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Age determination analysis of a single uranium particle for safeguards

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Abstract

An analytical technique was developed to determine the age of uranium particles. After the chemical separation of uranium and thorium, the ^{230}Th/^{234}U ratio was measured using single-collector inductively coupled plasma mass spectrometry and a ^{233}U-based reference material comprising a certain amount of ^{229}Th as a progeny nuclide of ^{233}U. The results allowed us to determine the purification age of two certified materials, i.e., U-850 and U-100, which was in good agreement with the reference purification age (61 y). Moreover, the age of a single U-850 particle was determined with a difference of − 28 to 2 years from the reference date.

Keywords Age determination · Uranium particles · Safeguards · Isotope ratio · ICP–MS · Anion-exchange separation

Introduction

The analysis of safeguards environmental samples has been adopted by the International Atomic Energy Agency (IAEA) for the detection of undeclared nuclear activities, where isotopic and quantitative analyses of nuclear materials have been performed in environmental swipe samples collected during IAEA safeguards inspections [1, 2]. Determining the age of nuclear materials can reveal important and detailed data on nuclear activity, as it can provide hints about their origin and history. To date, several studies have focused on determining the age of nuclear material for nuclear safeguards and forensics purposes using the ^{230}Th–^{234}U or ^{231} Pa–^{235}U chronometer for uranium [3–12] and the ^{241}Am–^{241}Pu or ^{236}U–^{240}Pu chronometer for plutonium [13–17].

The nuclear materials contained in safeguards environmental swipe samples collected from nuclear facilities are expected to be found in small quantities in the form of micron-sized particles. Therefore, the age dating in the field of swipe sample analysis for safeguards should focus mainly on individual nuclear particles. In previous studies, we have determined the age of plutonium for single plutonium or uranium–plutonium mixed particles [18–20]. However, the determination of the age of uranium, which is one of the most interesting elements in safeguards, is more challenging compared to plutonium, because the number of daughter atoms grown from their parent nuclide is small due to the long half-lives of ^{234}U and ^{235}U compared to those of ^{240}Pu and ^{241}Pu. Several studies have reported the age determination of micron-sized particles consisting of uranium oxides. Pointurier et al. [7] determined the age (40 years) of 1%-enriched uranium samples of a few micrograms (10^{-6} g) by spiking of ^{229}Th and ^{233}U reference solutions, chemical separation using anion-exchange columns, and determination of the ^{230}Th/^{234}U ratio by combination of inductively coupled plasma mass spectrometry (ICP–MS) and thermal ionization mass spectrometry measurements. They determined 6–25 fg of ^{230}Th in their analysis. Meanwhile, further ultra-trace analytical technique should be used for the IAEA safeguards environmental samples to determine the age of micron-sized uranium particles. Fauré et al. [10] determined the age of uranium oxide particles (0.8–2.8 μm in diameter) of U-100, U-850, U-900, and U-970 by secondary ion mass spectrometry (SIMS). They directly measured ^{230}Th/^{234}U ratio in a particle which may contain sub-fg of ^{230}Th. Szakal et al. [21] determined the purification age of individual uranium micron-sized particles by large geometry secondary ion mass spectrometry (LG–SIMS). In many research works on the U–Th age determination, the ^{230}Th/^{234}U ratio was measured by SIMS/LG–SIMS, or isotope dilution method for determining uranium and thorium in a sample separately.

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In our laboratory, a batch of ^{233}U spike solution have been stored for determining the total mass of uranium in the IAEA safeguards environmental samples by the isotope dilution method. It was found that our batch of the CRM 111-A was contaminated with trace plutonium, and the uranium in this CRM 111-A was chemically purified in 2004. Almost all other elements, including the long-lived thorium isotopes (^{229}Th and ^{230}Th) were also chemically eliminated by this purification. The progeny nuclides of the purified ^{233}U, including ^{229}Th were growing in equilibrium in this bottle. This aged ^{233}U solution was naturally spiked with ^{229}Th, whose ^{229}Th/^{233}U atomic ratio is calculable, and let us come up with this idea to simply determine the purification age of a single uranium particle by adding this ^{229}Th–^{233}U spike to the samples.

Herein, we demonstrated a method for determining the age of uranium particles using the ^{229}Th–^{233}U spike solution. Uranium oxide particles with known purification age were used, while the ^{230}Th–^{234}U chronometers along with the chemical separation of femtograms (fg) of thorium from uranium were applied for the accurate determination of the purification age. This analytical technique could be further applied to individual uranium particles collected from safeguards environmental swipe samples.

