The Determination of Plutonium in Soil Samples

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ABSTRACT

The contents of plutonium-239 in soil were determined by using $^{239}$Pu as yield tracer. The samples were decomposed by nitric acid treatment under ultrasonic vibration and the separation of plutonium from other elements was carried out by using anion exchange resin. The surface soils showed the plutonium content of about 1~4 mCi/km$^2$ and their $^{239}$Pu/$^{89}$Sr activity ratios were 2~5%. From these results, it was concluded that $^{239}$Pu in soil at present was brought mainly by the fall-out due to the nuclear bomb test explosion.

INTRODUCTION

This work was carried out to determine the content of plutonium-239 in soil and to study the activity ratio of Pu-239/Sr-90 in samples.

Though, at first, the determination of plutonium in soil was tried by the analytical method for fall-out sample$^1$, it was found that some modification of the method was necessary, because a large amount of soils contained many inorganic matters such as alkali and alkaline earth metals, aluminium, iron and others. As the nitrate form anion exchange method was found to be favorable for the initial separation of plutonium on the basis of the experiments$^2$ made by tracer, this system was adopted for the separation of plutonium from other elements.

Apparatuses and chemicals were similar to those which were used in the preceding report$^3$.

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SAMPLES

Soil samples were taken in Akita district in October 1967, and the content of Sr-90 in these samples had been analysed by Japan Analytical Chemical Research Institute3). Data of these samples were summarized in Table 1.

Table 1. Data for soil samples

<table>
<thead>
<tr>
<th>No. of sample</th>
<th>property</th>
<th>location</th>
<th>sampling area (cm²)</th>
<th>depth (cm)</th>
<th>total amount of dried soil (g)</th>
<th>Sr-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A1 a</td>
<td>silty soil</td>
<td>Akita</td>
<td>706.5</td>
<td>0~10</td>
<td>9076</td>
<td>769±26 98.7±3.3</td>
</tr>
<tr>
<td>2A1 b</td>
<td></td>
<td></td>
<td></td>
<td>10~30</td>
<td>19158</td>
<td>129±11 35.0±3.0</td>
</tr>
<tr>
<td>2A1 c</td>
<td></td>
<td></td>
<td></td>
<td>30~50</td>
<td>17844</td>
<td>9.6±1.2 2.4±0.3</td>
</tr>
<tr>
<td>2A2A2</td>
<td>paddy field soil</td>
<td>Akita</td>
<td>157</td>
<td>0~15</td>
<td>1966</td>
<td>607±29 76.0±3.6</td>
</tr>
<tr>
<td>2A4 a</td>
<td>humous soil</td>
<td>Akita</td>
<td>706.5</td>
<td>0~10</td>
<td>3682</td>
<td>2130±61 110±3.3</td>
</tr>
<tr>
<td>2A5A</td>
<td>clayey soil</td>
<td>Akita</td>
<td>400</td>
<td>0~5</td>
<td>955</td>
<td>3349±80 79.9±1.9</td>
</tr>
<tr>
<td>2A5B</td>
<td></td>
<td></td>
<td></td>
<td>5~10</td>
<td>1753</td>
<td>1111±47 48.7±2.1</td>
</tr>
<tr>
<td>OoteA</td>
<td>Surface soil in the pond</td>
<td>Kanazawa</td>
<td>&lt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ANALYTICAL PROCEDURE

1. Leaching and concentration of plutonium

The powdered dry soil of 50~120 g was put into a 300 ml conical beaker together with an aliquot of plutonium-238 tracer solution4). The leaching of plutonium was carried out by 8M nitric acid solution under ultrasonic wave vibration (Nippon Denshi Kagaku Co., Ltd. Ultrasonic Cleaner SUC-4003) at about 60°C for two days and this procedure was repeated for one more day after adding fresh 8M nitric acid solution to the residue separated after centrifugation.

