An Analytical Method for the Determination of Plutonium in Plant Materials

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An analytical method for the determination of plutonium in plant materials has been investigated. Plutonium was separated from sample solutions by using two anion-exchange columns. In the first stage, the higher valent plutonium Pu(IV, V, VI) in the sample solution was reduced to trivalent plutonium in the presence of sulfurous acid in a 6 M hydrochloric acid solution; the trivalent plutonium was then separated from some metallic ions by using anion-exchange column. Next, the trivalent plutonium was oxidized to quadrivalent plutonium in the presence of hydrogen peroxide in a 9 M hydrochloric acid solution; the quadrivalent plutonium was adsorbed on another anion-exchange column. Column was washed with 9 M hydrochloric acid, and then with an 8 M nitric acid solution; the plutonium on the resin was then eluted with a diluted hydrochloric acid solution containing sulfurous acid. In the final stage, plutonium was electrodeposited on a stainless-steel disk together with the molybdenum carrier. By this method, the recovery rate of plutonium in the sample solution was $97.0 \pm 3.4\%$ in seven repeated experiments. In addition, plutonium-238 and plutonium-239+240 in several kinds of herbs imported to Japan from Europe were determined.

Keywords Plutonium determination, plant material, anion-exchange resin, redox, electrodeposition, α -ray spectrum

Plutonium is a noticeable radioactive element, due to the fact that it is adsorbable in bone marrow of the human body. Therefore, many analytical procedures for the determination of its nuclides (plutonium-238, 239, 240) in environmental samples have been reported. In the separation of plutonium from environmental samples, ion-exchange and liquid-extraction methods are generally used, since quadrivalent plutonium is strongly adsorbed on an anion-exchange resin in high concentrations of hydrochloric acid and nitric acid solution¹⁻⁴, and is extractable in organic solvents containing trioctylamine or bis(2-ethyl hexyl) phosphoric acid from a nitric acid solution.⁴⁻⁷ However, since the recovery rate of plutonium from a sample solution is usually low and quite often varies⁸⁻¹⁰, an internal standard has been used for correcting the recovery rate of plutonium-238 or plutonium-239+240. If plutonium can be recovered quantitatively, the use of an internal standard might be unnecessary. One of the possible cause of the low recovery rate of plutonium is that hexavalent plutonium is very stable in concentrated hydrochloric acid or nitric acid and cannot be easily reduced to quadrivalent plutonium with hydrogen peroxide.

In this study, all plutonium ions in sample solutions were first reduced to the trivalent state with sulfurous acid in 6 M hydrochloric acid. This trivalent plutonium was then oxidized to quadrivalent plutonium by hydrogen peroxide and the quadrivalent plutonium was

adsorbed on an anion-exchange column. In the final stage, plutonium on the resin was eluted by a 1 M hydrochloric acid solution containing sulfurous acid and was then electrodeposited on a stainless-steel disk. By the proposed method, $97.0 \pm 3.4\%$ of plutonium in the ash of plant materials were recovered.

Experimental

Reagents and apparatus

All chemicals used were of analytical reagent grade. An iron(III) chloride solution (1 mgFe/ml) was prepared by dissolving 0.484 g of iron(III) chloride hexahydrate in 100 ml of 6 M hydrochloric acid. A molybdenum carrier solution (10 μ gMo/ml) was prepared by diluting the stock solution (containing 0.184 g of ammonium molybdate tetrahydrate in 100 ml of water) with distilled water. One, 6 and 9 M hydrochloric acid, and 8 M nitric acid were prepared. As a tracer of plutonium analysis, plutonium-236 was used. Two ion-exchange columns were prepared by filling Amberlite CG-400 Cl type resin (100–200 mesh) into two glass tubes (1 cm i.d. $\times$ 20 cm) to a height of 5 cm. One of them (A) was washed with 50 ml of 6 M hydrochloric acid after passing through 50 ml of 1 M hydrochloric acid; the other (B) was washed with 50 ml of 9 M hydrochloric acid after passing through 50 ml of 1 M hydrochloric acid.

