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Combined application of alpha-track and fission-track techniques for detection of plutonium particles in environmental samples prior to isotopic measurement using thermo-ionization mass spectrometry

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ABSTRACT

The fission track technique is a sensitive detection method for particles which contain radio-nuclides like ^{235}U or ^{239}Pu. However, when the sample is a mixture of plutonium and uranium, discrimination between uranium particles and plutonium particles is difficult using this technique. In this study, we developed a method for detecting plutonium particles in a sample mixture of plutonium and uranium particles using alpha track and fission track techniques. The specific radioactivity (Bq/g) for alpha decay of plutonium is several orders of magnitude higher than that of uranium, indicating that the formation of the alpha track due to alpha decay of uranium can be disregarded under suitable conditions. While alpha tracks in addition to fission tracks were detected in a plutonium particle, only fission tracks were detected in a uranium particle, thereby making the alpha tracks an indicator for detecting particles containing plutonium. In addition, it was confirmed that there is a linear relationship between the numbers of alpha tracks produced by plutonium particles made of plutonium certified standard material and the ion intensities of the various plutonium isotopes measured by thermo-ionization mass spectrometry. Using this correlation, the accuracy in isotope ratios, signal intensity and measurement errors is presumable from the number of alpha tracks prior to the isotope ratio measurements by thermal ionization mass spectrometry. It is expected that this method will become an effective tool for plutonium particle analysis. The particles used in this study had sizes between 0.3 and 2.0 μm.

1. Introduction

The International Atomic Energy Agency (IAEA) has adopted environmental sampling as a new method for the strengthened safeguard system [1,2]. The objectives of this method are both to check declared activities and to detect undeclared in nuclear plants. One of the analytical methods for environment sampling is particle analysis, a powerful tool for nuclear safeguards to detect undeclared nuclear activities. In this method, isotope ratios of nuclear material present in individual particles are measured in pieces of cotton cloth wiped on surfaces so as to collect dust (particulate material). Two commonly used analytical methods to perform such investigations are secondary ion mass spectrometry (SIMS) [3–5] and fission track-thermal ionization mass spectrometry (FT-TIMS) [6–8]. In the former, the particles of interest are rapidly detected followed by the individual isotopic measurements. The latter is a high-sensitivity method for measurement of precise isotopic abundance of major and minor isotopes of plutonium and uranium. The major advantage of this method is its specific ability to detect and then to analyze particles which contain the highest proportion of fissile radio-nuclides, i.e. highly enriched uranium particles useable for the manufacturing of nuclear weapons.

Accuracy of the isotopic measurement of the small amount of nuclear material (uranium or plutonium) in particles is one of the important concerns in particle analysis. It is notably necessary to analyze a single particle, so as to avoid the so-called mixing effect. The particles that are commonly present in the swipe sample are uranium and plutonium. Samples containing either of these particles can be detected with a high sensitivity using the fission track technique. However, it is difficult to use this method to detect plutonium particle alone from a mixed sample of uranium and plutonium. This opened up a new avenue of research to develop a new method in order to overcome the disadvantage.

All isotopes of uranium and plutonium decay by emission of alpha particles, except ^{241}Pu which undergoes beta decay with a half-life of 14.325 years to produce ^{241}Am [9]. The specific radioactivity (Bq/g) under alpha decay of plutonium is several orders of magnitude higher than that of uranium, and thus the formation of an alpha track by uranium can be disregarded under suitable conditions. This suggests that the number of alpha tracks can be used

