Radiochemical analysis of plutonium, americium and curium isotopes in radioactive waste samples

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1. Introduction

Highly radioactive wastes produced from nuclear facilities contain hazardous radionuclides such as plutonium, uranium, americium and curium. Long-lived Pu, U, Am and Cm isotopes should be isolated from such solutions before a disposal. These nuclides are alpha emitters, except for Pu-241 which is a beta emitter.

The activity concentrations of Pu-238, Pu-239,240, Am-241 and Cm-244 are determined by an alpha spectrometer (AP) after a radiochemical separation. Also, the activity concentration of Pu-241 is determined by a liquid scintillation counter (LSC). Reliable determination of the activity concentrations in the waste of the major actinide elements such as plutonium, americium and curium is necessary to classify level of a radioactive waste sample.

In this work, the Pu, Am and Cm isotopes were purified from hindrance nuclides and elements with an anion exchange resin and a TRU resin in radioactive waste samples, and the activity concentrations of the Pu, Am and Cm isotopes were determined by radiation counting methods after an alpha source preparation. Also, the activity ratios of the Pu, Am and Cm isotopes were determined by radiation counting methods and a mass spectrometric method.

2. Experimental

2.1 Pretreatment of the samples

A liquid waste sample (10 mL) leached from the radioactive sample with HNO_3 was evaporated to a dryness on a hot plate and the residue was dissolved in a concentrated nitric acid solution. To compensate for a chemical recovery, Pu-242 (0.1 Bq) and Am-243 (0.1 - 0.5 Bq), as yield tracers, were added into a sample. The residue was dissolved with 30 mL of 8 M HNO_3. The sample solution was filtered with a 0.45 m membrane filter. The oxidation state of the Pu isotopes was adjusted to a tetravalent state with 0.2 M $NaNO_2$ [1].

2.2 Separation of Pu and Am with anion exchange resin and TRU resin

The sample solution with an 8 M HNO_3 medium was passed through a pre-conditioned anion exchange resin (Bio-Rad, 100 - 200 mesh) column (inner diameter; 10 mm, resin bead length; 80 mm) with 8 M HNO_3 at a rate of 0.5 mL/minute. The column was then washed with 20 mL of 8 M HNO_3 to remove the Am and U isotopes. The effluent was evaporated to a dryness and reserved for a subsequent separation of the Am isotopes. Columns were washed with 20 mL of 9 M HCl to desorb the Th. Finally, Pu was eluted with 20 mL of 0.36 M HCl / 0.01 M HF[2], which does not form a chloride complex on the anionic exchange resin.

The TRU Spec column (bed volume; 1.3 mL, length; 2.6 cm) was used to separate Am from U, and it was conditioned with 30 mL of 2 M HNO_3. 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.

2.3 Measurement of the Pu, Am and Cm isotopes

The activity concentrations of Pu-239,240, Pu-238, Am-241 and Cm-244 were measured by an AP[3]. The measured activities for Pu-239,240, Pu-238, and Pu-241 were corrected for their chemical yield by using the observed activities of Pu-242. Also, the chemical yields for Am-241 and Cm-244 were obtained by measuring the alpha activity of Am-243, because the chemical property of the Cm isotopes was similar to that of the Am isotopes. After the α -spectrometric measurement for Pu-239,240 and Pu-238, the Pu sample coprecipitated with Nd on the membrane filter was dissolved with 10 mL of 8 M HNO_3. The dissolved solution was divided into two fractions, where one was used for measuring Pu-241 by a LSC and the other was used for measuring Pu-239, Pu-240 and Pu-241 by a TIMS / IDMS[4].

3. Results and discussion

3.1 Radiochemical separation of the Am isotopes from the interference elements

If the separated Am fraction from the radioactive waste sample contains lanthanides and Pb-210, it is necessary to remove them from the Am fraction, because lanthanides degrade the alpha spectra and Pb-210 through its grand daughter Po-210 (major α -energy; 5.30 MeV) which interferes with the measurement of Am-243 (major α-energy; 5.27 MeV), which is a yield tracer for the Am separation. Therefore, an anion exchange resin method is generally used for removing lanthanides and Pb-210 from the Am fraction. The activity concentrations and chemical recoveries of Am-241 purified with the TRU resin and the anion exchange resin were similar to those with only TRU resin. Also, the peak resolution of Am-241 (FWHM : about 43.0 keV) with the TRU resin and the anion exchange resin were similar to that with the TRU resin (FWHM : about 43.5keV). Therefore, in this study, the Am isotopes were purified with the TRU resin without using an additional anion exchange resin, thus saving on the analytical time and reducing the analytical cost.

3.2 Activity concentrations of the Pu, Am and Cm isotopes in radioactive waste samples

The activity concentrations of Pu-238, Pu-239,240, Am-241 and Cm-244 were measured by the AP as well as the activity concentrations of Pu-239 and Pu-240 were measured by the TIMS in the radioactive samples. After measuring Pu-238 and Pu-239,240 by the AP, the activity concentrations of Pu-239 and Pu-240 were measured by the TIMS and the Pu-241 were measured by the LSC. The activity concentrations of Pu-239 and Pu-240 were calculated from the atomic ratios of Pu-240/Pu-239 measured by the TIMS using the IDMS techniques. The Pu, Am and Cm isotopes in the radioactive waste samples were clearly separated from the other nuclides and elements. The activity concentrations of the Pu, Am and Cm isotopes in the radioactive waste samples were variable, depending on the origin of the radioactive waste samples.

It is interesting to compare the correlation between the radionuclides. The correlation of the Pu-238 activity concentrations with the activity concentrations of Pu-239,240 is highly significant (R = 0.957). The correlation of the Pu-238 activity concentrations with the activity concentrations of Pu-241 is, also, highly significant (R = 0.953). The correlation between the Pu-239,240 activity concentrations measured by the AP with the TIMS is highly significant (R = 0.916). The activity concentrations of the Pu-239,240 measured by the TIMS were summed by Pu-239 with Pu-240, which were measured independently by the TIMS. Also, the correlation between the activity concentrations of the Pu-241 measured by the LSC with the TIMS is highly significant (R = 0.984). The correlations of the Am-241 activity concentrations with the activity concentrations of Pu-239,240 and Pu-241 are not significant (R = 0.152 for Pu-239,240, R = 0.282 for Pu-241), even though Am-241 was produced from the decay of Pu-241. Also, no significant correlation of Am-241 activity concentrations was observed with the Pu-238 activity concentrations (R = 0.385). However, the correlation of the Am-241 activity concentrations with the Cm-244 activity concentrations is highly significant (R = 0.994).

4. Conclusion

After the Pu isotopes in the radioactive waste samples were separated from the other nuclides with an anion exchange resin, the Am isotopes were purified with a TRU resin and an anion exchange resin or a TRU resin. Activity concentrations and chemical recoveries of Am-241 purified with the TRU resin were similar to those with the TRU resin and anion exchange resin. In this study, to save on the analytical time and cost, the Am isotopes were purified with the TRU resin without using an additional anion exchange resin.

The correlation of the Pu-238 activity concentrations with the activity concentrations of Pu-239,240 and Pu-241 is highly significant. The correlations between the Pu-239,240 activity concentrations measured by AP with the TIMS, and between the activity concentrations of Pu-241 measured by the LSC with the TIMS, were found to be significant.

5. References

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