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# A new method for isotope ratio measurement of uranium in trace amount by thermal ionization mass spectrometry: The continuous heating method

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ABSTRACT

A new method for isotope ratio measurement with thermal ionization mass spectrometry (TIMS), "continuous heating method", was developed in order to determine an accurate isotope ratio of uranium ranging from sub-picograms to several dozen picograms. In this method, signals were measured during evaporation of an entire sample in the same way as in the "total evaporation method"; however, part of the higher detected signals was used for calculation of the isotope ratio. The continuous heating method can measure the ratios with high reproducibility regardless of the sample amount and the skill of operators because procedures of measurement and data calculation were standardized, enabling accurate correction of the mass discrimination effect. By using the optimized procedures, the relative standard deviation ($2\sigma$) of $^{235}$U/$^{238}$U ratio in CRM U350 particle (35% $^{235}$U enrichment) with a diameter of about 1 μm was less than 2%. When $^{235}$U/$^{238}$U ratios in IRMM 184 (natural uranium) solution samples of uranium of 0.4, 4 and 44 pg measured by the continuous heating method were compared with those measured by the conventional method and the total evaporation method, which were well-known methods of TIMS, there was no difference in the case of measurement of a larger amount of samples. However, the continuous heating method showed the most accurate result for the smallest amount of samples.

## 1. Introduction

Isotope ratios of uranium have been studied in various fields such as nuclear science, nuclear safeguards, environmental science and geoscience, because the isotope ratios vary by artificial nuclear activity and geochemical effects. Recently, due to the needs of measurement of small amounts of uranium, such as sub-picograms in a sample, there has been an increase in the study of such measurement [1–5]. Because a fine particle containing small amounts of uranium can easily be inhaled into human the body, it induces radiation exposure, thus the measurements of the particle are performed from the viewpoint of radiation protection [1]. In analysis of environmental sample for nuclear safeguards, the isotope ratio measurements of the uranium contained in a particle are one of the effective tools to detect undeclared nuclear activity [6].

Thermal ionization mass spectrometry (TIMS) has been the primary technique for determination of isotope ratios, because of its excellent precision. Two measurement methods have already been developed; a conventional method and a total evaporation method. The two methods have been used to measure accurate isotope ratios in large amounts of sample ranging between nanograms and micrograms in many studies [7–9]. To obtain accurate results by using the conventional method, strict control of measurement conditions and stable signals is needed. In the case of measurement of a sample containing a small amount of uranium, detected signals are small and unstable. This means that preliminary measurement and skilled experience of an operator are required to decide the optimum condition before measurement of a real sample. However, it is difficult to divide a sample having a small amount of uranium for the preliminary measurement. In addition, a particulate sample cannot be used to perform the preliminary measurement. Hence it is hard to analyze the sample having a small amount of uranium by the conventional method.

The total evaporation method also has a problem for the measurement of a sample having a small amount of uranium. In this method, the isotope ratios are obtained from integrated values of signals of each isotope measured during evaporation of a whole sample, however, not all signals from the evaporated sample are, in practice, integrated. At the early stage of evaporation, weak signals were obtained with an evaporation filament (EF) at low temperature. The operator uses these signals for conditioning of instrument parameters such as focusing. After heating up the EF, the signals above a decided threshold are measured to calculate the isotope ratios [9–10]. The signals below the threshold are negligible if the

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sample amount is large enough, but they cannot be ignored for the measurement of the trace amount of sample. It is desirable that all signals except for background are integrated for the measurement. However, it is difficult to distinguish between the signal and the background because the signals at the beginning and the end of the measurement are small and unstable. Moreover, signals of a minor isotope are sometimes below the detection limit even when signals of a main isotope are detected.

In this study, a new method, "the continuous heating method", was developed for measurement of isotope ratio in ultra-trace amounts of uranium by TIMS. This method enabled measurement of an isotope ratio with high reproducibility regardless of the sample amount and skill of operator by standardizing the measurement conditions and the data calculation procedure.

