A Quantitative Sequential Separation Method of ^{90}Sr, ^{241}Am and Pu Isotopes in Environmental Soil Samples Using an anion exchange and Sr-Spec Resin

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Abstract

This paper presents a quantitative method of sequential separation of ^{90}Sr, ^{241}Am and Pu nuclides in environmental soil samples with an anion exchange and Sr-Spec resin. The Pu isotopes were purified with an anion exchange resin. Strontium-90 was separated from other hinrance elements with Sr-Spec resin after oxalate co-precipitation. Americium-241 was purified from lanthanides with anion exchange resin after oxalate and iron co-precipitations. The measurement of α-emitters was carried out by α-spectrometry. Strontium-90 was measured by a low level β counter. The radiochemical procedure of ^{90}Sr, ^{241}Am and Pu nuclides investigated in this study has been validated by application to IAEA and SRM-Reference soils.

1. Introduction

The determination of low levels of fallout radionuclides such as ^{90}Sr, ^{241}Am and Pu isotopes

requires lengthy and tedious chemical processes, which include techniques such as ion exchange, liquid-liquid extraction, and precipitation for separating and preconcentrating the nuclides [1-3]. In some cases, the sample material available for analysis is not infinite in number so that a radiochemical method is necessary by which Sr, Pu, Am, Th and U can be separated from one sample and determined in sequence. Also, in an emergency situation a rapid and reliable analytical method of radionuclides is desirable. Recently, several studies have been reported on the combined procedure for the determination of radionuclides in soils or sediment samples with extraction chromatographic materials such as TRU Spec, TEVA Spec resins and Diphonix[4-7]. However, these methods are somewhat difficult for applying for very low levels of fallout radionuclides due to limit of amount of sample. Also, extraction chromatographic materials are a little expensive, therefore, it is not suitable to determine Pu and Am isotopes for routine environmental samples.

In order to reduce analysis cost and turnaround time in conventional methods, a simultaneous methods to determine ^{90}Sr, ^{241}Am and Pu nuclides in environmental samples have become increasingly important. In this study, an extraction chromatography method using anion exchange resin and Sr Spec resin was developed for rapidly and reliably determining low levels of ^{90}Sr, ^{241}Am and Pu isotopes in environmental samples. The developed analytical method for ^{90}Sr, ^{241}Am and Pu isotopes was validated by application to IAEA-Reference soils.

2. Experimental methods

2.1 Sample decomposition

Fifty g of ash were weighed into a Teflon beaker. About 20 ml of 1 M HNO$_3$ were added to produce a slurry. Thirty mg of strontium carrier and spikes of ^{243}Am and ^{242}Pu tracers were added for ensuring isotopic equilibrium with the analyte nuclides. Then 50 ml of 48 % HF

were added, and the mixture was stirred and boiled gently to promote dissolution and removal silica. When the mixture has been evaporated to a paste, a second addition of 30 ml of 48 % HF was made and the evaporation was repeated. Then 50 ml of 65 % HNO_3 were added and the mixture was again evaporated to a paste. This evaporation was repeated two more times with 50 ml of 65 % HNO_3 and 2 g boric acid. The residue was dissolved with 50 ml of 8 M HNO_3 and was centrifuged and filtered through a membrane filter (0.2 µm pore size).

2.2 Plutonium separation by anion exchange

About 2 ml of H_2O_2 was added into the solution to adjust oxidation state of Pu (IV). The sample solution was heating for removing H_2O_2. After cooling, the sample solution was passed through a pre-conditioned anion exchange column with 8 M HNO_3 at the rate of 1 ml/minute. The column was then washed with 100 ml of 8 M HNO_3 for removing hindrance nuclides. The passing and washing solutions were collected for analysis of Am and Sr nuclides. Columns were washed with 150ml 9 M HCl to desorb Th. Finally, Pu was stripped with 30 ml of 0.36 M HNO_3 - 0.01 M HF.

2.3 Preconcentration of Am and Sr by oxalate precipitation

The combined effluent from the anion exchange column was evaporated to about 20 ml and diluted to 200 ml with double distilled water. Twenty g of oxalic acid were added and the pH of the solution was adjusted to 3.0 with 25 % ammonia so that both Am and Sr were co-precipitated. Under these conditions in many cases, most of the Fe, Al and Ti remains in solution in the form of oxalate complexes. The precipitate was centrifuged and washed with 25ml double distilled water three times. After 100 mg of Ca (II) is added into the solution, the procedure of calcium oxalate precipitation was carried out once more. The oxalate precipitate was destroyed by evaporation with 65 % HNO_3 (3×20 ml) or electric furnace at 450 ^{0}C.

