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Determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) in environmental samples using radiochemical separation combined with radiometric and mass spectrometric measurements

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ABSTRACT

This paper reports an analytical method for the determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) in environmental samples using anion exchange chromatography in combination with extraction chromatography for chemical separation of Pu. Both radiometric methods (liquid scintillation counting and alpha spectrometry) and inductively coupled plasma mass spectrometry (ICP-MS) were applied for the measurement of plutonium isotopes. The decontamination factors for uranium were significantly improved up to 7.5×10^5 for 20 g soil compared to the level reported in the literature, this is critical for the measurement of plutonium isotopes using mass spectrometric technique. Although the chemical yield of Pu in the entire procedure is about 55%, the analytical results of IAEA soil 6 and IAEA-367 in this work are in a good agreement with the values reported in the literature or reference values, revealing that the developed method for plutonium determination in environmental samples is reliable. The measurement results of $^{239+240}$Pu by alpha spectrometry agreed very well with the sum of ^{239}Pu and ^{240}Pu measured by ICP-MS. ICP-MS can not only measure ^{239}Pu and ^{240}Pu separately but also ^{241}Pu. However, it is impossible to measure ^{238}Pu using ICP-MS in environmental samples even a decontamination factor as high as 10^6 for uranium was obtained by chemical separation.

1. Introduction

Plutonium has been deposited in the present environment as a result of global fallout and releases from other nuclear activities during the past 70 years [1]. Plutonium isotopes are regarded as not only radioactive pollutants from the viewpoints of radioecology and toxicology [2–5], but also useful tracers for better understanding of environmental processes owing to their high particle affinity [6,7]. The most interesting isotopes of plutonium in the environment are ^{238}Pu (87.7 yr), ^{239}Pu (24,110 yr), ^{240}Pu (6563 yr) and ^{241}Pu (14.4 yr), among which ^{239}Pu and ^{240}Pu are the most important ones due to their long half-lives and relatively high abundance. Besides, the atomic ratios of ^{240}Pu/^{239}Pu varying with release conditions of Pu and the type or design of the device can serve as a fingerprint for tracing the source of plutonium contamination [8].

Accurate and precise determination of plutonium isotopes is the foundation for their environmental studies because their radioactivity levels are extremely low in the environment. Except ^{241}Pu, all other mentioned isotopes of plutonium are alpha emitters without suitable γ- rays to be measured. Due to their distinct nuclear properties, different techniques have to be used for the measurement of these Pu isotopes. Radiometric methods used for Pu measurement are mainly liquid scintillation counting (LSC) and alpha spectrometry, although X-ray spectrometry has also been used for measuring Pu isotopes in high level samples or hot particles [9]. Liquid scintillation counting is often used to measure ^{241}Pu which is a low-energy beta emitter with maximum energy of 20.8 keV [1,8]. Alpha spectrometry is normally used for the determination of ^{238}Pu and $^{239+240}$Pu. Because this method is difficult to distinguish ^{240}Pu (5168 keV) from ^{239}Pu (5155 keV), the sum activity of ^{239}Pu and ^{240}Pu is normally measured [1,10]. In recent years, mass spectrometric methods including ICP-MS and accelerator mass spectrometry (AMS) have being rapidly developed for the determination of plutonium isotopes owing to their advantages like the rapidity of analysis, high sensitivity and the provision of isotopic information on ^{239}Pu and ^{240}Pu separately, etc. [1,10–15] However, it is still difficult to use the mass spectrometric methods for measuring ^{238}Pu in environmental

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samples because of serious isobaric interference from more abundant ^{238}U [1] and its low mass concentration.

For the determination of Pu isotopes using whatever the abovementioned detection techniques, a completed separation of Pu from matrix and other interfering radionuclides is needed. Qiao et al. [16] reported a separation method using sequential injection extraction chromatography coupled to ICP-MS for the determination of Pu isotopes in environmental samples, which could be applied to analyze up to 200 g Danish soil. However, the matrix composition in environmental samples collected from different places varies significantly. For example, when we analyzed some Chinese soil samples (10 g) using one 2-mL extraction chromatographic (TEVA) column, it was observed that due to the high content of matrix elements, the volume of sample solution after co-precipitation and valence adjustment was so large that Pu penetrated the TEVA column during the stage of sample loading, resulting in nearly complete loss of Pu in this process. This work aims to solve this problem by improving the analytical method applying co-precipitation, anion-exchange and extraction chromatography. Both radiometric methods (liquid scintillation counting and alpha spectrometry) and ICP-MS were applied for the measurement of all 4 Pu isotopes.

