CrossMark

A comparison of two calibration methods of the ^{229}Th spike for uranium age dating by ^{230}Th/^{234}U radiochronometer

Yan Chen[1] · Yong-Gang Zhao[1] · Li-Li Li[1] · Zhi-Yuan Chang[1] · Liu-Chao Zhu[1] ·
Guo-Ping Xiao[2] · Sheng-Hui Huang[1]

Abstract ^{230}Th/^{234}U radiochronometer was commonly used for uranium age determination which could help to reveal the origin of the nuclear material. ^{229}Th was a relatively appropriate spike for measuring ^{230}Th by isotope dilution mass spectrometry and its concentration needs to be calibrated before using as spike. A prepared ^{229}Th solution which was used as Th isotope spike for age dating of CRM U850 sample were calibrated separately by ^{232}Th and ^{230}Th standard materials. The calibrated results were compared and evaluated.

Keywords Uranium age · ^{229}Th spike · Calibration · ICP-MS

Introduction

Uranium age could be defined as the time since the uranium material was last subjected to a separation process capable of separating uranium from its radioactive-decay daughters [1, 2]. It is a dynamic fingerprint of nuclear material and could help to reveal the origin of the nuclear material and trace back the possible route of the sample to its source, which could be verified against the declared origin in nuclear forensics [3, 4].

Several isotope ratios such as ^{230}Th/^{234}U, ^{231}Pa/^{235}U and ^{214}Bi/^{234}U have been successfully applied for the determination of the age of uranium [5–7]. However, in case of ^{231}Pa/^{235}U lack of suitable isotopic spike inhibits its application, while for ^{214}Bi/^{234}U ratio the method is restricted only to highly enriched uranium (HEU) samples or old nuclear materials due to the slow ingrowth of this daughter nuclide [8]. ^{230}Th/^{234}U isotope ratio was commonly used for uranium age dating. For most samples of uranium, ages determined with this ^{230}Th-^{234}U chronometer are considered as "model ages" by R. W. Williams [9], because they are based on the assumptions of (a) some initial amount of ^{230}Th in the sample, and (b) closed-system behavior of the sample since production. Under the condition of meeting these assumptions the accuracy of dates determined with the ^{230}Th-^{234}U chronometer only relies upon accurate ^{230}Th and ^{234}U measurements.

In the developed isotopic dilution mass spectrometric methods for determining ratio of ^{230}Th/^{234}U, ^{229}Th solution was used as spike for ^{230}Th. It was usually prepared by separating the ^{229}Th from old ^{233}U solution [7–9]. The ^{229}Th solution should be calibrated by reverse isotope dilution measurement with another isotope standard material before use. Usually, it is a long and complicated process to determine the age of uranium material.

Both the ^{230}Th and ^{232}Th isotope standard reference material could be used for ^{229}Th calibration [10]. The aim of this study was to develop a more exact ^{229}Th calibration method for the age determination of uranium materials using ^{229}Th solution as spike by isotope dilution multi-collector inductively coupled plasma mass spectrometry.

✉ Yan Chen
cy@ciae.ac.cn

1 Department of Radiochemistry, China Institute of Atomic Energy, P.O. Box 275-8, Xinzhen Fangshan District, Beijing 102413, China

2 CNEC High Temperature Reactor Holdings Co.,LTD, No. 81 Zizhuyuan Road, Haidian District, Beijing 100089, China

Experimental

Instrumentation and materials

The mass spectrometric analysis was carried out using an inductively coupled plasma mass spectrometer equipped with 7 Ion counters, 1 Daly detector and 9 Faraday cups (Micromass Isoprobe-T, GV). The 1.5 mg uranium oxide reference material (CRM 850) was dissolved in 10 mL HNO_3 for age analysis. The ^{233}U isotopic standard (IRMM051) was used to spike the samples for ^{234}U measurements. ^{229}Th spike for ^{230}Th analysis were calibrated by natural Th-solution (Relative standard uncertaintyof certified value is 0.3% ($k = 1$), SPEXertificate) and ^{230}Th standard material provided by LLNL (prepared from NIST 4342A, Relative standard uncertainty of certified value is 0.19% ($k = 1$)). Standard solutions (prepared from ERM-199, CRM U030, CRM U200 and working standard UTB900) were used to correct for instrumental mass discrimination and relative detector gain factors. The TEVA (100–150 µm) extraction chromatographic resin was used for chemical separation. All sample preparation procedures were carried out under clean room conditions (Class 100,000).