2.4 Separation of Am from Sr by iron precipitation

The residue was dissolved in about 100 ml of 1 M HNO_3. Five milligrams of Fe (III) were added, and the heated solution was neutralized to pH 8 or 9 with concentrated ammonia solution. Am, rare earth elements (REEs), U and Th coprecipitate with hydrated ferric oxide precipitation, while Sr and Ca remain in solution. The precipitate was centrifuged and the solution was collected for analysis of Sr nuclides. After the precipitate was dissolved with 9 M HCl, hydrated ferric oxide precipitation were successively preformed once more to separate completely Am from Sr and Ca.

2.5 Separation of Am from Fe and U by anion exchange

The ferric hydroxide precipitate containing Am, rare earths and U was dissolved in 20 ml of 9 M HCl. The solution was passed through a pre-conditioned anion exchange column with 9 M HCl. The column was then washed with 30 ml of 9 M HCl for removing hindrance nuclides. U and Fe are co-absorbed with thorium on an anion exchanger from 9 M HCl solution, while americium and REEs pass through the column.

2.6 Separation of Am from rare earth elements by ion exchange

The passing and washing was evaporated to dryness and converted to nitrate with 65 % HNO_3 (3×1 ml). The residue was taken up with 20 ml of 1 M HNO_3 – 93 % CH_3OH with gentle heating and stirring. Columns were prepared from Bio Rad AG 1×4 resin (mesh; 100-200, inner diameter; 1 cm, column length; 1.2 cm). Columns were conditioned with 100 ml of 1 M HNO_3 - 93 % methanol. Samples were loaded onto the columns followed by washing with 50 ml of 1 M HNO_3 - 93 % methanol. Americium is sorbed on the column together with REEs and traces of Pb and U, etc., while any remaining traces of Fe pass through. Columns were

washed with 80 ml of 0.1 M HCl - 0.5 M NH₄SCN - 80 % methanol to remove REEs and traces of U. A wash with 20ml of 1M HNO₃- 93 % methanol was performed. Am was stripped with 50 ml of 0.5 M HCl.

2.7 Separation of strontium with Sr-Spec

 The solution collected from iron precipitation was dissolved in 20 ml of 6 M HNO₃. The column of Sr Spec resin was 20 ml of 6 M HNO₃. Sample solutions were loaded to the column, then the columns were washed with 20 ml 6 M HNO₃ to remove most of the alkaline earth metal interferences such as Ca, K and Ba. Sr is stripped with 20ml distilled water.

2.8 Source preparation of Pu, Am Sr nuclides

The purified Pu fraction was evaporated to dryness. The residue was dissolved in 1 ml of concentrated HCl and evaporated to dryness. Pu isotopes was electroplated on stainless steel platelets[8]. The source preparation of Am is similar to that of Pu.

A 600 mg of oxalic acid was added to the strip solution. Strontium oxalate was precipitated from alkaline solution by adjusting to pH 9-10 with ammonia water. The precipitate was filtered through pre-weighed filter paper. The chemical recovery for strontium was determined by gravimetry. Samples were dissolved in 8 ml of 0.1 M HCl and mixed with 12 ml liquid scintillation cocktail. Strontium-90 was analyzed by liquid scintillation counting.

3. Results and discussion

3.1 Plutonium oxidation state adjustment

Many reducing and oxidizing reagents such as H_2O_2, $NaNO_2$, $Fe(NH_2SO_3)_2$, Na_2SO_3 and hydrazinium hydroxide (N_2H_5OH) have been used to stabilize Pu (IV). In this study, four

valence adjustment methods of Pu were tested and presented in Table 1. The chemical yields of plutonium with H_2O_2 was found to be lower than other the redox-systems. Therefore, only H_2O_2 without $NaNO_2$ is not sufficient to stabilize Pu oxidation state (IV), because the oxidation state of Pu is not stable during the separation step with an anion exchange column. Also, Qingjiang reported that the traces of ^{238}U and ^{234}U were detected in the purified Pu fraction, using H_2O_2 to adjust Pu valence state (IV)[9]. The high chemical yields of plutonium using redox-systems such as H_2O_2 - $NaNO_2$, N_2H_5OH - $NaNO_2$ and Na_2SO_3 - $NaNO_2$ were obtained in the IAEA Reference soil. However, when H_2O_2 - $NaNO_2$ is applied for valence adjustment of plutonium, it needs a standing time after adding H_2O_2 - $NaNO_2$ to the sample solution, as the Pu (III) is rapidly oxidized by H_2O_2 - $NaNO_2$; but the Pu (V, VI) are rather slowly reduced to Pu (IV)[10]. Also, valence adjustment of Pu with N_2H_5OH - $NaNO_2$ is somewhat tedious and complicated, though the reaction is more powerful and effective than other regents. It was reported that $Pu^{4,5,6+}$ was easily reduced by Na_2SO_3 and then the Pu^{3+} was oxidized to Pu^{4+} by $NaNO_2$, using Na_2SO_3 - $NaNO_2$. Therefore, Na_2SO_3 and $NaNO_2$ agents are recommendable for adjusting Pu^{4+}, because oxidation and reduction of Pu are fast and quantitative.