The sample solution thus obtained by decanting the supernatants after centrifugation was filtered through a Toyo filter paper No. 5C to remove the finest precipitates. The filtrate was concentrated by evaporation and diluted to about 8 liters with hot distilled water. Then, solid ammonium carbonate of 60~80 g and concentrated sodium hydroxide solution were poured into the solution, on stirring by a magnetic stirrer, until the pH value of the solution became higher than 13 so as to dissolve perfectly aluminium hydroxide precipitate. In this process, pluto-
nium coprecipitate with ferric hydroxide and some uranium may also coprecipitate in spite of the presence of a large amount of carbonate ion. After standing over one night, the precipitate was separated by decanting the supernatant after centrifugation and washed several times with hot distilled water. After the precipitate was dissolved in concentrated nitric acid solution by warming on a hot plate followed by the addition of about 4 l of distilled water, the coprecipitation process was repeated by adding solid of ammonium carbonate and concentrated ammonia solution until pH of the solution became the value of 5~7. Sometimes, before the second coprecipitation process, the extraction was carried out either with iso-propyl ether from 6M hydrochloric acid solution or with di-isoo-butyl-ketone (DIBK) from 8M hydrochloric acid solution to remove the large amounts of iron. The precipitate after the second coprecipitation process was dissolved in concentrated nitric acid and the concentration of nitric acid solution was adjusted to be about 8 molar, the concentration being checked by sodium carbonate-methyl orange titration.

2. Ion exchange, electrodeposition and a spectrometry

Based on the over-all results obtained by tracer experiments shown in Fig. 1, the separation of plutonium from other element was carried out as follows.

About 25 ml of 8M nitric acid sample solution prepared by the above-mentioned procedure was fed to the nitrate form Dowex-1×8 resin column (12 mm inner diameter, 5 cm height, wet resin column volume 5~6 ml). After the column was washed by several column volumes of 8M nitric acid solution to elute uranium and other salts, the elution by several column volumes of 10M hydrochloric acid solution and 0.5M oxalic acid solution were stepwise carried out to elute thorium.

![Diagram](image-url)

**Fig. 1.** The elution diagram of actinide elements by a series of acids from Dowex-1×8 anion exchange resin.
and plutonium, respectively.

The effluent by 0.5 M oxalic acid solution was dried up with a few drops of concentrated perchloric acid solution to decompose oxalic acid. After taking up the resultant with 1 ml of 0.1 M hydrochloric acid solution, 0.35 ml of 2 M ammonium formate solution, 3 ml of 4 M sodium chloride solution and 0.65 ml of distilled water were added. The solution thus prepared was transferred into a polyethylene electrodeposition cell and plutonium was electrodeposited on a stainless steel plate in 2~3 hours at 0.2~0.3 A. In this conditions, the yield of electrodeposition of plutonium was about 70% in tracer experiments. The electrodeposited plutonium was determined by alpha spectrometry by a double gridded ionization chamber connected with a 100 channel pulse height analyser. The alpha spectrum in Fig. 2 showed that a considerable amount of uranium was found with plutonium owing to the insufficient washing by 8 M nitric acid solution. Therefore, the further purification was needed to separate plutonium from uranium completely. The alpha spectrum for the sample “Oote A” in the Fig. 3(II) was obtained by feeding the 0.5 M oxalic acid effluent directly to the oxalate form Dowex-1×8 resin column, where plutonium passed through as mentioned in the tracer experiments.

The alpha spectrum of plutonium for the sample “2A2A2” in Fig. 3 (III) is one example purified by another 10 M hydrochloric acid solution anion exchange resin system and 0.5 M oxalic acid elution. This purification method was applied to all samples except the sample “Oote A.”
RESULTS AND DISCUSSIONS

The analytical results of the soil samples are shown in Tables 2 and 3. As the natural activity ratios of Pu-238/Pu-239 had been found to be about 0.04 for fall-out samples\(^5\), this activity ratio value was used for the correction of the chemical yields obtained by plutonium-238. The values of plutonium content in the samples of 2A1b and 2A1c in Table 3 show only the upper limit, because the net activities of plutonium-239 were found to be below the limit of reliable determination as compared with the background counts of detector. For the samples of 2A5A and 2A4a, the values of plutonium-239 contents show only lower limits, because plutonium-238 recoveries were too low and the activities of this nuclide were only about two times of background.

