analytical chemistry

Effect of Ashing Temperature on Accurate Determination of Plutonium in Soil Samples

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Ⓢ Supporting Information

ABSTRACT: An acidic leaching method using HNO_3 is widely employed to release the global fallout Pu from soil samples for further chemical separations in radioecology and toxicology studies and in many applications using Pu as a useful tracer. In the method's sample ash treatment step to decompose organic matter in soil, various ashing temperatures (400−900 °C) are used; however, the effect of ashing temperature on the accurate Pu analysis has not been well investigated. In this study, two standard reference soils (IAEA-soil-6 and IAEA-375) were used to determine the ashing temperature effect (from 375 to 600 °C) on the HNO_3 leaching method. The Pu analytical results of both standard reference materials showed that lower $^{239+240}Pu$ activity was

observed when the ashing temperature exceeded 450 °C, and the $^{239+240}Pu$ activity continued to decrease as the ashing temperature was raised. Approximately 40% of the Pu content could not be leached out by concentrated HNO_3 after ashing for 4 h at 600 °C. The Pu loss was attributed to the formation of refractory materials, which are insoluble in HNO_3 solution. This hypothesis was confirmed by the XRD analysis of soil samples, which revealed that plagioclase-like silicate materials were formed after high-temperature ashing. To ensure Pu release efficiency in HNO_3 leaching, we recommend 450 °C as the ideal ashing temperature. This recommendation is also useful for analysis of other important artificial radionuclides (e.g., ^{137}Cs, ^{90}Sr, ^{241}Am) for which an ashing process is needed to decompose the organic content in soil samples.
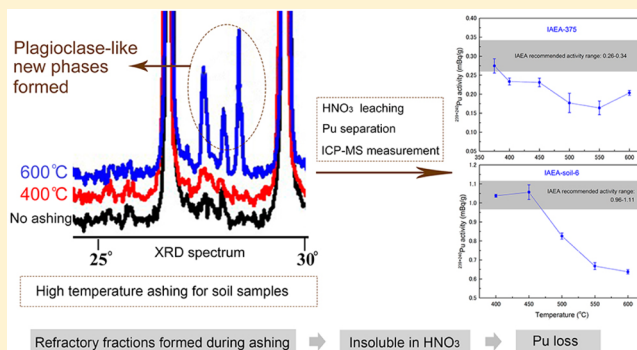
The global fallout plutonium in soil, introduced by nuclear detonations in the past century, has been extensively studied not only for the purpose of radiological assessments,[1−4] but also in various studies in which Pu is used as a geochemical tracer, such as soil erosion,[5−8] sediment dating,[9,10] desertification studies,[11] and estimation of aerosol residence time in the stratosphere.[12] Usually, in these applications, large amounts of soil samples are needed for Pu analysis. To shorten the analytical time and improve efficiency, a quick digestion method, the HNO_3 leaching method, has been commonly employed.[13−17]

Generally, the HNO_3 leaching method uses concentrated HNO_3 (or 8 M HNO_3) to dissolve the Pu component in the soil samples after high-temperature ashing, and that is followed by chemical separation and Pu measurement. However, during the ashing step, which is intended to decompose the organic matter and avoid interferences with the subsequent chemical separation, various ashing temperatures (400−900 °C) have been used by different researchers.[13,18−21] Different ashing temperatures may cause additional uncertainties for Pu analysis.

For example, a low temperature cannot decompose the organic matters thoroughly, whereas a high temperature may produce some refractory particles that cannot be dissolved by simple HNO_3 leaching.[22] It was observed that, at an ashing temperature of 900 °C, the $^{239+240}Pu$ activities in a series of soil and sediment standard samples were lower than the certified values.[18] Thus, an appropriate ashing temperature should be identified and accepted by researchers to improve the reliability and accuracy of the HNO_3 leaching method.

