

## **A Correction Method for the Peak Tailing Backgrounds for Accurate Isotope Ratio Measurements of Uranium in Ultra Trace Levels using Thermal Ionization Mass Spectrometry**

**Jong-Ho Park, Inhee Choi, Sujin Park, Myungho Lee, and Kyuseok Song\***

*Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea*

*\*E-mail: sks@kaeri.re.kr*

*Received September 19, 2011, Accepted October 15, 2011*

A new method in thermal ionization mass spectrometry (TIMS) was developed to correct peak tailing backgrounds in the isotope ratio measurements of uranium in ultra trace levels for higher accuracy. Two different uranium standard reference materials (U005 and U030) were used to construct databases of signal intensities at mass 234 u and mass 236 u, which correspond to the two uranium minor isotopes, and signal intensity of  $^{238}\text{U}$ . Correlations between peak tailing backgrounds and  $^{238}\text{U}$  were obtained by least-squares regression on calculated backgrounds at mass 234 u and mass 236 u with respect to the signal intensity of  $^{238}\text{U}$  followed by separation of the peak tails of the two major isotopes of uranium ( $^{235}\text{U}$  and  $^{238}\text{U}$ ), which enables us to obtain a master equation for peak tailing background correction on all kinds of samples. Verification of the correction method was carried out using U010 and IRMM-040a.

**Key Words :** Uranium, Background, Peak tailing, Isotopic analysis, Nuclear safeguards

### **Introduction**

As the recent fast growth of atomic energy industries requires a high degree of transparency, the importance of the isotope ratio measurements of uranium in environmental samples with high accuracy and precision is being improved.<sup>1-8</sup> The high precision of the isotope ratio measurements is ensured by utilizing state-of-the-art instruments, such as the thermal ionization mass spectrometer (TIMS)<sup>2-4,7-14</sup> and the multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS).<sup>15-18</sup> On the other hand, high precision itself does not necessarily guarantee that the measurement is accurate. Instead, some calibration and/or correction are additionally required to reduce the systematic errors by covering detector calibration and mass bias correction.<sup>4</sup>

In general, background is not considered as a significant correction factor to improve measurement accuracy, especially when the target of a measurement is a process sample which contains more than a few micrograms of nuclear materials and fission products. Since the actual ion signal intensities in the mass spectrum stemming from the sample are relatively large with respect to that of background, there is often no need to apply background correction for accuracy improvement. As the amount of target materials becomes smaller, however, the importance of the background contribution gradually increases up to a point where it results in a significant bias to the isotope ratio measurements. A typical environmental sample contains a small amount of uranium ranged from a few tens of picogram to a few nanograms, which fall into this case.

A possible origin of uranium background in the mass spectrum is the impurity contained in the reagents used in

chemical preparation. This can be removed or significantly reduced by using ultra pure grades of reagents, such as triple distilled water and a suprapur grade of nitric acid. In the case of TIMS, an additional background contribution comes from the impurity in the filament used for sample loading, evaporation, and ionization. A degassing process described in the experimental section reduces the uranium impurity in a filament to negligible levels.<sup>19</sup>

The peak tailing caused by energy dispersion of ions is another source of background in the isotopic analysis by mass spectrometry. Ion scatterings by gas molecules in a flight tube and ion reflections from a chamber wall are the main causes of the energy dispersion of ions affecting abundance sensitivity.<sup>20</sup> Therefore, some ions with dispersed energy interfere with the ions with different masses. Peak tailing must be considered seriously when the peak of a minor isotope is adjacent to that of an extremely abundant isotope. The isotopic analysis of uranium minor isotopes, such as  $^{234}\text{U}$  and  $^{236}\text{U}$ , is a case in point. The two isotopes in mass spectrum are close to the uranium major isotopes,  $^{235}\text{U}$  and  $^{238}\text{U}$ , of which the abundances are typically 3 and 5 orders of magnitude higher than those of the minor isotopes, respectively.