For the electrodeposition of plutonium onto a

stainless-steel disk, a regulated DC power supply was used with a platinum anode kept in an electrolytic cell. The diameter of a stainless-steel disk (cathode) was 23 mm and its thickness was 0.5 mm. For measurements of the α -ray spectrum, a multichannel analyzer (CANBERRA Series 40) was used, together with a silicone surface barrier detector (ORTEC CA-035-600).

Procedure

The ash obtained from 10 g of dried plant materials is digested with 20 ml of (1+1) nitric acid plus 2 ml of hydrofluoric acid; the digested solution is evaporated by using a sand bath. The residue is then transferred into a 200-ml beaker with 20 ml of 6 M hydrochloric acid; the solution is again evaporated by using a sand bath. The procedure of evaporation with hydrochloric acid is repeated two times. The residue is transferred into a 100-ml conical flask with 50 ml of 6 M hydrochloric acid (if necessary, the solution is filtered with a glass filter). Next, after 1 ml of a 6% sulfurous acid solution is added to the solution, it is warmed for 5 min in a water bath kept at 80°C. After cooling of the conical flask with water, the solution is passed through an anion-exchange column-A; the column is washed twice with 20 ml of 6 M hydrochloric acid. All of the passed solution is collected in a beaker, and the solution is evaporated to about 10 ml. The concentrated solution is transferred to a 100-ml conical flask with 50 ml of 9 M hydrochloric acid. To the solution, 3 drops of a 30% hydrogen peroxide solution are added and the solution is warmed for 40 min in a water bath kept at 80°C in order to oxidize trivalent plutonium to quadrivalent plutonium. After cooling the conical flask, the solution in the flask is passed through column-B. The column is then washed two times with 20 ml of 9 M hydrochloric acid and then with 80 ml of 8 M nitric acid. The quadrivalent plutonium in the column is eluted by 60 ml of 1 M hydrochloric acid solution containing 1 ml of 6% sulfurous acid solution. The eluate is collected in a 100-ml beaker. To the eluate, 10 drops of (1+1) sulfuric acid are added; the solution is concentrated until only sulfuric acid remains. After adding 1 ml of a molybdenum carrier solution to the residue, it is diluted with 10 ml of a 20% ammonium sulfate solution. After 1 drop of 0.1% Methyl Red solution is added to the solution, it is neutralized with (1+1) ammonia water until the color of the solution changes to yellow. Next, 1 drop of (1+1) sulfuric acid is added in order to adjust the pH of the solution to 2. The solution is then transferred into an electrolytic cell and the plutonium in the solution is electrodeposited on a stainless-steel disk, together with molybdenum dioxide, by passing a current of 0.2 A for 3 h. Prior to stopping the current, 2 drops of (1+1) ammonia water are added to the electrolyte and the stainless-steel disk is removed from the electrolytic cell. The disk is first washed with water and then with acetone. The electrodeposited plutonium isotopes are counted using an α -ray spectrometer.

Results and Discussion

Reduction of quadrivalent or sexivalent plutonium to trivalent plutonium

It is well known that quadrivalent and sexivalent plutonium are stable in concentrated hydrochloric acid or nitric acid solutions. Therefore, the reduction from quadrivalent or sexivalent plutonium to trivalent plutonium was studied by using sulfurous acid in the presence of iron(III) ions, since it was thought that iron(III) ions could be reduced to iron(II) ions by sulfurous acid, and that the resulting iron(II) ions would reduce quadrivalent or sexivalent plutonium to trivalent plutonium. We next placed 0.1 ml of a plutonium tracer solution (valency of plutonium is not certified), 50 ml of 6 M or 9 M hydrochloric acid, 1 ml of iron(III) chloride solution and 1 ml of 6% sulfurous acid solution into a 100-ml conical flask. The solution was warmed in a water bath kept at 80°C for an adequate period of time. After cooling the flask with water, a solution prepared with 6 M hydrochloric acid was passed through column-A, and a solution prepared with 9 M hydrochloric acid was passed through column-B. Column-A was washed twice with 20 ml of 6 M hydrochloric acid and column-B twice with 20 ml of 9 M hydrochloric acid. The eluent and the washed solutions were collected in a 100-ml beaker, and the plutonium in the solution was electrodeposited together with the molybdenum carrier on a stainless-steel disk. The recovered plutonium on the stainless-steel disk was compared with a standard of 0.1 ml of plutonium tracer solution dried on a stainless-steel disk.

