

Sequential Radiochemical Analytical Procedure for Pu, Am, U and Np Isotopes in Soil and Radioactive Waste Samples

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1. Introduction

Recently, several studies have been reported on the combined procedure for the determination of the radionuclides in environmental samples with extraction chromatographic materials such as TRU Spec, TEVA Spec resins and Diphonix [1-4]. However, the combined methods for the nuclides in soil or sediment samples are limited because it is somewhat difficult to purify the radionuclides due to major salts ions in the soil. Also, these combined methods were focused on only the actinides such as Pu and Am isotopes, not including the Np and U isotopes.

In this study, an extraction chromatography method using such as anion exchange resin and TRU Spec resin was developed for rapidly and reliably determining the low levels of Pu, Np, Am and U isotopes in environmental samples and radioactive waste samples. The developed analytical method for Pu, Np, Am and U isotopes was validated by an application to IAEA-Reference samples.

2. Methods and Results

2.1 Pu and Np separation with anion exchange resin

The sample solution with 8 M HNO₃ media was passed through a pre-conditioned anion exchange column with 8 M HNO₃ at the rate of 0.5 ml/minute. The column was then washed with 20 mL of 8 M HNO₃ for removing the hindrance nuclides. Columns were washed with 20 ml of 9 M HCl to desorb Th. This effluent was evaporated to a dryness and reserved for a subsequent separation of Am from U. Finally, Pu and Np were eluted with 20 mL of 0.36 M HCl / 0.01 M HF, which does not form a chloride complex on the anionic exchange resin [5]. Also, the sample solution with 9 M HCl - 0.1 M HNO₃ media was passed through a pre-conditioned anion exchange column (Bio-Rad, 100-200 Mesh) with 9 M HCl - 0.1 M HNO₃ at the rate of 0.5 ml/minute. The column was then washed with 20 mL of 9 M HCl - 0.1 M HNO₃ followed by 5 mL of 8 M HNO₃ and 5 mL of 4 M HNO₃ to elute the U and Am. This effluent was evaporated to a dryness and reserved for subsequent separation of Am from U. The column was then washed with 10 mL of 9 M HCl to remove Th, which was discarded. Finally, Pu and Np were eluted

with 20 mL of 0.36 M HCl / 0.01 M HF and held for electrodeposition.

The Pu separation with the anion exchange resin has been carried out mainly in a nitric acid media because most of the handling processes of nuclear fuel are in a nitric acid media. However, with the anion exchange method in a 8 M HNO₃ media, the tracer level of U was often detected in the final Pu fraction during routine analyses. This means that a small quantity of uranium adsorbed on the anion exchange column in the 8 M 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. To overcome the demerits of the conventional Pu separation method in a nitric acid media, Pu can be separated from other elements in a hydrochloric acid media. In this study, 9 M HCl / 0.1 M HNO₃ media was used for a purification of Pu instead of using only 9 M HCl media, because the Pu adsorbed on the resin from the 9M HCl solution may be reduced to the trivalent state in the resin phase, and loosened and removed from the resin column as the elution with HCl proceeds [6]. Pu, Am and U isotopes were electroplated on stainless steel platelets and measured by an alpha spectrometer [7].

The concentrations of ^{239,240}Pu in the IAEA-375 and IAEA-326 were consistent with the reference values reported by the IAEA. Though there was no significant difference in the chemical recoveries for Pu between the 9 M HCl / 0.1 M HNO₃ media and the 8 M HNO₃ media, the Pu separation method in the chloride system has some advantages when compared with a nitrate-based system ; the concentration of HCl and the temperature of the operation are not critical, and a complete loading can be obtained whether the Pu is in the (IV) or the (VI) state. The Pu complex with HCl on the resin was stronger than the Pu complex with HNO₃ [8]. The more rapid reaction rate of the chlorocomplex with the resin ensures a quantitative adsorption of the plutonium in the presence of competing complexes. Though the chloride-based anion exchange system has disadvantages in that the decontamination from certain impurities and fission products is lower and the solution is more corrosive to most metal equipment, by loading the Pu in 9 M HCl/0.1 M HNO₃, Th is not initially retained on the anion resin resulting in a better separation of Th from Pu. Therefore, the chloride system can be used in analytical procedures to separate the various valence states of plutonium, as well as to separate it from transplutonium elements.

