Environmental ^{241}Pu Determination Using Alpha / Beta Distinguish Technique with Liquid Scintillation Measurement

Yasuhiro Uezu, Naoto Miyagawa, Hiromi Katagiri
Japan Nuclear Cycle Development Institute
4-33 Muramatsu Tokai-Mura Ibaraki, Japan

INTRODUCTION

^{241}Pu emits beta ray (maximum energy: 21 keV) and its half life (14.4y) is shorter than other Pu isotopes. ^{241}Pu in the environment was introduced from atmospheric nuclear testing. It accounts for most of the radioactivity produced by the Pu isotopes. ^{241}Pu is parent nuclide of ^{241}Am (half life ; 432y, alpha ray; 5.5MeV and gamma ray; 60keV) and ^{237}Np (half life; 2.1×10^{6}y and alpha ray; 4.8MeV). So, it is an important nuclide for environmental assessment [1), (2)]. Fig. 1 shows the decay scheme of ^{241}Pu. In the case of ^{241}Pu measurement, it is necessary to use the liquid scintillation counter (LSC) which the counting efficiency for the low energy beta ray is high.

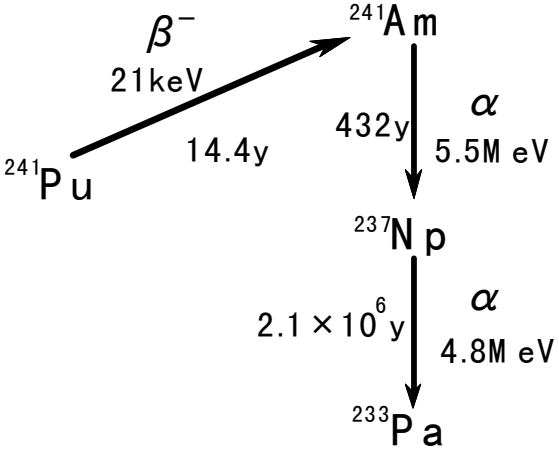

Fig. 1 Decay Scheme of ^{241}Pu

On the other hand, silicon semiconductor detector (SSD) which has high energy resolution [3] is available to measure Pu(alpha) isotopes such as $^{238,\ 239+240}$Pu in the samples. In the conventional analysis method, two kinds of tracers were used for chemical yield correction. This conventional analysis method is shown in Fig.2 [1].

In this analysis method, the sample needed to be divided for LSC and SSD measurement. The sample was divided into two fractions for ^{241}Pu measurement and calculation of chemical yield. So, ^{236}Pu and ^{242}Pu were used as the chemical yield tracer. Accordingly, the analytical method is applied only to the environmental samples in which the concentration of ^{241}Pu is relatively high.

Then, the discrimination method using a pulse shape analysis was used to improve the detection limit. The purpose of this investigation has been to develop a new procedure for the simultaneous determination of ^{239,240}Pu and ^{241}Pu using a liquid scintillation counter. The principle of pulse shape discrimination and results of its application to environmental samples are described in this report.

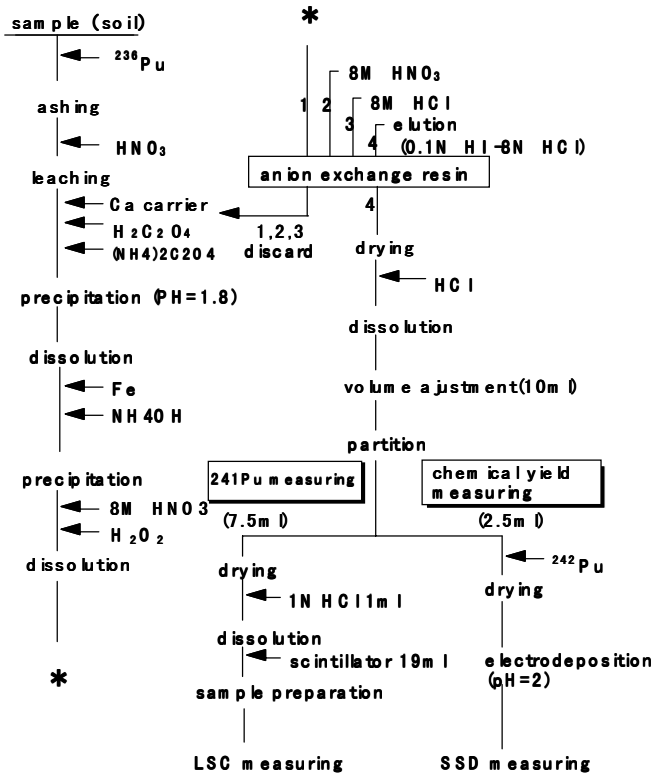

Fig. 2 Diagram of conventional analytical method of 241Pu in soil samples

PRINCIPLE

・α/β DISCRIMINATION METHOD

The liquid scintillation counting method has following features; (1) It is effective for beta ray measurement. (2) It is difficult to separate alpha rays from each other.

