A Technique to Minimize Impurity Signal from Blank Rhenium Filaments for Highly Accurate TIMS Measurements of Uranium in Ultra-Trace Levels

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Abstract: As background significantly affects measurement accuracy and a detection limit in determination of the trace amounts of uranium, it is necessary to minimize the impurities in the filaments used for thermal ionization mass spectrometry (TIMS). We have varied the degassing condition such as the heating currents and duration times to reduce the backgrounds from the filaments prepared with zone-refined rhenium tape. The most efficient degassing condition of the heating current and the duration time was determined as 3.5 A and 60 min, respectively. The TIMS measurement combined with the isotope dilution mass spectrometry (IDMS) technique showed that the uranium backgrounds were determined to be in a few fg level from blank rhenium filaments. The background minimized filaments were utilized to measure the uranium isotope ratios of a U030 (NIST) standard sample. The excellent agreement of the measurement with the certified isotope ratios showed that the degassing procedure optimized in this study efficiently reduced the impurity signals of uranium from blank rhenium filaments to a negligible level.

Key words: Uranium, Background, TIMS, Isotopic Analysis, Safeguard, Isotope Ratio

Introduction

Highly accurate and precise determination of isotopic ratios and concentrations of uranium plays essential roles in ensuring the nuclear transparency of a country.[1] Thermal ionization mass spectrometry (TIMS) is one of the most powerful techniques in the isotopic and quantitative analysis of uranium contained in swipe samples and environmental samples with ultra-trace levels.[2–7] The instrument is equipped with a good vacuum system as well as a multi collector system with one or more ion counters (IC), a series of faraday cups, and high performance amplifiers. These elements with high linearity reduce dark noise, the fluctuation of signal intensity, and random error, which are the key factors affecting accuracy and precision.

In most cases, a small background is not considered as a significant correction factor to improve measurement accuracy. It is true especially when the target of measurements is process samples which contain over a few micrograms of nuclear materials and fission products. When the actual intensities from target materials in the mass spectrum are strong compared to that of the background, there is no need to apply any background correction for accuracy improvement. As the amount of target materials becomes small, however, the importance of background gradually increases, resulting in a serious distortion in isotope ratio measurements.

The impurity in the reagents used in the chemical preparation of samples is one of the possible origins of uranium background. Therefore, it is required to use ultra pure grades of reagents, such as triple distilled water and a suprapur grade of nitric acid, to significantly reduce the impurities. Furthermore, the measurement of a process blank, which has experienced all the physical and chemical processes as a target sample has, but contains no target material, is always carried out to evaluate the background arising from the impurities for correction.

In the case of TIMS, additional background comes from the impurities in filaments used for sample loading, evaporation, and ionization. Although zone-refined rhenium filaments contain less impurity than normal rhenium filaments, a degassing treatment with high temperature under vacuum conditions is necessary to reduce the background to a negligible level. Since the degassing process affects the surface quality of the filaments as well as the background level, it is necessary to find optimized conditions for degassing.[8]

In this study, we have varied the heating current and the duration time to determine degassing conditions for the most efficient background reduction with maintaining the surface quality of zone-refined rhenium filaments followed by quantifying the background level in blank filaments. An isotopic analysis of a uranium standard reference material has been performed using the filaments degassed under the optimized condition to verify the applicability of the background minimization technique.

Experimental

The filaments were prepared with zone-refined rhenium tape (0.04 mm and 0.7 mm in thickness and width, respectively, Thermo Scientific) and wire emitter holders by spot welding.

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A double-filament system employed a pair of filaments for measurement. One filament, named as the evaporation filament, was used for sample loading and sample evaporation with high temperature, while the other filament, named as the ionization filament, was used for sample ionization. For the background measurements, also called as blank measurements, no sample was loaded on the evaporation filaments.

