



Uranium Isobaric Effect Correction for Determination of Pu-238 in Spent Nuclear Fuel by Thermal Ionization Mass Spectrometry†

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The correction for ^{238}U isobaric effect was investigated to determine the ^{238}Pu isotope content. It is generally difficult to get rid of uranium effect on the measurement of ^{238}Pu by mass spectrometry because plutonium cannot be purely separated from spent nuclear fuel and uranium exists on filament and in reagents as the impurities. The effect of ^{238}U was corrected by measuring Pu^+ and UO^+ in the sample spiked with ^{233}U and subtracting the uranium effect from the measured values. We controlled the heating currents of vaporization and ionization filaments to get the different ions of U^+ , Pu^+ , UO^+ and PuO^+ using thermal ionization mass spectrometry. For the Pu-U mixed solution, uranium was detected at lower filament temperature compared to plutonium, and the UO^+ peak was larger than the U^+ peak. The $^{238}\text{U}/^{233}\text{U}$ ratio was obtained by measuring the $^{238}\text{UO}^+/^{233}\text{UO}^+$ ratio at low temperature in a mixed solution of plutonium and ^{233}U (> 98 atom %) and then the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio was obtained by measuring the $(^{238}\text{Pu}+^{238}\text{U})/^{239}\text{Pu}$ and $^{233}\text{U}/^{239}\text{Pu}$ ratios at high temperature. For the plutonium standard solution, New Brunswick Laboratory-Certified Reference Material, Plutonium oxide (NBL CRM No. 122-PuO₂), the ^{238}Pu isotope composition obtained after ^{238}U correction was approximately 15 % lower than the measured value before the correction. The ^{238}Pu isotope composition after the ^{238}U correction for the plutonium solution that separated from the spent nuclear fuel was 30 % lower than the measured value.

Keywords: Uranium isobaric effect correction, Pu-238 determination, Spent nuclear fuel, Thermal ionization mass spectrometry.

INTRODUCTION

To determine the burning behaviour of a nuclear fuel in a reactor, the measured uranium and plutonium isotopic ratios in the spent nuclear fuel are important^{1,2}. Because the spent nuclear fuel is a highly radioactive sample, a small amount of sample must be treated in the analysis. For the isotopic ratio analysis of the sample, thermal ionization mass spectrometry (TIMS) is generally used³⁻⁶. However, the ^{238}Pu content in the plutonium isotopes has been determined using an α -spectrometer (instead of TIMS) because of the isobaric effect by ^{238}U , which has the same mass as ^{238}Pu . Therefore, the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio is typically obtained from the $^{238}\text{Pu}/(^{239}\text{Pu} + ^{240}\text{Pu})$ ratio that is measured by an α -spectrometer and the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio that is measured by TIMS⁷. However, the determination using an α -spectrometer also has some issues, such as the inaccurate measurement by the peak tailing that occurs because the ^{239}Pu + ^{240}Pu and ^{238}Pu detection energies are adjacent to each other. Therefore, the $^{238}\text{Pu}/^{239}\text{Pu}$ analytical method using TIMS,

considering the ionization characteristics of uranium and plutonium, is typically employed⁸⁻¹⁰. Aggarwal *et al.*⁸ studied the method by measuring the ^{238}U and ^{238}Pu peaks individually by adjusting the filament temperature near the Pu-U mixed sample. Alamelu *et al.*⁹ also investigated the metal ions and metal oxide ions generated at various filament temperatures and at various U/Pu concentration ratios for the ^{238}Pu that was measured using TIMS.

In this study, the ^{238}U isobaric effect was corrected for the determination of the ^{238}Pu isotopic ratio using ^{233}U spike and TIMS. For the ^{238}U isobaric effect correction, the $^{238}\text{U}/^{233}\text{U}$ ratio was obtained by measuring the uranium oxide ratio at low temperature, where PuO^+ , Pu^+ and U^+ are not generated for the mixed sample solution of the ^{233}U spike and plutonium. The measured and corrected ^{238}Pu values that were obtained using TIMS and the measured value obtained by the α -spectrometer for the plutonium solution that was separated from the spent nuclear fuel were compared with each other.