In the present study, IAEA reference soil samples IAEA-soil-6 and IAEA-375 were used to evaluate the effect of different ashing temperatures (375−600 °C) on Pu analysis. Lower $^{239+240}Pu$ activities were observed when the ashing temperature was increased. When ashed at high temperature, the formation of refractory fractions was proposed to be responsible for the incomplete release of Pu from soil samples. This proposed

cause was discussed by examining the chemical change in two ways: via X-ray diffraction analysis and comparison of the Pu results with those of the total digestion method. Finally, an optimal ashing temperature for the HNO_3 leaching method is recommended.

■ EXPERIMENTAL SECTION

Standard Soil Samples. Two soil standard reference materials (IAEA-soil-6 and IAEA-375) were used to investigate the ashing temperature effect on the release efficiency of Pu. IAEA-soil-6 standard samples were collected in Upper Austria, and their Pu content was assumed to be from global fallout.[23] The approximate composition of IAEA-soil-6 reference material is summarized in Supprting Information (SI) Table S-1. It is noted that this material was characterized by a high content of SiO_2 (38.5%). IAEA-375 soil samples were collected in Russia in July 1990, and their Pu content was assumed to be from global fallout and radionuclides released in the Chernobyl accident.[14,24] The elemental composition of the IAEA-375 reference material is summarized in Table S-2. It is noteworthy that the latter may be contaminated with hot particles resulting from the Chernobyl accident; significantly elevated activities may be observed for anthropogenic radionuclides in some subsamples.[25]

Instrumentation. The ashing process for soil samples was conducted in a muffle furnace (FUW 253PA, Advantec, Tokyo, Japan). An example of temperature increment conditions was heating from room temperature to 450 °C during 10 min, followed by maintaining the temperature at 450 °C for 4 h.

To evaluate the ashing temperature effect on Pu release in soil samples by HNO_3 leaching, 15 samples of IAEA-soil-6 (∼1.5 g amount for each sample) and 18 samples of IAEA-375 (∼2 g amount for each sample) were transferred to individual 30 mL ceramic crucibles (CW-B1, ASONE Corp., Tokyo, Japan), and then ashed at 375−600 °C. After heating at the target temperature for 4 h, the samples were cooled to room temperature in the muffle furnace until ready for subsequent acid leaching/digestion. Weight loss ranges of 0.9−4.4% and 9.2−11.7% were found after ashing for IAEA-soil-6 and IAEA-375 samples respectively, and the actual values depended on the ashing temperature. The crystal structures of the ashed soils were obtained using powder X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer (Karlsruhe, Germany) using Cu Kα radiation.

To measure Pu isotopes, a high efficiency sample introduction system (APEX-Q) equipped with a conical concentric nebulizer was combined with SF-ICP-MS (Element 2, Thermo Scientific, Bremen, Germany). Details of this analytical system have been described in previous study.[26] Low-resolution mode was used to take advantage of the maximal instrument sensitivity. All the measurements were made in the self-aspiration mode with an uptake rate of ∼0.2 mL/min to reduce the risk of contamination from the peristaltic pump tubing. The SF-ICP-MS was optimized on a daily basis using 0.1 ng/mL U standard solution to provide optimum intensities and peak shapes. The instrument detection limit of Pu was as low as 0.14 fg/mL.

Reagents. All solutions were prepared using analytical grade reagents, including HCl, HNO_3, HF, H_3BO_3, HBr, $HClO_4$, H_2O_2, $NaNO_2$, NH_4I, and $NH_2OH·HCl$. Ultrapure grade HNO_3 obtained from Tama Chemicals (Tokyo, Japan) was used for preparation of the final sample solution for ICP-MS measurement. Milli-Q water (18.2 MΩ cm) was used for sample preparation. The two anion-exchange resins, AG 1 × 8 (100−200 mesh, Cl-form) and AG MP-1 M (100−200 mesh, Cl-form), were obtained from Bio-Rad (Hercules, CA, U.S.A.). ^{242}Pu (CRM 130, Pu spike assay and isotopic standard, New Brunswick Laboratory, NJ, U.S.A.) was used to spike the soil samples as a yield tracer. The mixed Pu isotope standard solution (NBS-947) with a certified $^{240}Pu/^{239}Pu$ atom ratio of 0.242 was employed for mass bias correction.

