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Development of an analysis method of minor uranium isotope ratio measurements using electron multipliers in Thermal Ionization Mass Spectrometry

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ABSTRACT

A simple analytical procedure was developed to measure with high accuracy the isotope ratio of minor isotope of natural uranium present in small quantities using a thermal ionization mass spectrometer (TIMS). The reduction of quantities used for analysis and the measurement of non-abundant isotopes are of prime interest in the nuclear industry. Indeed it is necessary to reduce the analyst received dose and the effluent released, as well as realizing measurement at trace level. The new generation of TIMS is equipped with a multicollection system of electron multipliers: discrete dynode electron multiplier (SEM) and continuous dynode electron multiplier (MIC), that improve the sensitivity compared to faraday cups. The procedure developed was verified using Certified Reference Material IRMM 052. Results were evaluated relying on NF T 90-210 norm regarding method validation. First, the isotope ratio $^{234}U/^{238}U$ was examined by total evaporation using the SEM and MIC to measure ^{234}U and the faraday cup to measure ^{238}U. In a second approach, the isotope ratio $^{235}U/^{238}U$ was studied by total evaporation using the SEM to measure ^{235}U and the faraday cup to measure ^{238}U. The classical method with peak-jumping SEM measurement was also used. Total evaporation method employing only the faraday cup was used to confront the results obtained. The analyzable quantity was reduced from 250 ng to 50 ng for the $^{235}U/^{238}U$ isotope ratio and from 1270 ng to 50 ng for the $^{234}U/^{238}U$ isotope ratio with acceptable uncertainties thanks to the use of electron multipliers. For all experiments were the accuracy was achieved, the calculated uncertainties were below to 0.28% for the $^{235}U/^{238}U$ isotope ratio and 5% for the $^{234}U/^{238}U$ isotope ratio.

1. Introduction

The determination of isotope ratio with high accuracy is very important for different applications such as: environmental, geological, forensics or in the nuclear industries. The natural isotopic composition of an element is affected by the geological history, the age and the water permeability of the mineral. The knowledge of such characteristic is useful to identify and understand the processes affecting an element, and determine the ages of the minerals [1,2]. The interpretation of the isotopic composition of uranium (both natural and enriched) is of prime interest for the International Atomic Energy Agency (IAEA) for monitoring nuclear installations in order to verify the material conformity to the nuclear grade specification, to identify material origins and to control the nuclear activities [1,3–7]. Uranium mineral has an isotope ratio $^{235}U/^{238}U$ relatively constant whatever its origin [1]. In the nuclear field, the modification of this isotope ratio gives information about the enrichment level of nuclear material. The safeguard authorities requirement for ^{235}U abundance measurement uncertainty by TIMS is set to 0.28% [8]. The isotopic abundance of ^{234}U provides information about the type of activities conducted in the nuclear installations: enrichment or reprocessing [3,9]. However, ^{234}U stays a minor isotope with an isotopic abundance below 0.1% whatever its origins: enriched uranium, spent nuclear fuel, reprocessed uranium or depleted uranium. Moreover, the reduction of the analyzable quantities is important to realize environmental measurement where uranium is present at trace level. Finally in the nuclear industry the reduction of the analyzable quantities reduces the radioactive effluent generated and the exposure to the sample radiation by the analyst.

Thermal ionization mass spectrometry (TIMS) is a reference technique for uranium isotope measurement [9–15]. TIMS allows measurement of isotope ratio with high trueness and precision, allowing the knowledge of isotope ratio with an uncertainty sometimes lower than 0.1% [10,11,13,16–18]. The sample measurement with a low quantity of analyte or the isotope detection with low

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abundance (less than 0.1%) is very challenging due to the low intensity of the ion bean affecting the measurement trueness and precision. This is a reason why some methods and technologies have been developed in order to improve sensitivity, accuracy or detection.

The major development for the low quantities measurements is the use the electron multipliers [9,13–15,18,19]. They are used to further extend the sensitivity of the instrument by several orders of magnitude. It is useful for the minor isotope ratio determination or for low quantities of analyte. These types of detector operate by converting the ions hitting the detector into secondary electrons, which are amplified then detected. Multiple ion counting can be done with discrete dynode electron multipliers (secondary electron multiplier) or with continuous dynode electron multipliers (channel electron multipliers or Channeltron) or a combination of both. Due to their small size, these detectors can be moved, which improves the isotope measurement. Indeed, it is possible to perform static measurements [17,20].

After a brief description of the TIMS's detector optimization, the results obtained for the $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope ratio will be discussed in term of measurement trueness and precision. Different configurations using discrete and continuous dynode electron multipliers were studied in order to determine the best and most simple analytical method. Several quantities of uranium were investigated to challenge the limits of the different configurations. Each configuration was compared to the use of the faraday cups (FC) only.

2. Experimental

2.1. Reagent

All solutions were prepared in 8 M nitric acid (Merck suprapur). This 8 M nitric acid solution was prepared by diluting high purity nitric acid with deionized water (resistivity 18.2 MΩ cm).