3.2 Separation of plutonium from other elements

Pu (IV) and Th (IV) are strongly sorbed on the resin as anionic nitrate complexes while U (VI) is only weakly sorbed. Also, Am (III) and Sr (II) as well as Fe (II), Ca (II), Mg (II), Al (III), Ti (IV), REEs and other soil matrix components are not retained on the anion resin column and therefore pass completely through it. The column was then washed with 100 ml of 8 M HNO_3 for removing hindrance nuclides such as traces of U isotopes weakly sorbed on the column. Thorium was desorbed from the column by passing through 200 ml of 9 M HCl. Plutonium (IV) is retained by the column as anionic chloride complexes. Finally plutonium

was stripped from the column by passing through 20 ml of 0.36 M HCl/0.01 M HF solution or 50 ml of 0.1 M NH$_4$I/9 M HCl solution. HF or NH$_4$I reduces Pu (IV) to Pu (III), which dose not from an anionic chloride complex. As presented Table 1, the chemical yields with 0.36 M HCl/0.01 M HF were similar to those with 0.1 M NH$_4$I/9 M HCl. However, in the stripping Pu isotopes, 0.36 M HCl/0.01 M HF is preferable due to small volume (20 ml) of 0.36 M HCl/0.01 M HF (0.1 M NH$_4$I/9 M HCl; 50 ml).

3.3 Precipitation of U, Am and Sr on oxalate and iron

It is well known that transuranium elements are coprecipitated with metal oxalate [1]. In the analysis of environmental samples, purification from abundant elements such as iron, aluminium, titanium, and some anions as phosphate is essential. Calcium is one of the abundant elements in the environment and it is precipitated with oxalic acid from acidic solutions. Transuranium elements as well as lanthanides precipitate from rather acidic media, leaving many interfering elements in solution. The coprecipitation of transuranium elements on calcium oxalate and the interferences by some metal ions were measured as a function of pH of the solution. The results are plotted in Fig. 1. In these experiments, americium was coprecipitated with calcium oxalate at a pH higher than 0.5; yttrium precipitated from pH 0.2 to 3.5 while iron phosphate and calcium hydrophosphate did not start to precipitate till the pH was raised to 1.5 and 3.0, respectively. Iron without phosphate anions did not precipitate even at a pH of 5.0. Thus, actinides and lanthanides are coprecipitated with calcium oxalate effectively from acidic solutions at pH 1.5, while other major ions such as aluminum, iron, titanium, and phosphate are left in solution. After this coprecipitation, calcium was easily separated from americium by ferric hydroxide precipitation.

3.4 Validation of the anion exchange method

The determination of Pu isotopes with an anion exchange resin was validated by its

application to IAEA-Reference sample. As shown in Table 2, the concentrations of ^{90}Sr, ^{241}Am and ^{239,240}Pu in the IAEA-375 sample were consistent with the reference values reported by the IAEA. Therefore, the sequential separation method investigated in this study make it possible to be used for determining low levels of fallout ^{90}Sr, ^{241}Am and Pu isotopes in the environment.

4. Conclusions

In this work, with an anion exchange and Sr-Spec resin, a quantitative method of sequential separation of ^{90}Sr, ^{241}Am and Pu nuclides was developed in environmental soil samples. A sequential methods of ^{90}Sr, ^{241}Am and Pu nuclides can reduce analysis cost and time. With sequential method, the concentrations of ^{90}Sr, ^{241}Am and ^{239,240}Pu in the IAEA-375 sample were closed to the reference values reported by the IAEA.

Acknowledgements

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Table 1. Comparison of the chemical yield of plutonium in soils by redox-systems and stripping agent

Oxidizing agent	Reducing Agent	Stripping Agent	Chemical yield ^{242}Pu (%)
	H_2O_2	0.01 M HF/0.36 M HCl	67.2 ± 7.4
H_2O_2 or $NaNO_2$	H_2O_2 or $NaNO_2$	0.01 M HF/0.36 M HCl	82.7 ± 5.7
N_2H_5OH	$NaNO_2$	0.01 M HF/0.36 M HCl	85.8 ± 9.0
N_2H_5OH	$NaNO_2$	0.1 M NH_4I/9 M HCl	84.7 ± 6.0
Na_2SO_3	$NaNO_2$	0.01 M HF/0.36 M HCl	86.2 ± 6.8
Na_2SO_3	$NaNO_2$	0.1 M NH_4I/9 M HCl	83.7 ± 7.5

Table 2. Concentration of ^{90}Sr, ^{239,240}Pu and ^{241}Am in the IAEA-375 Reference soil

with sequential method

	Chemical yield (%)	Concentration of radionuclides (Bq/kg)	
		Recommended value	Sequential method
^{90}Sr	67.8 ± 5.2	108	106 ± 7.8
^{239,240}Pu	86.3± 8.4	0.30	0.34 ± 0.06
^{241}Am	69.4 ± 7.1	0.13	0.12 ± 0.05