The shape of pulse for alpha ray is different from that of beta ray in LSC measurement generally. Fig. 3 shows the respective decay times in scintillation measurements[(4)].

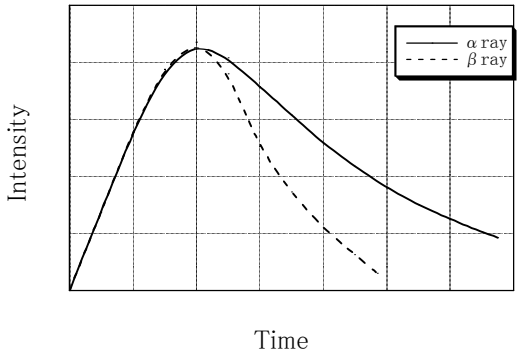

Fig. 3 Spectra of decay times for alpha and beta rays

So, alpha and beta ray can be separated each other using this difference of their decay times in scintillation measurement.

Fig. 4 is the spectra of ^{241}Pu and ^{239,240}Pu in LSC measurement. The peak of alpha nuclides is appeared in low energy about ten times smaller than original energy in liquid scintillation measurement.

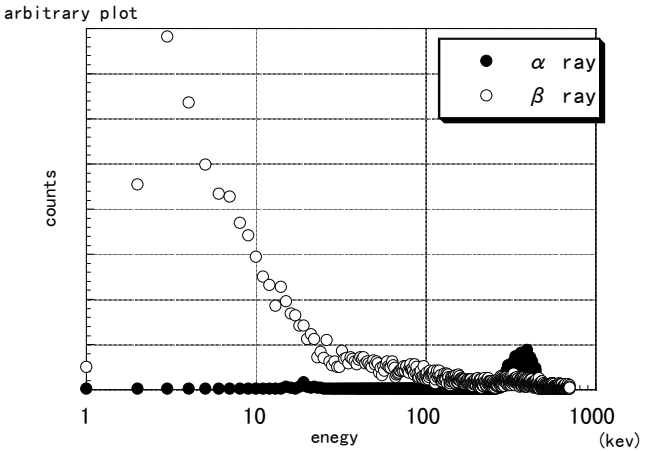

Fig. 4 The Spectra of ^{241}Pu and ^{239,240}Pu in LSC Measurement

The relationship between discriminator setting and spill over at alpha ray and beta ray simultaneous measurement is shown in Fig. 5.The discriminator setting means the delay time in the decay of the nuclide measured in LSC. And, spill over means the proportion of beta ray in alpha ray counting region and alpha lay in beta ray counting region in the time-related discrimination.

In this discrimination method, when discriminator setting is high, beta ray will be counted as alpha lay. When discriminator setting is low, they are counted as beta lay,.

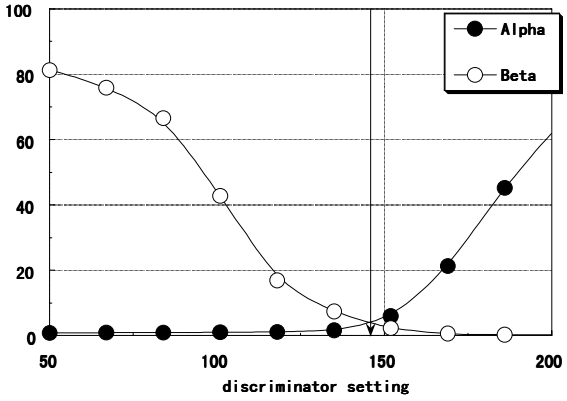

Fig. 5 Relationship of Discriminator Setting and Spill over of Alpha and Beta ray

To discriminate between alpha ray and beta ray, spill over should be minimized. Therefore, it is required that the background counts is lowered by decreasing spill over in ^{241}Pu and $^{239+240}$Pu measurement.

· THE CALUCLATION METHOD OF ACTIVITY FOR 241PU ANALYSIS

Generally, ^{242}Pu or ^{236}Pu is used as a chemical yield tracer for analysis of Pu isotopes in environmental samples. Since the energy resolution in the LSC measurement is inadequate, it is possible to discriminate the tracer from the other Pu(alpha) isotopes. Therefore, SSD is used to obtain the chemical yield in the ^{241}Pu measurement.