Figure 1 shows the recovery rate of the plutonium obtained from a 6 M or 9 M hydrochloric acid solution containing sulfurous acid and iron(III) ions, or only sulfurous acid.

As shown in Fig. 1, the recovery rate of plutonium

Fig. 1 Recovery rate of plutonium in anion-exchange chromatography as a function of the condition for preparing the feed solution. ●, 6 M HCl with sulfurous acid plus iron(III) ions; ○, 6 M HCl with sulfurous acid only; ■, 9 M HCl with sulfurous acid plus iron(III) ions; □, 9 M HCl with sulfurous acid only.

from a 6 M hydrochloric acid solution containing both sulfurous acid and iron(III) ions or only sulfurous acid were quantitative. However, the recovery rate from 9 M hydrochloric acid solution was very much lower than that from 6 M hydrochloric acid.

These results suggest that quadrivalent or sexivalent plutonium is stable in a 9 M hydrochloric acid solution and is not reduced with sulfurous acid. However, since the recovery rate of plutonium from 9 M hydrochloric acid containing both sulfurous acid and iron(III) ions was higher than that containing only sulfurous acid, the iron(III) ions seemed to function as the catalyzer in reducing quadrivalent or sexivalent plutonium to trivalent plutonium.

Oxidation of trivalent plutonium to quadrivalent plutonium and elution of plutonium from an anion-exchange column

In the preceding experiments, it was shown that quadrivalent and sexivalent plutonium in a 6 M hydrochloric acid solution were easily reduced to trivalent plutonium with sulfurous acid. Therefore, the trivalent plutonium solution obtained by passing through column-A after being reduced with sulfurous acid was concentrated to about 10 ml; the concentrated solution was transferred into a 100-ml conical flask with 50 ml of 9 M hydrochloric acid. Next, in order to oxidize trivalent plutonium to quadrivalent plutonium, 3 drops of 30% hydrogen peroxide were added to the solution. The solution was warmed for 40 min in a water bath kept at 80°C. After cooling the flask with water, the solution was passed through freshly prepared column-B. The column was washed two times with 20 ml of 9 M hydrochloric acid and then with 80 ml of 8 M nitric acid. Thereafter, quadrivalent plutonium on the resin was eluted by reducing to trivalent plutonium with 60 ml of 1 M hydrochloric acid solution containing 0.06% sulfurous acid. The elution curve of plutonium is shown in Fig. 2.

Fig. 2 Elution of plutonium from anion-exchange column-B by 1 M hydrochloric acid solution containing sulfurous acid.

Recovery rate of plutonium from a full-scale sample solution

Since a sample solution prepared from the ash of plant materials contains various kinds of metallic ions, the effect of interference of these ions was investigated for the recovery rate of plutonium from the sample solution. After the addition of 0.1 ml of a plutonium tracer solution into a sample solution prepared from the ash of 10 g dried tea leaves, the plutonium in the solution was analyzed according to the proposed method, with the exception that the warming time during the reducing procedure by sulfurous acid was modified.

Figure 3 shows whether or not all of the higher valent plutonium was reduced to trivalent plutonium by sulfurous acid and further oxidized to quadrivalent plutonium. As shown in Fig. 3, the recovery rate of plutonium was quantitative when the warming time was less than 10 min. The recovery rate, however, decreased drastically upon prolonging of the warming time.

From the experiments mentioned above, it was shown that the sulfurous acid was decomposed by metallic ions. These results also showed that the produced trivalent plutonium might be oxidized by some metallic ions, since the recovery rate of plutonium from a 6 M hydrochloric acid solution without sample ash was quantitative when the warming time was prolonged, as shown in Fig. 1. However, we did not attempt to clarify the situation of the concerned metallic ions any further in this study. Therefore, in the following described experiments, the solution was warmed for 5 min and the reproducibility of this method for the determination of plutonium was tested. The results from seven experiments for sample solutions containing 0.01 Bq of plutonium-236 showed that the recovery rate and its standard deviation were $97.0 \pm 3.4\%$ for a counting time of 20 h.