The measurement was performed with TIMS (TRITON, Thermo Scientific) schematically described in Figure 1. A differential pumping system consisting of a turbo-molecular pump and two ion-getter pumps maintained the ultra-high pressure of the system. In the thermal ionization source electrically floated by +10 kV, a double-filament system evaporated, and then, immediately ionized the sample by considerably high temperature (~1800 ^{o}C) followed by pushing the ions with accelerating voltage to a analyzer. A magnetic sector analyzed the ions spatially by masses, which were then transduced into electrical current by a combination of faraday cups and a secondary electron multiplier (SEM).

The acid digestion of uranium standard reference material (SRM U030, National Bureau of Standards) with concentrated nitric acid (65%, Merck) followed by being diluted with 1 M HNO_3 prepared from triple distilled water was performed to prepare a uranium standard solution in 1 ppm of concentration.

Results and Discussion

Determination of an optimized degassing condition

Blank filaments were baked in a degassing device equipped with a filament heating system and a high vacuum chamber maintained by a turbo-molecular pump. Three different heating currents (2, 3.5, and 4.5 A) were applied to filaments for different duration times (30, 60, and 90 min). The higher currents correspond to higher temperatures although it was not possible for the surface temperature of the filaments to be monitored while degassing. The estimated temperature was approximately 1500 ^{o}C at 3.5 A.

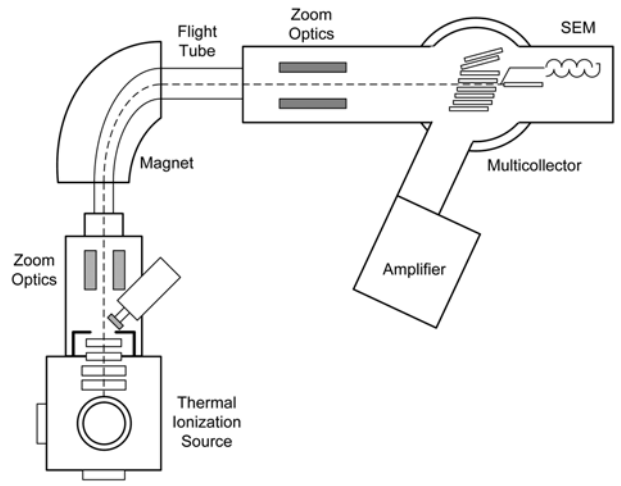

Figure 1. The schematic diagram of TIMS.

The surface conditions of each filament were observed using a scanning electron microscope (SEM, JSM-6610LV, JEOL). As shown in Figure 2, impurities of the filaments (black spots in Figure 2a) were clearly removed by degassing although slight surface cracks were produced with the expansion and contraction of the surface by the heating current at 3.5 A (Figure 2b). The cracks grew further at higher currents (4.5 A, Figure 2c) resulting in the deformation of some filaments. However, the preliminary experiments showed that the crack did not affect the evaporation and/or ionization of samples including background uranium.

