Contribution of the Faraday cup coupled to 10^{12} Ω current amplifier to uranium 235/238 and 234/238 isotope ratio measurements by thermal ionization mass spectrometry

Alexandre Quemet[*], Melody Maloubier, Alexandre Ruas

CEA, Nuclear Energy Division, Radio Chemistry & Processes Department, F-30207 Bagnols sur Cèze, France

ABSTRACT

This work highlights the possibility of improving, for given deposited quantities, the accuracy of uranium isotope ratio determination by Thermal Ionization Mass Spectrometry (TIMS) using Faraday cups coupled to a 10^{12} Ω current amplifying system. This system improves the electronic sensitivity compared to the same Faraday cups coupled to 10^{11} Ω current amplifiers. The analytical procedure developed in a previous work (Quemet et al., 2014) was applied in order to study the improvements in accuracy using the Faraday cups equipped with 10^{12} Ω current amplifier. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios were measured on the Certified Reference Material IRMM 052 (natural uranium). Results were evaluated relying on NF T 90–210 norm regarding method validation. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios were studied by total evaporation using different configurations. First, ^{234}U or ^{235}U was measured with a Faraday cup coupled to a 10^{12} Ω current amplifier and ^{238}U was measured with a Faraday cup coupled to a 10^{11} Ω current amplifier. Then, ^{234}U or ^{235}U was measured by discrete dynodes electron multiplier and ^{238}U was measured with a Faraday cup coupled to a 10^{12} Ω current amplifier. In comparison to the configurations using the 10^{11} Ω current amplifier, the analyzable quantity was reduced from 250 ng to 100 ng for the $^{235}U/^{238}U$ isotope ratio and from 50 ng to 3 ng for the $^{234}U/^{238}U$ isotope ratio with extended uncertainty below 0.28% for the $^{235}U/^{238}U$ isotope ratio, in compliance with the International Target Values (ITV 2010), and below 5% for the $^{234}U/^{238}U$ isotope ratio.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Accurate measurements for the uranium isotope ratios are well recognized in the nuclear field [1,2]. The $^{235}U/^{238}U$ isotope ratio allows determining the enrichment level of uranium. Safeguard authorities requirement for ^{235}U abundance measurement uncertainty by Thermal Ionization Mass Spectrometry (TIMS) is set to 0.28% (k = 1) [3]. The detection of ^{234}U is of prime interest in nuclear forensics [4]. Also, for a given sample, the relative amount of ^{234}U dramatically changes its radiotoxicity [5]. However, the ^{234}U isotope abundance is generally very low (0.1% of the total uranium) in materials handled in the nuclear industry.

The accuracy (*i.e.* measurement trueness and precision) of low signal measurements (low analytes quantity or low isotope abundance) is limited by the detection system used for mass spectrometry. The emergence of high resistance amplifiers (*i.e.* coupled to 10^{12} Ω or 10^{13} Ω current amplifiers) allows the decrease of the analyzable quantity by TIMS [6–8]. The signal to noise ratio is in theory three times higher for the 10^{12} Ω current amplifiers than for 10^{11} Ω at a given ion current [9]. This study investigates the accuracy improvement for natural uranium isotope ratios using current amplifiers equipped with 10^{12} Ω resistors. The study of the natural uranium is representative of a wide array of nuclear samples found in the nuclear industry: ^{235}U isotope abundance is between 3.2% and 4.4% for uranium used as fuel in light water reactor, and is as low as 0.2% for depleted uranium [10,11]. The ^{234}U isotope is enriched and depleted along the uranium cycle and in greater relative extent than the ^{235}U isotope [10].

In a previous study [1], the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios were measured using Faraday cups equipped with a 10^{11} Ω current amplifiers, discrete dynode secondary electron multipliers and continuous dynode electron multipliers. For the $^{234}U/^{238}U$ isotope ratio, the analyzable quantity was reduced from 1270 ng down to 50 ng with an enlarged uncertainty lower than 5%, by using electron multipliers compared to a configuration using only Faraday cups equipped with 10^{11} Ω current amplifiers. In that previous

work [1], the lowest analyzable quantity for the $^{235}U/^{238}U$ isotope ratio (50 ng) was achieved by peak-jumping measurement using discrete dynode secondary electron multipliers. For the $^{235}U/^{238}U$ isotope ratio determination with the total evaporation method, the lowest analyzable quantity was equal to 250 ng for a configuration using only Faraday cups equipped with $10^{11}\,\Omega$ current amplifiers [1]. For all the experiments where the target accuracy was achieved, the calculated uncertainties were below 0.28% for the $^{235}U/^{238}U$ isotope ratio, in compliance with the International Target Value [3], and below 5% for the $^{234}U/^{238}U$ isotope ratio.

This present study aims to continue the previous work [1], by studying the improvements in accuracy using a Faraday cup coupled to $10^{12}\,\Omega$ current amplifier for the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ uranium isotope ratios measurements. The results obtained with the different configurations using discrete dynode electron multiplier and Faraday cups coupled to 10^{11} and $10^{12}\,\Omega$ current amplifiers were discussed in terms of measurement trueness and precision in order to determine the best and most simple analytical method. The results of analyses using the $10^{12}\,\Omega$ current amplifiers were compared to those obtained with the conventional $10^{11}\,\Omega$ current amplifiers. The results were evaluated according to the NF T 90–210 norm regarding method validation [12].

