



## Original Article

# A comparative study of ultra-trace-level uranium by thermal ionization mass spectrometry with continuous heating: Static and peak-jumping modes

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## ABSTRACT

For ensuring nuclear safeguards, we report the analytical signal-detection performance of thermal ionization mass spectrometry (TIMS) with continuous heating for the measurement of isotopic ratios in samples containing ultra-trace amounts of uranium. As methods for detecting uranium signals, peak-jumping mode using a single detector and static mode using multiple detectors were examined with U100 (10% <sup>235</sup>U-enriched) uranium standard samples in the femtogram-to-picogram range. Uranium isotope ratios,  $n(^{235}\text{U})/n(^{238}\text{U})$ , were measured down to levels of 1 fg and 3 fg in static and peak-jumping modes, respectively, while  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  values were measured down to levels of 100 fg in both modes. In addition, the dependency of the <sup>238</sup>U signal intensity on sample quantity exhibited similar tendencies in both modes. The precisions of the isotope ratios obtained in the static mode over all sample ranges used in this study were overall slightly higher than those obtained in peak-jumping mode. These results indicate that isotope ratio measurements by TIMS with continuous heating are almost independent of the detection method, i.e., peak-jumping mode or static mode, which is characteristic of isotope-ratio measurements using the TIMS method with continuous heating. TIMS with continuous heating is advantageous as it exhibits the properties of multiple detectors within a single detector, and is expected to be used in various fields in addition to ensuring nuclear safeguards.

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## 1. Introduction

Thermal ionization mass spectrometry (TIMS) is a key analytical technique used to ensure nuclear safeguards and in nuclear forensics for the accurate isotopic analyses of uranium (U) and plutonium (Pu), in which the isotopic signatures of uranium and plutonium play crucial roles. TIMS enables highly precise and accurate measurements with small uncertainties compared to other mass spectrometry techniques. For ensuring nuclear safeguards, isotopic information obtained through the analysis of environmental samples collected by International Atomic Energy Agency (IAEA) inspectors from nuclear facilities is used to detect undeclared nuclear activity and nuclear materials [1–4]. The isotopic abundances of major (<sup>235</sup>U and <sup>238</sup>U) and minor (<sup>234</sup>U and <sup>236</sup>U) uranium isotopes provides information about nuclear activities

conducted within nuclear facilities, such as the enrichment and reprocessing of nuclear materials [5]. In addition, plutonium isotope ratios provide fingerprints that identify the type of nuclear reactor, nuclear fuel burnup, and nuclear weapon [6]. IAEA environmental samples require high quality analysis results even when the amounts of nuclear material they contain are small. The small amounts of uranium and plutonium present in environmental samples provide major analytical challenges. Consequently, their quantities are often measured very close to instrumental detection limits; clearly special sensitive techniques are required for the analysis of these samples.

TIMS with multiple ion counting (MIC) is a well-established analytical tool for isotopic analysis, and is employed in many fields including environmental monitoring, nuclear forensics, and nuclear safeguarding [7–12]. The MIC system generates a large number of counts for each isotope relative to single-detector ion counting. MIC or static measurements enable the simultaneous detection of the isotopes of interest using multiple detectors. In particular, the MIC system is advantageous when the sample

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**Table 1**  
TIMS detector configuration for the static determination of uranium.

Step	IC1 (SEM)	IC2 (SEM)	IC3 (SEM)	IC4 (CDD)
1	$^{234}\text{U}$	$^{235}\text{U}$	$^{236}\text{U}$	$^{238}\text{U}$

quantity is limited as the counting statistics are improved by a factor of two or more. In addition, the MIC system eliminates the need for drift correction algorithms usually required for single-collector measurements. In contrast, in single-ion counting or peak-jumping (PJ) measurements, different isotopes are sequentially introduced into the same detector by changes in the magnetic field; consequently peak-jumping measurements consume more sample than static measurements.