Experimental

Materials and reagents

Two types of uranium certified reference materials (CRM), U-850 (85% enriched ^{235}U, 0.6437% ^{234}U) and U-100 (10% enriched ^{235}U, 0.0676% ^{234}U) as U_3O_8 now distributed by New Brunswick Laboratory (NBL), USA, whose uranium purification was completed on December 31, 1957 and January 8, 1959 [6], respectively, were used for the analysis of this study. The atomic ratios of ^{234}U and ^{230}Th in the uranium samples were determined by spiking a CRM 111-A solution (99.4911% enriched ^{233}U, NBL, USA) stored in our laboratory, where uranium was chemically purified on August 5, 2004 by anion-exchange chromatography. The feed CRM 111-A (807 µg of ^{233}U) was dissolved in 2 mL of 10 M HCl–0.1 M HNO_3, and loaded on an anion-exchange column (inner diameter: 3.5 mm, length 130 mm, volume: 1.25 mL). Then, 6.4 mL of 10 M HCl–0.1 M HNO_3, 7 mL of 10 M HCl, and 14.2 mL of 10 M HCl–0.1 M HI were eluted in order to remove trace plutonium as a contaminant. The thorium (Th(IV)) was not retained on the anion-exchange resins, and eluted to the waste fractions. The amount of remaining ^{229}Th in the purified CRM 111-A were negligible to determine the uranium purification age; less than 6×10^{-9} of ^{229}Th/^{233}U atomic ratio, which was estimated from the analytical results of similar experiments of thorium and uranium separation. On this date, the progeny nuclides, including ^{229}Th, were also removed from the CRM. The amount of ^{229}Th increased as a decay product of ^{233}U, and the calculated atomic ratio of ^{229}Th/^{233}U in the spike solution as of September 2019 was 6.56×10^{-5}. The decay-corrected ^{229}Th/^{233}U, ^{234}U/^{233}U, and ^{230}Th/^{229}Th ratios of CRM 111-A were in good agreement with the experimental results measured by ICP–MS within the uncertainty. Thus, the calculated atomic ratio was used to determine ^{230}Th, which is the ^{234}U progeny nuclide produced in uranium particles.

Highly pure HCl and HNO_3 (TAMAPURE AA-100 and/or AA-10, TAMA Chemicals Co. Ltd., Japan) were used for all chemical treatments. Water was deionized (resistivity: 18.2 MΩ cm) with the Milli-Q system (Millipore Corp., USA), while quartz glass beakers and columns and small PFA jars (capacity: 7 mL) were purified before their use by soaking in HNO_3 (analytical grade) and rinsing with Milli-Q water.

Sample preparation

Sixteen and twelve samples with varying number of particles were prepared for the CRM U-850 and U-100, respectively. In particular, 2–210 particles with a diameter of 3–17 µm (equivalent to 0.7–126 ng of the total uranium content) were included in U-850, whereas 23–375 particles with a diameter of 2–15 µm (equivalent to 9.9–356 ng of the total uranium content) were included in U-100. Five sets of single U-100 particles (diameter: 6–20 µm) ranging between 0.9 and 16.3 ng and six sets of single U-850 particles (diameter: 8–10 µm) ranging between 0.9 and 3.4 ng were also prepared. The total uranium amount in each sample was calculated by the isotope dilution mass spectrometry method based on the measured ^{234}U/^{233}U isotopic ratio, the CRM isotopic abundance, and the CRM 111-A amount added to each sample. The CRM uranium oxide particles were collected and transferred to a 5×5 mm piece of silicon wafer (Semitec Co. Ltd., Japan) using a manipulator attached to a scanning electron microscope (SEM, JSM-7800F, JEOL Ltd., Japan) [22]. There was no electrostatic charging during the particle transfer due to using a glass-needle coated with gold. Figure 1 shows a typical SEM image of a U-850 particle. The silicon wafer loaded with the uranium particles was then placed into a small PFA jar, and 1.8 mL of 8 M HNO_3 and 0.2 mL of 6 M HCl were poured into the jar. The PFA jar lid was tightly screwed and the jar was heated on a hot plate at 180 °C for 7 h to completely dissolve the uranium particles. After removing the silicon wafer, 0.22 mL of the CRM 111-A solution (2.3 ng-U mL^{-1}), in which 0.5 ng of ^{233}U is containing, was spiked into this acid-digested solution in the PFA jar, followed by evaporation to dryness. The dried residue was dissolved again using 0.7 mL of 15 M HNO_3 to achieve a more efficient mixing of the contents, and the solution was evaporated to dryness. The dried residue was dissolved again in 0.7 mL of 9.5 M HCl to form the corresponding hydrochlorides