2.2. Certified reference materials

To calibrate the electron detectors, uranium CRM U500 standard solution obtained from the National Institute of Standard and Technology (NIST) at 0.96 µg/µL (±5%, $k = 2$) was used. This standard solution has a ^{234}U isotopic abundance (0.5181 ± 0.0008%) higher than natural uranium, necessary to obtain of an adequate intensity for the ^{234}U isotope.

The assessment of the investigated procedure was carried out on the certified reference material IRMM 052. This solution is certified for the following isotope ratios: $^{235}U/^{238}U$ (0.0072718 ± 0.0000030, $k = 2$), $^{234}U/^{238}U$ ($0.00005548 \pm 0.00000022$, $k = 2$) and $^{236}U/^{238}U$ ($0.000000151 \pm 0.000000045$, $k = 2$). The initial solution concentration was 1.2711 g kg^{-1} (±0.05%, $k = 2$). Solutions of 250, 100, 50, 30, 20, 10, 3 and 1 ng/µL (±5%, $k = 2$) were prepared from the IRMM 052 standard in 8 M nitric acid. Dilutions were performed gravimetrically with a high precision balance.

2.3. Instrumentation

Isotope measurements were performed on a Thermo Scientific Triton Thermal Ionization Mass Spectrometer, equipped with a glove box. The analyzer is a low resolution magnetic field (resolution around 400). The multicollector is equipped with 7 movable Faraday cups, a fixed discrete dynode Secondary Electron Multiplier (hereafter referred to as SEM), located behind the central faraday cup, and 3 movable continuous dynode electron multipliers operated in ion counting mode (hereafter referred to as MIC, abbreviation of Multi-Ion Counting). Faraday cups are equipped with high-ohmic resistors (10^{11} Ω). 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.

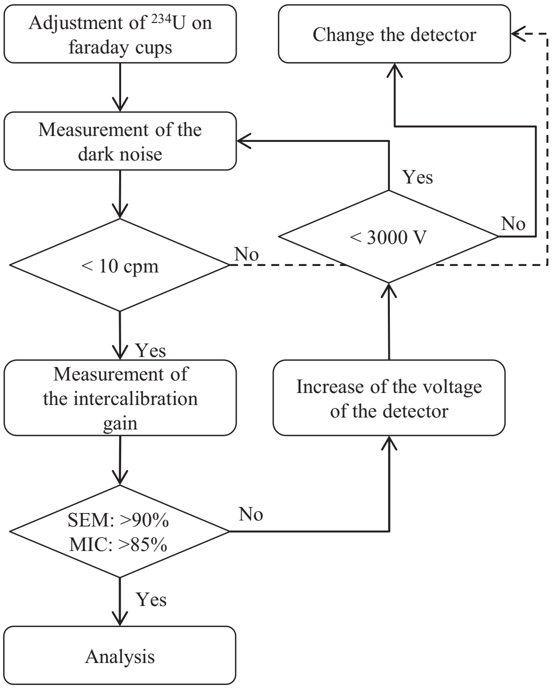

Fig. 1. Process for the electron multiplicators (MIC and SEM) calibration.

Uranium samples were loaded onto the outgassed zone of a refined Re filament. A double Re-filament configuration was used to control independently the evaporation and the ionization temperature. These filaments, provided by ATES, are obtained from a 99.995% pure Re metal. 1 µL of diluted solutions (described in Section 2.2) was deposited onto the filament. After deposition, the sample preparation was dried with a 0.5 A current. Then the current was progressively increased to 2 A over 10 s.

2.4. Detectors optimization

Intercalibration gains of the faraday cup detectors were measured daily by an automatic process [21]. The gains were extremely stable with a repeatability lower than 0.001%. Baselines were measured before each intercalibration gain and before each analysis.

For the SEM and the MIC, one of the major sources of uncertainty is the dead time, which is the time interval required between the impact of two ions to identify each ion as an independent event [2]. The dead time of each detector was implemented by the manufacturer. It was set up at 24 ns for the SEM and 70 ns for the MIC.

For the SEM and the MIC, two parameters have to be measured before starting an analysis: the dark noise and the intercalibration gain. The process of the calibration is schematized in Fig. 1.

In the first place, dark noise measurements were performed with the isolation valve closed for the SEM and the MIC. Each measurement takes about 10 minutes with an integration time set at 1 s. A dark noise level lower than 7 cps was observed for the SEM and the MIC. In practice the dark noise level measurement was also realized before each measurement, analysis or intercalibration.

In order to measure SEM/FC or MIC/FC intercalibration gains, 400 ng of the certified reference material U500 was deposited in order to obtain adequate intensity on $^{234}U^{+}$: 1.5 mV for the MIC and 5 mV for the SEM, and to measure the corresponding yield, given by the following formula:

$$\text{Yield} \quad (\%) = \frac{I_{\text{SEM/MIC}}}{I_{\text{FC}}/1.6 \times 10^{-8}} \times 100 \qquad (1)$$