Pu Separation Method. Three acidic leaching or digestion methods were used in this study: HNO_3 leaching, HNO_3−HF leaching, and HNO_3−HF−$HClO_4$ digestion. Detailed descriptions of their procedures can be found elsewhere: the HNO_3 leaching method from Bu et al.;[27] the HNO_3−HF leaching method from Zheng et al.;[28] and the HNO_3−HF−$HClO_4$ digestion method from Zhang et al.[29] For the HNO_3 leaching method, in brief, 1−3 g ashed soil samples and 20 mL conc. HNO_3 were transferred to a capped 120 mL Teflon vessel and digested at 160 °C for 4 h after 0.57 pg ^{242}Pu was added as a yield tracer. After filtration and adjusting the acidity to 8 M HNO_3, 0.41g $NaNO_2$ was added to take Pu to the tetravalent state.[27]

In the HNO_3−HF leaching method, an ashed soil sample (1−3 g) was mixed with 0.57 pg of ^{242}Pu tracer in a capped 120 mL Teflon vessel and digested by heating on a hot plate after adding 20 mL 10 M HNO_3/1 M HF. After leaching, the solution was heated to dryness, and the residues were dissolved in 30 mL 8 M HNO_3. $NaNO_2$ was also added to adjust the oxidation state, and then 0.3 g of boric acid was added to convert unreacted HF to BF_4^-.[28]

The HNO_3−HF−$HClO_4$ digestion method used 40 mL of HNO_3 and 10 mL of HF for digestion after adding 0.57 pg of ^{242}Pu tracer. The samples were then evaporated to dryness, followed by adding 3 mL of $HClO_4$. Next, 3 mL conc. HNO_3 was added and the solution was evaporated to dryness, this step was repeated twice. The residue was dissolved in 50 mL 1 M HNO_3, and 4 mg Fe^{3+} was added as carrier, then 2.5 mL of $NH_2OH·HCl$ (80 g/L) was added to change Pu to Pu(III), and Pu was further coprecipitated with $Fe(OH)_3$. The precipitate was dissolved in 1.5 mL conc. HNO_3, and then 50 mL 8 M HNO_3 was added to the solution along with 0.41 g of $NaNO_2$ to adjust the oxidation state of Pu to Pu (IV).[29]

After acid leaching or digestion, the samples were subjected to the subsequent two-stage anion chromatographic chemical separation as described by Bu et al.[27] In brief, Pu was separated from the sample matrix using an AG 1 × 8 anion-exchange column. The obtained Pu fraction was further purified using an AG MP-1 M anion-exchange column with HBr for Pu elution. After removing any trace of HBr, the sample was finally dissolved in 4% HNO_3 in preparation for the SF-ICP-MS analysis. Details on SF-ICP-MS measurements of Pu isotopes are reported elsewhere.[26]

■ RESULTS AND DISCUSSION

Effect of Ashing Temperature on the Release of Pu Using HNO_3 Leaching Method. The Pu analytical results are shown in Table S-3 for IAEA-soil-6 samples (temperature from 400 to 600 °C), treated by the HNO_3 leaching method. A $^{239+240}Pu$ activity range from 0.625 to 1.087 mBq/g was obtained, equal to or lower than the IAEA recommended $^{239+240}Pu$ activity value: 0.96−1.11 mBq/g. The $^{240}Pu/^{239}Pu$ atom ratios derived from the current analysis ranged from 0.183

to 0.203, consistent with the reported range of 0.17−0.22.[13−15,17,30−35]

For a better understanding of the ashing temperature effect on the release of Pu in the HNO_3 leaching method, Pu analytical results (temperature-averaged) of IAEA-soil-6 samples are plotted in Figure 1. For samples ashed at
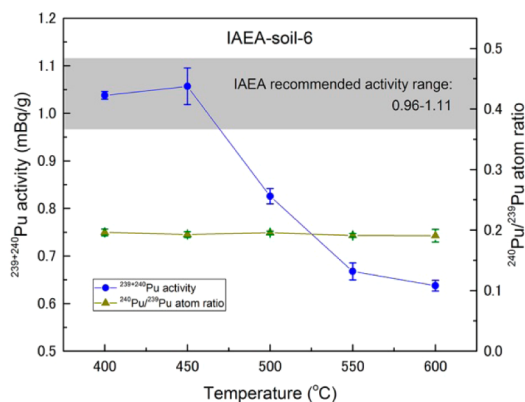