2. Experimental

2.1. Reagents and samples

All reagents including nitric acid (HNO_3), hydrochloric acid (HCl), ammonia ($NH_3 \cdot H_2O$), sodium hydroxide (NaOH), potassium disulfite ($K_2S_2O_5$), sodium nitrite ($NaNO_2$), ferric chloride ($FeCl_3 \cdot H_2O$), hydroxylammonium chloride ($NH_2OH \cdot HCl$), sulfuric acid (H_2S0_4) and methylblue used in the experiment were of analytical reagent grade. All solutions used in this work were prepared using high purity de-ionized water (18.2 MΩ cm, Sartorius Stedim Biotech, Aubagne Cedex, France).

The working solution of ^{242}Pu (0.1037 Bq g^{-1} in 2 mol L^{-1} HNO_3) was diluted from NBL-CRM 130 purchased from New Brunswick Laboratory (Argonne, IL). Uranium standard solution was purchased from NIST (Gaithersburg, MD). ^{3}H standard solutions (1.009 Bq g^{--1} for NIST-4361C and 5038 Bq g^{-1} for NIST-4926E) purchased from the National Institute of Standard and Technology (Gaithersburg, MD 20899, USA) were used as standard for ^{241}Pu measurement by LSC. The anion-exchange resin (Bio-Rad AG 1-×4, 50–100 mesh) was packed in an Econo-Column® (1 cm in diameter and 15 cm in length, Bio Rad Laboratories Inc.) and preconditioned with 8 mol L^{-1} HNO_3. For separation using extraction chromatography, TEVA resin (100–150 μm, TRISKEM International, Bruz, France) was swelled in de-ionized water and packed into an Econo-Column® with size of 0.7 cm in diameter and 5 cm in length and preconditioned with 1 mol L^{-1} HNO_3.

Information concerning the samples analyzed in this work is summarized in Table 1. An artificial sample (NPL inter-comparison sample B-2) containing certain amounts of ^{3}H, ^{90}Sr, ^{147}Pm and ^{241}Pu in 2 mol L^{-1} HNO_3 was used to investigate and compare ICP-MS and liquid scintillation counting (LSC) methods for the determination of ^{241}Pu. A Danish sediment collected from Rømø, Denmark in 2012 and a Chinese soil collected from northeast China in 2009 were used throughout for method development. Besides, two certified reference materials, IAEA-soil 6 (Austrian soil) and IAEA-367 (Marshal land ocean sediment) were also analyzed for validation of the methods. Two replicates were processed for each sample.