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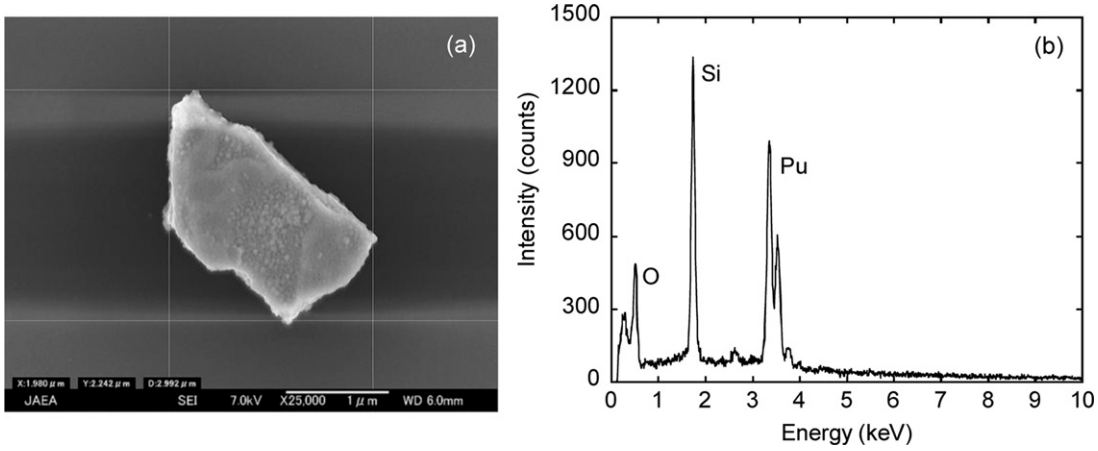

Fig. 1. SEM image (a) and EDX spectrum (b) of a plutonium particle on a Si planchet.

as an indicator for discriminating uranium and plutonium. Because the number of alpha tracks reflects the number of atoms of a plutonium particle, it can be used as an indicator of the extent of signal intensity when the isotope ratio of plutonium particle is analyzed provided the all plutonium particles are made of the same certified reference material. Information on the isotope ratio measurements such as signal intensity and measurement precision can be estimated from the number of alpha tracks prior to mass spectrometry analysis.

In this study, a method for detecting the particle containing plutonium from a mixed sample of plutonium and uranium is described using an alpha track technique in addition to the particle detection method by fission track technique that we developed. In addition, the correlation between the number of alpha tracks produced by plutonium particles and the isotope ratio measurement of the particles is described. We also described the production of plutonium particles used in this study.

2. Experimental

2.1. Preparation of particulate plutonium

Well-defined, monodisperse plutonium oxide particles are produced by a vibrating orifice aerosol generator (VOAG) system connected to a furnace system [10,11]. However, in the present study, a simpler method was developed that does not involve a VOAG method. The procedure for production of particles is described below. Isotopic standard reference material (SRM-947, plutonium solution, NIST, USA) was used for production of particulate plutonium. The plutonium solution with a concentration of 0.33 μg Pu/μL was subjected to a chemical purification using an anion exchange resin in order to remove americium and uranium. The purified plutonium solution of 30 μL was pipetted into a Teflon vessel, evaporated and then dissolved in 3 μL of 8 M HNO_3 by heating. The obtained solution was pipetted into a 1 mL volumetric round-bottomed flask made of silica glass and then evaporated to form a pinpoint dried residue. The flask containing the pinpoint dried residue was heated at 800 °C for 20 s to produce plutonium oxide. After cooling, *n*-dodecane (10 μL) was added into the flask and the dried residue was crushed with a silica glass rod to form particles. A further 90 μL of *n*-dodecane was added to the flask, which was then placed in an ultrasonic bath for 20 min in order to prevent particle agglomeration. The *n*-dodecane solution which contains plutonium particles was pipetted onto a Si planchet with a diameter of 25 mm. Then, the *n*-dodecane was evaporated by heating to obtain the plutonium particles. The *n*-dodecane played the role of particle dispersant. With pure water as the dispersant instead, the obtained particles tented to aggregate at the edges of the water on the Si planchet and strongly adhere to the surface of the planchet once the water had been evaporated, making it difficult to pick up the particles. In this method, the control of particle size is difficult because the lump of plutonium is crushed with a glass rod. Scanning electron microscope (SEM) revealed particle size distribution of around 0.3–2 μm with a maximum at approximately 1 μm. Both *n*-dodecane and pure water afforded plutonium particles of similar size distribution. Fig. 1 shows the SEM image and energy dispersive X-ray (EDX) spectrum of a plutonium particle prepared in this study. The EDX spectrum has peaks assigned to plutonium and oxygen, suggesting that the particle may be made of plutonium oxide. It was confirmed that the isotope ratio of the particle measured using thermal ionization mass spectrometry (TIMS) is consistent with that of SRM-947 solution. The particles prepared in this study are suitable for use as plutonium particles of known isotopic ratio, although they are not spherical like the particles obtained by the VOAG method. In addition, this method can be performed in a fume hood in a radioactivity-controlled area because only a small amount of plutonium solution, on the order of a few dozen microliters, is used for preparing plutonium particles; this method can also be applied for preparing plutonium–uranium mixed particles.