The correction of a chemical yield of ^{241}Pu is carried out using the following equations.

$$\text{Observed activity Ratio } (R) = \frac{{}_{Total}Pu\ (\alpha)_{LSC}}{{}_{Total}Pu\ (\alpha)_{SSD}} \quad \cdots (1)$$

$$\text{Activity of } {}^{241}Pu \text{ in total sample} = \frac{1}{R} \times {}^{241}Pu_{LSC} \quad \cdots (2)$$

${}_{Total}Pu\ (\alpha)_{SSD}$: Activity of Pu tracer and Pu (α) in sample by SSD measurment

${}_{Total}Pu\ (\alpha)_{LSC}$: Activity of Pu tracer and Pu (α) in sample by LSC measurment which was calculated from their quenching curve

${}^{241}Pu_{LSC}$: Activity of ${}^{241}Pu$ in LSC measurment sample which was calculated from their quenching curve

The radioactivity of each Pu (alpha) isotopes in a sample is measured by SSD. After chemical preparations, all the Pu isotopes on the electorodepositted disks are measured by LSC.

In LSC counting, activity of ^{241}Pu and total Pu(alpha)$_{LSC}$ are obtained. The radioactivity of $^{241}Pu_{LSC}$ is calculated from its quench curve. But, it does not contain the ratio of electorodepositting and dissolution from SSD samples. Thus, the radioactivity of ^{241}Pu is calculated from that of $^{241}Pu_{LSC}$ divided by the observated activity ratio.

EXPERIMENT

・THE BASAL CONDITION

The optimum conditions need to be set to discriminate alpha ray from beta ray. Before LSC measurement, optimum conditions need to be determined. Table 1 shows the used equipment for LSC measurement.

Table 1 Used Equipment of This Experiment

equipment	name
measuring instrument	Packard 2550 TR/AB
vial	Wheaton Liquid Scintallation Vial 20ml
vial cap	Wheaton Polypropylene
scintillator	Packard Ultima Gold (Naphthalene based)
	Packard Ultima Gold XR (〃)
	New England Aquasol-II (Xylene based)
	Dojin Kagaku Scintisol EX-H (〃)

In this experiment, ^{241}Am and ^{90}Sr were selected as an alpha source and a beta source in order to set up spill over for these scintillators.

^{3}H was used in order to determine the efficiency of ^{241}Pu, because their maximum energies are almost equal. The Pu solution (1M HCl 1ml) and each scintillator were mixed and cooled over 12 hours to ensure certain the optimum conditions. The region of interest and measuring time were adjusted for the actual liquid scintillation measurement.

ANALYSIS OF THE ENVIRONMENTAL SAMPLES

The analytical method of ^{241}Pu in the environmental samples referred to Japan Nuclear Cycle Development Institute, Tokai Works, standard procedures for environmental analysis [5]. The analysis flow is shown in Fig. 6.

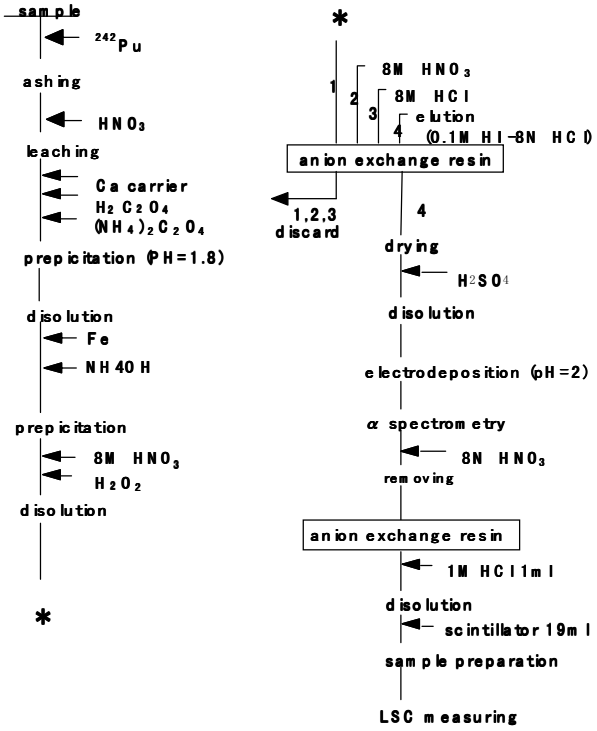

Fig. 6 Diagram of analytical method

After purification of Pu by the anion exchange resin, the entire sample is measured by alpha spectrometry with SSD. The Pu component is removed from the electrodeposited disk by HNO_3 and H_2O_2. The solution is run through the anion exchange resin again, and is refined. The refined solution is evaporated to dryness and is then dissolved with 1M HCl because the NO_3^- has a large quenching effect in the LSC measurement. This solution is mixed with scintillator to be a sample of ^{241}Pu measurment. After sample preparation, it is measured by LSC Packard 2550TR/AB. It has two discrimination systems. One is pulse height discrimination. The other is pulse shape discrimination. In the measurement, alpha ray and beta ray shall be discriminated using the different pulse shapes of their decay time.