2.2. Sample preparation for Pu determination

For the analysis of soil and sediment, a known amount of sample (1–60 g, depending on the concentration level of plutonium) was first ashed at 550 °C overnight to decompose the organic matter. After spiked with a known amount of ^{242}Pu (30–60 mBq, depending on the sample amount) as a chemical yield tracer, the sample was leached with *aqua regia* on a hotplate at 150 °C for 30 min and then at 200 °C for 2 h to release plutonium into solution (to be mentioned that this method is suitable for normal environmental samples. For samples with refractory actinide fraction (e.g., hot particle), plutonium might not be completely dissolved by acid leaching and a total dissolution methods such as alkali fusion should be used). After being filtered through GF/A filter, plutonium in the leachate was co-precipitated with iron hydroxides by adding $NH_3 \cdot H_2O$, the precipitate was washed with 6 mol L^{-1} NaOH to remove major matrix components (e.g. Ca, Mg, Al, V, etc.). The obtained precipitate was dissolved with 1–5 mL of concentrated HCl, then 200–500 mg of $K_2S_2O_5$ was added to reduce the overall Pu to Pu(III), whereupon $NH_3 \cdot H_2O$ was added to adjust pH to 9–10. The precipitate thus obtained was dissolved with 3–5 mL of concentrated HCl and some volume of concentrated HNO_3, with the consequent oxidation of Pu(III)–Pu(IV) by NO_2^- in the HNO_3 solution. Then the sample solution was adjusted to 8 mol L^{-1} HNO_3 to be loaded to the preconditioned AG 1-×4 anion-exchange column. After rinsing the column with 8 mol L^{-1} HNO_3 and 9 mol L^{-1} HCl, respectively, to remove most uranium, thorium and matrix elements, Pu was eluted with 0.1 mol L^{-1} $NH_2OH \cdot HCl$ in 2 mol L^{-1} HCl. The separated Pu was further purified using a 2-mL TEVA column to get better decontamination of uranium. Prior to the TEVA column purification, Pu was co-precipitated with $Fe(OH)_2$ after adding 100 mg of Fe^{3+} ($FeCl_3$), then redox pair of $K_2S_2O_5$-$NaNO_2$ was used to adjust overall Pu to Pu(IV). The final sample solution prepared in 1 mol/L HNO_3 medium was loaded to a TEVA column. After rinsing with 1 mol L^{-1} HNO_3 and 6 mol L^{-1} HCl, Pu was finally eluted with 20 mL of 0.1 mol L^{-1} $NH_2OH \cdot HCl$ in 2 mol L^{-1} HCl. The eluate was evaporated to dryness on a hot-plate followed by adding few milliliter of concentrated nitric acid and heating under

Table 1
Information of the samples analyzed in this work.

Sample	Sample amount	Description	Sampling area/location
Artificial sample	~160 mL	Composition: ^{3}H, ^{90}Sr, ^{147}Pm, ^{241}Pu in 2 mol L^{-1} HNO_3	Inter-comparison sample B-2 prepared by NPL, 2012
Danish sediment	~30 g	Low-level environmental sediment	Mixed sediment from a sediment core collected in Rømø, Denmark, in 2012
Chinese soil	~60 g	Low-level environmental soil	The top 10 cm of 2 mm sieved soil from 2 soil cores collected from northeast China in 2009
IAEA-soil 6	~30 g	Low-level environmental soil	IAEA reference material, collected from Austria
IAEA-367	~1 g	Contaminated sediment	IAEA reference material, collected from Marshall land, ocean sediment

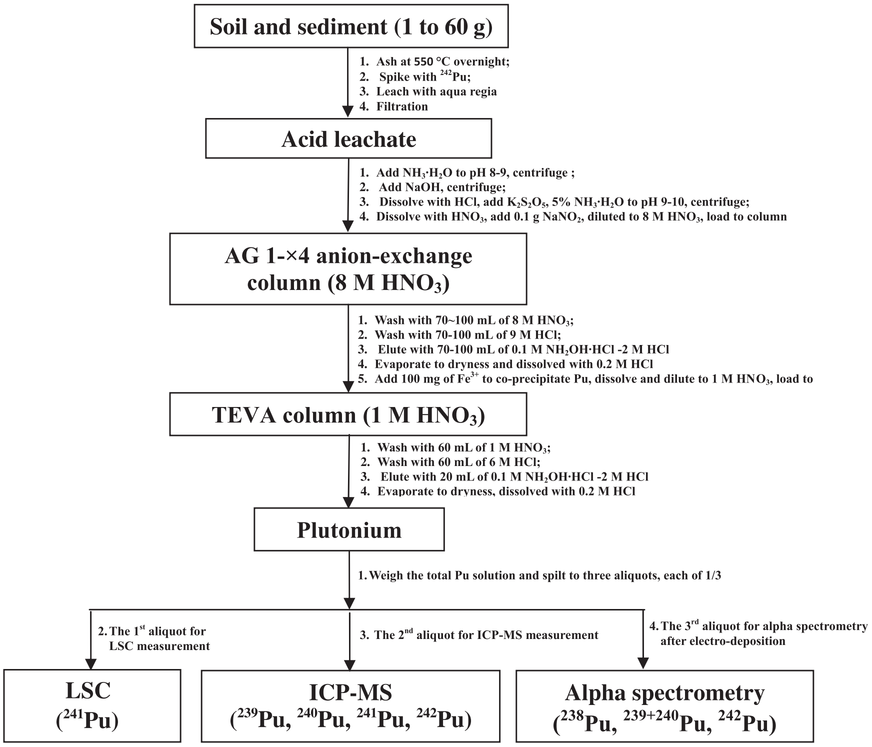

Fig. 1. Schematic diagram of procedure for determination of plutonium isotopes in solid environmental samples.