^{229}Th spike calibration by ^{232}Th

The primary ^{229}Th solution which is as ^{229}Th spike used for the ^{230}Th determination was prepared by separating the Th from an old ^{233}U solution. The ^{229}Th concentration in the primary solution obtained was determined by reverse isotope dilution ICP-MS measurement applying a 0.870(7) µg g^{-1} ^{232}Th standard solution which was obtained by successively diluting the certified natural Th-solution with 2% HNO_3 solution. Three aliquots of 0.5 mL ^{229}Th solution were added in 0, 5 and 2.5 mL 0.870(7) µg g^{-1} ^{232}Th standard solution respectively. After being isotopic equilibrium, $^{229}Th/^{232}Th$ atom ratios in three samples were measured by MC-ICP-MS. Both the ^{229}Th and ^{232}Th ionic beams were collected by faraday cups (FC).

^{229}Th spike calibration by ^{230}Th

The primary ^{229}Th solution was successively diluted with 2% HNO_3 solution to get around 100 pg g^{-1} ^{229}Th solution (named as solution2). Each dilution was approximately 100-fold and 30-fold respectively. Three aliquots of 0.8 mL solution2 were added in around 0, 80 and 80 pg ^{230}Th standard reference solution which was from gravimetrically diluting ^{230}Th standard reference material (NIST 4342A) respectively. After being isotopic equilibrium, $^{229}Th/^{230}Th$ ratios in three samples were measured by MC-ICP-MS. Both the ^{229}Th and ^{230}Th ionic beams were collected by ionic counters (IC).

Sample preparation for ^{234}U determination

Approximately 15 µg aliquot of the dissolved uranium oxide sample (CRM 850) was used for the analysis. The sample was diluted twice successively with 2% ultrapure nitric acid solution. Each dilution was approximately ten-fold and 100-fold respectively. The ^{234}U concentration following the second dilution was determined by isotope dilution ICP-MS measurement using ^{233}U standard as spike.

Sample preparation for ^{230}Th determination

The separation method of Th from U in Ref. [2] was adopted. Approximately 300 µg aliquot of the dissolved uranium oxide sample (CRM 850) was placed in a Teflon cup and spiked with approximately 2 pg of ^{229}Th spike gravimetrically, respectively. The Th-content of the sample was separated from uranium by 1.6 mL TEVA resin. In order to further purify the sample, the extraction chromatographic separation was repeated.

Data evaluation

All raw data were corrected taking into account instrumental mass bias using linear correction. The overall uncertainty was calculated taking into account the uncertainty of the weight measurements, spike concentrations, isotope ratios measurement and half-lives according to "A Guide to Expression of Uncertainty in Measurement" (ISO/1995).

Results and discussion

The ^{229}Th concentration in the working solution obtained was determined twice by reverse isotope dilution ICP-MS measurement applying certified natural Th-solution with different additive quantum. CRM U200 was used to correct instrumental mass bias. The results were showed in Table 1. The twice determined isotope concentrations were identical within the range of number of significant digit.