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EXPERIMENTAL

A thermal ionization mass spectrometer (TIMS, Finnigan MAT 262) with variable multi-collector Faraday cups and a secondary electron multiplier detector was used for the simultaneous determination of the isotopes. The configuration of the Faraday cups for the measurement of the plutonium and uranium isotopes is shown in Table-1. REIMEP-16 samples from the Regulation European inter-laboratory Measurement Evaluation Program and a NBL CRM No. 122-PuO₂ standard were used as plutonium reference samples. The plutonium standard was purified by eliminating the fission products (Am, etc.) via radioactive decay. An IRMM-040a (U-233 spike) from the Institute for Reference Materials and Measurements, European Commission, Joint Research Center was used for the correction of the isobaric effect of uranium-238 in the measurement of the plutonium-238 isotope.

TABLE-1
FARADAY CUP CONFIGURATION FOR
MEASURING THE ISOTOPES OF Pu AND U

Isotope	Faraday cup No.	Isotope	Faraday cup No.
Pu-242	4	Pu-239	7
Pu-241	5	Pu-238, U-238	8
Pu-240	6	U-233	9

Separation of plutonium from spent nuclear fuel: The spent nuclear fuel used in the experiment was UO₂-Gd₂O₃ (5.98 wt %) with a ²³⁵U initial concentration of 2.611 wt %, an average burn up of 40.5 GWd/tU and a burning time of 1425 days. This spent nuclear fuel was dissolved in a 1:1 nitric acid solution by heating for 8 h at 90 °C. From the dissolved solution, plutonium was separated using the anion exchange resin (BIO-RAD AG 1 × 8, Cl⁻ form, 100-200 mesh).

RESULTS AND DISCUSSION

Blank test of sample loading filament: The uranium impurity was measured for a commercial rhenium filament. The mass spectrum for a rhenium filament without any sample was scanned in the range of 230-242 (*m/z*) using a SEM (secondary electron multiplier) detector as shown in Fig. 1. The mass (*m/z*) peak for ²³⁸U and the small peaks for the other impurities were detected. The rhenium filament was degassed for 2 h at 2000 °C and 10⁻⁷ torr to eliminate impurities. The 238/239 (*m/z*) ratios of the REIMEP-16 samples were measured using the non-degassed and the degassed filaments individually as shown in Table-2. The values measured using the non-degassed filaments were larger by 40-900 % compared with the certified values. After the filament was degassed, the impurity amount was reduced significantly and only 0.08-1.1 % were detected. Thus, the uranium in the filament was not completely eliminated. Therefore, a ²³⁸U isobaric effect correction was needed for the determination of the ²³⁸Pu isotope ratio.

Ionization characteristics of uranium and plutonium:

Prior studies have reported that the evaporation and ionization temperatures of the uranium and plutonium in a U-Pu mixed sample were different each other when the U and Pu isotope ratios were measured by TIMS^{8,9}. The ²³⁸U isobaric effect correction using these characteristics was examined for measuring

TABLE-2
COMPARISON OF ²³⁸Pu/²³⁹Pu MEASURED USING THE
NON-DEGASSED AND DEGASSED RHENIUM
FILAMENTS FOR THE REIMEP-16 SAMPLES

Sample	Reference value (²³⁸ Pu/ ²³⁹ Pu)	²³⁸ Pu/ ²³⁹ Pu measured using non-degassed Re filament	²³⁸ Pu/ ²³⁹ Pu measured using degassed Re filament
A	0.00006696	0.000675133	0.000067015
B	0.00006615	0.000385352	0.000066685
C	0.00006551	0.000089857	0.000065971
D	0.00006504	0.000111103	0.000065753