The total evaporation (TE) method for TIMS was developed to overcome mass fractionation, which is a drawback of the conventional method for the isotopic analyses of uranium and plutonium [13–15]. In the TE method, the ion signal of the analyte is controlled at a defined target intensity by adjusting the evaporation filament current while maintaining the ionization filament at a constant current. The ion signals of all isotopes are measured with multiple collectors until the entire sample has been exhausted; the magnetic field and focus are not modified during the analysis of a single sample filament. The isotope ratios are calculated from the integrated intensities. However, the signal intensities are overestimated because the background and peak-tailing contributions from the more abundant isotopes cannot be corrected in situ. The determination of minor isotopes in the TE method were improved in the modified total evaporation (MTE) method, which is based on the same principal as the TE method for major isotopes. In the MTE method, the total evaporation of a sample is interrupted on a regular basis in order to measure background, to calibrate the internal yield of the SEM detector, for peak centering, and ion beam focusing [10,16]. These interruptions facilitate the determination of high quality  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  ratios without compromising the quality of the  $^{235}\text{U}/^{238}\text{U}$  ratio. However, the MTE method requires long measurement times, and requires large amounts of sample, of the order of several tens of picograms or more.

On the other hand, thermal ionization mass spectrometry with continuous heating was developed to measure uranium and plutonium isotope ratios at trace levels [17]. Briefly, the continuous-heating method differs from the MTE method in how it determines the isotope ratio after the evaporation filament is heated at a constant rate for sample consumption. The features of the continuous-heating method include:

- The evaporation-filament current is continuously increased until the sample is completely evaporated.
- Higher-intensity data are used to calculate isotope ratios.
- The measurement conditions and isotope-ratio calculation processes are standardized.

These features enable highly accurate and highly reproducible measurements irrespective of the amount of sample and the skill of the operator. In particular, the continuous-heating method is effective for measuring the isotope ratios of ultra-trace amounts of uranium and plutonium [18,19]. In this study, we verify the effectiveness of the continuous-heating method for isotope ratio measurements of ultra-trace amounts of uranium, in the femtogram-to-picogram range, using the two detection modes, namely peak-jumping and static.

**Table 2**  
TIMS integration and idle times for the peak-jumping determination of uranium.

Step	Mass ( $m/z$ )	Integrated time (s)	Idle time (s)
1	234	4.194	0.5
2	235	4.194	0.5
3	236	4.194	0.5
4	238	4.194	0.5

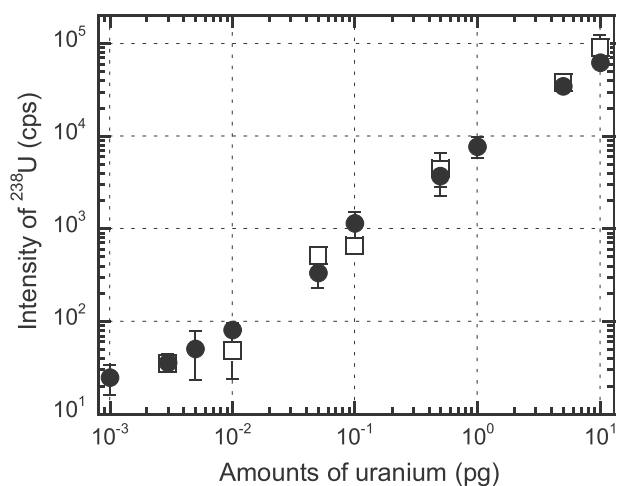
## 2. Material and methods

### 2.1. Sample preparation

A CRM U100 uranium isotope standard solution (10%  $^{235}\text{U}$ -enriched, NBL, USA) was diluted with 1 M ultrapure nitric acid (Merck, Germany) to obtain uranium masses ranging from 1 fg to 10 pg. A 1  $\mu\text{L}$  drop of each sample solution was loaded onto a pre-degassed zone-refined Re filament and dried by applying a current of 0.6 A for 200 s and 2.0 A for 50 s. In order to avoid cross-contamination with natural uranium, Teflon bottles and pipette tips were rinsed prior to use with 1 M  $\text{HNO}_3$ , 50% tetramethylammonium hydroxide (TMAH, TAMAPURE-AA, Tama Chemicals Co., Ltd., Japan), and deionized Milli-Q water, in a clean hood of a class 100 (ISO Class 5) laboratory. A CRM U350 uranium isotope standard solution (35%  $^{235}\text{U}$ -enriched, NBL, USA) was used to correct for mass bias.