2.2. Sample preparation for alpha and fission tracks

Plutonium oxide particles prepared from plutonium solution (SRM-947) and uranium oxide particles (NBL 950a, NU) were used. The sizes of particles used were 2 μm or less. They were collected on a cotton cloth (TexWipe 304, 10 cm × 10 cm, TexWipe) by wiping the particles. The particles were recovered from the cotton cloth by filtration and were collected on a polycarbonate membrane filter under vacuum pumping. The filter-recovered particles were put in a 1 mL volumetric flask and 160 μL of a mixture of 1,2-dichloroethane and dichloromethane was added to them. The mixture was stirred until the polycarbonate filter was dissolved completely. The polycarbonate solution containing the particles was poured on a clean silica glass plate, and was dried to form a thin polycarbonate film containing the particles. Further information on the preparation method of particle layer can be obtained from the reference [6]. Two kinds of particle layer were prepared; one containing only plutonium and the other containing a mixture of plutonium and uranium. Subsequently, a fission track detector (Makrofol, Goodfellow Camdridge Ltd., UK) with a thickness of 20 μm was stacked on the particle layer, and the assembled stack was irradiated with a fluence of 3.6×10^{15} thermal neutrons cm^{-2} at the Japan Research Reactor (JRR)-3, Japan Atomic Energy Agency (JAEA). After irradia-

Table 1
The number of alpha tracks calculated from plutonium and uranium particles under various conditions.

Particles	Exposure time (day)	Particle diameter (μm)	Radioactivity[a] (Bq)	Number of αT[b]
Pu (SRM 947)	7	0.5	3.65E−03	1104
		1	2.92E−02	8831
		3	7.89E−01	238,447
	30	0.5	3.65E−03	4731
		1	2.92E−02	378,849
		3	7.89E−01	1,021,917
NU (natural composition)	7	0.5	1.14E−08	0
		1	1.13E−07	0
		3	3.05E−06	1
	30	0.5	1.14E−08	0
		1	1.13E−07	0
		3	3.05E−06	4
U100 (10% ^{235}U enriched)	7	0.5	1.39E−08	0
		1	1.12E−07	0
		3	3.01E−06	6
	30	0.5	1.39E−08	0
		1	1.12E−07	0
		3	3.01E−06	27
U350 (35% ^{235}U enriched)	7	0.5	3.34E−08	0
		1	2.64E−06	1
		3	7.21E−05	22
	30	0.5	3.34E−08	0
		1	2.64E−06	4
		3	7.21E−05	93
U850 (85% ^{235}U enriched)	7	0.5	8.47E−07	0
		1	6.77E−06	2
		3	1.83E−04	55
	30	0.5	8.47E−07	1
		1	6.77E−06	9
		3	1.83E−04	237

[a] A sum of the radioactivity of each isotope.
[b] The number of alpha tracks corresponds to all the tracks induced by the alpha-emitter radio-nuclides present in the particles. It was assumed that the emitted particles were all detected within the range of 2π-geometry in the calculation, although a portion of the emitted particles may not be detected by the range of incident angle of particles on the detector.

tion, an alpha track detector (CR-39, BARYOTRAK, FUKUVI Chemical Co. Ltd., Japan) with a thickness of 0.9 mm was stacked on the particle layer, and the assembled stack was left for one week in order to create detectable alpha tracks.

2.3. Etching of detectors

The alpha track and fission track detectors were etched in a 7 M NaOH at 70 °C for 3 h and 6 M NaOH at 55 °C for 15 min, respectively. After etching, the appearances of alpha and fission tracks were observed using a digital microscope (VHX-200, KEYENCE, Japan).

2.4. Isotope ratio measurements

A small square portion of the particle layer containing one particle was cut out using a N_2 laser (LMD, Leica Microsystems) and then transferred onto a TIMS filament. Isotope ratio measurements by TIMS (TRITON, Thermo Fisher Scientific, USA) were performed by using a continuous heating method [12]. The instrument is equipped with a secondary electron multiplier in an ion counting mode. A double filament assembly made of zone-refined Re was used.