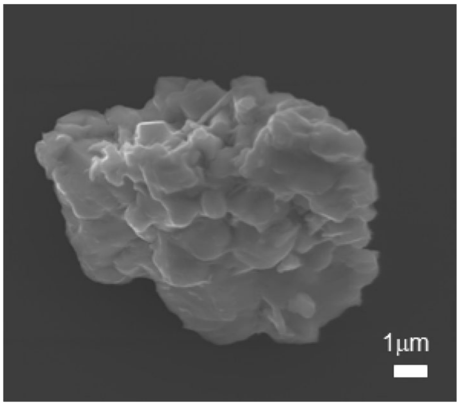

Fig. 1 SEM image of a U-850 particle (Sample ID: 29)

and the resulting solution was evaporated again to eliminate the nitrate ions. The final dried residue was dissolved in 0.7 mL of 8.5 M HCl. Then, thorium and uranium contained in the solution were chemically separated by anion-exchange chromatography using an anion-exchange resin (MCI GEL, CA08Y, Mitsubishi Chemical Corporation, Japan) packed into a quartz glass column (inner diameter: 2 mm, length: 16 mm, volume: 0.05 mL). The feed solution was loaded onto the column and thorium and uranium were sequentially eluted using 0.7 mL of 8.5 M HCl and 0.5 mL of 0.2 M HCl, respectively. The obtained thorium and uranium fractions were then evaporated to dryness and redissolved in 0.3 mL of 15 M HNO_3. After further evaporation to dryness, the residues were dissolved in 7 mL of 0.81 M HNO_3 and these solutions were used for the ICP–MS measurements. All operations, including the sample preparation and the ICP–MS measurements, were performed in clean rooms (ISO Class 6) at the Clean Laboratory for Environmental Analysis and Research (CLEAR) of the Japan Atomic Energy Agency (JAEA) [23]. Moreover, to evaluate the performance of the single anion-exchange separation method, the decontamination factor and the recovery yield were estimated by separating five aliquots of a solution containing 270 ng of the CRM U-850 and 6 ng of the CRM 111-A and measuring the intensity of the ^{229}Th and ^{233}U signals in the spikes.

Instrumentation and purification age calculation

The isotope ratios of thorium and uranium were measured using an ICP–MS instrument (ELEMENT-2, Thermo Fischer Scientific Inc., USA) under the conditions shown in Table 1. Specifically, the thorium isotope ratios were measured using the ICP–MS instrument attached to a desolvation inlet system (APEX-Q, Elemental Scientific Inc., USA). This inlet system enhanced the sensitivity by a factor of three. The mass bias was corrected by measuring the isotope ratio of the CRM U-015 (NBL, USA) solution and using the following equation:

Table 1 Operating conditions for the ICP–MS measurements

Parameter	Settings
[ICP–MS]	
RF power	1250 W
Cooling gas flow rate	17.0–17.4 L min^{-1}
Auxiliary gas flow rate	0.80 L min^{-1}
Sample gas flow rate	0.55–1.00 L min^{-1}
Solution uptake rate	0.12–0.14 mL min^{-1}
Sampling time per isotope	50 ms
Scan per replicate	200
Number of replicate (for U)	5
(for Th)	10
Resolution (M/ΔM)	300
[APEX-Q desolvation system]	
Spray chamber temperature	100 °C
Condenser temperature	2 °C
Nitrogen flow rate	1.5 mL min^{-1}
Additional gas (Ar) flow rate	0.31–0.52 L min^{-1}

$$R_t = R_m(1 + C)^{\Delta M} \tag{1}$$

where R_t is the certified isotope ratio, R_m is the measured isotope ratio, ΔM is the mass difference, and C is the mass discriminator factor. In addition, the uranium age (t) was determined using Eq. (2):

$$t = \frac{1}{\lambda_{U234} - \lambda_{Th230}} \times \ln\left(1 + \frac{\lambda_{U234} - \lambda_{Th230}}{\lambda_{U234}} \times R\right) \tag{2}$$

where R represents the ^{230}Th/^{234}U ratio in the sample and λ_{U234} and λ_{Th230} are the decay constants of ^{234}U and ^{230}Th, respectively, calculated based on the half-life of ^{234}U (2.455 (6) $\times 10^5$ y [24]) and ^{230}Th (7.54 (3) $\times 10^4$ y [25]), respectively.