### 2.2. Instrumentation

The isotope ratio measurements were performed using a thermal ionization mass spectrometer (Triton, Thermo Fisher Scientific, Germany) equipped with three secondary electron multipliers (SEMs), one compact discrete diode (CDD), and seven Faraday cups. In this study, the SEMs and CDD were used to measure the uranium isotope levels because of the ultra-trace natures of the samples. The static mode simultaneously measures the four isotopes of interest ( $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ , and  $^{238}\text{U}$ ) using the three SEMs and one CDD with the detector configuration shown in Table 1. The  $^{187}\text{Re}$  signal of the filament was used to determine the efficiency of the center faraday cup and four ion counters (three SEMs and one CDD). In the case of a double filament system, the  $^{187}\text{Re}$  signal of the evaporation filament was maintained at about 5 mV (corresponding to about



**Fig. 1.** Average intensity of the  $^{238}\text{U}$  signal as a function of uranium sample concentration over the 1 fg to 10 pg range ( $n = 5$ ) (Solid circles: static mode; open squares: peak-jumping mode).

312,000 counts on the SEM/CDD) by controlling the current. Using this signal, the ratio between center faraday cup and ion counters was measured and the correction factor was determined so that this ratio was constant. Each correction factor used the average value of six measurements. The obtained correction factor was used to correct the number of ion counter signals. In contrast, the peak-jumping (PJ) mode sequentially measures the four isotopes of interest using a single SEM. The optimized integration and idle times for the PJ mode are listed in Table 2. Double filament assemblies composed of zone-refined Re were used. Prior to use, the filaments were subjected to a heating routine involving degassing for 20 min at 4500 mA under a vacuum greater than  $5 \times 10^{-6}$  mbar in a

filament bake-out device (Thermo Finnigan) to reduce background signals from the filament.

### 2.3. Isotope ratio measurements

Isotope ratios in the uranium samples were measured using thermal ionization mass spectrometry with continuous heating