200 °C to decompose the hydroxylamine and eliminate the hydrochloric acid. The residue was finally dissolved in 3–6 mL of 0.2 mol L^{-1} HCl, and the solution was weighed and split to three aliquots for the measurement of plutonium isotopes using different techniques. A flow chart of the analytical procedure for the determination of Pu isotopes is illustrated in Fig. 1.

An artificial sample solution (2012 NPL inter-comparison sample B-2) was also analyzed, some 80 mL of sample solution was weighed in a beaker and about 10 mg of Fe^{3+} ($FeCl_3$) and 1 Bq of ^{242}Pu were added and purified by an AG 1- × 4 anion-exchange column for the LSC measurement. While for the ICP-MS measurement, the sample solution was separated by a TEVA column after about 10 mg of Fe^{3+} ($FeCl_3$) and 12 mBq of ^{242}Pu were added. The separation procedures using AG 1- × 4 or TEVA were the same as those described above.

2.3. *Detection of Pu isotopes*

One aliquot of the solution obtained from the chemical separation was taken to a 20 ml LSC vial, after addition of 10 mL of scintillation cocktail (Ultima Gold LLT, PerkinElmer Inc.), ^{241}Pu was measured using a liquid scintillation counter (Quantulus™ 1220, PerkinElmer Inc.) for 3 cycles and 60 min. of each cycle. The second aliquot was diluted to 5 mL by addition of 0.5 mol L^{-1} HNO_3 and 50 µL of 100 µg L^{-1} In (III) (as $InCl_3$) as internal standard for measurements of ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu by an ICP-MS system (X Series II, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs- skimmer cone under hot plasma conditions. A high efficiency ultrasonic nebulizer (U5000AT+, CETAC, USA) was used for sample introduction to the ICP-MS. The third aliquot was evaporated to dryness; the residue was then dissolved with 7 mL of 0.05 mol $L^{-1}H_2SO_4$. After the solution was transferred to an electro-deposition cell, 2 drops of methylblue and NH_4OH solution were added to adjust the pH to 2.5. Plutonium was finally electrodeposited on a stainless steel disc at a current of 0.7 A cm^{-2} for 1–2 h for measurements of ^{238}Pu and $^{239+240}$Pu by alpha spectrometer (Canberra, USA) [18].

3. Results and discussion

3.1. *Separation of Pu from sample matrix and interferences*

For the analysis of plutonium isotopes in environmental solid samples, especially when the activity level of Pu isotopes in the sample is extremely low, a big size sample normally needs to be handled in order to get accurate results. However, large amounts of matrix elements and interferences such as Ca, Mg, Al, U, Th, Am, etc. in samples of big size cause serious problems for the accurate determination of Pu isotopes, especially for mass spectrometric measurements. An anion-exchange chromatography using AG 1- × 4 column in combination with extraction chromatography using TEVA column were used in this work in order to get a better chemical separation of Pu isotopes from matrix components and interfering radionuclides.

Table 2 shows the chemical yields of Pu and decontamination factors for ^{238}U in the overall chemical separation procedure. Pu chemical yields of 33–80% with an average of 55% were obtained for the entire chemical separation procedure using the AG 1- × 4 anion-exchange chromatography combined with TEVA extraction chromatography. The relatively low Pu recoveries might be a consequence of relatively large losses of Pu during the anion-exchange process. The high content of matrix elements in the loading solution might also contribute to the high loss of Pu because of competitive absorption of some matrix anion onto the column. According to our previous experiences [19], the retention of Pu on AG 1- × 4 resin of 50–100 mesh is influenced by the flow rate in the uploading step, it is better to control the flow rate to ≤ 1.0 mL min^{-1} to ensure a high retention of Pu on the column. In this work, the ion exchange chromatographic separation was operated manually, the flow rate could not be precisely controlled,

Table 2
Concentration of ^{238}U in final elution and decontamination factor of the method for ^{238}U.