The ^{229}Th concentration in the working solution were obtained according to the gravimetrical dilution and the calibrated Th isotope concentration in dilution2 which was repetitively determined twice by reverse isotope dilution ICP-MS measurement applying ^{230}Th standard reference solution. CRM U005 and CRM U200 were used to correct

Table 1 Isotope concentrations of ^{229}Th spike calibrated by ^{232}Th

sample	Th isotope	Concentration (g g^{-1})	Standard uncertainty
1	^{232}Th	9.461×10^{-6}	8.1×10^{-8}
	^{229}Th	3.170×10^{-7}	2.7×10^{-9}
	^{230}Th	1.305×10^{-9}	1.1×10^{-11}
2	^{232}Th	9.461×10^{-6}	8.2×10^{-8}
	^{229}Th	3.170×10^{-7}	2.8×10^{-9}
	^{230}Th	1.305×10^{-9}	1.1×10^{-11}
Average	^{232}Th	9.461×10^{-6}	8.1×10^{-8}
	^{229}Th	3.170×10^{-7}	2.8×10^{-9}
	^{230}Th	1.305×10^{-9}	1.1×10^{-12}

Table 2 Isotope concentrations of ^{229}Th spike calibrated by ^{230}Th

sample	Th isotope	Concentration (g g^{-1})	Standard uncertainty
3	^{232}Th	9.492×10^{-6}	9.1×10^{-8}
	^{229}Th	3.208×10^{-7}	3.1×10^{-9}
	^{230}Th	1.320×10^{-9}	1.2×10^{-11}
4	^{232}Th	9.651×10^{-6}	5.2×10^{-8}
	^{229}Th	3.262×10^{-7}	1.7×10^{-9}
	^{230}Th	1.3426×10^{-9}	6.8×10^{-12}
Average	^{232}Th	9.57×10^{-6}	$1.4 \times 10^{-7*}$
	^{229}Th	3.235×10^{-7}	$4.8 \times 10^{-9*}$
	^{230}Th	1.331×10^{-9}	$1.6 \times 10^{-11*}$

*Estimated by range method and range coefficient was 1.13

determined Th isotope ratios of primary ^{229}Th solution. $\left(^9/_x\right)_{\text{mm}}$ was the determined Th isotope ratios of spiked aliquot primary ^{229}Th solution by ^{232}Th or ^{230}Th standard reference material. m and n were the weight of aliquot primary ^{229}Th solution and weight of ^{232}Th or ^{230}Th standard reference material respectively. x_s was the concentration of ^{232}Th or ^{230}Th standard reference material.

$$\begin{cases} \dfrac{9_p}{x_p} = \left(^9/_x\right)_{\text{pm}} & (1) \\ \dfrac{9_p \cdot m}{x_p \cdot m + x_s \cdot n} = \left(^9/_x\right)_{\text{mm}} & (2) \end{cases}$$

9_p could be expressed to Eq. (3) by the solution of Eq. (1) and Eq. (2).

$$9_p = \frac{n \cdot x_s \cdot \left(^9/_x\right)_{\text{pm}} \cdot \left(^9/_x\right)_{\text{mm}}}{m \cdot \left[\left(^9/_x\right)_{\text{pm}} - \left(^9/_x\right)_{\text{mm}}\right]} \tag{3}$$

Linear propagation of uncertainty on the weight of aliquot primary ^{229}Th solution m, weight of ^{232}Th or ^{230}Th standard reference material n, the concentration of ^{232}Th or ^{230}Th standard reference material x_s, the determined Th isotope ratios of primary ^{229}Th solution $\left(^9/_x\right)_{\text{pm}}$, and the determined Th isotope ratios of spiked aliquot primary ^{229}Th solution $\left(^9/_x\right)_{\text{mm}}$ results to:

$$u(9_p) = \sqrt{\begin{array}{c} \left(9_p \cdot \dfrac{u(n)}{n}\right)^2 + \left(9_p \cdot \dfrac{u(x_s)}{x_s}\right)^2 + \left(9_p \cdot \dfrac{u(m)}{m}\right)^2 + \\ \left(9_p \cdot \dfrac{\left(^9/_x\right)_{\text{mm}}}{\left(^9/_x\right)_{\text{pm}} - \left(^9/_x\right)_{\text{mm}}} \cdot \dfrac{u\left[\left(^9/_x\right)_{\text{pm}}\right]}{\left(^9/_x\right)_{\text{pm}}}\right)^2 + \left(9_p \cdot \dfrac{\left(^9/_x\right)_{\text{pm}}}{\left(^9/_x\right)_{\text{pm}} - \left(^9/_x\right)_{\text{mm}}} \cdot \dfrac{u\left[\left(^9/_x\right)_{\text{mm}}\right]}{\left(^9/_x\right)_{\text{mm}}}\right)^2 \end{array}} \tag{4}$$

instrumental mass bias and relative detector gain factors. The results were showed in Table 2. The relative deviation between two determined isotope concentrations was in 2%.