The use of a retarding potential quadrupole lens (RPQ), a kind of energy filter to eliminate the ions with inappropriate energy, improves the abundance sensitivity by a factor of several hundreds.<sup>21</sup> On the other hand, it decreases detection sensitivity and increases dark noise, which are critical drawbacks to the isotopic analysis of ultra trace levels of elements since a relatively large amount of sample is required and the precision is sacrificed. The backgrounds from the peak tailing of the uranium major isotopes can be subtracted from

the total signal intensities corresponding to the uranium minor isotope by estimating the backgrounds using off-peaks measurements.<sup>4</sup> In this method, a measurement at mass 233.5 u, mass 234.5 u, mass 235.5 u, and mass 236.5 u is performed in each multi-dynamic mass cycle to calculate the backgrounds at mass 234 u and mass 235 u by averaging the intensities of corresponding off-peak. Although this method enables us to correct the peak tailing effect using the backgrounds measured in-situ, an additional sample amount is necessary for this measurement step.

Makishima *et al.* used a different correction method employing a linear relationship between the <sup>238</sup>U signal intensity and the background at mass 234 u estimated at the off-peak masses.<sup>18</sup> They suggested that the peak tailing contribution of <sup>238</sup>U at mass 234 u is approximately 10<sup>-8</sup>. However, it is considered that their method is not appropriate to be applied to other samples with different isotopic ratios of <sup>235</sup>U and <sup>238</sup>U since the tailing background at mass 234 u originates not solely from <sup>238</sup>U but also from <sup>235</sup>U. Although <sup>235</sup>U is usually less abundant than <sup>238</sup>U, the contribution of <sup>235</sup>U to the tailing background at mass 234 u should not be neglected due to the closeness in mass. In the same manner, this method is inappropriate for correcting the background at mass 236 u. Therefore, a new correction method for the peak tailing effect, which is universally suitable for the analysis of environmental samples, is required.

In this study, we have separated the contributions of the two uranium major isotopes to the tailing backgrounds at mass 234 u and mass 236 u to correct the peak tailing effect for an accurate isotopic analysis of uranium in ultra trace levels. Two different uranium standard solutions are used to deduce correlations between each major isotope and the tailing backgrounds at mass 234 u and mass 236 u. The applicability of this correction method is evaluated by using other uranium standards.

### Experimental

The measurement was performed by TIMS (TRITON, Thermo Scientific). A differential pumping system consisting of a turbo-molecular pump and two ion-getter pumps maintained the ultra-high vacuum of the system. In the thermal ionization source, the double filament assembly evaporated and ionized the sample by a temperature of ~1800 °C. A magnetic sector separated the ions spatially by masses (i.e., mass to charge ratio), which were then detected by a combination of faraday cups and a secondary electron multiplier (SEM).

Prior to sample loading, the filaments prepared from zone-refined rhenium ribbon (0.04 mm and 0.7 mm in thickness and width, respectively, Thermo Scientific) were degassed under vacuum (~10<sup>-7</sup> mbar) at 4.5 A for 60 min. A preliminary experiment showed that the <sup>238</sup>U background from the impurity in an assembly of double-filament was significantly reduced by the degassing procedure.<sup>19</sup> The background at mass 238 from an assembly of double-filament was approximately a few cps corresponding to less than one

**Table 1.** Detector configurations for data acquisition

Step	SEM <sup>a</sup>	FAR <sup>b</sup> -H1	FAR-H2	FAR-H3	Integration time (s)
1	234 amu			238 amu	4
2	235 amu		238 amu		2
3	236 amu	238 amu			4

<sup>a</sup>SEM: Secondary Electron Multiplier. <sup>b</sup>FAR: Faraday Cup

femtogram. Since this amount is a negligible level compared to the amount of the actual sample (1 ng), no further corrections regarding the <sup>238</sup>U background from filaments were made.

The data acquisition method consisted of three steps as shown in Table 1. In each step, a secondary electron multiplier (SEM) without RPQ, and a corresponding faraday cup were used for the simultaneous detection of uranium isotopes, which cancels out signal fluctuation during data acquisition. The integration times for the steps were 4s and 2s for the minor isotopes and <sup>238</sup>U, respectively.