Samples	Sample amount[a](g)	Chemical yield of Pu (%)[b]	^{238}U in final elution (pg mL^{-1})	Decontamination factor for ^{238}U[c]
Danish sediment	~10	42.3 ± 2.1	1	3.1×10^4
	~10	64.6 ± 3.4	1	6.4×10^4
Chinese soil	~20	40.0 ± 2.0	3	6.8×10^5
	~20	59.4 ± 3.1	3	7.5×10^5
IAEA soil 6	~10	38.1 ± 2.1	5	1.6×10^5
	~10	80.5 ± 4.1	6	1.7×10^5
IAEA-367	~0.33	80.0 ± 4.1	18	3.6×10^3
	~0.33	33.1 ± 1.7	1	6.3×10^3

[a] The sample amount was calculated by the weight of the aliquot for ICP-MS measurement, the total weight of the final Pu solution and the original sample weight.
[b] Uncertainties are expanded uncertainties using a coverage factor of $k=1$.
[c] The uncertainties of decontamination factors for ^{238}U are lower than 10%.

therefore Pu might not be efficiently retained on the column during the loading process. However, this unsatisfied chemical yield of Pu did not affect the accuracy of the analytical results of Pu, which could be demonstrated by the analysis of the standard reference materials as shown in this article.

In soil and sediment samples, the concentration of ^{238}U is typically higher by more than 10^6-fold than that of plutonium [13]. The large amount of ^{238}U can cause serious problem in the accurate measurement of ^{239}Pu with ICP-MS, because the formation of uranium hydrides (i.e., ^{238}U^{1}H$^+$) and the tailing effect from the ^{238}U$^+$ peak contribute to the mass range of ^{239}Pu. Sufficient removal of uranium is very important for accurate measurement of ^{239}Pu. The decontamination factor of uranium in the separation procedure depends on the matrix and the initial uranium concentration in the sample [20], which is calculated as the ratio of the initial amount of ^{238}U in the sample leachate and the final amount of ^{238}U in the separated solution. As shown in Table 2, the ^{238}U concentrations in the final eluate were generally in the level of 1–18 pg mL^{-1}, close to the detection limit of the ICP-MS to ^{238}U. The decontamination factors for uranium were calculated up to 7.5×10^5 for 20 g of soil and 1.7×10^5 for 10 g of soil or sediment, respectively, which were significantly improved (about one order of magnitude) compared to those of former reports (10^3–10^5) [13,17,19,21,22]. The relatively low decontamination factor of ^{238}U for the small size sample in this work should be attributed to its relatively low initial ^{238}U amount and that the ^{238}U concentration in the final solution was close to the detection limit of the measurement method.

3.2. Performance of the analytical method

The detection limit is a critical parameter of the developed method, and very important for the analysis of samples with low concentrations of the analyte. In this work, the detection limit (Ld) is calculated based on Currie equation for a 95% confidence interval

$$\mathrm{Ld} = [2.71 + 4.65(B_c)^{1/2}]/t/\eta$$

here B_c is the procedure blank counts, t is the counting time of blank samples(s), η is the counting efficiency of the equipment (cps/fg/mL for ICP-MS, and cps/Bq for LSC and alpha spectrometry) [23].

The detection limits of ICP-MS for sample solutions of 2 mL were calculated to be 0.543 fg mL^{-1} for ^{239}Pu, 0.467 fg mL^{-1} for ^{240}Pu, and 0.405 fg mL^{-1} for ^{241}Pu, which corresponds to absolute detection limits of 2.50 μBq for ^{239}Pu, 7.85 μBq for ^{240}Pu, and 3.09 mBq for ^{241}Pu, respectively. This calculation is based on the ICP-MS measurement parameters of 30 ms dwell time and 200 sweeps for plutonium isotopes. The detection limit of LSC measurement for ^{241}Pu with 1 h counting time was calculated to be 41 mBq, which corresponds to 2.05 mBq g^{-1} for 20 g sample. The detection limit of alpha spectrometry of 3 days counting time is about 0.05 mBq for ^{238}Pu and $^{239+240}$Pu (Table 3).

