Determination of Americium in a Nitric Acid Medium Using Second-Order Derivative Spectrophotometry

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A second-order derivative spectrophotometric method has been developed for the determination of microgram quantities of trivalent americium in a nitric acid medium containing plutonium and uranium. The second-order derivative absorbance of the americium at 503.5 nm is used for the quantitative analysis. In the determination of 5.8 µg/ml and 3.9 µg/ml of americium, the presence of a 100-fold amount of plutonium and a 600-fold amount of uranium could be tolerated, respectively. The trivalent americium, in the concentration range of 1-11 µg/ml has been determined with good precision. The detection limit was 0.3 µg/ml at 3 times the standard deviation (3σ). The relative standard deviation was less than 2.1% for a sample of uranium-plutonium mixed oxide. The proposed method does not require the complicated separation step of plutonium and uranium.

Keywords Americium, second-order derivative spectrophotometry, plutonium, uranium, uranium-plutonium mixed oxide

Americium-241, an alpha emitter with a half-life of 433 years, is produced from 241Pu by beta decay with a half-life of 14.4 years and a gamma-ray is emitted along with alpha decay.1 Therefore, in facilities that produce a uranium-plutonium mixed oxide (MOX) fuel, the analytical method for 241Am is very important concerning the quality control of MOX fuel and the shielding design of a glove-box.

The determination of 241Am in various aqueous samples has usually been performed by coulometric methods2-3, radiometric method4-6 and absorption spectrophotometry.7-10 For a sample containing Pu and U, a tedious separation step is required such as solvent extraction and ion exchange. Americium-241 in an acidic aqueous solution can exist in various oxidation states, similar to the other actinide elements.4-6 Nevertheless, Am(III) is stable in nitric acid11, and the major peaks in the absorption spectrum of Am(III) occur at 503 and 811 nm.12

This study was concerned with the direct determination of a microgram amount of Am(III) in the presence of Pu and U. The use of derivative spectrophotometry allowed the direct determination of the objective ion without any separation step, and eliminated background interference.13-15

Experimental

Apparatus

The alpha activities of Pu and Am are several orders of magnitude higher than that of U, which makes it necessary to perform all analytical operations in a glove-box. A modified apparatus was installed in a glove-box. A Hitachi Model 150-20 UV-VIS spectrophotometer with a 1 cm cell was used for the normal and derivative spectrophotometry. A schematic diagram of the improved spectrophotometer is shown in Fig. 1. A cell chamber equipped with a quartz window was tightly welded to the base of the glove-box. The quartz window was exactly adjusted to the optical axis of the spectrophotometer. A Hiranuma Comtite-8 was used for titrating Pu and U. A NAIG E-series pulse-height analyzer equipped with a silicon surface barrier detector was used for the alpha spectrometry of 241Am. A certified 241Am standard source was purchased from the Japan Radio Isotope Association.

Fig. 1 Schematic diagram of improved spectrophotometer.
Reagents

A Pu(IV) stock solution (20 mg/ml) and an Am(III) stock solution (180 µg/ml) were prepared by ion exchange separation16 using a Bio-Rad AG 1X-8 (100 - 200 mesh) after dissolving PuO2 powder (nuclear fuel grade) in 8 M HNO3, and were standardized by potentiometric titration17 for Pu(IV) and alpha spectrometry for Am(III), respectively. A U(VI) stock solution (35 mg/ml) was prepared by dissolving UO2 powder (nuclear fuel grade) in 8 M HNO3, and standardized by potentiometric titration.18 The working solutions were prepared by diluting the stock solutions with 1 M HNO3. All of the chemicals used were of analytical reagent grade. The two kinds of MOX fuels used were obtained from the Plutonium Fuel Development Facility of Power Reactor and Nuclear Fuel Development Corporation (PNC).

Procedure

After transferring a reagent blank solution to the cell, it was placed in a cell holder and scanned from 550 to 450 nm to set up the baseline. Replace the blank solution in the sample cell with the sample solution, and a repeat the spectral scan at a scan speed of 50 nm/min with a 2.00 nm band-pass. Then record the 2nd-order derivative spectrum. Read the derivative amplitude at 503.5 nm for the determination of Am(III). For constructing the calibration curve, record the 2nd-order derivative spectra for 1 - 11 µg/ml of Am(III), and plot of the derivative amplitudes versus the Am(III) concentration were made.

Results and Discussion

Ordinary and the second-order derivative spectrum of Am(III)

For the working solutions of Am(III) and Pu(IV), the ordinary spectra were measured. Figures 2(a) and (b) show the typical absorption spectra of Am(III) and Pu(IV). Significant peaks of Am(III) were confirmed at 503.5 and 811.4 nm without the various absorption maxima of Pu(IV); Am(III) was perfectly separated from Pu(IV). From Figs. 2(a) and (b), the absorption spectrum of Am(III) at around 810 nm is similar to that of Pu(IV). However, each absorption maximum at around 500 nm differs slightly. Next, the 2nd-order derivative spectrum of Am(III) was measured. As can be seen in Fig. 3, Am(III) has two zero points at around 501 and 505 nm, and has a trough (the absorption maxima) at 503.5 nm. On the basis of these results, the zero point-to-trough measurement technique was used in the present study.

The calibration curve for the determination of Am(III) was linear in the range of 1 - 11 µg/ml. For 2.9 µg/ml of Am(III) in nitric acid, the detection limit was 0.3 µg/ml at 3 times the standard deviation (3σ) for ten measurements.