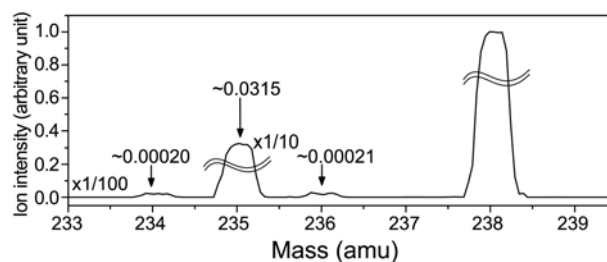
Acid digestion of uranium certified reference materials (U005, U010, U030, National Bureau of Standards, IRMM-040a, Institute of Reference Materials and Measurements) with nitric acid (Suprapur, Merck) were performed to prepare uranium standard solutions followed by dilution with 1 M HNO<sub>3</sub>.

### Results and Discussion

Figure 1 shows a mass spectrum of U030. The approximate intensities of <sup>234</sup>U, <sup>235</sup>U, and <sup>236</sup>U with respect to <sup>238</sup>U were 0.00020, 0.0315, and 0.0021, respectively.

**Mass Bias Correction with <sup>235</sup>U/<sup>238</sup>U Ratio.** Thirteen and eight isotopic measurements for U005 and U030, respectively, were carried out. The ion signals at mass 234 u, mass 235 u, and mass 236 u in cps were measured with the corresponding ion signals at mass 238 u in volt simultaneously as described in Table 1. The continuous heating method,<sup>12</sup> in which data collection was performed with a gradual increase in the current of evaporation filament (EF) up to 4500mA, was applied. As the EF current was raised with a fixed ionization current, the ion signals increased until a certain temperature, and then decreased once the sample was entirely consumed. Therefore, considerable numbers of data sets at different <sup>238</sup>U intensities were accumulated for statistics.

For determination of the isotope ratios, only the data sets,



**Figure 1.** A mass spectrum of U030.

whose  $^{238}\text{U}$  intensity fell in the range of 15-100% with respect to the maximum  $^{238}\text{U}$  signal intensity, were chosen for data analysis to avoid unnecessarily large uncertainty arising from relatively small signal intensities. The weighted mean and the weighted standard deviation for the isotope ratios were calculated by applying weights ( $w_i$ ) defined as follows:

$$w_i = \frac{I_i^{235}}{\sum_i I_i^{235}} \quad (1)$$

where  $I_i$  is the signal intensity of  $^{235}\text{U}$  in “the range of 15-100%” described above. The signal intensity of  $^{235}\text{U}$  detected by SEM, instead of that of  $^{238}\text{U}$  detected by faraday cups, was used to obtain the weights due to the relatively small uncertainty.

Table 2 shows the measured  $n(^{235}\text{U})/n(^{238}\text{U})$  ratios of the uranium standard solutions acquired by averaging the thirteen and the eight measurements of U005 and U030, respectively. Mass bias correction factors (C) were calculated as the ratios of the certified  $n(^{235}\text{U})/n(^{238}\text{U})$  value to the measured isotopic ratio values, multiplied by the measured signal intensities of mass 234 u and mass 236 u:

$$C = \frac{R_{\text{Cert}}(n(^{235}\text{U})/n(^{238}\text{U}))}{R_{\text{Meas}}(n(^{235}\text{U})/n(^{238}\text{U}))} \quad (2)$$

$$I_{\text{Corr}}^{\text{mass}_i} = I^{\text{mass}_i} \cdot C \quad (3)$$

where  $R_{\text{Cert}}(n(^{235}\text{U})/n(^{238}\text{U}))$  and  $R_{\text{Meas}}(n(^{235}\text{U})/n(^{238}\text{U}))$  are the certified and the measured isotope ratios of  $^{235}\text{U}$  and  $^{238}\text{U}$ , respectively,  $I^{\text{mass}_i}$  and  $I_{\text{Corr}}^{\text{mass}_i}$  are the signal intensity and corrected signal intensity at mass  $i$ , respectively, with the superscript ( $\text{mass}_i$ ) representing the background masses of interest, which were mass 234 u and mass 236 u in this study.