The ionization filament was heated up until the ^{187}Re intensity became 100 mV, and then the ion lens system was optimized to obtain maximum intensity. After the ^{187}Re intensity was readjusted to 100 mV, the measurement process was commenced. The evaporation filament (EF) was gradually raised to 4000 mA (corresponds to a temperature of 1730 °C) in order to evaporate the sample. The signal of ^{239}Pu appeared at the EF current of 1200 mA (corresponds to a temperature of 810 °C), and the highest intensity was observed at approximately 2000 mA (corresponds to a temperature of 1280 °C). The intensities of each isotope were measured with a peak-jumping sequence. For details of the isotope ratio calculation, refer to the continuous heating method [12].

3. Results and discussion

3.1. Detection of plutonium-containing particles

Alpha particles emitted by alpha-emitter radio-nuclides register as tracks in a detector. The number of alpha tracks depends on the exposure time for detecting alpha particles and the radioactivity of alpha-emitter radio-nuclides. The number of alpha tracks per particle ($N_{\alpha T}$) can be calculated by summing of all tracks induced by the alpha-emitter radio-nuclides present in the particle. The numbers of tracks induced by alpha decay in uranium and plutonium are given by

$$N_{\alpha T(Pu)} = N_{\alpha T(Pu\text{-}238)} + N_{\alpha T(Pu\text{-}239)} + N_{\alpha T(Pu\text{-}240)} + N_{\alpha T(Pu\text{-}242)} \quad (1)$$

$$N_{\alpha T(U)} = N_{\alpha T(U\text{-}233)} + N_{\alpha T(U\text{-}234)} + N_{\alpha T(U\text{-}235)} + N_{\alpha T(U\text{-}236)} + N_{\alpha T(U\text{-}238)} \quad (2)$$

The number of alpha tracks induced by each alpha-emitter radio-nuclide $N_{\alpha T(i)}$ can be calculated using the following equation.

$$N_{\alpha T(i)} = A_{(i)} \cdot t \cdot \varepsilon \quad (3)$$

where $A_{(i)}$ is the radioactivity of alpha-emitter radio-nuclide (i) [Bq]; t is the exposure time for detecting alpha particles [s]; and ε is the detection efficiency, which depends on the geometry between alpha-emitter radio-nuclide-containing particle and detector (0.5 for 2π-geometry). The radioactivity of each alpha-emitter radio-

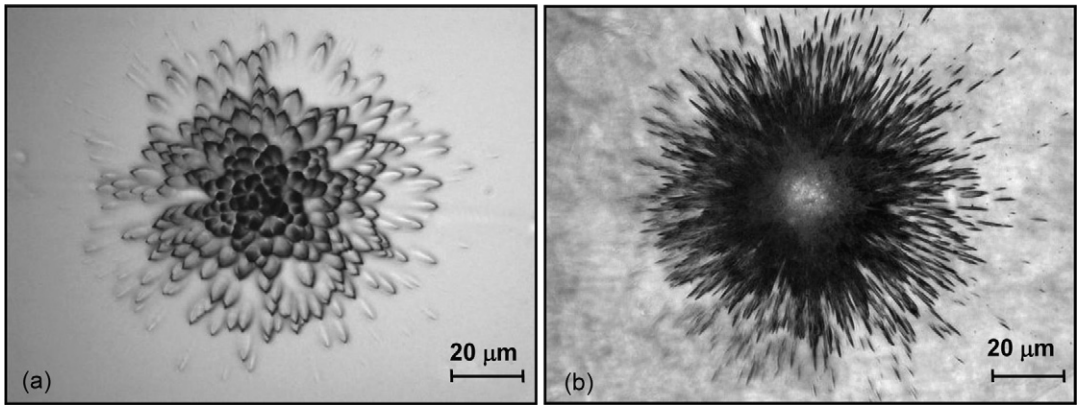

Fig. 2. Appearances of alpha tracks (a) and fission tracks (b) by a plutonium particle.

nuclide $A_{(i)}$ can be derived using the specific radioactivity $S_{(i)}$ [Bq/g] and the mass $m_{(i)}$ of an alpha-emitter radio-nuclide (i) [g]:

$$A_{(i)} = S_{(i)} \cdot m_{(i)} \quad (4)$$

Assuming spherical particles of diameter d, $m_{(i)}$ can be calculated using following equation.

$$m_{(i)} = \frac{B_{(i)}}{100} \cdot \frac{\pi d^3}{6} \cdot \rho \quad (5)$$

where $B_{(i)}$ is the isotopic abundance of alpha-emitter radio-nuclide (i) in the particle [%] and ρ is the density of particle [g/cm^3].