## 2. Experimental

### 2.1. Instrumentation

Isotope ratio measurements were performed with a TIMS (Triton, Thermo Fisher Scientific, USA). The instrument is equipped with a SEM (Secondary Electron Multiplier) and eight Faraday detectors. Only the SEM in an ion-counting mode was used because the sample had a trace amount of uranium and thus the intensities were weak. A double filament assembly with zone-refined rhenium filaments (Thermo Fisher Scientific) was used. Before its use, the filaments were degassed in a filament degassing device (Thermo Fisher Scientific) for 20 min with a current of 4.5 A (about 1800 °C) under a vacuum lower than $5 \times 10^{-6}$ mbar.

The background caused from impurity of the assembly was measured as follows. Current of an ionization filament (IF) was raised until the $^{187}$Re intensity became 100 mV and then the current of the EF was increased to 4000 mA, which let the assembly degas again. After degassing twice, the background from the assembly was evaluated by measuring the signal intensities of masses of 234, 235, 236 and 238; the mass number of uranium isotopes, with a peak-jumping sequence of 10 scans. In addition, in order to minimize the background from the assembly, an assembly with an average intensity of the mass 238 of 10 cps or less was used for the measurement.

### 2.2. Samples

Two kinds of samples were used. One was a uranium isotopic reference material solution (IRMM 184, natural uranium, Institute for reference materials and measurements, Belgium). An aliquot of 0.4 μl of the solution (U concentration: 1.1, 11 and 111 pg/μl) was loaded on the EF and dried up. The amounts of uranium on the EF were 0.4, 4 and 44 pg. The other was a particle sample of uranium isotopic reference material (CRM U050, 5% $^{235}$U enriched, and CRM U350, 35% $^{235}$U enriched, New Brunswick Laboratory, USA). The particle was picked up by manipulator attached to a scanning electron microscope (JSM-6700F, JEOL, Japan) and transferred onto the center of each EF [11].

Uranium isotopic reference material solution (CRM U500, 50% $^{235}$U enriched, New Brunswick Laboratory, USA) was used for mass fractionation correction.

### 2.3. Analytical procedure

The current of the IF was heated up until $^{187}$Re intensity became 100 mV and then the ion lens system was optimized to obtain the maximum intensity. After the $^{187}$Re intensity was readjusted to 100 mV, the measurement was commenced. The current of the EF was gradually raised to 4000 mA to evaporate a sample. A typical intensity profile of mass 238 is shown in Fig. 1. The signal of $^{238}$U appeared at the EF current of 1500 mA and the highest intensity was observed at about 2900 mA. In order to maintain the high intensity for a long time at around 2900 mA, the rate of increase of the EF current was manually changed in a stepwise fashion (Table 1).

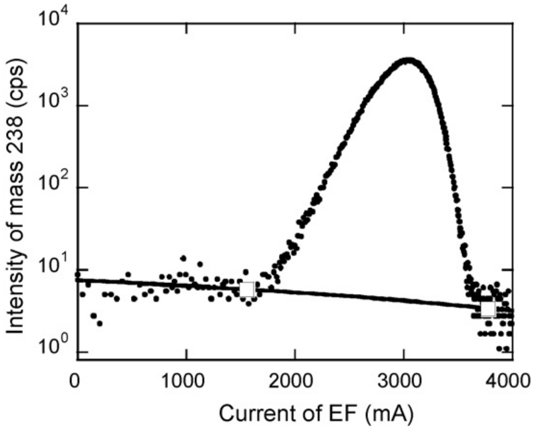

**Fig. 1.** A typical intensity profile of mass 238 and background correction line □: Start and end points to determine background correction line.