**Correlation between Background and  $^{238}\text{U}$  Signal Intensity.** The backgrounds at mass  $i$  ( $I_{\text{Backgr}}^{\text{mass}_i}$ ) were calculated by the differences between the measured signal intensities ( $I_{\text{Corr}}^{\text{mass}_i}$ ) and the corresponding theoretical intensities ( $I_{\text{Theo}}^{\text{mass}_i}$ ) estimated by applications of the certified ratios to the measured  $^{238}\text{U}$  signal intensities ( $I^{238}$ ):

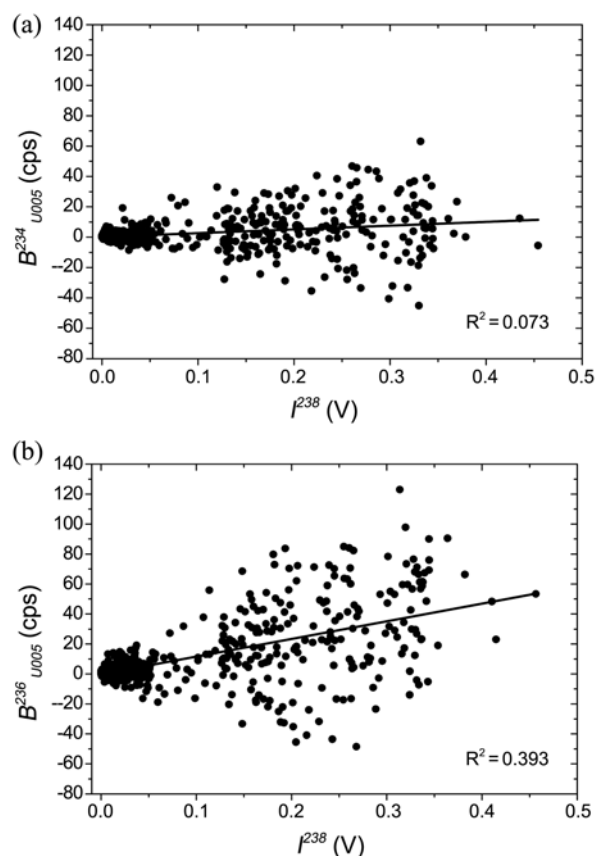
$$I_{\text{Theo}}^{\text{mass}_i} = I^{238} \cdot R_{\text{Cert}}(n(^{\text{mass}_i}\text{U})/n(^{238}\text{U})) \quad (4)$$

$$I_{\text{Backgr}}^{\text{mass}_i} = I_{\text{Corr}}^{\text{mass}_i} - I_{\text{Theo}}^{\text{mass}_i} \quad (5)$$

The calculated background data sets ( $I_{\text{Backgr}}^{\text{mass}_i}$  versus  $I^{238}$ ) for a standard reference material were merged into a data-

**Table 2.** Measured and certified isotope ratios of  $^{235}\text{U}$  and  $^{238}\text{U}$  for U005 and U030

CRM	$n(^{235}\text{U})/n(^{238}\text{U})$		Mass bias correction factor (C)
	Measured	Certified	
U005	0.0049373	0.0049194	0.99637
U030	0.031509	0.031430	0.99748



