

Studies on the adjustment of the oxidation states of Pu oxidation states for the analysis of Pu isotopes in soil samples

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1. Introduction

The major oxidation states of Pu in acidic solutions are Pu(III), Pu(IV), Pu(V) and Pu(VI). Reducing and oxidizing reagents such as H₂O₂, NaNO₂, Na₂SO₃ and N₂H₅OH have been used to adjust the Pu oxidation state. Nuclear counting methods can be applied for determining the amounts of Pu isotopes in very low level Pu concentrations with a high sensitivity. For micro molar concentration ($> 10^{-6}$ M) of Pu, absorption spectroscopic techniques can be used for a quantitative determination of the oxidation states of Pu in an aqueous solution. Each oxidation state shows a completely distinctive absorption spectrum composed of characteristic, narrow and intense bands. Several investigations [1-3] have been performed for a determination of the Pu oxidation states in a nitric acid media by the absorption spectroscopic method. However, there have been very few studies on the spectroscopic properties of the Pu oxidation states in a hydrochloric acid medium.

Over the years, the redox states of plutonium have been stabilized by a complexation with various ligands. Among these, a nitrate anion has played a historically critical role in the processing and purification of plutonium. Also, a chloride anion has played a significant part in the separation and purification of plutonium for a very low level of Pu in environmental samples. The objective of this work is to measure various oxidation states of plutonium and to investigate the stability of the plutonium oxidation states with a laps of time in a HCl medium by using a UV-Vis-NIR spectrophotometer. Also, the adjustment method for the Pu oxidation states to Pu(IV) and Pu(VI) in a HCl medium was applied for determining the Pu isotopes in IAEA reference soils.

2. Methods

2.1 Preparation and measurement of the Pu(III), Pu(IV) and Pu(VI) solutions

The preparation of the Pu(III), Pu(IV), Pu(VI) and Pu(V) solutions was carried out in a glove box at room temperature. The oxidation state of Pu(III) was prepared by adding 0.1 mL of 0.5 M NH₂OH·HCl (10 times for the concentration of Pu) to the Pu stock solution. The oxidation state of Pu(IV) was prepared by adding 0.1

mL of 0.5 M NaNO₂ to the Pu stock solution. Also, the oxidation state of Pu(VI) was prepared by evaporating the Pu stock solution to an incipient dryness with an excess of concentrated HNO₃, by repeating the procedure with an excess of concentrated HClO₄, and finally dissolving the moist residue with 1 M HCl solution. The oxidation state of Pu(V) was prepared by adding 0.1 mL of 1 M NH₂OH·HCl to the Pu(VI) solution. The preparation of Pu(III), Pu(IV) and Pu(VI) solutions was carried out at room temperature. A high-resolution UV-Vis-NIR spectrophotometer (Cary 5, Varian) was used to measure the Pu oxidation states with a high valence spectral purity. After placing a Pu(III) solution into a semi-micro absorption quartz cell (Hellma, path length; 10 mm, volume; 1.4 ml) with a PTFE stopper, the plutonium solution in the 1M HCl medium was scanned (scanning speed: 600 nm/min.) in the wavelength range from 400 to 1200 nm. Other Pu oxidation states were measured by the same method mentioned above.

2.2 Radiochemical analysis of Pu in a soil sample

A total of 20 g soil was weighed into a porcelain dish and ashed in a muffle furnace with a gradual heating program up to 600 °C to eliminate any organic matter. To compensate for a chemical recovery, ²⁴²Pu was added into the calcinated soil sample. The calcinated samples were dissolved with 10 mL of concentrated HNO₃ and 10mL of HF (48 %) and evaporated to a dryness. The samples were leached with 30 mL of 9 M HCl, stirred on a hot plate, and finally the sample solution was filtrated with a 0.45 μm membrane filter. About 3 mL of 0.5 M NaNO₂ was added to the filtrated solution to adjust it to Pu(IV). Also, the sample solution adjusted to Pu(VI) was prepared by evaporating the filtrated solution to an incipient dryness with an excess of concentrated HNO₃, by repeating the procedure with an excess of concentrated HClO₄, and finally dissolving the moist residue with 30 mL of 9 M HCl solution. The sample solutions adjusted to Pu(IV) and Pu(VI) were passed through a pre-conditioned anion exchange (Bio-Rad, AG 1-X 8) column with 9 M HCl at a rate of 0.5 mL/min. The column was washed with 30 mL of 8 M HNO₃ to remove the U isotopes and 20 mL of 9 M HCl to desorb the Th isotopes. Finally the plutonium was eluted with 20 mL of 0.36 M HCl/0.01 M HF. The purified Pu

fraction was electroplated onto stainless steel platelets and measured by an alpha spectrometer.