Application of the proposed method to plant materials

The nuclear power reactor accident in the USSR on 26 May, 1986, released a large amount of radioactive

Fig. 3 Recovery rate of plutonium from a full-scale sample solution. The solution was warmed in a water bath to reduce higher valent plutonium to trivalent plutonium.

Table 1 Concentrations of radioactive cesium and plutonium in herbs imported to Japan from Europe

Sample ^a	¹³⁷ Cs Bq/kg	²³⁸ Pu Bq/kg	²³⁹⁺²⁴⁰ Pu Bq/kg	²³⁸ Pu/ ²³⁹⁺²⁴⁰ Pu	²³⁹⁺²⁴⁰ Pu/ ¹³⁷ Cs
Sage leaves Turkey ^b	1413±26	0.058±0.010 (0.062±0.010)	0.185±0.014 (0.200±0.018)	0.31	1.3×10 ⁻⁴
Sage leaves Greece ^b	1271±26	0.109±0.013 (0.123±0.014)	0.208±0.014 (0.205±0.018)	0.52	1.6×10 ⁻⁴
Laurel leaves Turkey ^b	687±18	0.028±0.006	0.056±0.009	0.50	0.8×10 ⁻⁴
Time leaves Spain ^b	1203±21	0.022±0.008	0.036±0.011	0.61	0.4×10 ⁻⁴
Chamomile flowers West Germany ^b	237±12	0.104±0.012 (0.113±0.013)	0.146±0.014 (0.145±0.014)	0.71	6.2×10 ⁻⁴

a. Dried sample. b. The country producing the sample. Parenthesis shows the concentration of plutonium determined by the addition of internal standard.

nuclides into the atmosphere, contaminating many plants and vegetables in Europe. Due to the fact that some plant materials have been imported to Japan from Europe, their radioactivities have been carefully checked in our laboratory. For example, plant materials, such as herbs, were found to be conspicuously contaminated by cesium-134 and cesium-137. The concentration levels of these radiocesium indicated the possibility that some imported materials might be contaminated with long half-life nuclides, such as plutonium.

In this report, the radioactive levels of plutonium in various kinds of herbs imported in 1986 or 1987 were investigated by using the proposed method, both with or without the addition of an internal standard.

As shown in Table 1, the results obtained without an internal standard are consistent with those determined by the addition of an internal standard; it has been clarified that the proposed method is useful for the determination of plutonium in plant materials. In addition, the results of measurements of plutonium show that the activity ratio of plutonium-239+240 to cesium-137 was of the order of 1×10^{-4} and that of plutonium-238 to plutonium-239+240 was about 0.5.

References

1. M. C. Bortoli, *Anal. Chem.*, **39**, 375 (1967).
2. N. A. Talvitie, *Anal. Chem.*, **43**, 1827 (1971).
3. Y. Inoue and M. Sakanoue, *J. Radiation Research*, **11**, 98 (1970).
4. "Plutoniumu Bunsekihou (Analytical Methods for Plutonium, in Japanese)", Radioactivity measurements Series 12, The Science and Technology Agency Japan, 1979.
5. T. Nomura, K. Sumazaki, S. Motoyama and N. Suzuki, PNC Technical Report, p. 118 (1973).
6. N. P. Singh, S. A. Ibrahim, N. Cohen and M. E. Wrenn, *Anal. Chem.*, **51**, 1978 (1979).
7. R. P. Bernabee, D. R. Percival and F. D. Hindman, *Anal. Chem.*, **52**, 2351 (1980).
8. J. C. Veselsky, *Microchim. Acta* [Wien], **1**, 79 (1978).
9. C. W. Sill, *Health Physics*, **29**, 619 (1975).
10. B. F. Myasoedov and F. I. Pavlotskaya, *Analyst* [London], **114**, 255 (1989).

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