Table 3
The detection limit of ICP-MS and radiometric methods for the determination of Pu isotopes.

Detection method	Nuclide	Detection limit[a]
ICP-MS	^{239}Pu	0.543 fg mL^{-1}, 2.50 μBq
	^{240}Pu	0.467 fg mL^{-1}, 7.85 μBq
	^{241}Pu	0.405 fg mL^{-1}, 3.09 mBq
Alpha spectrometry	^{238}Pu, $^{239+240}$Pu	0.05 mBq for 3 days counting
LSC	^{241}Pu	41 mBq for 1 h counting

[a] The detection limit of ICP-MS measurement was calculated for 2 mL of sample solution.

Analytical results for plutonium isotopes in samples and standard reference materials measured using ICP-MS, alpha spectrometry and LSC are summarized in Table 4. The measured values in the two replicates of all samples agree very well for ^{239}Pu and ^{240}Pu by ICP-MS and $^{239+240}$Pu by alpha spectrometry with a deviation of less than 6% for IAEA-367 and $<3\%$ for other 3 samples (Table 4), indicating a high analytical precision of the presented method for these two isotopes of Pu. According to the paired samples t-test between the analytical results of $^{239+240}$Pu by alpha spectrometry and ICP-MS ($t\text{-Stat} = -1.57 < t_{\mathrm{crit}}$ for $n=8$), the sum activity of the measured ^{239}Pu and ^{240}Pu by ICP-MS is in a good agreement with the measured $^{239+240}$Pu activity by alpha spectrometry for the same sample within a deviation of $<10\%$ for IAEA-367 and $<5\%$ for other 3 samples (Table 4). Relatively high concentrations of Pu isotopes in the sediment sample IAEA-367 were observed, but the deviation of the analytical results of ^{239}Pu and ^{240}Pu in this sample was relatively high for both ICP-MS and alpha spectrometry. This might be attributed to the less homogeneity of plutonium in this sample and the small sample size (about 0.3 g) used for the analysis. Relatively higher deviation ($>10\%$) was observed for the measurement of ^{238}Pu in 2 samples (Table 4). This is mainly attributed to the low level of ^{238}Pu in these samples, and the measured values in the two samples are close to the detection limit of alpha spectrometry. The concentrations of ^{238}Pu in another two samples are too low to be measured.

The atomic ratio of ^{240}Pu/^{239}Pu obtained by ICP-MS (Table 4) can be used to identify the potential source of plutonium contamination. The measured ^{240}Pu/^{239}Pu atomic ratios in both Danish sediment (0.188 ± 0.009) and Chinese soil (0.179 ± 0.010) agree very well with the global fallout value of 0.18 ± 0.02 [24], indicating that the major source of the plutonium in both sampling areas are the global fallout.

Due to the higher detection limit of LSC for ^{241}Pu (41 mBq), ^{241}Pu concentration could not be measured in 4 solid samples by

Table 4
Analytical results of plutonium isotopes measured by ICP-MS, alpha spectrometry and LSC[a].