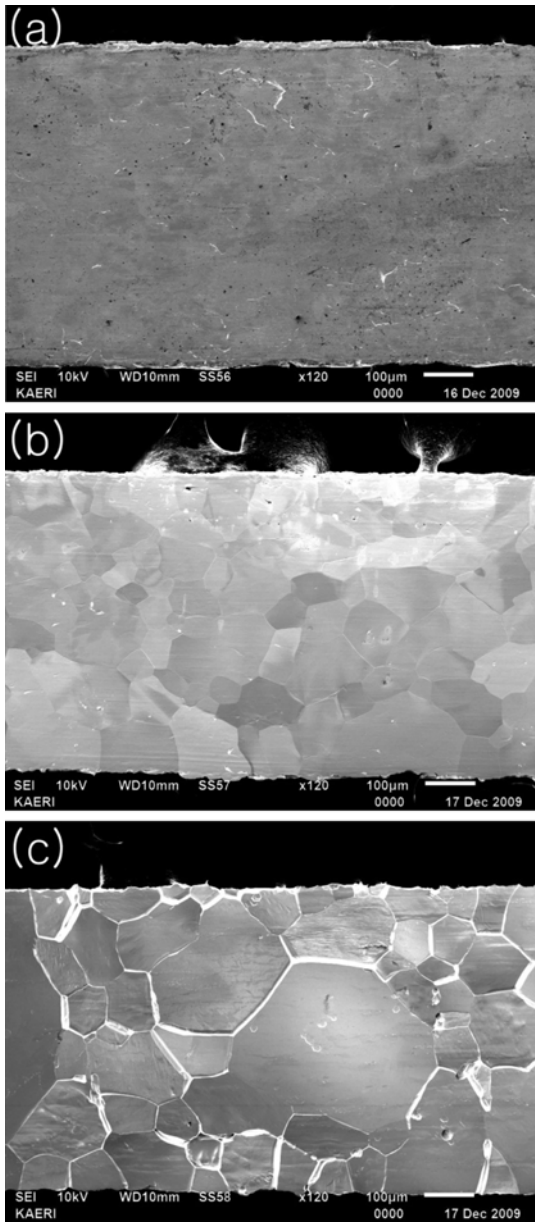

Figure 2. SEM images of the blank zone-refined rhenium filaments without degassing treatment (a), and with degassing treatment at 3.5 A (b), and at 4.5 A (c) for 60 min.

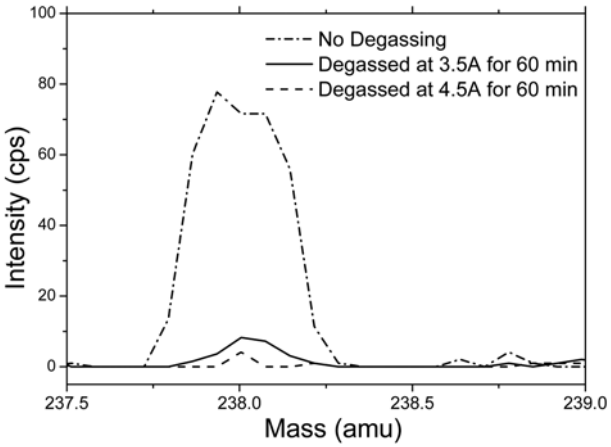

Figure 3. ^{238}U background from the blank filaments treated with various heating conditions.

Uranium background from the blank filaments was measured using a secondary electron multiplier as a transducer. No reduction in uranium background was observed on the filaments degassed at 2 A as the temperature was not believed to reach the melting point of uranium oxide (1150 °C for U_3O_8). On the other hand, the uranium backgrounds from the filaments degassed at 3.5 A or 4.5 A were reduced by an order of magnitude as shown in Figure 3. Compared to the heating conditions at 3.5 A, relatively small additional reduction in uranium impurities under the 4.5 A condition was observed. Regarding the degassing duration, further degassing was required for the filaments with 30 min heating. The uranium background was minimized by a factor of ten when the heating process lasted for 60 min while no additional background elimination was found on the condition of 90 min duration. Therefore, based on the surface conditions and the uranium background intensity as discussed above, we determined the most efficient degassing condition to be 3.5 A and 60 min for the heating current and the duration time, respectively.

The uranium background was determined by isotope dilution mass spectrometry (IDMS) with ^{233}U internal spike using the following equation;[9,10]

$$c(^{238}U,x) = \frac{R_y - R_b}{R_b - R_x} \cdot \frac{1}{R_y} \cdot \frac{m_y}{m_x} \cdot c(^{233}U,y)$$

where,

R_b : amount ratio n(^{233}U)/n(^{238}U) in the blend
R_x : amount ratio n(^{233}U)/n(^{238}U) in the sample
R_y : amount ratio n(^{233}U)/n(^{238}U) in the spike
m_x : mass of the sample
m_y : mass of the spike
$c(^{238}U,x)$: amount content of ^{238}U kg^{-1} in the sample
$c(^{233}U,y)$: amount content of ^{233}U kg^{-1} in the spike

IRMM-040a was selected as a spike for uranium quantification as it consists mostly of ^{233}U (over 98%), a fissile artificial isotope of uranium, which is not contained in normal uranium samples. Consequently the employment of IRMM-040a minimizes any chance of interference with the ^{238}U in samples. The uranium background from the filaments degassed under the optimized condition was estimated as 1.2 ± 0.7 fg, which is considered to be negligible in uranium measurements for uranium with over pg level.