Two calibration methods could be expressed in the Eqs. (1–2). Assumed 9_p was the ^{229}Th concentration of primary ^{229}Th solution and x_p was the ^{232}Th or ^{230}Th concentration of primary ^{229}Th solution. $\left(^9/_x\right)_{\text{pm}}$ was the

For calibration by ^{230}Th, the uncertainty on the weight of aliquot primary ^{229}Th solution m was including of uncertainty of dilution process. Two representative uncertainty budgets for the ^{229}Th spike calibration by ^{232}Th and ^{230}Th were given in Table 3.

The calibrated Th isotope concentrations by two methods were close, but in calibration by ^{232}Th, the twice

Table 3 The uncertainty budget for calibrated ^{229}Th concentration in spike

Calibration by ^{230}Th			Calibration by ^{232}Th		
Calibrated ^{229}Th concentration in spike $3.262(17) \times 10^{-7}$ g g^{-1} ($k = 1$)	Contribution to combined uncertainty	Relative Uncertainty components	Calibrated ^{229}Th concentration in spike $3.170(27) \times 10^{-7}$ g g^{-1} ($k = 1$)	Contribution to combined uncertainty	Relative Uncertainty components
Concentration of ^{230}Th standard reference material	22.4%	1.2×10^{-3}	Concentration of ^{232}Th standard reference material	97.8%	8.4×10^{-3}
Weighing sample	0.1%	2.8×10^{-6}	Weighing sample	0.1%	8.5×10^{-6}
Standard reference material for Mass bias correction	22.9%	1.2×10^{-3}	Standard reference material for Mass bias correction	1.9%	1.6×10^{-4}
Standard reference material ratio measurement	6.7%	3.5×10^{-4}	Standard reference material ratio measurement	0.1%	1.1×10^{-5}
Sample Ratio measurement	46.8%	2.4×10^{-3}	Sample Ratio measurement	0.1%	8.2×10^{-6}
Dilution process	1.2%	5.9×10^{-5}	Dilution process	–	–
Total	100%	5.2×10^{-3}	Total	100%	8.6×10^{-3}

determined isotope concentrations were identical within the range of number of significant digit and in calibration by ^{230}Th, there was a deviation between twice measurements. The difference between two calibration methods could also be concluded by the math theory. For convenience, the computation (3) of ^{229}Th concentration in primary solution could be simplified into Eq. (5), as assuming the amount of ^{232}Th or ^{230}Th in original primary solution could be ignored. x is the added true amount of ^{232}Th or ^{230}Th standard material. 229 is the amount of ^{229}Th in primary ^{229}Th solution.

$$229 = x \cdot \left(^{229}/_x\right)_{\text{measure}} \tag{5}$$

When the uncertainty of measurement could be ignored, we could assume that

$$\left(^{229}/_x\right)_{\text{measure}}$$

is the true isotope ratio value and Δx is the distance between reference value used for calculation and true value x. Then ^{229}Th concentration in primary solution could be expressed by Eq. (6).

$$229 = (x + \Delta x) \cdot \left(^{229}/_x\right)_{\text{measure}} \tag{6}$$

By math operation, the Eq. (7) could be gotten from Eq. (6).

$$229 = 229 + 229 \cdot \frac{\Delta x}{x} \tag{7}$$

Similarly, when added different amount of th isotope standard expressed by kx. The apparent amount used for calculation is equal to the value of k multiplied by sum of x and Δx. The calculated expression of ^{229}Th concentration in primary solution from Eq. (8) is the same to the Eq. (7).

$$229 = k(x + \Delta x) \cdot \left(^{229}/_{kx}\right)_{\text{measure}} \tag{8}$$

That means when adding different amount of Th standard material, if the uncertainty of measurement could be very little to be ignored the calibrated ^{229}Th concentration in every determination are same. Because the Δx is a fixed value which is independent on the measurement process. From the uncertainty budget in Table 3, we can see the contribution from the measurement to total uncertainty could be ignored relative to the standard reference material. So it could be explained the twice calibrated ^{229}Th concentration were identical.