Plutonium content of surface soils (0~15 cm depth) in 1967, October, varied from about 1.6 mCi/km\(^2\) (2A5A+2A5B) or 3.9 mCi/km\(^2\) (2A2A2) (Tables 2 and 3). These results are slightly higher than the value of about 1 mCi/km\(^2\) of the cumulative deposition of plutonium-239 in Tokyo by Miyake et al.\(^5\). And such circumstances are interesting in relation to the fact that about two times higher values have been found in Akita district for other fall-out nuclides such as strontium-90 as compared with the same nuclide in Tokyo. On the other hand, if the value of 6.5 pCi/kg for the soil sample of Brestigny sur Orge (S. & O.), France, in the year of 1964, is converted to the unit of mCi/km\(^2\) as the representative data on French soils\(^6\), the value of about 2 mCi/km\(^2\) is estimated for French surface soil, because this sample was taken in the cylindrical form of 8.9 cm \(\phi \times 20\) cm depth. If the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (cm)</th>
<th>cpm/sample weight (g)</th>
<th>Chemical yield (%)</th>
<th>dpm/kg</th>
<th>pCi/kg</th>
<th>mCi/km(^2)</th>
<th>(^{239})Pu/(^{240})Sr activity ratio (%)</th>
<th>Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A1a</td>
<td>0~10</td>
<td>0.62,100</td>
<td>22.7</td>
<td>55.4</td>
<td>24.9</td>
<td>3.2</td>
<td>3.2</td>
<td>Akita</td>
</tr>
<tr>
<td>2A5A</td>
<td>0~5</td>
<td>0.076,80.2</td>
<td>2.1</td>
<td>8.4\times10</td>
<td>3.8\times10</td>
<td>0.91</td>
<td>1.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>2A5B</td>
<td>5~10</td>
<td>0.17,120.2</td>
<td>8.7</td>
<td>34.7</td>
<td>15.6</td>
<td>0.68</td>
<td>1.4</td>
<td>&quot;</td>
</tr>
<tr>
<td>2A2A2</td>
<td>0~15</td>
<td>0.28,80.0</td>
<td>11.5</td>
<td>69.2</td>
<td>31.2</td>
<td>3.9</td>
<td>5.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>2A4a</td>
<td>0~10</td>
<td>0.12,65.0</td>
<td>2.4</td>
<td>2.4\times10</td>
<td>6.3\times10</td>
<td>3.9</td>
<td>2.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>OoteA</td>
<td>Surface soil in the pond</td>
<td>&lt;5  0.62,48.9</td>
<td>5.9</td>
<td>44.0</td>
<td>19.8</td>
<td>Kanazawa</td>
<td>Kanazawa</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Plutonium content of surface soil. 1967, Oct.
Table 3. Plutonium content of soils at various depth from the surface

<table>
<thead>
<tr>
<th>Sample</th>
<th>depth (cm)</th>
<th>cpm* / weight (g)</th>
<th>G.I.C.** efficiency (%)</th>
<th>Chem. yield (%)</th>
<th>dpm/kg</th>
<th>pCi/kg</th>
<th>mCi/km²</th>
<th>239Pu/239Sr Activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A1a</td>
<td>0~10</td>
<td>0.62/100</td>
<td>49.3±1.5</td>
<td>22.7</td>
<td>55.4</td>
<td>24.3</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>2A1b</td>
<td>10~30</td>
<td>≤.0.006/100 (&lt;B.G.)</td>
<td>9.0</td>
<td>≤1.4</td>
<td>≤0.6</td>
<td>≤0.1</td>
<td>≤0.5</td>
<td></td>
</tr>
<tr>
<td>2A1c</td>
<td>30~50</td>
<td>&lt;.0.01/100 (~B.G.)</td>
<td>21.7</td>
<td>&lt;1.3</td>
<td>&lt;0.6</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2A5A</td>
<td>0~5</td>
<td>0.07/80.2</td>
<td></td>
<td></td>
<td>2.1</td>
<td>8.4×10</td>
<td>3.8×10</td>
<td>0.9</td>
</tr>
<tr>
<td>2A5B</td>
<td>5~10</td>
<td>0.17/120.2</td>
<td></td>
<td></td>
<td></td>
<td>8.7</td>
<td>34.1</td>
<td>15.5</td>
</tr>
<tr>
<td>2A5C</td>
<td>10~20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* B.G. 0.016±0.001 cpm/250 keV (4.85~5.60 MeV)
** Estimated by an aliquot of the standard solution of 239Pu. (total 0.1332 μCi-IAEA.)

