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Development and comparison of high accuracy thermal ionization mass spectrometry methods for uranium isotope ratios determination in nuclear fuel

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Abstract

This study presents the development and the comparison of high accuracy methods for uranium isotope determination by thermal ionization mass spectrometry. Two methods for uranium minor isotope ratio determination were compared in term of accuracy, analysable quantity, analysis time and versatility: the total evaporation and the classical method with multi-dynamic sequences. The mathematical correction of the abundance sensitivity and the detector calibration within the classical method helps decreasing the uncertainties and the biases compared to the total evaporation method. This comparative study was conducted within the framework of the “2017 Nuclear Material Round Robin” participation organized by the International Atomic Energy Agency.

Keywords

TIMS; minor isotope ratio; multi-dynamic sequence; total evaporation method

Introduction

Uranium is the most essential element of the nuclear fuel cycle. It is present at different steps with different isotope composition: in uranium mine (natural uranium), in the enrichment process (depleted and enriched uranium), in the fuel fabrication (enriched uranium), in power reactor and in the reprocessing process (reprocessed uranium). Accurate measurements for uranium isotope and concentration are necessary in the nuclear field [1–3]. Knowing the isotope composition and uranium concentration is also of prime interest for safeguards and forensics purposes: the ^{235}U isotope abundance indicates the enrichment level of the nuclear material, the ^{234}U isotope abundance determination provides information on the material origin and finally, the ^{236}U isotope is a marker of uranium origin (natural, fallout from nuclear test or accident) [1,2,4,5].

One of the reference techniques for the isotope ratio measurement is the Thermal Ionization Mass Spectrometry (TIMS) [6]. Two TIMS measurement methods are commonly used: the classical and the total evaporation method [6–8]. In the classical method, the different isotopes are collected in a limited period of the sample evaporation and the isotope ratios are mathematically corrected of the isotope fractionation. Isotope fractionation comes from an evaporation difference between the light and the heavy isotopes, causing a bias on measured isotope ratios. In the total evaporation method (TE method), the isotopes are collected during the entire sample evaporation. Thus, this method is barely affected by the isotope fractionation and is a reference technique for major isotope ratio determinations like $^{235}\text{U}/^{238}\text{U}$ [1,2,7].

The analyses of the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios can be more complicated. First, weak signals close to the detection limit make accurate measurements difficult. The most commonly used detector for isotopic analysis by TIMS is the Faraday cup coupled to a $10^{11} \Omega$ current amplifier. This detector is highly stable helping reaching a high accuracy measurement (*i.e.* measurement trueness and precision). However, this detection system is not adapted for weak signals. The development of the 10^{12} and $10^{13} \Omega$ current amplifiers helps improving the Faraday cup sensitivity [1,9]. When the isotope abundance becomes even lower, it is necessary to use other types of detectors such as the

65 Secondary Electron Multiplier (SEM). The SEM improves dramatically the TIMS
66 sensitivity [1,2]. However, the low stability of the SEM makes low uncertainty
67 measurements difficult [1]. The abundance sensitivity is another cause of bias for the
68 minor isotope ratios measurement: it is the contribution of the major isotope peak tail (*i.e.*
69 ^{235}U or ^{238}U) to the minor isotope detection (*i.e.* ^{234}U or ^{236}U). The retardation filter
70 associated with the SEM decreases the abundance sensitivity by 2 orders of magnitude,
71 improving the measurement bias [1,2]. It is also possible to correct the abundance
72 sensitivity with a mathematical correction. In that case, different measurement sequences
73 can be dedicated to the abundance sensitivity measurement. Also, abundance sensitivity
74 measurement requires the use of the classical method. Another possibility to overcome
75 the isotope fractionation and correct the peak tailing is the Modified Total Evaporation
76 method (MTE). This method consists in interrupting the total evaporation process
77 regularly to perform corrections and signal optimization [10]. This method has the
78 benefits of both the total evaporation method to overcome the isotope fractionation and
79 the classical method to apply corrections using several sequences.

