very close to the procedural blanks (0.02 ng/g). Similar results were obtained for ^{238}U in the soil samples digested by lithium metaborate fusion, and the U concentrations in the TEVA eluates (0.09 ng/g) were close to the corresponding procedural blank (0.08 ng/g). The overall decontamination factors of ^{238}U were calculated to be $(2-4) \times 10^4$ for the three sample digestion methods. Moreover, the purification by using a small TEVA column could assist in the further concentration of Pu in the final eluate sample for ICP-MS measurement.

To further understand the extraction and elution behaviors of U on anion exchange and extraction chromatography resins and the U interference to ^{239}Pu , the ^{238}U and ^{239}Pu count rates in the eluates measured by tandem quadrupole ICP-MS in the NH_3/He mode are compared in Table 2. The abundance sensitivity of uranium to $m/z=239$, including the tailing of $^{238}\text{U}^+$ and the polyatomic

interference of $^{238}\text{U}^1\text{H}^+$ by tandem quadrupole ICP-MS, was estimated to be less than 5×10^{-5} .¹⁵ The average contribution of uranium at $m/z=239$ by using a single AGMP-1M column was calculated to be 0.55 cps for acid digestion and 2.38 cps for lithium metaborate fusion, which was 2-10 times as high as those of the blanks at $m/z=239$, and even much higher than the ^{239}Pu count rates for the low-level sample S-2. After the TEVA purification step, the interference count rates to $m/z=239$ for all three sample digestion techniques dropped to the blank level (0.2 cps) and would not contribute much to the ^{239}Pu measurement. Therefore, the TEVA purification step is preferred as it provides reliable analytical results, especially for the analysis of low-level Pu (i.e., < 0.01 mBq or 5 fg). Furthermore, a single AGMP-1M anion exchange purification may still be adequate for the determination of Pu isotopes in samples with relatively high Pu levels (i.e., > 0.02 mBq or 10 fg).

Elimination of Pb interference. Other potential interfering polyatomic ions at $m/z=239$, 240 and 242 could also be formed in the plasma by a combination of interference elements (e.g., Hg, Pb, Tl, Bi) in the sample solution with gaseous elements (e.g., O, S, Cl, Ar).³⁹ In this work, the interferences at 242 m/z were negligible since a sufficient amount of ^{242}Pu spike was added to overlook the error from these interferences. The total Hg concentrations of samples S-1, S-2 and S-3 ranged from 0.99 $\mu\text{g/g}$ to 1.21 $\mu\text{g/g}$ (Table S2). The count rates of Hg at m/z of 199, 200, 202, 204 in the NH_3/He mode were measured to be 0 cps, confirming a complete elimination of Hg via the reaction of Hg^+ with NH_3 . Thus, only the interferences of $^{206/207/208}\text{Pb}$, $^{203/205}\text{Tl}$ and ^{209}Bi in each chemistry step of the three samples by different digestion techniques are discussed below.

No obvious discrepancies of the Pb isotopes in the acid leaching step by two acid digestion methods can be found (Fig. S2). No significant change in the Pb count rates was observed in the coprecipitation step for the leaching solutions by acid digestion, whereas the Pb count rates by lithium metaborate fusion decreased up to 46%-72%. This might be explained by the removal of some gelatinous Pb precipitate in the PEG-6000 flocculation process.

Table 2. Comparison of ^{238}U and ^{239}Pu Count Rates of Three Sample Digestion Techniques in the NH_3/He Mode

Sample digestion method	Sample	^{238}U , cps		^{239}Pu , cps
		AGMP-1M	TEVA	
	Instrument blank	6.67		0.03
8M HNO_3	S-1	$(1.19 \pm 0.05) \times 10^4$	$(1.4 \pm 1.1) \times 10^3$	46.9 ± 2.9
	S-2	$(2.38 \pm 0.27) \times 10^4$	$(4.2 \pm 7.2) \times 10^2$	0.69 ± 0.12
	S-3	$(1.17 \pm 0.24) \times 10^4$	$(7.8 \pm 2.7) \times 10^2$	72.9 ± 1.2
	Blank	$(4.4 \pm 1.5) \times 10^2$	$(1.12 \pm 0.99) \times 10^3$	0.18 ± 0.03
Aqua regia	S-1	$(2.23 \pm 0.26) \times 10^4$	$(1.6 \pm 1.1) \times 10^3$	38.3 ± 1.3
	S-2	$(1.75 \pm 0.15) \times 10^4$	$(1.3 \pm 2.3) \times 10^2$	0.80 ± 0.22
	S-3	$(2.25 \pm 0.57) \times 10^4$	$(6.5 \pm 4.5) \times 10^2$	65.4 ± 1.4
	Blank	$(3.8 \pm 6.6) \times 10^2$	$(8.3 \pm 8.3) \times 10^2$	0.14 ± 0.05
Lithium metaborate fusion	S-1	$(4.9 \pm 2.1) \times 10^4$	$(2.0 \pm 1.2) \times 10^3$	20.4 ± 1.7
	S-2	$(1.24 \pm 0.35) \times 10^5$	$(1.8 \pm 1.5) \times 10^3$	0.67 ± 0.28
	S-3	$(6.5 \pm 1.3) \times 10^4$	$(4.8 \pm 1.0) \times 10^3$	28.8 ± 1.2
	Blank	$(6.0 \pm 3.5) \times 10^3$	$(1.77 \pm 0.44) \times 10^3$	0.25 ± 0.50