Samples	ICP-MS measurement					Alpha spectrometric measurement		LSC measurement
	^{240}Pu/^{239}Pu atom ratio	^{239}Pu (mBq g^{-1})	^{240}Pu (mBq g^{-1})	^{239}Pu+^{240}Pu (mBq g^{-1})	^{241}Pu (mBq g^{-1})	$^{239+240}$Pu (mBq g^{-1})	^{238}Pu (mBq g^{-1})	^{241}Pu[c] (mBq g^{-1})
Danish sediment	0.186 ± 0.006	0.574 ± 0.011	0.392 ± 0.014	0.966 ± 0.018	3.47 ± 1.41	0.931 ± 0.038	0.066 ± 0.009	< Ld[d]
	0.189 ± 0.007	0.569 ± 0.010	0.394 ± 0.009	0.963 ± 0.013	2.79 ± 0.31	0.925 ± 0.031	0.056 ± 0.006	< Ld[d]
Chinese soil	0.176 ± 0.006	0.301 ± 0.006	0.194 ± 0.008	0.495 ± 0.010	1.21 ± 0.77	0.467 ± 0.028	< Ld[b]	< Ld[d]
	0.182 ± 0.007	0.284 ± 0.009	0.190 ± 0.007	0.475 ± 0.011	1.12 ± 0.45	0.467 ± 0.029	< Ld[b]	< Ld[d]
IAEA soil 6	0.186 ± 0.005	0.680 ± 0.018	0.465 ± 0.004	1.144 ± 0.019	0.94 ± 0.19	1.133 ± 0.055	0.030 ± 0.007	< Ld[d]
	0.191 ± 0.012	0.645 ± 0.020	0.452 ± 0.027	1.097 ± 0.034	2.31 ± 0.65	1.002 ± 0.037	0.025 ± 0.005	< Ld[d]
IAEA-367	0.296 ± 0.008	19.342 ± 0.545	21.015 ± 0.632	40.357 ± 0.835	79.88 ± 5.99	35.354 ± 1.277	< Ld[b]	< Ld[d]
	0.290 ± 0.009	20.881 ± 0.904	22.185 ± 0.862	43.065 ± 1.249	127.48 ± 47.58	38.280 ± 1.924	< Ld[b]	< Ld[d]
Inter-comparison sample B-2	–	–	–	–	0.87 ± 0.06	–	–	0.92 ± 0.04
	–	–	–	–	0.89 ± 0.03	–	–	0.85 ± 0.06

[a] The analytical results of two replicates are presented. Uncertainties are expanded uncertainties using a coverage factor of $k=1$.

[b] The detection limit (Ld) for ^{238}Pu and $^{239+240}$Pu by alpha spectrometry counting for 3 days is 0.05 mBq.

[c] For the inter-comparison sample B-2, the data of ^{241}Pu were decay corrected to the reference date on 1st Oct. 2012, and for the other samples, to the reference date on 19th May 2013.

[d] The absolute detection limit (Ld) of the method using LSC is 41 mBq with 1 h counting time, corresponding to 137 mBq g^{-1} for 0.3 g of sample and 4.1 mBq g^{-1} for 10 g of sample.

Table 5
Comparison of the obtained Pu results for IAEA soil 6 and IAEA-367 with those literature/reference values.

Sample	References	^{240}Pu/^{239}Pu atom ratio	$^{239+240}$Pu (mBq g^{-1})	^{238}Pu (mBq g^{-1})	^{241}Pu[f] (mBq g^{-1})
IAEA soil 6	Ref. [12]	0.17–0.18	0.97[c]; 0.92–0.96[d]	–	0.51–3.08
	Ref. [13]	0.18 ± 0.01	1.00 ± 0.003	–	–
	Ref. [10]	0.195 ± 0.001	1.004 ± 0.015[c]	–	–
	Ref. [25]	–	1.03 ± 0.16	< 0.2; < 0.036	–
	IAEA reference value	–	0.96–1.11	–	–
	95% confidence interval[a]	0.171–0.196	0.94–1.06	–	–
	This work[b]	0.189 ± 0.013	1.12 ± 0.04[e]; 1.07 ± 0.07[c]	0.028 ± 0.008	1.62 ± 0.57[e]
IAEA-367	Ref. [13]	0.30 ± 0.03	39.5 ± 1.23	–	–
	Ref. [12]	0.296–0.32	38.5[c]; 31.9–36.6[d]	–	46.28–59.65
	Ref. [26]	0.295–0.311	35.4–44.2	–	–
	Ref. [22]	0.297–0.310	34.9–38.5	–	–
	IAEA reference value	–	34.4–39.8	–	55.02
	95% confidence interval[a]	0.288–0.319	35.27–39.85	–	53.65–70.51
	This work[b]	0.293 ± 0.011	41.71 ± 1.49[e]; 36.82 ± 2.28[c]	< Ld	103.68 ± 39.47[e]

Ld = Detection limit.