The ^{230}Th/^{234}U ratio (R) was in turn determined based on Eq. (3):

$$\frac{^{230}\text{Th}}{^{234}\text{U}} = \left[\left(\frac{^{230}\text{Th}}{^{229}\text{Th}}\right)_{\text{Meas.}} - \left(\frac{^{230}\text{Th}}{^{229}\text{Th}}\right)_{\text{Sp.}}\right] \Big/ \left[\left(\frac{^{234}\text{U}}{^{233}\text{U}}\right)_{\text{Meas.}} - \left(\frac{^{234}\text{U}}{^{233}\text{U}}\right)_{\text{Sp.}}\right] \times \left(\frac{^{229}\text{Th}}{^{233}\text{U}}\right)_{\text{Sp.}} \tag{3}$$

where $(^{230}\mathrm{Th}/^{229}\mathrm{Th})_{\mathrm{Meas.}}$ and $(^{234}\mathrm{U}/^{233}\mathrm{U})_{\mathrm{Meas.}}$ are the isotope ratios of ^{230}Th/^{229}Th and ^{234}U/^{233}U measured by ICP–MS in the thorium and uranium fractions, respectively. Moreover, the ratios $(^{230}\mathrm{Th}/^{229}\mathrm{Th})_{\mathrm{Sp.}}$, $(^{234}\mathrm{U}/^{233}\mathrm{U})_{\mathrm{Sp.}}$, and $(^{229}\mathrm{Th}/^{233}\mathrm{U})_{\mathrm{Sp.}}$ represent the ratios in the CRM 111-A spike calculated from the ^{233}U and ^{234}U abundance data based on the CRM-111A reference sheet. The radioactive decay and growth after the uranium purification were also corrected. Considering that the CRM 111-A contains 0.1847 atomic% of ^{234}U and, that ^{230}Th is growing as a progeny nuclide of ^{234}U, the amount of ^{234}U, and ^{230}Th impurities in the CRM 111-A spike were estimated by calculating the radioactive decay and growth. The calculated amount of the ^{234}U and ^{230}Th impurities in the spike were subtracted from the measured values, which in turn facilitated the accurate age determination of uranium. The atomic ratio of ^{229}Th/^{233}U in the CRM 111-A, $(^{229}\mathrm{Th}/^{233}\mathrm{U})_{\mathrm{Sp.}}$, was calculated from the radioactive decay of ^{233}U and growth of ^{229}Th, assuming that no ^{229}Th was present in the purified ^{233}U spike. In addition, the combined uncertainty was estimated taking into account all uncertainties in the ICP–MS intensities, mass bias correction, certified values of the reference materials, and half-life values of each nuclide to comply with the principles described in the Guide to the Expression of Uncertainty in Measurement (GUM) [26].

Results and discussion

As shown in Table 2, the measured ratios of ^{229}Th/^{233}U, ^{234}U/^{233}U, and ^{230}Th/^{229}Th of the CRM 111-A were in good agreement with the corresponding calculated ratios within one standard deviation of each ICP–MS measurement. This result indicated that the uranium–thorium decay chain (*i.e.*, ^{233}U–^{229}Th and ^{234}U–^{230}Th) was closed in this system. Thus, the calculated values for the ^{229}Th/^{233}U, ^{234}U/^{233}U, and ^{230}Th/^{229}Th ratios of the CRM 111-A were used to further calculate the ^{230}Th/^{234}U ratio using Eq. (3). Based on Table 3, uranium and thorium were separated with a high chemical recovery yield, which was > 97% for uranium and 88–96% for thorium, while the decontamination factor of uranium in the thorium fraction was greater than 2×10^{6}. These results suggested that uranium and thorium were sufficiently separated and recovered in each fraction, thus allowing the precise determination of the purification age.

Table 2 Atomic ratios of thorium and uranium isotopes in the CRM 111-A

Ratios	Calculated values[a]	Measured values
^{229}Th/^{233}U	4.8×10^{-5}	$(4.6\pm0.6^{b})\times10^{-5}$
^{234}U/^{233}U	1.86×10^{-3}	$(1.91\pm0.08)\times10^{-3}$
^{230}Th/^{229}Th	1.20×10^{-3}	$(1.23\pm0.07)\times10^{-3}$

[a] Decay corrected values for July 8, 2015. (CRM 111-A was purified in 2004.)