Figure 1. Pu analytical results of IAEA-soil-6 samples treated by HNO_3 leaching method (ashed at 400−600 °C).

temperatures not exceeding 450 °C, the $^{239+240}$Pu activities were generally consistent with the reported range: 0.96−1.11 mBq/g. As the ashing temperature was increased, however, an obvious decreasing trend was observed. The lowest activity (average: 0.638 ± 0.011 mBq/g) was found for the 600 °C ashed samples, in which only ∼62% of the Pu was released. By comparison, the IAEA recommended average activity was 1.035 mBq/g. In contrast to $^{239+240}$Pu activity, the ^{240}Pu/^{239}Pu atom ratios did not show any significant difference at various ashing temperatures, and all the ratios were within the reported range. This may indicate no isotopic discrimination occurred during the ashing process, and all Pu isotopes were lost at the same rate.

In the case of IAEA-375 samples (Table S-4), unlike the IAEA-soil-6 case, no obvious ashing temperature effect was observed on the temperature-averaged $^{239+240}$Pu activities, which appeared to be irregularly distributed with large uncertainties. In addition, some subsamples showed significantly higher ^{240}Pu/^{239}Pu atom ratios (0.335−0.456) compared with the literature value, 0.22−0.31.[13,15,18,20,33,36] These discrepancies might be attributed to the influence of hot particles released from the Chernobyl accident. As pointed out by the IAEA data sheet of IAEA-375, some evidence has been presented to suggest that this material may be contaminated with hot particles resulting from the Chernobyl accident,[25] but the frequency of the occurrence of these hot particles is unknown. The IAEA suggested that Pu analysis of IAEA-375 would be especially welcomed, as to receive additional data about hot particles.[37] Fortunately, because of the smaller sample amount (about 2 g) and larger number of samples adopted in the current study, compared with other studies,[13,20,36] hot particle signals were successfully observed. Among the 18 analyzed IAEA-375 samples, 6 samples (400_sub_2, 450_sub_2, 500_sub_2, 550_sub_1, 550_sub_2, and 600_sub_1 in Table S-4) were considered to be seriously affected by hot particles, taking into account their much higher ^{240}Pu/^{239}Pu atom ratios and $^{239+240}$Pu activities compared with the reported values, 0.22−0.31 for the ^{240}Pu/^{239}Pu atom ratio;[13,15,18,20,33,36] and 0.26−0.34 mBq/g

for $^{239+240}$Pu activity.[25] The correlation between the ^{240}Pu/^{239}Pu atom ratio and the $^{239+240}$Pu activity for IAEA-375 samples is plotted in Figure 2, in which the samples heavily affected by hot
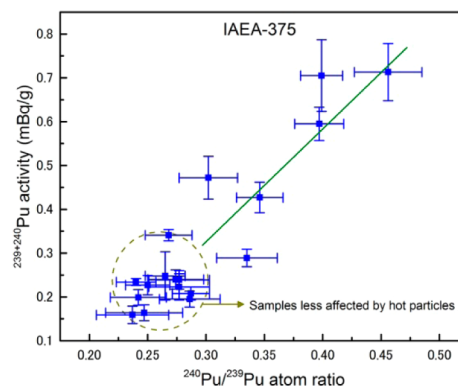

Figure 2. Correlation between ^{240}Pu/^{239}Pu atom ratio and $^{239+240}$Pu activity in IAEA-375 soil samples affected by hot particles.

particles were clearly separated from the less (or non-) hot-particle-affected samples. Taking the ^{240}Pu/^{239}Pu atom ratio as a Pu source indicator, a higher ratio means more hot particles were mixed in the soil sample, thus resulting in a linearly increased $^{239+240}$Pu activity. The highest ^{240}Pu/^{239}Pu atom ratio was found to be 0.456 ± 0.041, which was in good agreement with the reported values of 0.45−0.52 for Chernobyl hot particles.[38]