In the loading solution (8 M HNO₃, 9 M HCl), the oxidation states of Pu and Np were adjusted to IV and VI with NaNO₂, respectively. It was reported that Np (V) in nitric acid higher than 3 M in the presence of NO₂⁻ oxidizes to Np (VI) [9]. Under the same conditions Pu exists as Pu (IV). Because the distribution coefficient of Np (VI) on the anion exchange resin in nitric acid media is similar to U (VI) [10], most of Np was eluted into the loading and washing solution with U, so that only a tracer level of Np was detected in the eluting solution. However, in the 9 M HCl media, Np (VI) was so strongly adsorbed on the anion resin due to a high distribution coefficient on the anion resin that most of Np was detected in the eluting solution. There was no ²³⁷Np detected in the IAEA reference soil and radioactive waste samples. For detecting the level of ²³⁷Np in environmental or radioactive samples, mass analytical techniques with TIMS or ICP-MS are preferred rather than a radiation measurement.

2.2 Separation of Am from U with TRU resin

The U / Am residue that was separated from the Pu was dissolved in 30 mL of 2 M HNO₃. TRU Spec columns (bed volume; 1.3 mL, length; 2.6 cm) were used to separate the Am from the U, and they were conditioned with 30 mL of 2 M HNO₃. Samples were loaded onto the column followed by a washing with 20 mL of 2 M HNO₃. The column was then washed with 4 mL of 9 M HCl and the Am fraction was eluted with 20 mL of 4 M HCl. Uranium was eluted with 20 mL of a 0.1 M ammonium oxalate solution. Americium was purified from rare earth elements with the anion exchange resin [4]. The separated fractions of the Pu (Np), Am and U isotopes were evaporated to a dryness. Each residue was dissolved in 1 mL of concentrated HCl and evaporated to a dryness.

The concentrations of ²⁴¹Am and ²³⁸U in the IAEA-375 and IAEA-326 were within the confidence interval, though in the acid leaching method, the concentrations of ²³⁸U were a little lower than the other decomposition method due to an incomplete destruction of the soil matrix. Also, the chemical recoveries for Am and U isotopes with TRU resin in the 8.0 M HNO₃ media were lower than those in the 9.0 M HCl media. This result means that a lot of Fe which leached from the soil interfere adsorption of Am and U isotopes onto the TRU resin, even if ascorbic acid is added to the solution to reduce the Fe (III). Therefore, in the nitric acid media, it is necessary to remove Fe with an oxalic coprecipitation before loading the solution containing Am and U isotopes onto the TRU resin. However, in the 9 M HCl media, because lots of Fe strongly adsorbed onto the anion exchange resin, only a small position of Fe was eluted in the passing and washing solution so it is not necessary to remove Fe before loading the solution onto the TRU resin.

The activity concentrations of ²⁴¹Am were measured with high chemical recovery in the radioactive waste solution, though the activity concentrations of ²³⁸U were not measured in the radioactive waste solution. Also, to save on the analytical time of Am isotopes in the routine liquid samples, an anion-exchange procedure in acid-methanol for removing the rare earth elements (REEs) makes it possible to leave out because the concentration of REEs is very low in the liquid samples.

3. Conclusion

Sequential separation method of the Pu, Np, Am and U Isotopes in the soil and radioactive waste samples investigated in this study is rapid and reliable. The activity concentrations of the ^{239,240}Pu, ²⁴¹Am and ²³⁸U in the IAEA-375 and IAEA-326 were closed to the reference values reported by the IAEA. The chemical recoveries of the Pu, Np, Am and U Isotopes for the acid leaching methods were similar to those for the fusion method. In the Pu and Am separation with an anion exchange resin and TRU resin, a hydrochloric acid media is preferred rather than a nitric acid media. Np-237 was not detected in the IAEA reference soil and radioactive waste samples.

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