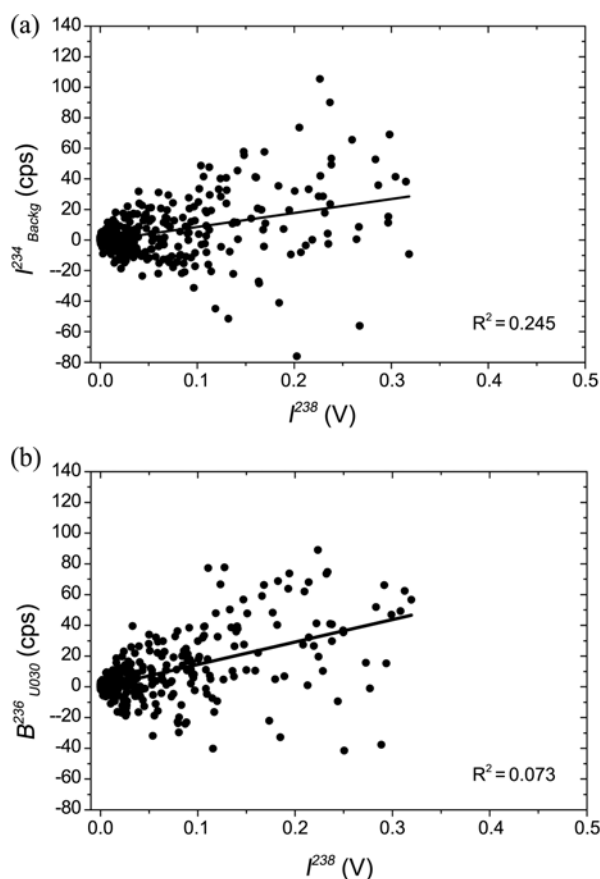
**Figure 2.** Linear regression for the backgrounds at mass 234 u (a) and mass 236 u (b) versus the signal intensity of  $^{238}\text{U}$  in U005.

base. Each database consists of 879 and 491 data sets for U005 and U030, respectively. A least-squares regression was carried out to obtain the correlations between the backgrounds and the measured  $^{238}\text{U}$  signal intensities (see Fig. 2 and Fig. 3), which are summarized in Table 3. The correlations were expressed as  $B_j^{\text{mass}_i}(\text{cps}) = a_j^{\text{mass}_i} \cdot I^{238}(\text{V})$ , where  $a$  is the slope of least-squares regression, named as ‘the background coefficient’, and the subscript ( $j$ ) represent the samples of interest. The intercepts having extremely small values were neglected considering the uncertainty range with a 95% confidence level. The uncertainty ranges in the background coefficients are expanded uncertainties  $U = k \cdot u_c$  following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement (GUM)<sup>22</sup> where  $k$  is a coverage factor and  $u_c$  is the combined standard uncertainty.  $k$  was set to 2 in this study.

**Separation of Peak Tailing Effects from the Two Major Uranium Isotopes.** Since the backgrounds, whose correlations with  $I^{238}$  were obtained above, simultaneously arise from the peak tails of the two major uranium isotopes,  $^{235}\text{U}$  and  $^{238}\text{U}$ , the application of the background coefficients in Table 3 is limited to the specific samples unless the two peak tails are separated.

The background coefficient of sample  $j$  at mass  $i$ , can be rewritten as follows (see Appendix):

$$a_j^{\text{mass}_i} = R_j \cdot P^{\text{mass}_i}(^{235}\text{U}) + P^{\text{mass}_i}(^{238}\text{U}) \quad (6)$$



**Figure 3.** Linear regression for the backgrounds at mass 234 u (a) and mass 236 u (b) versus the signal intensity of  $^{238}\text{U}$  in U030.

where  $R$  is the isotope ratio of  $^{235}\text{U}/^{238}\text{U}$  of a sample, and  $P^{mass_i}(^{235}\text{U})$  and  $P^{mass_i}(^{238}\text{U})$  are the individual background coefficients at mass  $i$  arising from the peak tails of  $^{235}\text{U}$  and  $^{238}\text{U}$ , respectively, which correspond to the values of simultaneous equations constructed using two different samples, such as U005 and U030 in this study. Table 4 shows the individual background coefficients at mass 234 u and mass 236 u obtained from the background coefficients listed in Table 3. The uncertainty ranges are expanded uncertainties  $U = k \cdot u_c$  following the ISO/BIPM GUM where  $k$  is the coverage factor and  $u_c$  is the combined standard uncertainty.  $k$  is set to 2 in this study.