[b] The error represents one standard deviation derived from five repetition of an ICP–MS measurement

Table 3 Performance of the chemical separation for the uranium–thorium dating

No	Recovery yield (%)		DF of U in the Th fraction
	Th	U	
1	88 ± 3	97 ± 1	$>4.8\times10^{6}$
2	96 ± 4	101 ± 1	2.5×10^{6}
3	90 ± 4	100 ± 1	2.1×10^{6}
4	94 ± 6	101 ± 2	$>7.2\times10^{6}$
5	92 ± 3	100 ± 1	$>5.5\times10^{6}$

The whole process blanks and detection limits determined for the investigated nuclides are shown in Table 4. Based on the three-sigma criterion, the detection limits of the target nuclides at these interested masses were determined using three times the standard deviation of the process blank count rate (cps) under the analytical conditions, 7 mL of the solution volume, and sensitivity (12.8 cps ppq^{-1} for ^{229}Th and ^{230}Th and 13.4 cps ppq^{-1} for ^{233}U and ^{234}U). The process blanks in the entire analysis were estimated to be 0.04 ng of natural uranium and 1 fg of ^{230}Th. The detection limit for ^{230}Th was calculated to be 1.3 fg, and was in line with the results of Pointurier et al., who have reported that the instrument detection limit for ^{230}Th is 1 fg by measuring a diluted 2% HNO_3 solution commonly used for the instrument rinsing [7].

Furthermore, according to Table 5, the determined purification ages for the U-850 particles agreed with the reference age (61 y) within the expanded uncertainty at the 95% confidence level. In the case of the U-850 particles, the difference between the determined ages and the reference purification age ranged between − 9.8 to 12 y and was 0.8 y in average, except for samples No. 4 and No. 5, where significantly low chemical recovery yields (~ 27% each) were obtained.

Table 4 Whole process blanks and detection limits determined for the investigated nuclides during the age determination analysis

Mass	process blank (counts s^{-1})	detection limit (fg in 7 mL of solution)
229	1.5 ± 0.4[a]	0.6
230	1.9 ± 0.8	1.3
233	2.4 ± 2.3	3.6
234	4.3 ± 0.7	1.1

[a] The error represents one standard deviation of three data obtained for three individual samples ($n = 3$)

Table 5 Analytical results of the purification age of the CRM U-850 particles

ID	Total U amount (ng)	Number of particles analyzed	^{230}Th/^{234}U atomic ratio [× 10^{-4}]	Purification age (year)[a]	Difference from the reference purification date (year)	Measured/calculated purification date
1	0.75	3	1.50 ± 0.46[b]	52 ± 38[c]	9.1	Feb-07-1967
2	0.98	3	1.40 ± 0.53	49 ± 44	12	Nov-03-1969
3	2.65	2	1.45 ± 0.29	51 ± 24	9.9	Dec-04-1967
4	4.18	7	1.14 ± 0.41	41 ± 36	20	Jan-20-1978
5	4.64	5	0.97 ± 0.60	36 ± 49	26	Jul-13-1983
6	4.73	15	1.97 ± 0.13	70 ± 11	−9.2	Oct-29-1948
7	6.12	16	1.95 ± 0.16	69 ± 14	−7.6	Jun-09-1950
8	6.17	16	1.76 ± 0.21	62 ± 17	−1.8	Mar-21-1956
9	7.21	11	1.70 ± 0.15	60 ± 13	0.4	May-30-1958
10	7.90	18	2.03 ± 0.35	71 ± 30	−9.8	Mar-31-1948
11	10.3	24	1.673 ± 0.085	59.1 ± 7.1	1.5	Jul-04-1959
12	18.0	37	1.68 ± 0.13	60 ± 11	1.0	Dec-16-1958
13	17.6	33	1.64 ± 0.11	58.0 ± 9.3	2.6	Aug-07-1960
14	94.4	172	1.688 ± 0.094	59.7 ± 7.9	1.0	Dec-16-1958
15	110	175	1.691 ± 0.039	60.0 ± 3.3	0.7	Sep-07-1958
16	126	210	1.684 ± 0.053	59.7 ± 4.4	1.0	Dec-16-1958

Average of difference from the reference purification date:0.8 years[d], and the reference purification date [6]: Dec-31-1957

[a] Reference age (i.e., elapsed year from the reference purification date on the date determined age): 61.1 years for ID 1–5, 60.6 years for ID 6, 8–9, 11–16, and 61.4 years for ID 7 and 10

[b] Combined uncertainty ($k = 1$)

[c] Expanded uncertainty (95% confidential level)