increases of plutonium-239 in soils by atmospheric precipitation for three years (from 1964 to 1967) are considered, it is interesting that plutonium contents in soils are not so different between Japan and France.

The activity ratio of Pu-239/Sr-90 varied from 2.5% to 5.1%. Although Pu-239 /Sr-90 ratio may change with the different migration characteristics of plutonium and strontium depending on the quality of soils, these results are of the same order value as other reported values; 1.8~4.1% for precipitation in Tokyo from 1960 through 1966⁵, and 4.4% in 1960 and 2.3% in 1964 in soil in France⁶. From these results, it may be reasonable that plutonium-239 in soils has been brought by the fall-out due to the nuclear bomb test explosion.

Plutonium contents of soils at various depths from surface in 1967 are shown in Table 3. Plutonium was not detected below 10 cm depth in the profiles of 2A1 series. It has been reported that plutonium remained in surface soil of 5 cm depth for more than 10 years at the desert in New Mexico⁷ and plutonium moved downward in soil slower than strontium⁸. Therefore, it is concluded that the sampling of soil must reach the depth of 10 cm in order to estimate the cumulative amount of plutonium in soils, even though many factors, such as quality of soil, pH value of soil, presence of inorganic and organic matters, and others⁹,¹⁰ may affect the adsorption of radioactive elements on soils. For example, the organic matters may affect the adsorption of plutonium on soils⁹, by forming complexes with plutonium.
AN IMPROVEMENT OF SEPARATION PROCEDURE

The mean overall chemical yield of plutonium was about 10% for four samples in this experiment. The method applying the ion exchange resin (the above-mentioned method or others\textsuperscript{10}), suffer from a large quantity of inorganic salts which may disturb the effective separation of the elements owing to the limited column volume of the resin and another reason for the low chemical yield may be due to

![Diagram](https://example.com/diagram.png)

**Scheme 1.** Analytical scheme for the extraction of plutonium with TOA (10\textdegree\textit{v/v}}\% in xylene)

(E): Extraction process

(W): Washing process

(S): Stripping process of plutonium

(c.f.): Centrifugation
the small area (5.5 mm diameter) of an electrodeposition plate for fission track study. In order to detect plutonium in less amount of soil sample and to assure the better counting statistics, it is desired to improve the chemical yield in the analytical procedure. Therefore, the solvent extraction procedures shown in Scheme 1 were examined by using plutonium-239 tracer, because it has been reported that only Pu(IV), Np(IV) and Th(IV) among many actinide elements could be easily extracted from nitric acid solution with TOA\(^1\).

The sample solution was prepared from soil (10 g) by the treatment in 8 M nitric acid solution and the coprecipitation with ferric hydroxide, followed by dissolving the precipitate with concentrated nitric acid solution and the adjustment of the nitric acid concentration to about 8 molar. By alpha spectrometry of the electrodeposition plate of plutonium, the yield of plutonium through the extraction process with TOA was found to be about 89\%, if the electrodeposition yield found by plutonium-238 spike was considered on the overall yield of plutonium-239.

In this way, it was concluded that the solvent extraction of TOA was an effective method as the separation procedure of plutonium from a large amount of soils.

This method was applied to soil samples at Nagasaki by other members of our laboratory, plutonium-236\(^2\) being used newly as chemical yield tracer. Analytical results and discussion for these samples are reported in another paper\(^3\).

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REFERENCES