From the above deducing we know the deviation of reference value of standard material didn't affect the point-to-point reproducibility of calibrated results. So it could be assumed the apparent added amount of Th isotope standard material is true value x and Δ^1 is the distance between measured isotope ratio value and true isotope ratio value. In calibrating by ^{230}Th, when the deviation of measurement could not be ignored, the calibrated ^{229}Th concentration in primary solution could be expressed by Eq. (9).

$$229 = x \cdot \left(\left(^{229}/_x\right)_{\text{true}} + \Delta^1\right) \tag{9}$$

Table 4 The determined uranium age of CRM U850

	Calibrated ^{229}Th concentration g g^{-1} spike	^{230}Th atoms g^{-1} primary solution	^{234}U atoms g^{-1} primary solution	^{230}Th/^{234}U atoms ratio	Age (years) ($k = 2$)
Calibration by ^{232}Th	3.170 (19) × 10^{-7}	2.1211 (99) × 10^{11}	1.3249 (24) × 10^{15}	1.6008 (81) × 10^{-4}	56.65 ± 0.58
Calibration by ^{230}Th	3.235 (40) × 10^{-7}	2.165 (15) × 10^{11}	1.3249 (24) × 10^{15}	1.634 (12) × 10^{-4}	57.81 ± 0.84

Fig. 1 Results of the age determination of CRM U850
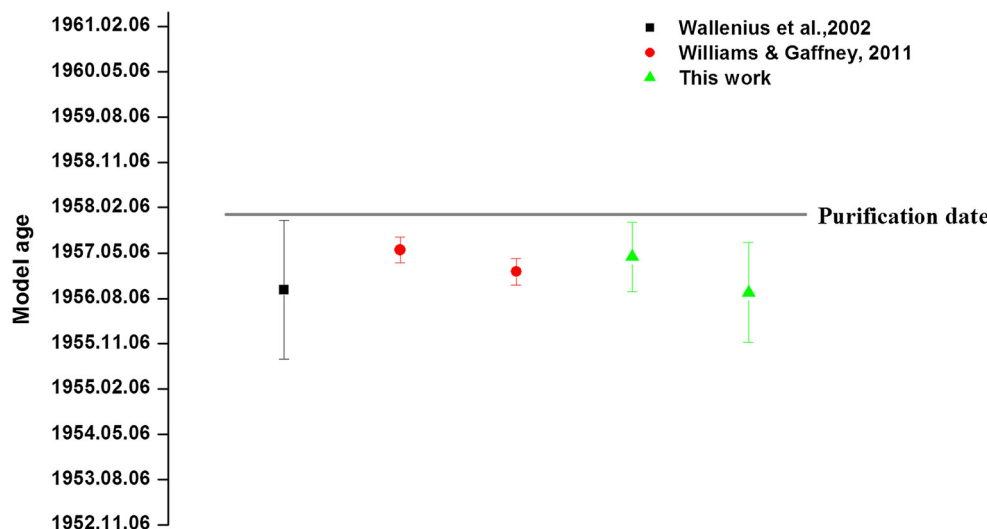
By math operation, the Eq. (10) could be gotten from Eq. (9).

$$229 = 229 + \Delta^1 \cdot x \tag{10}$$

Similarly, when adding different amount of Th isotope standard material, the calculated Eq. (11) of ^{229}Th concentration in primary solution is different with the Eq. (10). Deltas were different in every measurement due to fluctuant parameter. So it could be explained two calibrated results by ^{230}Th have deviation.