80 ATALANTE is a nuclear facility of the French Alternative Energies and Atomic Energy
81 Commission dedicated to research on the spent nuclear fuel reprocessing process and the
82 management of long-lived radioactive waste. The ATALANTE analysis laboratory is
83 devoted to elemental, isotopic and physico-chemical analyses and nuclear measurements
84 applied to samples of medium and high activity for the ATALANTE R&D programs. In
85 order to evaluate the laboratory performances and to guarantee the result reliability for
86 the uranium isotope ratio and concentration determination in diverse physico-chemical
87 forms such as pellets or dissolution solutions, the laboratory participates to different
88 Round Robin Test (RRT). The present study focuses on the “2017 Nuclear Material
89 Round Robin” organized by the International Atomic Energy Agency (IAEA) which aims
90 at determining the uranium isotope ratio and mass fraction in nuclear materials. The total
91 evaporation method using different detectors and the classical method using multi-
92 dynamic sequences for the minor isotope ratios measurement are compared in terms of
93 accuracy, simplicity of use and analysis duration.

94

Experimental

Materials, reagents and certified reference materials

All solutions were prepared using polypropylene flasks, except for the uranium solutions, which were prepared in PFA vials. 3 mol L⁻¹ and 8 mol L⁻¹ nitric acid solutions were prepared by diluting high purity nitric acid (Merck, Suprapur) with deionized water (resistivity: 18.2 MΩ.cm). A high precision scale (Mettler-Toledo, WXTP 205) was used to prepare all solutions. Weighings were repeated at least twice.

Analytical method validation for the uranium isotope determination was performed on the U015 Certified Reference Material (CRM) provided by the National Institute of Standard and Technology (NIST). The isotope composition of this CRM and the RRT sample are similar. This solution is certified for the ²³⁴U/²³⁸U (0.00008634(92), k = 2), ²³⁵U/²³⁸U (0.015565(16), k = 2) and ²³⁶U/²³⁸U (0.0001666(10), k = 2) isotope ratios.

Sample preparation

Each participant of the “2017 Nuclear Material Round Robin” received a uranium oxide pellet (UO₂) of about 5 g in a 20 mL HDPE vial (hereafter referred to as RTT sample). The RTT sample is a uranium fuel pellet fabricated in Brazil with a uranium isotope composition close to a low enrichment uranium oxide pellet before irradiation in Pressurized Water Reactor [11]. The TIMS requires working with liquid samples. Thus, the first preparation step was the dissolution of the pellet. It was weighed and about 15 mL of 8 mol L⁻¹ nitric acid was added. This solution (pellet + nitric acid) was heated at 135 °C in a PFA vial until complete dissolution. The pellet dissolution solution (hereafter referred to as RRT solution), which had a uranium concentration about 250 µg µL⁻¹, was diluted with 3 mol L⁻¹ in order to obtain solutions of concentration suitable for isotopic analysis: about 4 µg µL⁻¹ and 1 µg µL⁻¹.

Thermal Ionization Mass Spectrometer

The Thermo Fisher Triton TIMS used for the experiments and the deposit technique were previously described in detail [12]. The TIMS is equipped with 9 Faraday cups (all are movable except the central denoted C) which can be coupled to $10^{11} \Omega$ current amplifiers (9 are available and hereafter Faraday cups coupled with $10^{11} \Omega$ amplifiers are referred to as FC 11) or a $10^{12} \Omega$ current amplifier (1 is available and hereafter a Faraday cup coupled with a $10^{12} \Omega$ amplifier is referred to as FC 12). 4 Faraday cups are positioned in low masses (noted L1 to L4) and 4 Faraday cups are positioned in high masses (noted H1 to H4). The TIMS is also equipped with one fixed discrete dynode Secondary Electron Multiplier located behind the central Faraday cup (hereafter referred to as SEM). The SEM is combined with a high abundance filter (RPQ for Retarding Potential Quadrupole). The SEM calibration was performed using the method described in [12].

Isotopic analysis methods

The total evaporation method

The TE method applied in the present study was described in details in previous work for the $^{235}\text{U}/^{238}\text{U}$ major isotope ratio measurement [1,2,8,12]. The quantity of uranium deposit was 1 μg . This uranium amount allows the accurate determination of the $^{235}\text{U}/^{238}\text{U}$ isotope ratio in compliance with the International Target Value (ITV) [1,2]. The $^{238}\text{U}^+$ ion beam target intensity was measured using the FC 11 exclusively that was fixed at 15 V whereas the $^{235}\text{U}^+$ ion beam was measured either by FC 11 or FC 12.