In the AGMP-1M column separation step, the Pb count rates in the samples leached out by acids were close to those of the procedural blanks, which were 10 to 100-fold lower compared with those achieved by lithium metaborate fusion. The higher Pb count rates observed for the fusion method were consistent with the increased level of the procedural blank in the anion exchange step. However, the contamination source of this Pb background increase remains unclear and needs to be addressed in a future study. Hou *et al.*⁴¹ reported that the contribution with a Pb isotope signal intensity of 10^8 cps to $m/z=239$ was less than 0.03 cps in 0.5 M HNO₃ media in the NH₃/He mode. Thus, the contribution of Pb to $m/z=239$ by the acid leaching methods was calculated to be < 0.03 cps after the anion exchange purification step, while the Pb contribution by the fusion method was approximately 0.3 cps. For low-level soil samples digested by the fusion method, a further elimination of Pb interference using a small extraction chromatography column may be required.

After the TEVA purification step, the Pb count rates in the soil samples digested by fusion were close to the procedural blanks. The overall decontamination factor for the fusion method was about 10^3 , which was similar to the acid digestion results. The contribution of Pb (10^7 cps) to $m/z=239$ was calculated to be less than 3×10^{-3} cps, thus completely negligible. The total Pb concentrations of samples S-1, S-2 and S-3 were, respectively, 39.1 ± 2.3 $\mu\text{g/g}$, 26.5 ± 2.1 $\mu\text{g/g}$ and 25.6 ± 2.1 $\mu\text{g/g}$ (Table S2). Assuming that the amount of soil sample is 10 g and the chemical yield is 70%, the concentration of Pb in the final solution (3.5 mL) could be approximately 0.01 $\mu\text{g/mL}$. Therefore, the Pb interference found at $m/z=239$ should be very minor and much less problematic than ^{238}U .

Elimination of Tl and Bi interference. The remarkable discrepancies of the Tl and Bi count rates by using different sample digestion techniques can be seen in Supplementary Fig. S3 and S4. In the acid leaching step, the Tl and Bi count rates by acid digestion were significantly higher than those achieved by lithium metaborate fusion. During the fusion, the Tl and Bi compounds (particularly the halogenated Tl species) could be quite volatile at high temperatures (1000 °C). Thus, due to the severe loss of volatile Tl and Bi during high temperature fusion, it seems to be reasonable that the count rates of Tl and Bi in the digested samples by the acid leaching methods were much higher than those by the fusion method. In the AGMP-1M resin separation step, the Tl and Bi count rates were approximately 10^7 - 10^8 cps. Since the contribution of approximately 10^8 cps of Tl isotopes was less than 0.01 cps to $m/z = 239$ in the NH₃/He mode,⁴¹ the Tl interferences at $m/z=239$ after purification by a single AGMP-1M column were calculated to be far less than 0.01 cps for the three sample digestion methods. Therefore, the Tl and Bi interferences to Pu isotopes are completely negligible after anion exchange purification using a single AGMP-1M column. With a further purification using the TEVA column, the Tl and Bi count rates decreased to approximately 10^5 cps, which led to a much smaller interference

at $m/z=239$ ($<10^{-4}$ cps). Those demonstrate that the Tl and Bi interferences found at m/z 239 would be much less a concern compared to ^{238}U .

CONCLUSIONS

A comprehensive study regarding the influence of three commonly used sample digestion techniques on the accurate measurement of plutonium isotopes was carried out. The three sample digestion techniques of 8 M HNO₃, *aqua regia* and lithium metaborate fusion were found to be well suitable for the analysis of Pu from global atmospheric fallout in various types of environmental soil samples. The dissolution efficiency and the decontamination factors of the major interfering elements (U, Pb, Hg, Tl, and Bi) in different chemical separation steps were measured by tandem quadrupole ICP-MS in the He mode. When 10 g of soil sample was digested by the fusion method, a sizable fraction of U (> 50%) and Pb (46%-72%) could be efficiently removed in the subsequent polyethylene glycol (PEG) flocculation step, while a minimal amount (<3.4%) of Pu was lost. However, after anion exchange separation using the AGMP-1M resin, the U and Pb contributions to m/z -239 (2.38 and 0.3 cps) in the samples digested by the fusion method were significantly higher than those digested by the acid leaching methods (0.55 cps for U and < 0.03 cps for Pb). Therefore, compared to acid leaching with 8M HNO₃ and *aqua regia*, the influence of U and Pb on the accurate measurement of Pu in the samples digested by lithium metaborate fusion by using a single AGMP-1M anion exchange resin should be considered. Taking advantage of tandem quadrupole ICP-MS in the NH₃/He mode, the influence of Hg, Tl and Bi in the samples purified by using the AGMP-1M resin column and/or the TEVA resin column would be negligible for all three sample digestion methods.

ASSOCIATED CONTENT

Please contact the corresponding author for the Supporting Information (Fig. S1, S2, S3, and S4; Table S1 and S2).

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Notes

The authors declare no competing financial interest.

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