Table 1 shows the calculated number of alpha tracks produced by alpha decay of plutonium and uranium particles under various conditions by using Eqs. (1)–(5). As can be seen, the formation of alpha tracks in uranium is negligible under the conditions used. Fig. 2 shows the microscopic images of alpha tracks (a) and fission tracks (b) produced by a plutonium particle prepared in this study. Clear alpha tracks and fission tracks were formed. As can be seen from Table 1 and Fig. 2, the particles forming both tracks were determined to be plutonium, while the particles forming only fission tracks were determined to be uranium. Fig. 3 shows the microscopic images of fission tracks (a) and alpha tracks (b) in the same area of a mixed sample containing plutonium (SRM 947) and uranium (NU). One alpha track group is formed even though there were three fission track groups. In Fig. 3(a), the fission track group with the corresponding alpha track group is attributed to plutonium particle, whereas the one without the corresponding alpha track group is attributed to uranium particle. Accordingly, the position of plutonium particle on the particle layer corresponds to the position of the fission track group on the solid state track detector, provided that a corresponding alpha track group is also observed on the other solid state track detector.

3.2. Identification of plutonium-containing particles from alpha tracks

The method for identifying a plutonium particle corresponding to an alpha track is described. The alpha track and fission track detectors are superimposed. Therefore, the alpha track and fission track groups produced by the same particle are clearly superimposed and are easily identified. Fig. 4(a) shows both an alpha track group and the corresponding fission track group. The plutonium-containing particle corresponding to the fission track group is located after the fission track detector is piled up on the particle layer. As shown in Fig. 4(b), the plutonium-containing particle is at the center of the fission track. Here, the microscope is focused on the particle that is present under the fission track detector. Accordingly, the plutonium-containing particle is identified from the alpha track.

In order to detect a particle of interest, a precise coincidence between the positions of alpha track group and the corresponding fission track group, as well as between the positions of the particle and the corresponding fission track group is of great importance. The corresponding fissile radio-nuclides containing particles can be identified correctly and easily because a part of fission track detector and the particle layer was fixed on the silica glass plate [6]. However, an accurate superposition of the alpha track detector and the fission track detector is difficult because the alpha track detector is completely separated for etching. In this study, we used a U-shaped tool that is composed of transparent acrylic with thick-

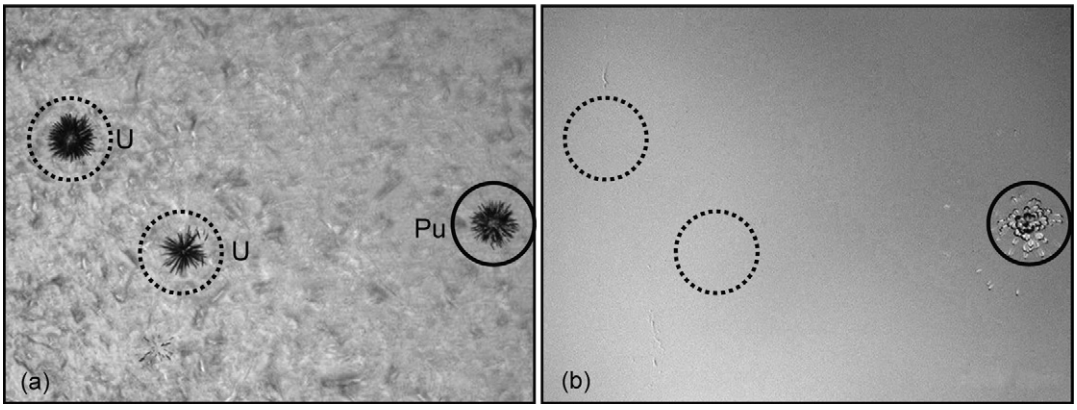

Fig. 3. Appearances of fission tracks (a) and alpha tracks (b) in the same area of sample containing both plutonium and uranium particles.