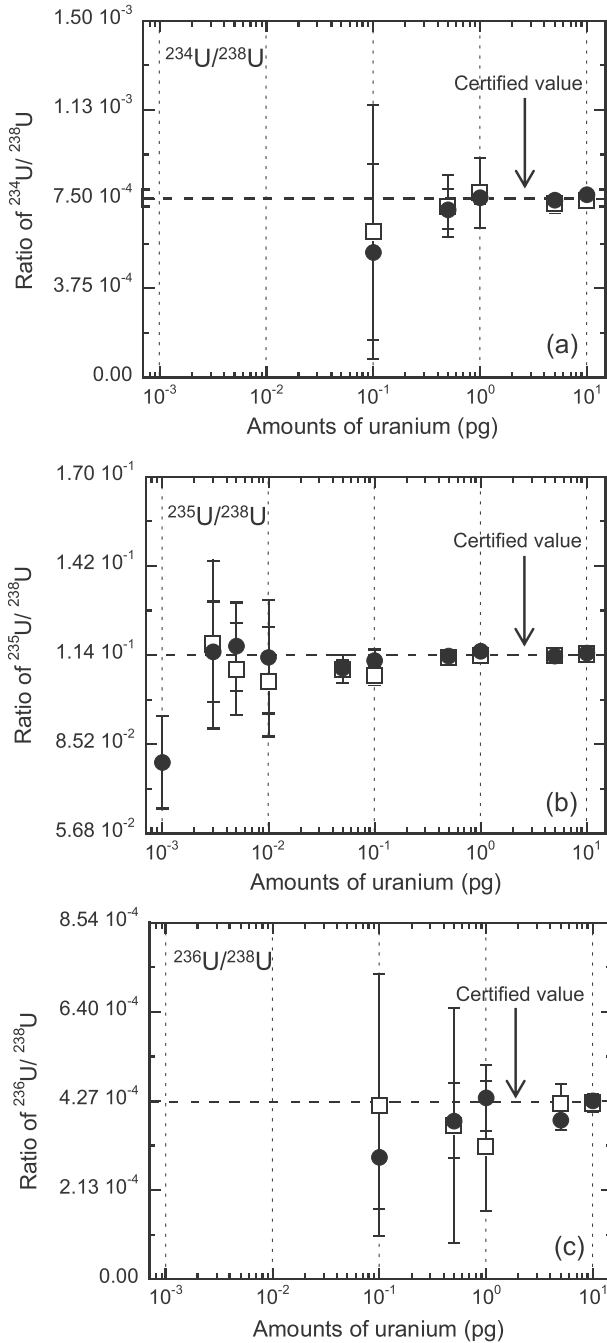


Fig. 2. Values of (a)  $n(^{234}\text{U})/n(^{238}\text{U})$ , (b)  $n(^{235}\text{U})/n(^{238}\text{U})$ , and (c)  $n(^{236}\text{U})/n(^{238}\text{U})$  as functions of the uranium-signal detection mode and sample quantity ( $n = 5$ ) (Solid circles: static mode; open squares: peak-jumping mode).

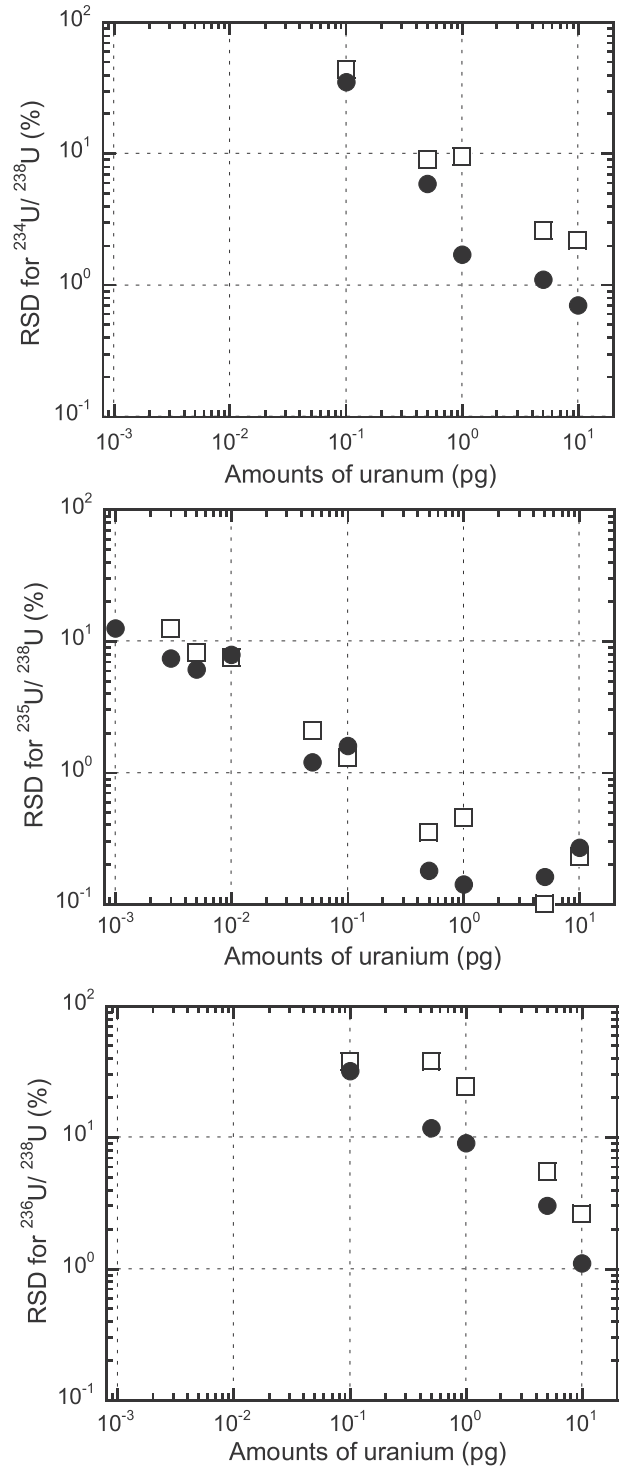


Fig. 3. Relative standard deviations (RSDs) in (a)  $n(^{234}\text{U})/n(^{238}\text{U})$ , (b)  $n(^{235}\text{U})/n(^{238}\text{U})$ , and (c)  $n(^{236}\text{U})/n(^{238}\text{U})$  as functions of the uranium-signal detection mode and sample quantity ( $n = 5$ ) (Solid circles: static mode; open squares: peak-jumping mode).