As shown in Table 4,  $P^{234}(^{235}\text{U})$  was over two orders of magnitude larger than  $P^{234}(^{238}\text{U})$  implying that the peak

**Table 3.** The background coefficients of U005 and U030 at mass 234 u and mass 236 u

CRM	Mass 234 u (cps/V)	Mass 236 u (cps/V)
U005	$a_{U005}^{234} = 24.7 \pm 5.9$	$a_{U005}^{236} = 117.7 \pm 9.6$
U030	$a_{U030}^{234} = 91.3 \pm 19.3$	$a_{U030}^{236} = 146.1 \pm 18.8$

**Table 4.** The individual background coefficients at mass 234 u and mass 236 u

Peak tail origin	Mass 234 u (cps/V)	Mass 236 u (cps/V)
$^{235}\text{U}$	$P^{234}(^{235}\text{U}) = 2510 \pm 761$	$P^{236}(^{235}\text{U}) = 1072 \pm 795$
$^{238}\text{U}$	$P^{234}(^{238}\text{U}) = 12 \pm 8$	$P^{236}(^{238}\text{U}) = 112 \pm 12$

tailing effect is drastically enhanced as the mass difference from the origin becomes smaller, which is consistent with the nature of the peak tailing effect. If the lower limit of  $P^{234}(^{238}\text{U})$  is considered, the enhancement in the peak tailing effect becomes even larger. Similar enhancements were observed in  $P^{236}(^{235}\text{U})$  versus  $P^{236}(^{238}\text{U})$ , and  $P^{234}(^{238}\text{U})$  versus  $P^{236}(^{238}\text{U})$ . It must be noted that  $P^{234}(^{235}\text{U})$  was approximately twice as  $P^{236}(^{235}\text{U})$ . The asymmetric shape of  $^{235}\text{U}$  peak implies that losing energy by ion scattering and ion reflection is more probable than gaining energy, which is also consistent with one of the general aspect of the peak tailing effect.

**Verification of the Correction Method.** Four measurements with 1 ng of U010 samples were performed by TIMS for the verification of the correction method. Isotope ratios of  $n(^{235}\text{U})/n(^{238}\text{U})$  of the samples, and the corresponding individual background coefficients in Table 4 were combined by eq. (6) to obtain  $a_{U010}^{234}$  and  $a_{U010}^{236}$ , which were 38 cps/V and 123 cps/V, respectively. As seen in Table 5, the accuracy of the isotope ratios was clearly improved by applying the correction method. Since the individual background coefficient at mass 236 u is greater than that at mass 234 u, the degree of improvement in accuracy was more remarkable in  $n(^{236}\text{U})/n(^{238}\text{U})$  than in  $n(^{234}\text{U})/n(^{238}\text{U})$ .

The versatility of the correction method was verified with IRMM-040a, a certified isotopic reference material, of which the major isotope is  $^{233}\text{U}$  instead of  $^{238}\text{U}$ . We focused on the peak tailing effect of  $^{233}\text{U}$  on mass 234 u. Assuming that the peak tails of  $^{235}\text{U}$  and  $^{238}\text{U}$  are negligible due to their low abundance, the background coefficient for mass 234 u is expressed as eq. (7).

**Table 5.** Uncorrected and corrected  $n(^{234}\text{U})/n(^{238}\text{U})$  and  $n(^{236}\text{U})/n(^{238}\text{U})$  in U010

Sample ID	$n(^{234}\text{U})/n(^{238}\text{U})$		$n(^{236}\text{U})/n(^{238}\text{U})$	
	Uncorrected	Corrected	Uncorrected	Corrected
Certified value	0.0000546(5)		0.0000688(7)	
U010 #1	0.0000551(42)	0.0000545(42)	0.0000701(36)	0.0000681(36)
U010 #2	0.0000560(64)	0.0000554(64)	0.0000713(72)	0.0000693(72)
U010 #3	0.0000553(36)	0.0000547(36)	0.0000711(19)	0.0000691(19)
U010 #4	0.0000554(49)	0.0000548(49)	0.0000703(34)	0.0000683(34)

Numbers in parentheses indicate expanded uncertainties  $U = k \cdot u_c$ .