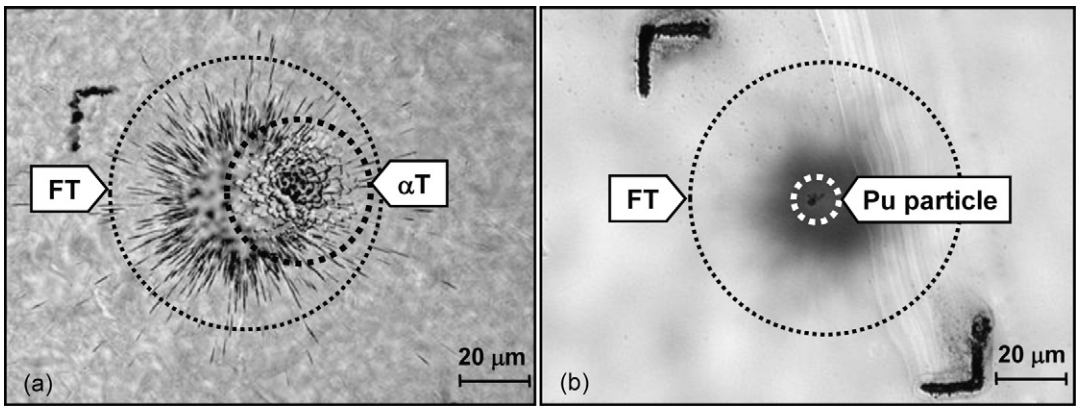

Fig. 4. Identification of a plutonium particle from the corresponding alpha track group. Microscopic images of an alpha track group superimposed on the corresponding fission track group (a) and a plutonium particle superimposed on the corresponding fission track group which was beforehand identified from the related alpha track group (b).

ness of 3 mm for adjusting the position of the two detectors. The widths of fission track detector and silica glass plate, on which the particle layer is fixed, are matched with the inside width of the U-shaped tool beforehand. The alpha track detector and the particle layer were put in this tool for the formation of alpha tracks. Thus, an accurate alignment of the alpha track detector with the particle layer, and, consequently, with the fission track detector, is possible only by using this tool after etching.