[17]. Briefly, the ionization filament was heated until the Faraday detector recorded a 100 mA  $^{187}\text{Re}$  signal. The ion lens system was then optimized to maximize the intensity of this signal. The  $^{187}\text{Re}$  signal was then readjusted to 100 mA and the measurement process was commenced using the SEM and CDD detectors. The evaporation filament current was raised, at a linear rate of 150 mA/min, to 5000 mA ( $\sim 2000^\circ\text{C}$ ) at which point the sample had evaporated entirely. In the TIMS method with continuous heating, the isotope ratios were calculated as follows. First, the peak area was determined in the measured signal profile, and the range for the isotope ratio measurements was determined within the peak area. The data within the selected range were used to calculate the isotope ratio following drift and background correction. In the continuous heating method, the data with the highest intensities over the measurement temperature range were used to calculate isotope ratios.

### 3. Results and discussion

Fig. 1 displays the intensity of the  $^{238}\text{U}$  signal as a function of sample quantity measured in the static and PJ modes of TIMS with continuous heating; each signal is an average of five measurements. The magnitudes of the  $^{238}\text{U}$  signals in both modes are similar over the sample quantities used in this study. The  $^{238}\text{U}$  signal was determined down to a level of 1 fg in static mode; however the  $^{235}\text{U}$  signal was not detected at this level, and none of the U isotopes were measured at levels of 1 fg in PJ mode, which is ascribable to the large amounts of sample required per cycle to measure  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ , and  $^{238}\text{U}$  levels in peak-jumping mode compared to static mode.

The dependence of  $n(^{235}\text{U})/n(^{238}\text{U})$  on the sample quantity is displayed in Fig. 2 (b);  $n(^{235}\text{U})/n(^{238}\text{U})$  values were measured down to levels of 1 fg and 3 fg in the static and peak-jumping modes, respectively, and are consistent, to within measurement error, with the certified values. Masses of 1 fg and 3 fg correspond to uranium particles with diameters of 0.06 and 0.09  $\mu\text{m}$ , respectively, assuming that the particles are perfectly spherical and consist of homogeneous  $\text{U}_3\text{O}_8$  with a density of  $8.38\text{ g cm}^{-3}$ . Relative standard deviations (RSDs) of 7.1% and 11.4% in the  $n(^{235}\text{U})/n(^{238}\text{U})$  values of a 3 fg sample were determined for the static and peak-jumping modes, respectively. The  $^{235}\text{U}/^{238}\text{U}$  ratio at a sample quantity of 1 fg was determined to be lower than the certified value, suggesting that precise detector-efficiency and background corrections need to be considered. In samples containing several fg of material, in

which  $^{235}\text{U}$  signal intensities of several cps are observed, the calculated value of the isotope ratio can vary greatly depending on the correction method used, even if the signal intensity changes by only 1–2 cps. Hence, a precise calibration method applicable to ultra-trace quantities of sample is required.

Fig. 2 (a, c) display the dependences of the minor isotope ratios, i.e.,  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$ , on the amount of sample. Minor isotope ratios were measured down to 100 fg in both modes, and are consistent with the certified value to within measurement error. A mass of 100 fg corresponds to a uranium particle with a diameter of 0.3  $\mu\text{m}$ , making the above-mentioned assumptions of particle shape, homogeneity, and density. RSDs in the  $n(^{234}\text{U})/n(^{238}\text{U})$  values of a 100 fg sample were determined to be 35.2% and 43.8% for the static mode and PJ modes, respectively, while RSDs of 32.0% and 37.5% were determined for the  $n(^{236}\text{U})/n(^{238}\text{U})$  values in the same sample using the static and PJ modes, respectively.