**Table 1**
Increasing rate of the current of the evaporation filament (EF).

| Current of the EF (mA) | Rate (mA/min) |
|---|---|
| 0–800 | 200 |
| 800–1800 | 100 |
| 1800–2700 | 50 |
| 2700–4000 | 20 |

Table 2 shows integration time and idle time of each isotope of uranium measured in a peak-jumping sequence. Integration times of mass 234 and 236 were lengthened twice as compared with those of mass 235 and 238 because of low abundance of $^{234}$U and $^{236}$U. Data collection was carried out until the current value of EF reached 4000 mA at which the sample evaporated entirely.

## 3. Results and discussion

### 3.1. Calculation of isotope ratio

This section describes the method of background correction and selection of the data for the calculation of isotope ratios. Before the background correction, a liner drift correction was applied to estimate intensities of mass 238 during measurements of intensities of mass 234, 235 and 236 because different isotope ion currents could not be measured simultaneously in the peak-jumping sequence.

For the background correction, a net intensity of $^{238}$U was estimated by subtracting background intensity from a measured intensity. The background probably arises from polyatomic ions of impurities in the filament assembly and dark noise of the SEM (or electronic noise). As a result of measurement of some blank filament assemblies, the intensity of mass 238 did not form a peak and decreased linearly with increasing the EF current. Thus, the background intensity beneath the peak was estimated by interpolation from the intensities outside the peak region (see

**Table 2**
Integration and idle times in a mass cycle.

| Step | Mass | Integration time (s) | Idle time (s) |
|---|---|---|---|
| 1 | 234 | 4 | 1 |
| 2 | 235 | 2 | 0.5 |
| 3 | 236 | 4 | 1 |
| 4 | 238 | 2 | 0.5 |

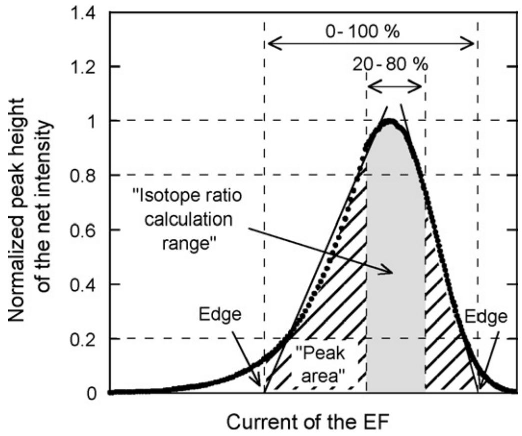

**Fig. 2.** Peak area and isotope ratio calculation range.

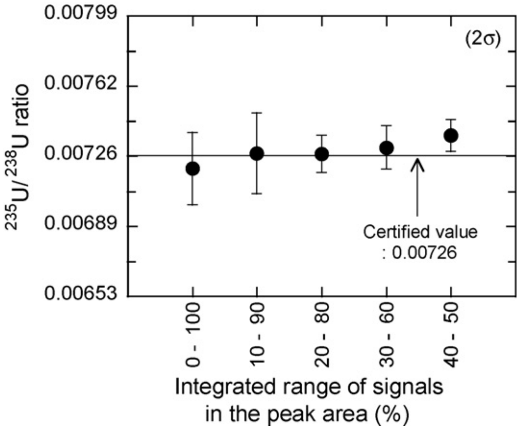

**Fig. 3.** Ratios of $^{235}U/^{238}U$ in IRMM 184 samples containing uranium of 4 pg ($n = 3$) as a function of integrated range of signals in the peak area.

Fig. 1). Net intensities of $^{234}U$, $^{235}U$ and $^{236}U$ were obtained by using the same procedure. Background correction lines were calculated at the same currents of the EF used in the estimation of mass 238.