Isotope Ratio Measurement of U030

In order to confirm that the minimized uranium background was on a negligible level, the isotope ratios of uranium in a standard reference material (U030) were determined using the filaments with degassing treatment. The total amount of U030 loaded on the filaments was approximately 1 ng. 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 was used for the simultaneous detection of uranium isotopes, which cancels out the signal fluctuation during data acquisition. The integration times for the steps were 4 s and 2 s for the minor isotopes and ^{235}U, respectively.

Table 2 shows the excellent agreement of the measurements with the certified values. The accuracies of the measurement were 1.29%, 0.78%, and 3.35%, for ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U, respectively. This implies that the uranium background from the filaments was minimized to a negligible level with the degassing treatment under the optimized condition.

Summary

The uranium background in zone-refined rhenium filaments was minimized to improve the accuracy of TIMS measurements for uranium containing in swipe and environmental samples with ultra-trace levels. The most efficient condition of the heating current and the duration time for degassing filaments was determined as 3.5 A and 60 min, respectively, which resulted in an order of magnitude decrease in uranium

Table 1. Detector configurations for data acquisition

Step	SEM	FAR-H1	FAR-H2	FAR-H3	Integration time (s)
1	234			238	4
2	235		238		2
3	236	238			4

Table 2. Uranium isotope ratios of U030 measured under the minimized background condition

	^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U
Certified Value	0.0001960(10)	0.03143(5)	0.0002104(10)
Measured Value*	0.0001935(76)	0.03168(28)	0.0002177(98)
Accuracy (%)**	1.29	0.78	3.35

*Numbers in parentheses indicate standard deviation
**Accuracy is defined as (measured value−certified value)/(certified value)

background from the blank filaments. Since this corresponds to 1.2 fg, no correction for uranium background from the degassed filaments is necessary when a sample amount exceeds pico-gram levels. The uranium isotope ratio measurement of a U030 sample enabled us to confirm that the minimized background of uranium in the degassed filaments was on a negligible level.

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References

1. Donohue, D. L. *J. Alloy Compd.* **1998**, 271-273, 11.
2. Cohen, A. S.; Belshaw. N. S.; O'Nions, R. K. *Int. J. Mass Spectrom. Ion Process.* **1992**, 116, 71.
3. Heumann, K. G.; Eisenhut, S.; Gallus, S.; Hebeda, E. H.; Nusko, R.; Vengosh, A.; Walczyk, T. *Analyst*, **1995**, 120, 1291.
4. Rubin, K. H. *Chemical Geology* **2001**, 175, 723.
5. Richter, S.; Goldberg, S. A. *Int. J. Mass Spectrom.* **2003**, 229, 181.
6. Lee, C. G.; Iguchi, K.; Esaka, F.; Magara, M.; Sakurai, S.; Watanabe, K.; Usuda, S. *Jpn. J. Appl. Phys.* **2006**, 45, 294.
7. Suzuki, D.; Saito-Kokubu, Y.; Sakurai, S.; Lee, C.-G.; Magara, M.; Iguchi, K.; Kimura, T. *Int. J. Mass Spectrom.* **2010**, 294, 23.
8. Jeon, Y. S.; Park, Y. J.; Joe, K. S.; Han, S. H.; Song K. *Analytical Science and Technology* **2008**, 21, 487.
9. Wolff, J. C.; Dyckmans, B.; Taylor P. D. P.; Bievre, P. D. *Int. J. Mass Spectrom. Ion Process.* **1996**, 156, 67.
10. Heumann, K. G. *Int. J. Mass Spectrom. Ion Phys.* **1982**, 45, 87.