Fig. 3 (a–c) display the RSDs of the various isotope ratios, namely (a)  $n(^{234}\text{U})/n(^{238}\text{U})$ , (b)  $n(^{235}\text{U})/n(^{238}\text{U})$ , and (c)  $n(^{236}\text{U})/n(^{238}\text{U})$ , as functions of sample quantity. It is noteworthy that the RSD of the major isotope ratio,  $n(^{235}\text{U})/n(^{238}\text{U})$ , is lower overall in the static mode than in the peak-jumping mode (Fig. 3). This tendency is also observed in the dependency of the RSDs of the minor isotope ratios,  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$ , on the sample quantity, which is ascribable to differences in the number of data points used in the isotope-ratio calculations. In general, the measurement error tends to decrease with increasing number of data points. Indeed, the number of data points in the isotope-ratio-calculation region is approximately three times larger in the static mode than in the peak-jumping mode, as shown in Table 3. Fig. 3 can also be used as a guide for estimating the magnitude of the relative standard deviation associated with the amount of sample used for isotope-ratio measurements at ultra-trace levels.

### 4. Conclusions

We compared the static mode, using multiple detectors, and the peak-jumping mode, using a single detector, for the measurement of the uranium isotope ratios of ultra-trace (femtogram-to-pico-gram) levels of uranium using TIMS with continuous heating. The signal intensities and accuracies of the isotope ratios determined using both modes were similar in the sample concentrations used in this study. The isotope ratios determined using the static mode, with a larger number of data points in the isotope-ratio calculation region, exhibited better precisions than those determined using the

**Table 3**

Isotope ratios of uranium standard solution (CRM U100) measured by TIMS with continuous heating method. Isotope ratios and average intensities are the mean value of five measurements.

Amount of U (pg)	No. of data <sup>a</sup>		Intensity of $^{238}\text{U}$ (cps) <sup>b</sup>		$^{234}\text{U}/^{238}\text{U}$				$^{235}\text{U}/^{238}\text{U}$				$^{236}\text{U}/^{238}\text{U}$			
					static		peak-jumping		static		peak-jumping		static		peak-jumping	
					ratio	1RSD (%)	ratio	1RSD (%)	ratio	1RSD (%)	ratio	1RSD (%)	ratio	1RSD (%)	ratio	1RSD (%)
0.1	26	7	1149	651	5.253E-04	35.2	6.104E-04	43.8	1.118E-01	1.5	1.071E-01	1.3	1.919E-04	32.0	4.170E-04	37.5
0.5	23	7	3714	4375	7.060E-04	5.9	7.204E-04	9.0	1.133E-01	0.2	1.125E-01	0.4	3.787E-04	11.8	3.674E-04	38.1
1.0	33	9	7702	4962	7.546E-04	1.7	7.763E-04	9.5	1.149E-01	0.1	1.134E-01	0.4	4.344E-04	9.0	3.184E-04	24.4
5.0	28	7	34295	37676	7.459E-04	1.1	7.296E-04	2.5	1.133E-01	0.2	1.132E-01	0.1	3.807E-04	3.0	4.199E-04	5.5
Certified value	-	-	-	-	7.535E-04	-	7.535E-04	-	1.136E-01	-	1.136E-01	-	4.225E-03	-	4.225E-03	-

<sup>a</sup> Number of data contained in the area for isotope ratio calculation.

<sup>b</sup> Average value of five measurements

peak-jumping mode. However, the differences in the precisions of the isotope ratios determined using the two modes are within a few percent, so that there is effectively no difference in the overall analytical performance of the two modes. These results suggest that similar analytical performance can be obtained in static mode using multiple detectors to peak-jumping mode using a single detector in TIMS with continuous heating. In addition, the use of only one detector it is expected to be useful for shortening long measurement times, which is one of the disadvantages of the TIMS system, and is a result of the continuous heating method, which uses only high-intensity data for the calculation of isotope ratios. Hence, this method is expected to be used in a variety of fields including nuclear safeguards and nuclear forensics.

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