To determine accurate isotope ratios by the continuous heating method, how to determine 'peak area' and how to select the data to be calculated in the peak area are important. First, the 'peak area' was determined as follows. Edges of the peak area were fixed by extrapolating the two points of 0.2 and 0.8 of the normalized peak height on each side of the peak to the axis of the EF current, under the assumption that the intensity increases or decreases linearly with the EF current (Fig. 2). The area inside both edges was defined as the 'peak area'. Secondly, selection of net intensities used for the calculation of isotope ratios was examined. It is advisable to use the higher net intensities for the calculation of isotope ratios because the higher intensities provide better reproducibilities and higher signal-to-noise ratio. In order to determine an appropriate range for isotope ratio measurement, isotope ratios were calculated while changing the integrated range of the net intensity included in the peak area (Fig. 3). The integration ranges along the horizontal axis in Fig. 3 shows the cumulative rate when the net intensities are integrated from the side of low EF current in the peak area (see Fig. 2). For instance, a result of the '0–100%' range shows a ratio of the integrated value of all intensities in the peak area and that of '20–80%' range was calculated from the intensities around the peak top. The results of the range of '10–90%' and '20–80%' were similar to the certified value. The range of '20–80%' was used to estimate the isotope ratios because of smaller uncertainty. The range was named the "isotope ratio calculation range". Next, the range was divided into five zones to obtain the uncertainty, and the intensities in each zone were integrated to calculate isotope ratios, and their average was decided as the final result.

### 3.2. Measurement of isotope ratio using the continuous heating method

The effect of background correction was validated by using CRM U050 particle samples. Bias from a certified value is calculated as follows:

$$\text{bias }(\%) = \left[\frac{({}^{x}\mathrm{U}/{}^{238}\mathrm{U})_{\mathrm{mes.}}}{({}^{x}\mathrm{U}/{}^{238}\mathrm{U})_{\mathrm{cer.}} - 1}\right] \times 100 \quad x = 234,\ 235,\ 236$$

where $({}^{x}U/{}^{238}U)_{mes.}$ and $({}^{x}U/{}^{238}U)_{cer.}$ are measured and certified values, respectively. In the continuous heating method, the correction of the background that originated in the filament assembly became possible by measuring the target mass before and after the sample evaporation. Isotope ratios of CRM U050 particles with a diameter of several μm ($n = 5$) were calculated with/without the background correction. The averages of bias with/without the background correction were −4% and 20% in the $^{234}U/^{238}U$ ratio, 0.5% and 0.6% in the $^{235}U/^{238}U$ ratio and −4% and 27% in the $^{236}U/^{238}U$ ratio, respectively. The method of background correction used in this study is especially effective in the measurement of isotope ratios including minor isotopes such as $^{234}U$ and $^{236}U$.

In order to evaluate the precision of an isotope ratio measured by the continuous heating method, IRMM 184 solution samples were used. The amounts of uranium were 0.4, 4 and 44 pg, which corresponded to $U_3O_8$ particles with diameters of 0.5, 1 and 2 μm, respectively. Table 3 shows the results of the $^{235}U/^{238}U$ ratio and maximum $^{238}U$ net intensity. The net intensity has increased in proportion to the amount of uranium. Isotope ratios in all samples were in good agreement with the certified value. The relative standard deviations (R.S.D.) depended on the amount of sample. The R.S.D. in the samples of 44 pg were about 1% and those in the sam-

**Table 3**
Ratios of $^{235}U/^{238}U$ and maximum net intensity of $^{238}U$ in IRMM 184 samples measured with the continuous heating method.

| Sample ID | $^{235}U/^{238}U$ ratio ± 2S.D. (R.S.D.) | Maximum of the net intensity (CPS) $^{238}U$ |
|---|---|---|
| Certified value | 0.0072623 ± 0.0000022 | – |
| 0.4 pg-1 | 0.0072 ± 0.0004 (5.8%) | 1857 |
| 0.4 pg-2 | 0.0074 ± 0.0007 (9.9%) | 1187 |
| 0.4 pg-3 | 0.0071 ± 0.0007 (9.2%) | 950 |
| 4 pg-1 | 0.0073 ± 0.0003 (4.0%) | 8302 |
| 4 pg-2 | 0.0073 ± 0.0003 (3.7%) | 16,955 |
| 4 pg-3 | 0.0072 ± 0.0002 (2.9%) | 8707 |
| 44 pg-1 | 0.00727 ± 0.00006 (0.86%) | 205,750 |
| 44 pg-2 | 0.00725 ± 0.00008 (1.1%) | 118,292 |
| 44 pg-3 | 0.00726 ± 0.00012 (1.7%) | 100,171 |