3. Results and discussion

3.1 Stability of Pu(III), Pu(IV), Pu(V) and Pu(VI) with time

The stability of plutonium oxidation states has an effect on chemical processing operations, nuclear-waste storage and treatment, and the reactivity and mobility of plutonium in the environment. From measuring the absorption spectrum for Pu(III), Pu(IV) and Pu(VI) in the 1 M HCl medium every week, it was found that the shapes of the absorption spectra of Pu(III) and Pu(VI) were unchanged at least for up to 1 month. However, in the case of Pu(IV), the peak intensities were dramatically reduced after 6 months. This result means that Pu(IV) is apt to form colloids or sub-nano particles and precipitates in the weak HCl medium with time, because the solubility of Pu(IV) in a HCl medium is smaller than those of Pu(III) and Pu(VI). After 10 minutes, the absorption spectrum of Pu(IV) was generated from Pu(III), however the background intensity was dramatically increased due to a formation of plutonium peroxide colloids in the HCl medium. After 48 hours, the absorption spectrum of Pu(IV) could not be measured because a lot of the plutonium peroxide colloids generated from Pu(IV) were precipitated in the HCl solution. As soon as Pu(V) was generated from Pu(VI) in the HCl solution, Pu(V) was reduced to Pu(III) after 180 min, because of disproportionation of Pu(V). As a result, it is possible to conclude that the stability of plutonium oxidation states in a 1 M HCl solution with elapsed time after a preparation is in the order Pu(III) \approx Pu(VI) > Pu(IV) > Pu(V).

3.2 Application to the separation of Pu isotopes

Pu isotopes can generally be separated from other nuclides in a high concentration of nitric acid media or hydrochloric acid media with an anion exchange resin, because the distribution coefficients of Pu on an anion exchange resin in high nitric and hydrochloric acid concentrations are very high. A Pu separation with an anion exchange resin has been mainly carried out in nitric acid media, because most of the handling processes of a nuclear fuel are in a nitric acid media. However, with the anion exchange method in a 8M HNO₃ solution, a trace level of U has often been detected in the final Pu fraction during routine analyses, because a small quantity of the uranium which has been adsorbed onto the anion exchange column in the 8M HNO₃ media is easily eluted into the final Pu solution when a lower concentration of hydrochloric acid (0.36 M HCl / 0.01 M HF) is used as an eluting reagent of the Pu isotopes. To overcome the demerits of the conventional Pu separation method in a nitric acid

medium, Pu can also be separated from other elements in a hydrochloric acid media.

The chemical recoveries of Pu(IV) in the 9 M HCl medium were similar to those of Pu(VI), though the distribution coefficient of Pu(VI) on the anion exchange resin (Bio-Rad, AG 1-X8) is higher than that of Pu(IV) in a HCl solution. Less than 10 % of the Pu was passed into the effluent without adsorbing onto the anion exchange resin. This means that an amine group in the anion exchange resin acts as a reducing agent in the HCl medium, particularly when dealing with micro-quantities. Therefore, a small quantity of the Pu adsorbed onto the resin from the 9 M HCl solution may be reduced to a trivalent state in the resin phase, and then loosened and removed from the resin column as the elution with HCl proceeds. However, more than 90 % of Pu(IV) and Pu(VI) were detected in the Pu fraction of the eluting solution.

This method for a determination of the Pu adjusted to Pu(IV) and Pu(VI) with an anion exchange resin in the 9 M HCl medium was applied to IAEA reference soil. The activity concentrations of ^{239,240}Pu and ²³⁸Pu in the IAEA-375 and IAEA-326 were consistent with the reference values reported by the IAEA. Also, there was no significant difference in the chemical recoveries for the Pu isotopes adjusted to Pu(IV) and Pu(VI) in the HCl medium. However, the method for a determination of the Pu adjusted to Pu(IV) is more convenient than that to Pu(VI). The adjusting step for Pu(VI) needs more time, because this step includes an evaporated dryness for the leaching solution extracted from a sample solution to adjust it to Pu(VI).

4. Conclusion

The stability of the plutonium oxidation states in a HCl solution with elapsed time after preparation was found to be in the following order: Pu(III) \approx Pu(VI) > Pu(IV) > Pu(V). The chemical recoveries of Pu(IV) in a 9 M HCl solution with an anion exchange resin were similar to those of Pu(VI). This method for a determination of the Pu isotopes with an anion exchange resin in a 9M HCl medium was applied to IAEA reference soils where the activity concentrations of ^{239,240}Pu and ²³⁸Pu in IAEA-375 and IAEA-326 were consistent with the reference values reported by the IAEA.

References

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