**Table 6.** Uncorrected and corrected  $n(^{234}\text{U})/n(^{233}\text{U})$  in IRMM-040a

Sample ID	$n(^{234}\text{U})/n(^{233}\text{U})$	
	Uncorrected	Corrected
Certified value	0.0093280(20)	
IRMM-040a #1	0.0093507(99)	0.0093336(99)
IRMM-040a #2	0.0093689(186)	0.0093517(186)
IRMM-040a #3	0.0093425(185)	0.0093253(185)
IRMM-040a #4	0.0093463(242)	0.0093292(242)

$$a_{IRMM-040a}^{234} = P^{234}(^{233}\text{U}) \quad (7)$$

As the individual background coefficients of  $P$  depend on the mass difference from the origin,  $P^{234}(^{233}\text{U})$  can be, as a first approximation, set equal to  $P^{236}(^{235}\text{U})$  in Table 4. It must be noted that  $P^{234}(^{235}\text{U})$  is only an approximation considering that mass 234 u is heavier than mass 233 and the peak tailing effect is uneven for lighter and heavier masses with respect to the origin. Table 6 shows that applying the correction method enhances the accuracy of the four measurements of the IRMM-040a samples.

### Conclusion

A correction method for the backgrounds at mass 234 u and mass 236 u originated from the peak tails of the major isotopes of uranium was developed for accurate isotopic measurements of uranium at ultra-trace levels. The isotopes of uranium in two different uranium certified reference materials were measured using TIMS to derive the correlations between the backgrounds of the minor isotopes and the ion signals of  $^{238}\text{U}$  followed by determining the corresponding background coefficients. The application of the correction method to the isotopic measurements of U010 and IRMM-040a improved the accuracy of the isotope ratios, especially  $n(^{236}\text{U})/n(^{238}\text{U})$ . The correction method can be potentially applied not only to TIMS, but also to other mass spectrometric techniques like ICP-MS.

**Acknowledgments.** This work was supported by the long-term nuclear research and development project of the Ministry of Science and Technology of Korea.

### Appendix

The background at mass  $i$  consists of the peak tails of  $^{235}\text{U}$  and  $^{238}\text{U}$  ( $B(^{235}\text{U})$  and  $B(^{238}\text{U})$ , respectively):

$$B_j^{mass_i} = B^{mass_i}(^{235}\text{U}) + B^{mass_i}(^{238}\text{U}) \quad (8)$$

It is noted that subscripts are unnecessary for the individual backgrounds from the peak tails due to independence on samples. To separate the two peak tails at mass  $i$ , the partial derivative of the background of sample  $j$  at mass  $i$  with respect to the signal intensity of  $^{238}\text{U}$ :

$$\frac{\partial B_j^{mass_i}}{\partial I^{238}} = \frac{\partial B^{mass_i}(^{235}\text{U})}{\partial I^{238}} + \frac{\partial B^{mass_i}(^{238}\text{U})}{\partial I^{238}} \quad (9)$$

Considering the isotope ratio of  $n(^{235}\text{U})/n(^{238}\text{U})$  of sample  $j$  and assuming that the peak tailing effect of  $^{238}\text{U}$  on mass 235 is negligible, peak tails at mass  $i$  are separated as follows:

$$\frac{\partial B_j^{mass_i}}{\partial I^{238}} = R_j \frac{\partial B^{mass_i}(^{235}\text{U})}{\partial I^{235}} + \frac{\partial B^{mass_i}(^{238}\text{U})}{\partial I^{238}} \quad (10)$$

Eq. (10) is the same as eq. (6) if the individual derivatives are substituted into the parameters defined above.