2. Experimental

Experimental details were described in Quemet et al. [1]. Compared to the previously published studies [1,13], the Thermo Scientific Triton Thermal Ionization Mass Spectrometer was upgraded with two Faraday cups. The instrument is now equipped with 9 movable Faraday cups which can be coupled to $10^{11}\,\Omega$ current amplifiers (9 available and hereafter referred to as FC 10^{11}) or a $10^{12}\,\Omega$ current amplifier (1 available and hereafter referred to as FC 10^{12}), one fixed discrete dynode Secondary Electron Multiplier (hereafter referred to as SEM in agreement with Thermo Scientific denomination), located behind the central Faraday cup, and 3 movable continuous dynode electron multipliers operated in ion counting mode (hereafter referred to as MIC in agreement with Thermo Scientific denomination). The SEM is combined with a RPQ retardation filter to improve the abundance sensitivity to about 10 ppb at mass M compared to mass M^{+1} or M^{-1}.

A double Re-filament configuration was used to control independently the evaporation and the ionization temperature. These filaments (Re metal, purity 99.99%) are provided by ATES. 1 μL of solution was deposited onto the filament previously outgassed. After deposition, the sample was dried with a 0.5 A current. Then the current was progressively increased from 0.5 A to 2 A in 10 s and was maintained at 2 A for 5 s.

Two different methods were used to measure the uranium isotope ratios: the total evaporation method and the classical method. In the total evaporation method, the ion beams coming from the uranium isotopes are collected by a multi-collection system until the sample is fully evaporated. This method was developed in order to overcome mass fractionation, the main cause of the TIMS measurement bias. In the classical or traditional method, the different isotopes are collected in a limited period of the sample evaporation. Then the isotope ratios are corrected of the mass fractionation by using an external normalization. This method is available in single or multi-collection mode. These two methods are described in detail in Quemet et al. [1].

The measurements performed with the SEM and the MIC in the previous study showed comparable results [1]. However, using a SEM is easier and the signal was more stable over time. Therefore, in the present study, the isotope ratio measurements using electron multipliers were only performed using the discrete dynode multipliers.

The method evaluation, according to the NF T 90–210 norm, is described at length in the previous study [1,12]. We recall the main calculations steps: a maximal bias (MB) was set by the Laboratory of Analysis and Materials Metrology (LAMM) at 0.28% when isotope ratio involved the two most abundant isotopes (^{238}U and ^{235}U) to satisfy the International Target Value (ITV) recommended by the IAEA [3] and 5% when isotope ratio involved ^{234}U and ^{238}U. For each method and each uranium quantity, five independent determinations were performed. The precision control consisted in verifying the repeatability, given by the relative standard deviation (RSD). The relative bias, or measurement trueness, of the method was calculated using Formula (1):

$$Bias(\%) = \frac{|Z - ref|}{ref} \times 100 \tag{1}$$

where Z is the average of the series and ref is the certified value of the reference.

Finally, the method was validated in terms of accuracy when the following inequality was verified:

$$|Z - ref| + 2 \times s < MB \tag{2}$$

where s is the standard deviation of the series.

According to the NF T 90–210 norm, Eq. (3), where u_{ref} is the uncertainty at k = 1 of the reference value and NB is the normalized bias, was used to determine whether the analytical method has a statistically significant bias or not. If NB > 2, the method is considered having a statistically significant bias.

$$NB = \frac{|Z - ref|}{\sqrt{s^2 + u_{ref}^2}} \tag{3}$$

The uncertainty estimations (Fig. 1, Tables S1 and S2 in Supplementary materials) take into account the standard deviation, the method bias and the reference value uncertainty.

3. Results and discussion

Uranium isotope measurements have been performed with quantities varying from 1270 ng down to 1 ng. Five measurements were performed for the different quantities and measurement methods. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios were determined by total evaporation method using two different detector configurations: FC 10^{12}/FC 10^{11} and SEM/FC 10^{12}. The $^{234}U/^{238}U$ isotope ratio was also determined by the classical method using peak-jumping SEM measurement.

Tables 1 and 2, Fig. 1 and Supplementary materials report the results obtained for the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios for each deposited quantity.

3.1. $^{234}U/^{238}U$ isotope ratio measurements

3.1.1. Total evaporation method using Faraday cups coupled to $10^{12}\,\Omega$ (^{234}U) and $10^{11}\,\Omega$ (^{238}U) current amplifiers

$^{234}U/^{238}U$ isotope ratio measurements have been performed using FC 10^{12} to measure ^{234}U and FC 10^{11} to measure ^{238}U (Table 1 and Fig. 1). The measurement trueness was lower than 5% for 1270 ng (2.0%), 250 ng (1.1%) and 100 ng (1.7%). The observed relative standard deviations (RSD) of the $^{235}U/^{238}U$ isotope ratio were 1.0% for 1270 ng, 1.9% for 250 ng and 7.4% for 100 ng. The RSD for a uranium quantity of 100 ng is higher than the set maximum bias (5%). The decrease in precision found for loadings filament with 100 ng led us to exclude such low filament loadings from validation. That is why this method was validated for uranium quantities from 1270 down to 250 ng.