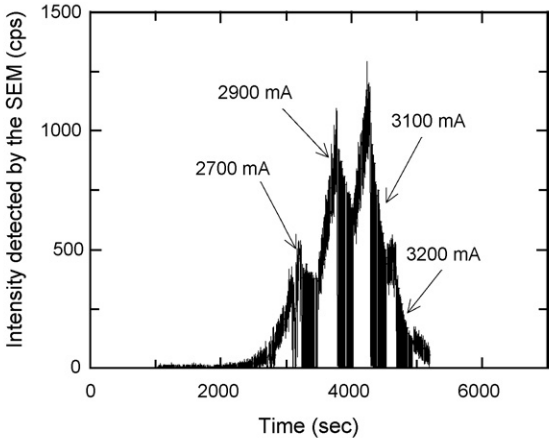

**Fig. 4.** Time chart of signal detected by SEM in IRMM 184 (U: 0.4 pg) measured by the conventional method. The current value in the figure shows the EF current when the isotope ratio is measured.

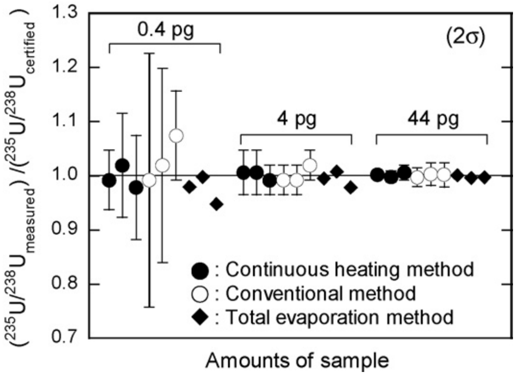

**Fig. 5.** Deviation of the measured ratios of $^{235}$U/$^{238}$U from the certified value in IRMM 184 samples of 0.4, 4 and 44 pg measured by the continuous heating method, the conventional method and the total evaporation method.

ples of 0.4 pg were less than 10%. These results indicate that the continuous heating method gives us isotope ratios with sufficient precision for measuring uranium ranging from sub-picograms to several dozen picograms.

### 3.3. *Comparison among the continuous heating method, the conventional method and the total evaporation method*

Isotope ratios of $^{235}$U/$^{238}$U in IRMM 184 samples of 0.4, 4 and 44 pg were measured by the continuous heating method, the conventional method and the total evaporation method. In the conventional method, the peak-jumping sequence of the SEM was used to determine intensities of each isotope. Five to seven blocks (20 cycles/block) were measured at the EF current of 2600–3200 mA. The isotope ratio was calculated with three blocks where higher intensity of $^{238}$U was detected, and the final result was an average of the three isotope ratios. On the other hand, results of the total evaporation method were calculated from integration of intensities measured by the continuous heating method. In this study, positive values of the net intensities that formed peaks were integrated for the calculation of isotope ratios.

Fig. 4 shows a profile of signals measured by the conventional method in the sample of 0.4 pg. The signals decreased drastically during the measurement. This trend was also observed for the samples of 4 and 44 pg. In the conventional method, it is necessary to measure the isotope ratios from steady signals with a constant current of the EF during measurement. In addition, the measurement conditions such as timing of the block measurement and the EF current should also be strictly arranged by each measurement [12]. However, since the signal decreases in the trace amount of a sample used in the present study while measuring it, and the decreasing tendency is different according to the sample, it is necessary to decide the measurement conditions such as the timing of the measurement and the heating pattern of filament while measuring it. Since measurement conditions are different in each sample, the effect of mass discrimination could not be corrected accurately. Although the measurement condition can be arranged to some degree by gaining experience of the measurement, the measurement precision depends on the operator and the above problem still remains.