RESULTS

・OPTIMUM CONDITIONS OF LSC MEASUREMENT

The scintillator names A, B, C and D are Ultima Gold, Ultima Gold XR, Aquasol-2 and Scintisol EX-H. Table 2 shows the Figure of Merit (the FOM value), B.G., efficiency and spill over setting for each scintillator. Pu(alpha) measurement ranges are 150-350 keV. The ^{241}Pu measurement ranges of A, C and D are in 1.5-7.0keV and that of B is in 1.5-7.5keV.

The background rates in the alpha region were 0.1-0.3cpm and they were about one thirtieth as compared to the conventional method. The background rates of xylene based scintillators were lower than those of naphthalene based scintillators. The spill overs of naphthalene based scintillators are smaller than those of xylene base scintillators. Efficiencies of Pu (alpha) were 88.3-96.9% using ^{242}Pu standard solution. However, beta efficiencies of xylene based scintillators were higher than those of naphthalene based scintillators.

Table 2 Result of Scintillator Test

Scintillator		Spillover (%)		Background (cpm)		Efficiency ^{3}H (%)	figure of merit ※3	
		α	β	α ※1	β ※2		α	β
Naphthalene based	A	4.28	3.64	0.3	4.6	20.9	3.1×10^{4}	95
	B	3.18	3.84	0.1	5.1	31.5	9.4×10^{4}	190
Xylene based	C	11.82	12.35	0.3	4.3	32.0	2.6×10^{4}	240
	D	12.00	12.38	0.2	3.4	35.4	3.9×10^{4}	370
	D' ※4	4.90	6.42	0.1	4.0	34.6	9.0×10^{4}	300

※1 150～350keV
※2 A、C、D、D'is 1.5～7.0keV、B is 1.5～7.5kev
※3 FOM=E^2/B.G.
※4 D'is added Naphthalen to D.

For beta ray, the FOM values of naphthalene based scintillators were higher than those of xylen based scintillators. FOM value of D (Scintisol EX-H) was the highest scintillator in the beta (^{241}Pu) region.

In order to improve the spill over performance, naphthalene, which is wavelength shifter for alpha ray, was added to D.

Fig. 7 shows the relationship between the concentration of naphthalene and spill over for beta ray. It is shown that as more naphthalene is added, the spillover is decreased, but when the concentration of naphthalene is higher than 20mg/ml, the spill over tends to increase.

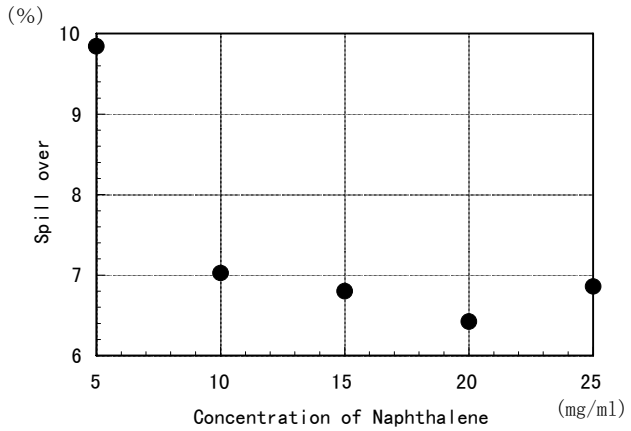

Fig. 7 Relationship between concentration of Naphtalene and Spillover for β ray

From these results, 20mg/ml naphthalene solution was added to D. The scintillator is called (D'). D' is used for ^{241}Pu analysis in environmental samples. The spill over of beta ray decreased from about 12% to about 6% by using D' solution. Fig. 8 shows their spill overs.