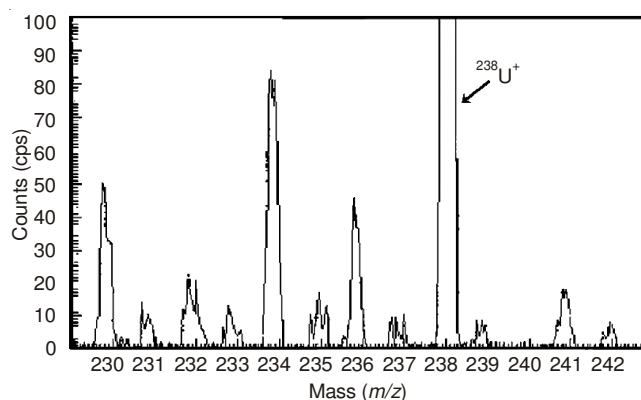


Fig. 1. Mass spectrum of the impurities from the non-degassed rhenium filament for the uranium and plutonium mass range (*m/z* 230-242). Detector: secondary electron multiplier (SEM)

the ²³⁸Pu isotope ratio. The mixed solution of the plutonium standard (NBL CRM No. 122 PuO₂) and the uranium nuclear fuel (²³⁵U 4 % enriched UO₂ pellet) was used for the ionization characteristic experiments. For the Pu-U mixed sample, the current of the rhenium filament was adjusted to produce the uranium oxide ion (UO⁺) and the mass spectrum is shown in Fig. 2. The ²³⁵U¹⁶O⁺ and ²³⁸U¹⁶O⁺ peaks were the most intense, while PuO⁺, Pu⁺ and U⁺ were not detected when the evaporation and the ionization current were 1.5 A and 4.0 A, respectively. Under these filament conditions, the ²³⁸U isotope ratio could be obtained by measuring the uranium oxide ion (UO⁺) ratio without PuO⁺ interference or Pu⁺ loss. As shown in Fig. 3, when the plutonium standard solution (NBL CRM No. 122 PuO₂) was loaded onto the rhenium filament and the evaporation and ionization currents were adjusted to 2.0 and 5.5 A, respectively, the Pu⁺ peak was the most intense, while the PuO⁺ peak was not detected. This result corresponds to the reports that the plutonium ion and plutonium oxide ion are produced at higher evaporation currents compared with the uranium in the Pu-U mixed solution^{8,9}.

Pu isotope ratio measurement and U isobaric effect correction for a reference sample and the spent nuclear fuel: Based on the results of the ionization characteristics of plutonium and uranium in the mixed solution, the ²³⁸Pu/²³⁹Pu ratio could be obtained by adding ²³³U to a plutonium solution. The ²³⁸U/²³³U isotopic ratio was obtained by measuring the ²³⁸U¹⁶O⁺/²³³U¹⁶O⁺ isotopic ratio of the uranium oxide ion produced at a relatively low temperature when the evaporation filament current was at 1.5 A and the ionization filament current was at 4.0 A. Under these conditions, plutonium oxide ion was not produced. The (²³⁸Pu+²³⁸U)/²³⁹Pu and ²³³U/²³⁹Pu were measured at higher temperatures when the evaporation filament current

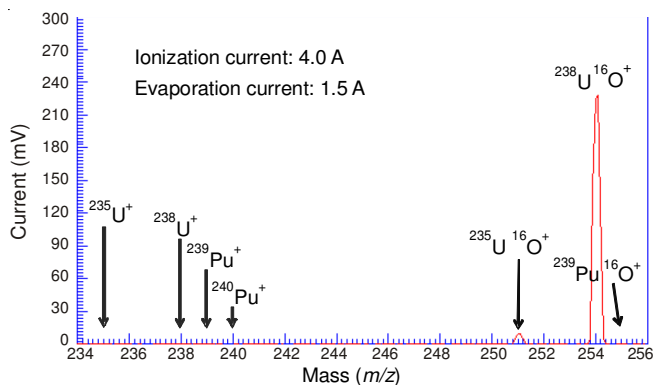


Fig. 2. Mass spectrum of the mixed sample of the ^{235}U 4 % enriched UO_2 solution and the CRM No. 122 PuO_2 (^{239}Pu 87 %) solution (ioni. fil. current: 4.0 A; eva. fil. current: 1.5 A)