$$229 = 229 + \Delta^2 \cdot kx \tag{11}$$

As the uncertainty budget in Table 3 shown, the largest contribution to combined uncertainty of ^{229}Th concentration calibrated by ^{230}Th was from sample ratio measurement. Standard reference material for Mass bias correction and concentration of ^{230}Th standard reference material were two significant contributors to combined uncertainty of ^{229}Th concentration. But for calibration by ^{232}Th the only one significant contributor was from the reference concentration value of ^{232}Th standard reference material. The difference may be due to that the precision of measurement by IC for relative low concentration sample is lower than the precision of measurement by FC for relative high concentration sample. The calibration process contribution to combined uncertainty of ^{229}Th concentration

calibrated by ^{232}Th could be less with one order of magnitude than the reference concentration value of ^{232}Th standard reference material. It was reflected by the twice identical determined isotope concentrations within the range of number of significant digit in calibration by ^{232}Th. It seems that the calibration method by ^{232}Th is superior to calibration method by ^{230}Th. The combined uncertainty of ^{229}Th concentration in single observation calibrated by ^{232}Th is a little higher than by ^{230}Th just because the relative uncertainty of used ^{232}Th standard reference material is 8.5‰ which is much larger than 2.5‰ of ^{230}Th standard reference material. Considering about the reproducibility of two independent measurements, the combined uncertainty of average ^{229}Th concentration in spike calibrated by ^{230}Th was larger than by ^{232}Th.

According to the weight of spikes and determined isotope ratios, the ^{234}U/^{230}Th ratio could be calculated. The model age was calculated according to simplified age-dating Eq. (12) where R is the ^{230}Th/^{234}U atomic ratio, and λ_1 and λ_2 are the decay constants of ^{234}U and ^{230}Th, respectively. Half-lives for ^{230}Th and ^{234}U of 75690 ± 230 years and 245250 ± 490 years were used for these decay constants, respectively [11].

$$t = \frac{1}{\lambda_1 - \lambda_2} \ln\left[1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right] \tag{12}$$

Table 5 The uncertainty budget for sample U850 using the ^{229}Th spike calibrated by ^{232}Th

CRM U850 determined age 56.65 ± 0.58 years ($k = 2$)			Contribution to combined uncertainty (%)
^{230}Th in U850	^{229}Th spike		35.76
	^{230}Th/^{229}Th analysis	Weighing spike	<0.01
		Weighing sample	<0.01
		Mass bias correction	31.74
		Ratio measurement	18.71
^{234}U in U850	^{233}U spike		6.67
	^{234}U/^{233}U analysis	Weighing spike	0.30
		Weighing sample	0.02
		Mass bias correction	5.92
		Ratio measurement	0.09
^{230}Th half-life			≪0.01
^{234}U half-life			0.77
Total			100

Table 6 The uncertainty budget for sample U850 using the ^{229}Th spike calibrated by ^{230}Th

CRM U850 determined age 57.81 ± 0.84 years ($k = 2$)			Contribution to combined uncertainty (%)
^{230}Th in U850	^{229}Th spike		68.55
	^{230}Th/^{229}Th analysis	Weighing spike	<0.01
		Weighing sample	<0.01
		Mass bias correction	15.67
		Ratio measurement	9.24
^{234}U in U850	^{233}U spike		2.13
	^{234}U/^{233}U analysis	Weighing spike	0.19
		Weighing sample	0.01
		Mass bias correction	3.78
		Ratio measurement	0.06
^{230}Th half-life			≪0.01
^{234}U half-life			0.37
Total			100

The results of age determination were shown in Table 4. The purification date was calculated: 1957-4-15 ± 209 days for CRM U850 with ^{229}Th spike calibrated by ^{232}Th and 1956-2-18 ± 301 days for CRM U850 with ^{229}Th spike calibrated by ^{230}Th. The U850 analyzed give the determined age older than the purification dates of record (1957-12-31). This indicates that excess ^{230}Th in U850 standard results from incomplete purification during production.