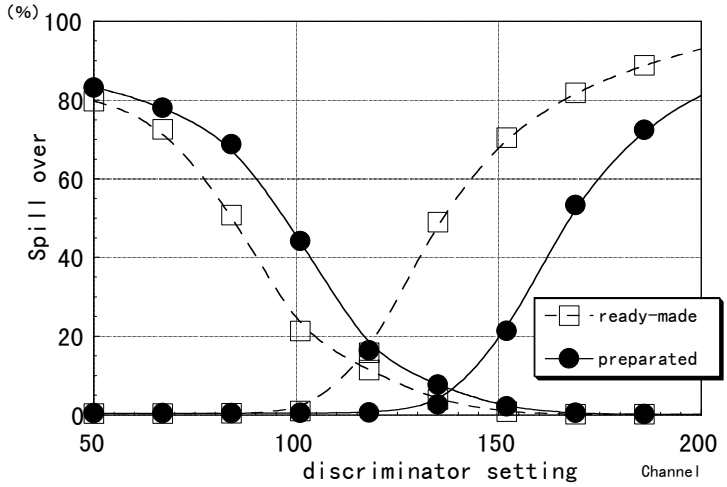

Fig. 8 Comparison between ready-made and preparated scintillstor

・THE APPLICATION TO THE ENVIRONMENTAL SAMPLES

The detection limit of ^{241}Pu is 1.4×10^{-1} Bq/kg·dry soil, quantity 200g , background counts 4.0cpm, 65% recovery percentage, 35% counting efficiency, measuring time 500 minutes. The detection limit of this method is about two times lower than the conventional method (2.2×10^{-1} Bq/kg·dry soil). It is considered that this new analytical method can be applied to many environmental samples.

This new method was applied to soil samples at Tokai Mura. The confirmation of the accuracy by the reproducibility of analysis was carried out with soil samples (200g).

Table 3 shows that the reproducibility of ^{241}Pu analysis in soil samples. The result of reproducibility is 16% which is sufficiently because sample of ^{241}Pu was removed from electrodeposited disk.

Table 3 The reproducibility of ^{241}Pu analysis in soil samples

Sample No.	^{239,240}Pu (Bq/kg・dry)	^{241}Pu (Bq/kg・dry)
1	$1.6\times10^{-1}\pm1.9\times10^{-2}$	$8.5\times10^{-1}\pm1.1\times10^{-1}$
2	$1.6\times10^{-1}\pm1.0\times10^{-2}$	$7.0\times10^{-1}\pm7.0\times10^{-2}$
3	$1.4\times10^{-1}\pm8.7\times10^{-3}$	$6.7\times10^{-1}\pm5.8\times10^{-2}$
4	$1.4\times10^{-1}\pm1.0\times10^{-2}$	$7.0\times10^{-1}\pm8.8\times10^{-2}$
Average	1.5×10^{-1}	7.0×10^{-1}
Standard Deviaton	1.1×10^{-2}	1.1×10^{-1}
Coefficiency Deviation	7.1%	16%

Table 4 shows the results of analysis of surface soil samples collected in 1996. Activity level of ^{241}Pu was 1.8×10^{-1} - 8.0×10^{-1} Bq/kg·dry. As a result, ^{241}Pu / ^{239,240}Pu activity ratios were 2.3 - 2.8 for 1996. The results were almost the same values as previous data [2), (6)] reported in 1988, if decay of ^{241}Pu was taken into account.

CONCLUSION

An analytical method of ^{241}Pu in environmental samples has been studied. This method uses a pulse shape discrimination method that is based on the difference of decay time between alpha and beta ray. Using a

scintillator with naphthalene added to xylene based one, FOM value was doubled. In addition, detection limit of ^{241}Pu was improved to about two times lower than the conventional method.

This ^{241}Pu analysis method needs a little more time than the conventional method, but it is very useful method because only one kind of tracer used.

Determined ^{241}Pu levels in soil samples around Tokai mura are similar to previously reported levels, which originated from atmospheric nuclear testing.

REFERENCES

1. Shuichi Sumiya et al; Development of an Analytical Method of ^{241}Pu in Environmental Samples : PNC Technical review, 66, 92-95, (1988)
2. Osamu Matsuoka;Safety Estimation of Plutonium (In Japanese):The Nikkan kougyou Shinbunsya, (1993)
3. Yu-fu Yu ; Determination of Plutonium-239+Plutonium-240 and Plutonium-241 in Environmental Samples Using Low-level Liquid Scintillation Spectrometry, *Analyst*. ,117, 439-442, (1992)
4. Charles Passo et al ; The essential of Alpha / Beta Discrimination, Packard Instrument Company., (1992)
5. Power Reactor and Nuclear Fuel Development Corporation; Manual of Standard Procedures for Environmental Sampling and Analysis, PNC TN8520, 94-009
6. Kanazawa University Low level Radioactivity Laboratory; Transuranium Elements (Np, Pu, Am) in Sediment Cores from Mikata Five Lakes,1987.4-1988.3