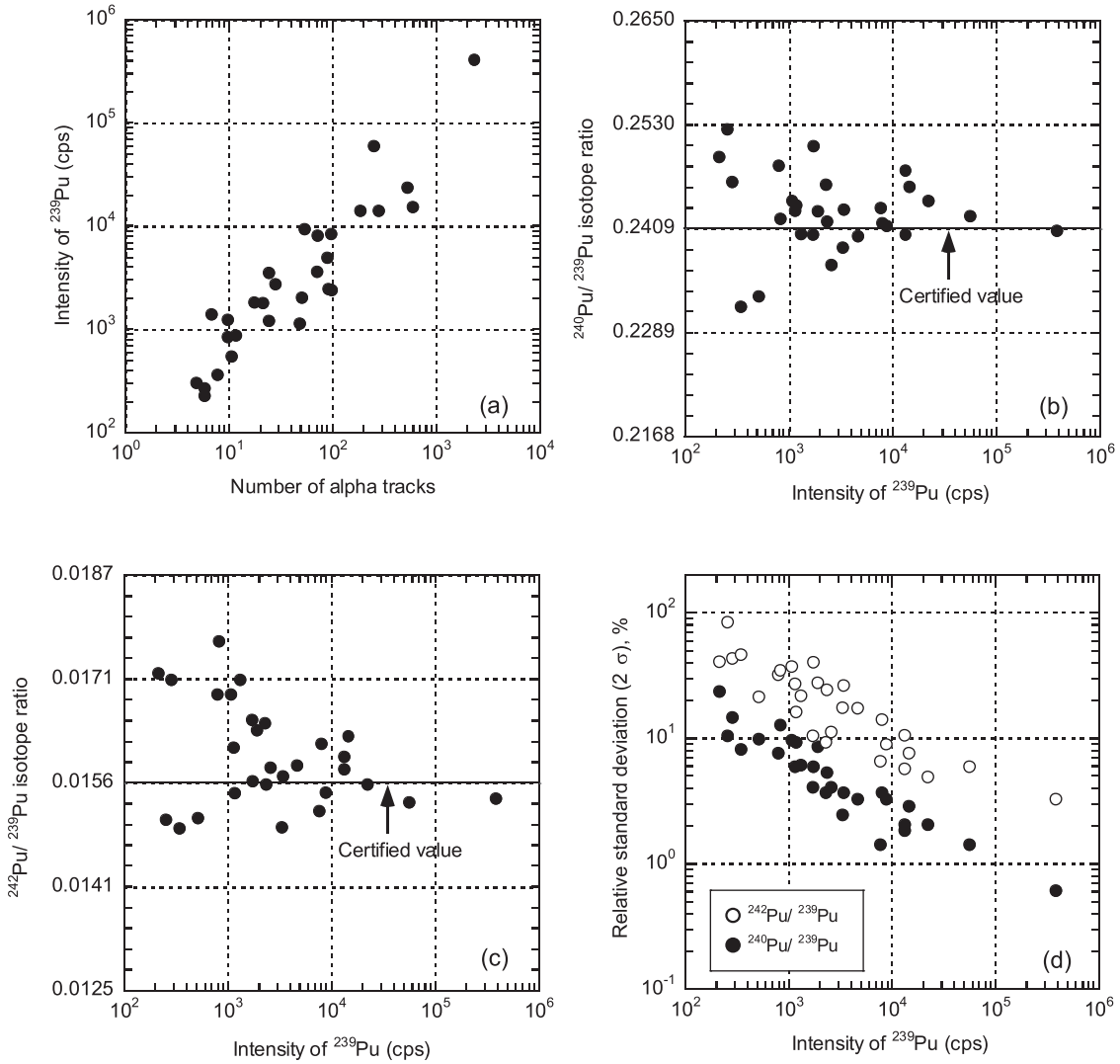

Fig. 5. Results of TIMS measurements and the number of alpha tracks. Correlation between the ^{239}Pu signal intensity by TIMS and the number of alpha tracks (a), the ^{240}Pu/^{239}Pu isotope ratio by TIMS and intensity of ^{239}Pu (b), the ^{242}Pu/^{239}Pu ratio by TIMS and intensity of ^{239}Pu (c) and the RSDs in ^{240}Pu/^{239}Pu, ^{242}Pu/^{239}Pu and intensity of ^{239}Pu (d).

3.3. Correlation between the number of alpha tracks and TIMS measurements

Here, the correlation between the number of alpha tracks and the TIMS measurement is described. Fig. 5(a) shows the correlation between the number of alpha tracks made by plutonium particles prepared from the SRM 947 solution and the signal intensity of ^{239}Pu measured by TIMS for the particle. The number of alpha tracks was counted with a hand tally-counter under a digital microscope. As shown in this figure, the signal intensity of ^{239}Pu increases in proportion to the number of alpha tracks. Fig. 5(b and c) shows correlations of the deviation from the certified value in the isotope ratios of ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu and the signal intensity of ^{239}Pu. It was found that the accuracy of isotope ratios improved with an increase in the signal intensity of ^{239}Pu, that is, an increase in the number of alpha tracks. The relative standard deviations (RSDs) of the ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotope ratios plotted against signal intensity of ^{239}Pu are shown in Fig. 5(d). The RSDs decrease with increasing signal intensity of ^{239}Pu. As can be seen from the correlation shown in Fig. 5, the signal intensity of ^{239}Pu and the accuracy and RSDs of isotope ratios are presumable from the number of alpha tracks produced by a plutonium particle. The correlation will be useful as a reference, although the correlation cannot be directly applied to the real-life samples.

4. Conclusions

A method was developed for detecting the plutonium-containing particles in an environmental sample using fission track and alpha track techniques. The plutonium-containing particles can be detected in the environmental sample containing many uranium and plutonium particles. In the current method, fission tracks and alpha tracks were detected for plutonium particles, although only fission tracks were detected for uranium particles. Also, it has been shown that number of alpha tracks emitted by a single particle has a close correlation with the presence of plutonium-containing particles as well as the results of TIMS measurements when all particles are made with the same certified plutonium isotopic reference material. Particularly, the method for identifying plutonium-containing particles developed in this study is found to be an effective tool for particle analysis where an analysis of a single particle is requested. The results obtained in this study suggest that an appropriate nuclear reactor is no longer necessary for detecting and localizing plutonium particles. In addition, it has been shown that the plutonium particles produced in this study can be used a reference material with known isotopic composition.

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