To eliminate the hot particles' influence on IAEA-375 samples, only those samples whose Pu analytical results (^{240}Pu/^{239}Pu atom ratios and $^{239+240}$Pu activities) were consistent with the reported values were considered for the evaluation of ashing temperature effect (Figure 3). Similar to
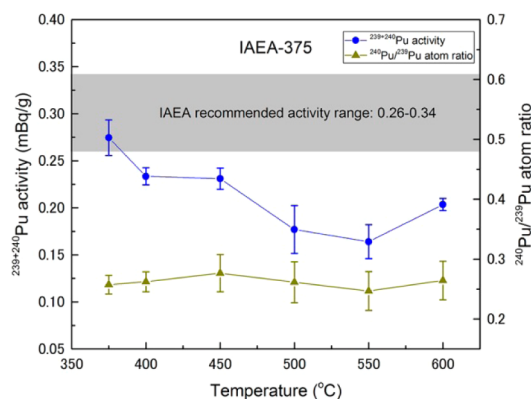

Figure 3. Pu analytical results of IAEA-375 samples treated by conc. HNO_3 leaching (ashed at 375−600 °C).

the IAEA-soil-6 case, the $^{239+240}$Pu activities decreased as the ashing temperature increased, with the exception of the 600 °C ashed samples, which might be slightly influenced by hot particles. Unlike the IAEA-soil-6 case, IAEA-375 samples ashed at 400 and 450 °C showed lower $^{239+240}$Pu activities than the IAEA recommended range. This was probably due to the fact that the IAEA-recommended $^{239+240}$Pu activity was based on measurements of large-sized samples in which the hot particles' influence might be included, and hence, the recommended values were overestimated. The highest Pu loss was found for the sample ashed at 550 °C, in which only 55% of the Pu was
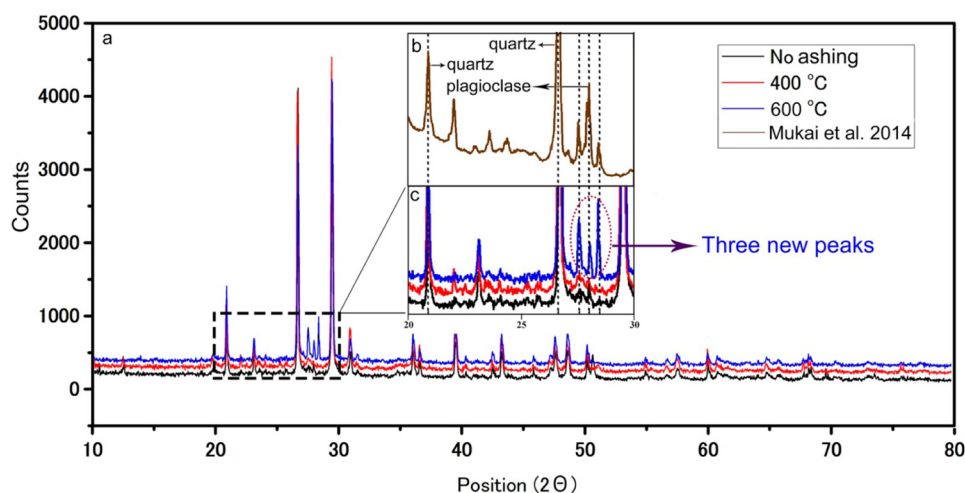
Figure 4. Spectrum of XRD analysis after ashing at different temperatures (a); XRD results derived from Mukai et al.[39] (b); and XRD spectra from this study (20°−30°) (c).

measured, compared with the IAEA recommended activity (0.30 mBq/g).

As discussed above, both standard reference materials had a decreasing trend for $^{239+240}$Pu activity when the ashing temperature exceeded 450 °C, indicating that a smaller Pu content was measured in these samples. Because all the experimental conditions were the same except the ashing temperature, we hypothesized that the high ashing temperature is responsible for the Pu loss by forming some refractory fractions in which some portion of the Pu was trapped and could not be leached out by HNO_3.