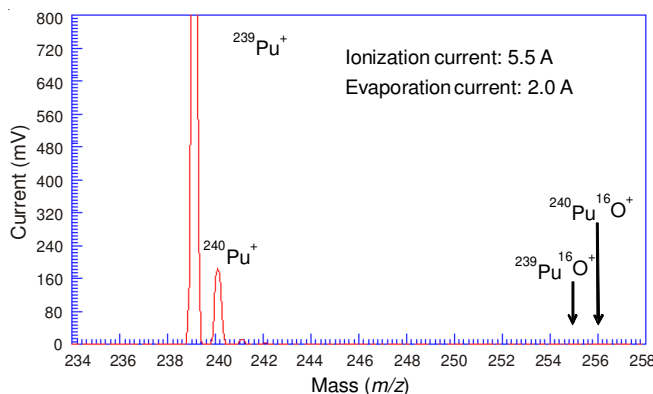


Fig. 3. Mass spectrum of the CRM No. 122 PuO_2 (^{239}Pu 87 %) solution (ioni. fil. current: 5.5 A; eva. fil. current: 2.0 A)

was at 2.0 A and the ionization filament current was at 5.5 A. The $^{238}\text{U}/^{239}\text{Pu}$ could be obtained from the $^{238}\text{U}/^{233}\text{U}$ and $^{233}\text{U}/^{239}\text{Pu}$ ratios. As a result, the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio was obtained by subtracting the $^{238}\text{U}/^{239}\text{Pu}$ ratio from the $(^{238}\text{Pu} + ^{238}\text{U})/^{239}\text{Pu}$ value. Using the reference sample, the ^{238}U correction effect was examined. The analytical results of the PuO_2 standard solution (NBL, CRM, No 122) in which the ^{233}U spike was added are shown in Table-3. As shown in Table-3, the ^{238}Pu value calculated by the radiation decay equation, $N = N_0 \cdot e^{-\lambda t}$, and the ^{238}Pu half-life was 0.04254 atom %. The measured ^{238}Pu value was 0.04886 atom % and the ^{238}Pu value corrected by ^{238}U was 0.04190 atom %. Therefore, the 15 % error for ^{238}Pu was reduced. The measured and corrected values of the ^{238}Pu isotopic ratio of the plutonium solution separated from the spent $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel are shown in Table-4. The ^{238}Pu measurement value was 1.254 atom % and ^{238}Pu value after the ^{238}U isobaric effect correction was reduced to 0.959 atom %, which is a 30 % decrease. The main reason for this decrease is the incomplete separation of plutonium from uranium.

TABLE-3
COMPARISON OF ^{238}Pu MEASURED
AND CORRECTED VALUES

CRM No. 122 (PuO_2)	Certified value (1 Jan. 1985)	Calculated value by decay time	Measured value	^{238}U corrected value
^{238}Pu (Atom %)	0.0521	0.04254	0.04886	0.04190

TABLE-4
COMPARISON OF THE ^{238}Pu MEASURED AND
CORRECTED VALUES FOR THE SOLUTION SEPARATED
FROM THE SPENT $\text{UO}_2\text{-Gd}_2\text{O}_3$ FUEL SAMPLE

Isotope	Measured value	^{238}U corrected value	Value measured by α -spectrometry
^{238}Pu (Atom %)	1.254	0.959	0.837

Conclusion

A ^{238}U isobaric correction method for determining the ^{238}Pu isotopic ratio in spent nuclear fuel was examined using a ^{233}U spike and by adjusting the filament temperature. Analysis was performed using TIMS. The filament was degassed to eliminate uranium impurity; however, it was not completely removed. For the ^{238}U isobaric effect correction, the $^{238}\text{U}/^{233}\text{U}$ ratio was obtained by measuring the uranium oxide ratio at low temperature, where plutonium oxide is not generated for the mixed sample solution of the ^{233}U spike and plutonium. The ^{238}Pu isotopic ratios were reduced by 15 and 30 % individually and were obtained for the plutonium standard solution (CRM No. 122 PuO_2) and the spent $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel by ^{238}U isobaric correction.

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