$$a_j^{mass_i} = R_j \cdot P^{mass_i}(^{235}\text{U}) + P^{mass_i}(^{238}\text{U}) \quad (6)$$

where  $a_j^{mass_i} = \frac{\partial B_j^{mass_i}}{\partial I^{238}}$ ,  $P^{mass_i}(^{235}\text{U}) = \frac{\partial B^{mass_i}(^{235}\text{U})}{\partial I^{235}}$ , and

$$P^{mass_i}(^{238}\text{U}) = \frac{\partial B^{mass_i}(^{238}\text{U})}{\partial I^{238}}$$

### References

- Donohue, D. L. *J. Alloy Compd.* **1998**, 271-273, 11.
- Stoffel(S), J. J.; Wacker, J. F.; Kelley, J. M.; Bond, L. A.; Kiddy, R. A.; Brauer, F. P. *Appl. Spectrosc.* **1994**, 48, 1326.
- Sahoo, S. K.; Yonehara, H.; Kurotaki, K.; Fujimoto, K.; Nakamura, Y. *J. Radioanal. Nucl. Chem.* **2002**, 2, 241.
- Richter, S.; Goldberg, S. A. *Int. J. Mass Spectrom.* **2003**, 229, 181.
- Esaka, F.; Watanabe, K.; Fukuyama, H.; Onodera, T.; Esaka, K. T.; Magara, M.; akrai, S.; Usuda, S. *J. Nucl. Sci. Technol.* **2004**, 41, 1027.
- Stirling, C. H.; Halliday, A. N.; Porcelli, D. *Geochim. Cosmochim. Acta* **2005**, 69, 1059.
- Lee, C.-G.; Iguchi, K.; Esaka, F.; Magara, M.; Sakurai, S.; Watanabe, K.; Usuda, S. *Jpn. J. Appl. Phys.* **2006**, 45, 294.
- Kraiem, M.; Richter, S.; Kühn, H.; Aregbe, Y. *Anal. Chim. Acta* **2011**, 688, 1.
- Cohen, A. S.; Belshaw, N. S.; O'Nions, R. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, 116, 71.
- Suzuki, K.; Miyta, Y.; Kanazawa, N. *Int. J. Mass Spectrom.* **2004**, 235, 97.
- Bürger, S.; Richiputi, L. R.; Bostick, D. A.; Turgeon, S.; McBay, E. H.; Lavelle, M. *Int. J. Mass Spectrom.* **2009**, 286, 70.
- Suzuki, D.; Saito-Kokubu, Y.; Sakurai, S.; Lee, C.-G.; Magara, M.; Iguchi, K.; Kimura, T. *Int. J. Mass Spectrom.* **2010**, 294, 23.
- Schoenberg, R.; Blanckenburg, F. *Int. J. Mass Spectrom.* **2005**, 242, 257.
- Jakopiè, R.; Richter, S.; Kühn, H.; Benedik, L.; Pihlar, B.; Aregbe, Y. *Int. J. Mass Spectrom.* **2009**, 279, 87.
- Hoffmann, D. L.; Prytulak, J.; Richards, D. A.; Elliott, T.; Coath, C. D.; Smart, P. L.; Scholz, D. *Int. J. Mass Spectrom.* **2007**, 264, 97.
- Hoffmann, D. L.; Spötl, C.; Mangini, A. *Chem. Geol.* **2009**, 259, 253.
- Newman, K.; Freedman, P. A.; Williams, J.; Belshaw, N. S.; Halliday, A. N. *J. Anal. At. Spectrom.* **2009**, 24, 742.
- Makishima, A.; Chekol, T. A.; Nakamura, E. *J. Anal. At. Spectrom.* **2007**, 22, 1383.
- Park, J.-H.; Choi, I.; Song, K. *Mass Spectrom. Lett.* **2010**, 1, 17.
- Pavlenko, V. A.; Pliss, N. S.; Sokolov, B. N.; Shcherbakov, A. P. *Int. J. Mass Spectrom. Ion Phys.* **1983**, 46, 55.
- Calsteren, P.; Schwieters, J. B. *Int. J. Mass Spectrom. Ion Processes* **1995**, 146/147, 119.
- Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization*, 1995; ISBN 92-6r-10188-9.