[d] Average without considering the difference for No.4 and No. 5

Table 6 Analytical results of the purification age of the CRM U-100 particles

ID	Total U amount (ng)	Number of Particles analyzed	^{230}Th/^{234}U atomic ratio [× 10^{-4}]	Purification age (year)[a]	Difference from the reference purification date (year)	Measured/calculated purification date
17	11.2	23	2.79 ± 0.28[b]	99 ± 24[c]	−38	Mar-19-1921
18	10.6	23	2.75 ± 0.67	99 ± 55	−38	Mar-19-1921
19	9.90	24	2.39 ± 0.28	85 ± 24	−24	Nov-26-1934
20	53.1	111	1.72 ± 0.16	61 ± 14	−0.3	Sep-21-1958
21	56.9	119	1.79 ± 0.25	63 ± 20	−2.5	Jul-13-1956
22	61.5	120	1.91 ± 0.53	68 ± 44	−7.7	May-01-1951
23	123	123	1.81 ± 0.14	64 ± 12	−3.3	Sep-17-1955
24	121	142	1.74 ± 0.23	62 ± 19	−0.8	Mar-05-1958
25	129	278	1.763 ± 0.048	62.4 ± 4.1	−1.7	May-09-1957
26	322	289	1.81 ± 0.19	64 ± 16	−3.9	Feb-03-1955
27	350	248	1.73 ± 0.13	61 ± 11	−0.9	Feb-07-1958
28	356	375	1.66 ± 0.15	59 ± 12	1.5	Jul-26-1960

Reference purification date [6]: Jan-08-1959

[a] Reference age (i.e., elapsed year from the reference purification date on the date determined age): 60.8 years for ID 17–25, and 60.4 years for ID 26–27

[b] Combined uncertainty ($k = 1$)

[c] Expanded uncertainty (95% confidential level)

Especially when the total amount of uranium particles analyzed was higher than 10 ng (No. 11–16); the determined age showed a difference of only three years from the reference age. However, according to Table 6, the precision of the age estimation for the U-100 particles was lower than that for the U-850 particles due to the ultra-trace contents of ^{230}Th and ^{234}U. As shown in Table 6, when more than 50 ng of U-100 particles were analyzed (No. 20–28), the difference from the reference date ranged between − 7.7 to 1.5 y. Consequently, this trace analytical method proved to be available for the determination of the purification age of uranium particles in uranium–thorium samples.

The contribution of uncertainty (uncertainty budgets) to the age determination of the representative samples was also investigated. As shown in Table 7, the ^{230}Th/^{229}Th ratio (0.202 ± 0.013) was the main contributor to the uncertainty for the U-850 particles, whereas both the ^{230}Th/^{229}Th (91–95%) and ^{234}U/^{233}U (5–8%) ratios contributed to the uncertainty for the U-100 particles. Moreover, Williams and Gaffney performed an age determination analysis using large amounts (of mg scale) of U-100 and reported that the contribution of the ^{230}Th/^{229}Th ratio measurement to the overall uncertainty was 55.19% [6]. Thus, we concluded that the ^{230}Th/^{229}Th ratio measurement uncertainty significantly contributes to the uncertainty of the purification age only when the sample amount is low. Therefore, the ^{230}Th/^{229}Th ratio should be measured with high accuracy to achieve a small uncertainty in the age determination when small sample amounts, such as particles, are used.

The purification age of single U-850 and U-100 particles was also determined (Table 8). For the U-850 particles, the difference from the reference purification age ranged between − 28 to 2 y, which was in good agreement with the actual age, although the uncertainties were large. In contrast, only the purification age of the U-100 particles No. 38 and No. 39, whose total uranium weight was more than 14 ng, could be determined. Figure 2 shows the relationship between the difference from the reference purification date and (a)the total uranium amount, (b)the ^{234}U amount, and (c)the ^{230}Th amount in the U-850 and the U-100 particles. Figure 2(a) shows the measured purification date of the U-100 particles whose total uranium amount is less than 14 ng was older than the reference date, but the difference was not found in the case of the U-850. By changing the horizontal axis of this figure to the ^{234}U amount (Fig. 2b) and ^{230}Th (Fig. 2c), the systematic error of the purification date can be identified. The systematic error was obviously confirmed in the case of less than 3 pg of ^{234}U and 0.5 fg of ^{230}Th in the measured U-100 particles. In the case of the U-850 particles, the all measured date were consistent with the reference date within the uncertainty. The all U-850 particles contained enough ^{234}U and ^{230}Th amount more than the critical values, which were estimated from the analytical results of U-100 particles. The purification date of the U-100 particles gradually decreased (older) as the ^{234}U and the ^{230}Th amount decreased. The cause of this systematic difference can be clarified by discussing the accuracy of ^{234}U and ^{230}Th amount in the analyzed uranium particle. The ^{234}U amount in a particle of sample ID 35 listed in Table 8, which sample was shown the largest difference from the reference purification date, was estimated to be 0.6 pg (^{234}U atomic abundance: 0.0676%). This amount is enough to obtain the ^{234}U/^{233}U isotopic ratio with high accuracy and good precision because several hundred counts were measured in the ICP–MS measurement. Whereas, the ^{230}Th amount of sample ID 35 was approximately 0.1 fg. In this case, around 0.2 cps of the ^{230}Th intensity can be expected in the ICP–MS measurement. This intensity is extremely lower than that of the ^{230}Th process blank (1.9 cps) listed in Table 4. As shown in the Table 7, accuracy and uncertainty of the measured ^{230}Th/^{229}Th ratio mainly contributed to the whole uncertainty and the lower limit of determination of the purification age