The results of the isotope ratios measured by the three methods were summarized in Fig. 5. All isotope ratios agreed closely with the certified value. The results measured by the conventional method could not correct the mass discrimination strictly as mentioned above. For the results of uranium of 0.4 pg, the continuous heating method had smaller uncertainties and better reproducibility compared with those of the conventional method and the total evaporation method. Notice that the result measured by the total evaporation method did not have an uncertainty unlike the other methods. The continuous heating method has a fixed measurement procedure for the calculation of the isotope ratio at each measurement. This enabled an accurate correction of the effect of the mass discrimination. The results in samples of 0.4 pg measured by the total evaporation method tended to be lower than the certified value as shown in Fig. 5 because the intensities of $^{235}$U at the start and the end of the measurement would be below the detection limit and thus the isotope ratio may be underestimated.

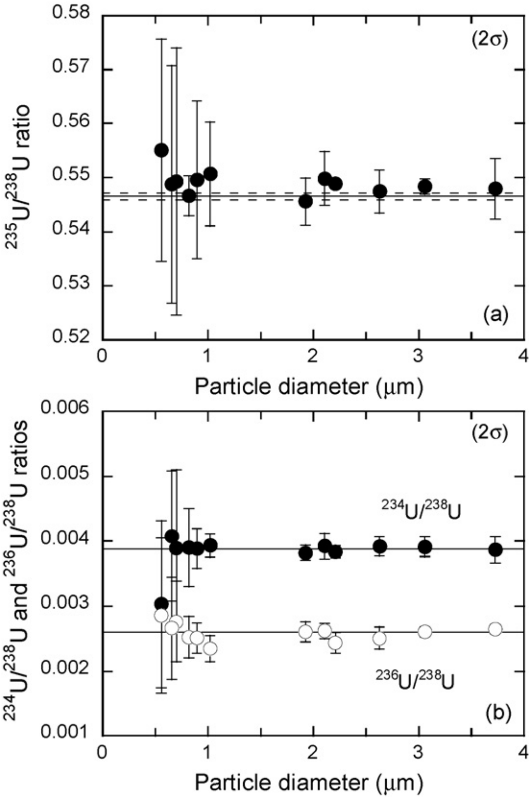

**Fig. 6.** Ratios of $^{235}$U/$^{238}$U (a), $^{234}$U/$^{238}$U and $^{236}$U/$^{238}$U (b) in CRM U350 particles measured by the continuous heating method. Particle diameter is the average between the lengths of the major and minor axes of each particle determined with the scanning electron microscope.

By using the continuous heating method, Fig. 6 shows the ratios of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ in the CRM U350 particles with diameters of 0.56–3.7 μm that correspond to weights of 0.76–228 pg under the assumption that chemical composition is $U_3O_8$ (density 8.39 g/cm$^3$). The measured ratios were in good agreement with the certified values. The R.S.D. of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios in the particles with a diameter above 1 μm were within 5%, 2% and 10%, respectively. The maximum R.S.D. of $^{235}U/^{238}U$ ratio for CRM U010 particles (1.3–3.4 μm) measured with the conventional method were reported as 2–6% [13]. These results indicated that the continuous heating method allowed small uncertainty regardless of different isotope ratios such as CRM U010 and CRM U350.

## 4. Conclusion

The continuous heating method by TIMS was developed to measure isotope ratios in a trace amount of uranium, and the main features are as follows: (1) parts of higher intensities were used to calculate the isotope ratio; (2) procedures of measurement and data calculation were standardized. These features enabled us to measure accurate isotope ratios regardless of the skillfulness of the operator and sample amount as compared with previous methods. It is expected that the continuous heating method will be used in various research fields as an effective tool for isotope ratio measurements of ultra-trace amounts of samples.

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