XRD Analytical Results. To verify our hypothesis, X-ray diffraction (XRD) analysis was performed to identify the phase change in the soil samples after ashing treatment. Soil samples ashed at 400 and 600 °C, together with a nonashed sample, were subjected to XRD measurements in which the diffraction data were recorded in the 2θ range of 10−80° with a step of 0.03° and a count time of 1 s. As shown in Figure 4a, the spectra obtained from soil samples, nonashed and ashed at 400 °C, had exactly the same distribution pattern, indicating that no phase change was observed after 400 °C heating. However, in the 600 °C case, three new peaks were observed between the angle 25° and 30°. New phases, for which the three new peaks stand, were formed in soil samples during the 600 °C ashing process.

For a better understanding of these newly formed components, a comparison between the present XRD spectra and a soil sample spectrum reported by Mukai et al.[39] was carried out; the results are shown in Figure 4. Mukai et al. collected a litter soil sample from a forest in Fukushima Prefecture and analyzed this sample by XRD. Their results showed the presence of quartz, plagioclase, and hornblende in the soil sample. Two obvious quartz peaks appeared at the same locations in both spectra (from 20° to 30°) (Figure 4b,c), providing a valid basis for comparing these two spectra in detail. Similarly, the three new peaks observed in this study also appeared in Mukai et al.'s spectrum, in which the middle peak was identified as plagioclase. Plagioclase, commonly present in the Earth's crust, refers to a series of silicate minerals that are known to be insoluble by nitric acid leaching. Thus, it was concluded in the 600 °C ashing temperature case, that the lost

Pu content during ashing was probably wrapped up by these newly formed plagioclase-like refractory fractions.

Validation of the Hypothesis Using Different Leaching/Digestion Methods. To validate the hypothesis, various leaching/digestion, including conc. HNO_3, HNO_3−HF, and HNO_3−HF−$HClO_4$, were utilized to treat IAEA-soil-6 samples after ashing at 550 °C. The $^{239+240}$Pu activity obtained from the conc. HNO_3 leaching method was 0.67 ± 0.02 mBq/g, significantly lower than the reported range: 0.96−1.11 mBq/g. For the HNO_3−HF leaching and HNO_3−HF-$HClO_4$ digestion methods, silicate fractions formed during ashing were dissolved by HF, resulting in the $^{239+240}$Pu activity (0.96 ± 0.03 mBq/g for HNO_3−HF leaching; 0.99 ± 0.02 mBq/g for HNO_3−HF−$HClO_4$ digestion) being within the reported range. Consequently, on the basis of the above discussion, it was confirmed that a high ashing temperature (500−600 °C) can lead to formation of some refractory silicates that remain insoluble in conc. HNO_3 and Pu loss in the HNO_3 leaching method.

CONCLUSIONS

In summary, standard reference soil samples, IAEA-soil-6 and IAEA-375, were used to evaluate the effect of ashing temperature on Pu analysis for the widely employed HNO_3 leaching method. Both standard reference materials showed Pu loss (without isotopic composition change) when the ashing temperature exceeded 450 °C. Pu release decreased as the ashing temperature was increased, and ∼40% of the Pu was lost after 600 °C ashing. The results of XDR analysis for IAEA-soil-6 samples revealed that refractory materials (silicate, e.g. plagioclase-like) were generated after the 600 °C ashing; however, these refractory fractions remain insoluble in concentrated HNO_3. Thus, the Pu content wrapped in these refractory fractions could not be released by HNO_3 leaching, resulting in the Pu loss observed for this method. To ensure the Pu release efficiency, the findings of this study suggest that the temperature for sample ashing in the HNO_3 leaching method should be controlled below 500 °C, and 450 °C is recommended. This suggestion is also useful for the determination of other artificial radionuclides (e.g., ^{137}Cs, ^{90}Sr, ^{241}Am) if an ashing process is needed. In addition, hot particle information in IAEA-375 standard reference soil was

presented, and it should be useful for studies using this soil as a quality control material for the validation of analytical methods and for the assessment of a laboratory's analytical work.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information contains four Tables (S-1, S-2, S-3, and S-4) as noted in text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b01472.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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