Table 7 Representative contributors to the whole uncertainty of the uranium purification age

Quantity	Value	%RSD	Uncertainty contribution (%)
U-850 particle (sample ID: 6)			
U mass (ng)	4.7		
^{230}Th/^{229}Th	0.202 ± 0.013	6.6	99.1
^{234}U/^{233}U	$(6.401 \pm 0.033) \times 10^{-2}$	0.52	0.6
^{234}U half-life	$(2.455 \pm 0.006) \times 10^5$	0.24	0.1
^{233}U half-life	$(1.592 \pm 0.002) \times 10^5$	0.13	0.0
U-100 particle (sample ID: 25)			
U mass (ng)	129		
^{230}Th/^{229}Th	0.469 ± 0.012	2.6	91.0
^{234}U/^{233}U	0.1768 ± 0.0013	0.76	8.0
^{234}U half-life	$(2.455 \pm 0.006) \times 10^5$	0.24	0.8
^{233}U half-life	$(1.592 \pm 0.002) \times 10^5$	0.13	0.2

Table 8 Analytical results of the purification age of single U-850 and U-100 particles

ID	Total U amount (ng)	^{230}Th/^{234}U atomic ratio [$\times 10^{-4}$]	Purification age (year)[a]	Difference from the reference purification date (year)	Measured/calculated purification date
U850					
29	0.90	1.60 ± 0.37[b]	57 ± 33[c]	3.6	Aug-17-1961
30	0.98	1.72 ± 0.43	60 ± 36	2.0	Jan-15-1960
31	1.38	1.94 ± 0.75	68 ± 63	−6.2	Oct-29-1951
32	1.52	2.08 ± 0.54	74 ± 47	−12	May-08-1946
33	1.76	2.35 ± 0.45	82 ± 38	−20	Feb-19-1938
34	3.40	2.58 ± 0.62	90 ± 52	−28	Dec-03-1929
Reference purification date [6] Dec-31-1957					
U100					
35	0.90	29.8 ± 5.3[b]	1068 ± 438[c]	−1007	N.D
36	2.32	11.4 ± 2.0	405 ± 167	−344	N.D
37	4.34	8.3 ± 1.5	296 ± 120	−234	N.D
38	14.0	2.45 ± 0.29	87 ± 25	−25	Oct-09-1933
39	16.3	2.88 ± 0.44	101 ± 36	−40	Dec-27-1918
Reference purification date [6] Jan-08-1959					

[a] Reference age (i.e., elapsed year from the reference purification date on the date determined age: 61.1 years for ID 29, 62.3 years for ID 30–34, and 61.3 years for ID 35–39

[b] Combined uncertainty ($k = 1$)

[c] Expanded uncertainty (95% confidential level)

in this analytical technique. Figure 3 shows the relationship between the ^{230}Th/^{234}U ratio of the U-100 particles (Table 8) calculated from Eq. (3) and the total uranium amount analyzed in this study. The ^{230}Th/^{234}U ratio (i.e., the purification age) in a single U-100 particle gradually increased as the total uranium amount decreased. Moreover, the three curves in Fig. 3 indicated that the gradual increase in the ^{230}Th/^{234}U atomic ratio in a U-100 particle was due to the contamination of ultra-trace ^{230}Th as a process blank. The determined ^{230}Th/^{234}U ratio was dotted ranging in the 1–2-fg curvature region, indicating that ^{230}Th contamination as a process blank from 1 to 2 fg randomly occured during the age determination analysis run of these U-100 paticles. This systematic error of the variation between 1 and 2 fg implied that the ^{230}Th process blank should be carefully controlled and accurately corrected at the fg level to accurately determine the purification age of a single low-enriched uranium particle. Figure 3 shows ^{230}Th contamination of 1–2 fg may happen during the age determination analysis run, including the chemical separation, the sample preparation of ICP–MS measurement. However, many of the particles containing ^{230}Th of approximately 1 fg were good agreement with the reference purification date within the uncertainty as shown in Fig. 2c. Consequently, the practical small particle-size limit for being able to analyze an age determination with the method in this work considered to be the particle containing ^{230}Th of 1 fg, which particle size were, then, estimated to be 5.9 µm in diameter for the U-850, and 12.6 µm in diameter for the U-100, respectively (in case of the age 61 y, and the form of spherical shape U_3O_8). The precise measurement of the isotope ratios using a multi-collector ICP–MS (MC–ICP–MS) and LG–SIMS would also contribute to the effective determination of the purification age.