Influence of acidity

The concentration of HNO3 in the test solution must be optimized. The influence of the acidity on the absorbance was examined over the range of 1 - 8 M HNO3. The result is shown in Fig. 4. The absorbance was decreased with an increase in the concentration of HNO3. It can be presumed that shifts in the position of these peaks and the changes in molar absorptivity are occurred.12 In the present study, 1 M HNO3 was chosen for the acidity in the sample because the difference in the sensitivity within this acidity was only a few percent.

Influence of plutonium and uranium

Americium-241 is often present together with a large
amount of Pu, since $^{241}$Am is produced from $^{241}$Pu decay by beta emission. Therefore, the influence of Pu(IV) was examined by varying the Pu(IV) to Am(III) concentration ratio over the range of 0 - 690. Figures 5 and 6 show the 2nd-order derivative spectrum of Am(III) in the presence of Pu(IV), and the influence of Pu(IV). It can be seen from Fig. 5 that Am(III) can be determined using 2nd-order derivative spectrophotometry. From Fig. 6, Pu(IV) did not affect the Pu/Am concentration ratio up to about 100, and above this ratio, the relative amplitude slightly decreased. Further, the precision of the present method was measured in the presence of Pu(VI) or U(VI). The results are listed in Table 1. The relative standard deviations were less than about 2.5% with the presence of Pu(VI), and less than about 4.0% with the presence of U(VI).

Result of Am(III) in prepared Pu(VI) and U(VI) mixtures
The influence of the presence of U(VI) and Pu(IV) was examined by varying the concentrations. The concent-

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**Fig. 4** Effect of nitric acid on absorbance of americium(III). Concentration of americium, 3.9 µg/ml; wavelength, 503.5 nm.

**Fig. 5** Second-order derivative spectrum of americium(III) in 1 M nitric acid solution in the presence of plutonium(IV). Concentration of americium and plutonium, 5.8 µg/ml and 170 µg/ml, respectively.

**Fig. 6** Effect of plutonium(IV) on relative amplitude value of americium(III). Concentration of americium, 5.8 µg/ml.

**Fig. 7** Effect of uranium(VI) on relative amplitude value of americium(III). Concentration of americium, 3.9 µg/ml.
Concentrations of Pu(IV) and U(VI) were determined in mixtures simulated from real samples of MOX. Table 1 shows the results together with the compositions and precisions. Along with an increase in the amount of Pu(IV) and U(VI), a decrease in the precision was observed.

Comparison with alpha spectrometry was conducted in order to compare alpha spectrometry and the present method. The dissolved samples with 8 M HNO$_3$ were evaporated to dryness, and 3 ml of 1 M HNO$_3$ was added. It was allowed to cool to room temperature. The sample was transferred into a 25 ml volumetric flask and diluted to the mark with 1 M HNO$_3$. This treated sample was submitted to the present method, and an aliquot was used for alpha spectrometry. Plutonium(IV) in the aliquot was separated by ion exchange separation using Bio-Rad AG 1X-8 (100 - 200 mesh). The determination of Am(III) was carried out for each method. Table 2 shows the results together with the precisions for each method. The relative standard deviations were less than 3.0% for alpha spectrometry and less than 2.1% for the present method. The proposed method allows for the determination of Am(III) in the presence of Pu(IV) and U(VI) without any complicated separation step.

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### Table 1 Determination of americium(III) in the presence of plutonium(IV) and/or uranium(VI) (n=3)

<table>
<thead>
<tr>
<th>Added Pu(IV)/µg ml$^{-1}$</th>
<th>Added U(VI)/µg ml$^{-1}$</th>
<th>Found Am(III)/µg ml$^{-1}$</th>
<th>RSD, %</th>
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<tr>
<td>170</td>
<td>—</td>
<td>5.8$^a$</td>
<td>2.3</td>
</tr>
<tr>
<td>510</td>
<td>—</td>
<td>5.9$^a$</td>
<td>1.6</td>
</tr>
<tr>
<td>—</td>
<td>240</td>
<td>3.9$^b$</td>
<td>3.0</td>
</tr>
<tr>
<td>—</td>
<td>2400</td>
<td>4.0$^b$</td>
<td>3.7</td>
</tr>
<tr>
<td>200</td>
<td>500</td>
<td>6.0$^a$</td>
<td>1.9</td>
</tr>
<tr>
<td>400</td>
<td>1100</td>
<td>5.8$^a$</td>
<td>6.9</td>
</tr>
<tr>
<td>800</td>
<td>2100</td>
<td>6.6$^a$</td>
<td>9.9</td>
</tr>
</tbody>
</table>

a. Taken Am(III), 5.8 µg ml$^{-1}$.
b. Taken Am(III), 3.9 µg ml$^{-1}$.

### Table 2 Comparison of alpha spectrometry and present method in uranium-plutonium mixed oxide samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha spectrometry (n=3)</th>
<th>Present method (n=5)</th>
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<tr>
<td></td>
<td>Mean / mg g$^{-1}$</td>
<td>RSD, %</td>
</tr>
<tr>
<td>A</td>
<td>10.2$^a$</td>
<td>3.0</td>
</tr>
<tr>
<td>B</td>
<td>7.1$^c$</td>
<td>2.0</td>
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a. 25% PuO$_2$ and 75% UO$_2$.

### References


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