[a] 95% confidence interval calculated from the mean of all mentioned literature/reference values ± standard deviation (95% confidence level).

[b] All values are the average of 2 replicates and analytical uncertainty ($k=1$).

[c] Alpha spectrometry.

[d] AMS.

[e] ICP-MS.

[f] Reference date is 19th May 2013.

LSC, and was only measured in the artificial sample B-2 by analyzing 80 g of the sample (Table 4). Although the activity concentrations of ^{241}Pu in the analyzed samples are higher than other isotopes of plutonium, the mass concentrations of ^{241}Pu are more than 2 orders of magnitude lower than the concentration of $^{239+240}$Pu. ^{241}Pu concentration in all analyzed samples were measurable by the ICP-MS due to its relatively lower detection limit for ^{241}Pu compared to that of the LSC, however, the accuracy of most of the data was not satisfied, reflected by relatively high deviations between the two replicates of most samples (Table 4). This is mainly attributed to the low mass concentration of ^{241}Pu in the samples, and the measured values are close to the detection limit of the measurement method of ICP-MS (3.09 mBq). In addition, the instability of ICP-MS signal for low level samples during the measurement process might also contribute to the high uncertainty of the measurement results. However, both ICP-MS and LSC provided good measurement results of ^{241}Pu for the sample B-2 with low analytical uncertainty, the deviation of the measurement results between the two replicate samples and between the two measurement methods was very small (< 5%). This is mainly because of large size of sample (80 g) was used for the analysis of this sample. All these suggested that sufficient amount of sample (especially for low level environmental samples) has to be analyzed in order to obtain a reliable analytical result.

Because Pu isotopes in the two IAEA reference materials were not certified, and only reference values are available, the analytical results of Pu isotopes in the two IAEA reference materials were compared with reference values and the values reported in the literature in Table 5. For the concentrations of $^{239+240}$Pu, the results measured by alpha spectrometry (1.07 ± 0.07 mBq g^{-1} for IAEA soil 6 and 36.82 ± 2.28 mBq g^{-1} for IAEA-367) fall in the range of the IAEA reference values. The ICP-MS results showed slightly high values (1.12 ± 0.04 mBq g^{-1} for IAEA soil 6 and 41.71 ± 1.49 mBq g^{-1} for IAEA-367) but still within the 95% confidence interval of all literature values [10,12,13,22,25,26]. Our results of ^{240}Pu/^{239}Pu atomic ratios, 0.189 for IAEA soil 6 and 0.293 for IAEA-367, agreed quite well, within the 95% confidence interval, with the values reported in the literature [10,12,13,22,25,26].

For the concentrations of ^{238}Pu and ^{241}Pu, there were very few reported values on the two IAEA materials [12,25]. ^{238}Pu concentration in IAEA soil 6 was measured to be 0.028 ± 0.004 mBq g^{-1} in this work, which fall in the concentration range reported by Tavčar et al. [25]. The measured ^{241}Pu concentration in IAEA-367 (103.68 ± 39.47 mBq g^{-1}) was significantly higher than the IAEA reference value and the one reported by McAninch et al. [12]. This is mainly attributed to the relatively high analytical uncertainty of the ICP-MS method for ^{241}Pu, and the influence of relatively high ^{240}Pu in this sample to the mass of ^{241}Pu might be another possible reason.

4. Conclusions

In this work, an improved analytical method was developed for the determination of different Pu isotopes in environmental samples. The decontamination factors for interference especially for big sample size were significantly enhanced using the AG 1-× 4 anion exchange chromatography in combination with TEVA extraction chromatography. A good agreement between the analytical results of the two IAEA materials and the literature or IAEA reference values reveals that the developed method for plutonium determination in environmental samples is reliable. Both alpha spectrometry and mass spectrometry play important roles in Pu determination and have irreplaceable functionality in measuring ^{238}Pu concentrations and isotopic ratios of ^{239}Pu/^{240}Pu, respectively. Sufficient sample amount is needed for ^{241}Pu measurement by LSC due to its relatively high detection limit.

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