Conclusions

The purification age of a high-enriched (1 ng) and a lower-enriched single uranium particles (tens ng) with micron-sized was accurately determined with the isotope dilution method using a ^{229}Th–^{223}U mixed spike. This mixed uranium spike was readily prepared by leaving a chemically purified ^{233}U spike solution to stand for a long time, thus increasing the ^{229}Th amount emerging as a progeny nuclide of ^{233}U. The results indicated that the main factor contributing to the whole uncertainty in the results was the uncertainty in the ^{230}Th/^{229}Th ratio measurement in the chemically separated thorium fraction. Thus, it was strongly suggested that the thorium isotopes should be accurately analyzed at the sub-fg to fg level, and that the ^{230}Th process blank should be carefully controlled at the sub-fg level. MC–ICP–MS will be thus applied as a powerful tool to achieve this ultra-trace analysis and the analytical results will be reported in the near future.

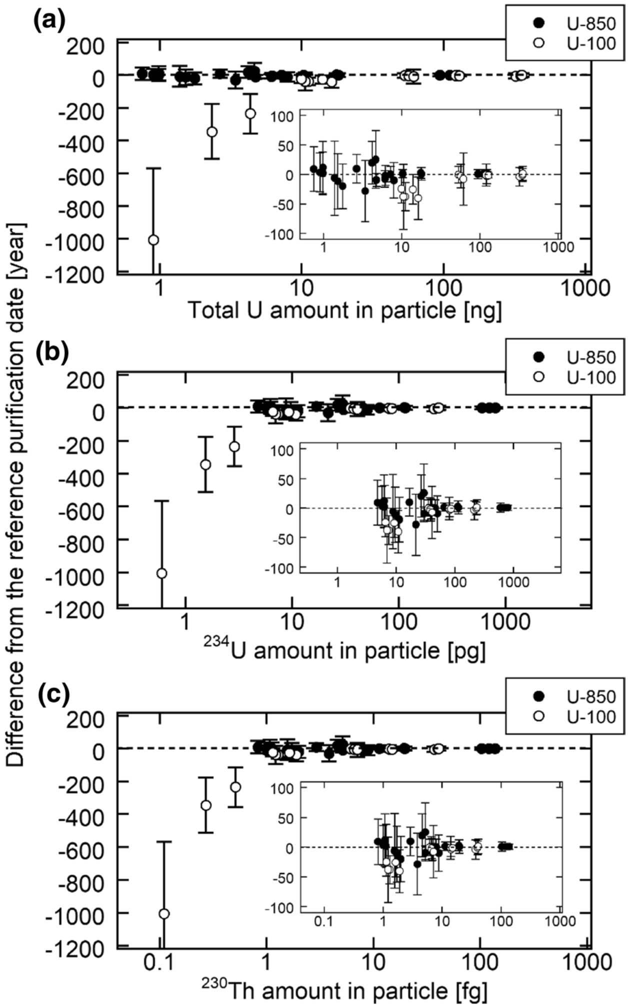

Fig. 2 Relationship between the difference from the reference purification date and **a** the total uranium, **b** the ^{234}U, and **c** the ^{230}Th amount in the U-850 and U-100 particles

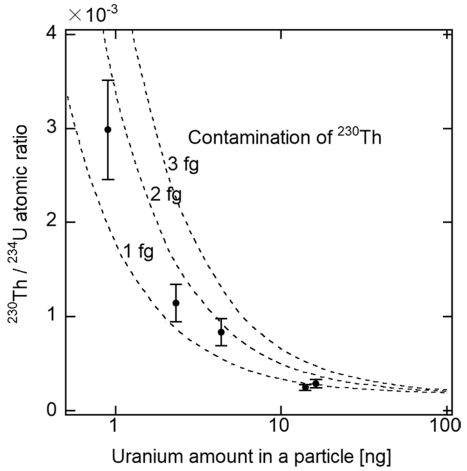

Fig. 3 Contribution of the ^{230}Th process blank to the ^{230}Th/^{234}U ratio in a single U-100 particle

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