The determined model age of CRM U850 and some results in the literature were shown in the Fig. 1. The data showed good agreement with the ages determined in the earlier works by Wallenius et al. [2] and Williams and Gaffney [8] using the ratio ^{234}U/^{230}Th. The ^{230}Th was determined with ^{232}Th spike in the work by Wallenius et al. and the ^{230}Th was determined with ^{229}Th spike which was calibrated by the NIST SRM 4342A ^{230}Th radioactivity solution in the work by Williams & Gaffney. The determined purification date of CRM U850 using the ^{229}Th spike calibrated by ^{232}Th which in this work was lying between the results in the literature was closer to the average model age of current published results than the determined purification date of CRM U850 using the ^{229}Th spike calibrated by ^{230}Th which was earlier than the results in the literature.

Two representative uncertainty budgets for the age-dating analyses were given for sample CRM U850 in Table 5, 6. The largest part of the uncertainty in these analyses comes from the ^{229}Th spike, of which the uncertainty on the Mass bias correction and ratio measurement for ^{230}Th/^{229}Th analysis were two significant contributors to combined uncertainty of determined U850 age. The accuracy concentration of ^{229}Th spike has a great effect on the result of determined age of Uranium material.

Conclusions

Precisely and accurately calibrating Th isotope spike was very important to determine uranium model age by ^{230}Th/^{234}U radiochronometer. Using higher concentration primary Th spike solution to be directly calibrated and be used as spike for uranium age dating could get more accuracy results than diluted to be calibrated especially in the case the uncertainty of standard materials for calibration were similar. Easily available ^{232}Th standard material could be used to calibrate ^{229}Th spike to get accuracy results instead of uncommon ^{230}Th standard material.

References

1. Morgenstern A, Apostolidis C, Mayer K (2002) Age determination of highly enriched uranium: separation and analysis of ^{231}Pa. Anal Chem 74:5513–5516
2. Wallenius M, Morgenstern A, Apostolidis C, Mayer K (2002) Determination of the age of highly enriched uranium. Anal Bioananl Chem 374:379–387
3. Varga Zsolt, Wallenius Maria, Mayer Klaus (2010) Age determination of uranium samples by inductively coupled plasma mass spectrometry using direct measurement and spectral deconvolution. J Anal At Spectrom 25:1958–1962
4. Varga Zsolt, Wallenius Maria, Mayer Klaus, Hrnecek Erich (2011) Alternative method for the production date determination of impure uranium ore concentrate samples. J Radioanal Nucl Chem 290:485–492
5. Eppich Gary R, Williams Ross W, Gaffney Amy M, Schorzman Kerri C (2013) 235U–231Pa age dating of uranium materials for nuclear forensic investigations. J Anal At Spectrom 28:666–674
6. Nguyen Cong Tam, Zsigrai József (2006) Gamma-spectrometric uranium age-dating using intrinsic efficiency calibration. Nuclear Instrum Methods Phys Res B 243:187–192
7. LaMont SP, Hall G (2005) Uranium age determination by measuring the ^{230}Th/^{234}U ratio. J Radioanal Nucl Chem 264:423–427
8. Varga Z, Surányi G (2007) Production date determination of uranium-oxide materials by inductively coupled plasma mass spectrometry. Anal Chim Acta 599:16–23
9. Williams RW, Gaffney AM (2011) ^{230}Th-^{234}U model ages of some uranium standard reference materials. Proc Radiochim Acta 1:31–35
10. Varga Z, Mayer K, Bonamici CE, Hubert A, Hutcheon I, Kinman W, Kristo M, Pointurier F, Spencer K, Stanley F, Steiner R, Tandon L, Williams R (2015) Validation of reference materials for uranium radiochronometry in the frame of nuclear forensic investigations. Appl Radiat Isot 102:81–86
11. Cheng H, Edwards RL, Hoff J, Gallup CD, Richards DA, Asmerom Y (2000) The half-lives of uranium-234 and thorium-230. Chem Geol 169:17–33