For the method validation, 6 measurements were performed using the FC 11 and the U015 CRM. Afterwards, for the RRT sample, the $^{235}\text{U}/^{238}\text{U}$ isotope ratio analyses were performed using different detector configurations: 5 analyses were performed using the FC 11 to collect ^{235}U and ^{238}U isotopes, and 5 analyses were performed using the FC 12 to collect ^{235}U and the FC 11 to collect ^{238}U . In fine the reported isotope ratio was the average of all the measurements.

The $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios were also acquired on the U015 CRM with the TE method at the same time as the $^{235}\text{U}/^{238}\text{U}$ isotope ratio measurements. 3 analyses were performed using the FC 12 to collect the ^{234}U isotope and the SEM to collect the ^{236}U isotope and 3 analyses were performed using the FC 12 to collect the ^{236}U isotope and the SEM to collect the ^{234}U isotope.

Classical method with multi-dynamic sequences

The TE method is an accurate and simple analytical method for major isotope ratio measurements (typically $^{235}\text{U}/^{238}\text{U}$ isotope ratio) [7]. However, the TE method has limitations for the minor isotope ratios measurements because these measurements require other corrections such as: the SEM calibration, changes in the peak centering and focusing during the filament heating, or peak tailing corrections [6]. Hence, the classical method is more adapted for minor isotope ratios determination (*e.g.* $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios) because it allows the application of corrections through different measurement sequences [2]. On the other hand, the classical method is affected by isotope fractionation, as it is its main cause of the measurement bias, and requires another mathematical correction. In the present study, when applying the classical method, the isotope fractionation was corrected using an internal normalization established from the major uranium isotope ratio. This isotope ratio (*e.g.* $^{235}\text{U}/^{238}\text{U}$ isotope ratio) was previously determined using the TE method for major isotope ratio determination.

A classical multi-dynamic method (hereafter referred to as CMD method) was developed to measure the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios. This method includes 4 measurement sequences performed one after the other in order to apply several corrections and collect all of the uranium isotopes (Table 1).

In the first sequence, the magnetic field was set to collect the ^{236}U isotope on the SEM. The other detectors (Faraday cups) were positioned to collect all of the other uranium isotopes: the ^{234}U isotope was collected on the FC 12 (L2 cup), the ^{235}U (L1 cup) and ^{238}U (H2 cup) isotopes were collected on a FC 11. An idle time of 1 s was applied and the measurement was performed with 5 integrations of 4 s. The idle time is necessary to

avoid any drift due to the different time response of the different detectors (the SEM is faster than the FC 11 and the FC 11 is faster than the FC 12).

In the second sequence, the magnetic field was modified to collect the ^{234}U isotope on the SEM. The H1 cup, not used in sequence 1, was positioned to collect the ^{235}U on a FC 11. This step was dedicated to the real-time SEM/FC inter-calibration. It was calculated using the $^{234}\text{U}/^{235}\text{U}$ isotope ratio in order to avoid any signal fluctuation and decrease the uncertainty. The inter-calibration was performed by comparing the $^{234}\text{U}/^{235}\text{U}$ isotope ratio measured in sequence 1 using FC 12 and FC 11 with the $^{234}\text{U}/^{235}\text{U}$ isotope ratio measured in sequence 2 using SEM and FC 11. An idle time of 1 s was applied. The measurement was performed with 5 integrations of 4 s in order to obtain a good estimation of the SEM/FC inter-calibration.

In the third sequence, the magnetic field of the sector field was modified so that the SEM was set at 235.7 amu (*i.e.* $^{236}\text{U} - 0.35$, ^{236}U mass being about 236.05 amu) for tailing contribution measurement. It was measured closer to the peak in order to make the linear interpolation more accurate. This step measured in parallel the tailing contribution at mass $^{234}\text{U} - 0.35$. The Faraday cups used in this sequence were the same as in sequence 1. The signal intensities measured during sequence 3 were weak compared to the signal intensities in sequence 1. An idle time is necessary to ensure that the Faraday cups response return to their background level before the measurement in sequence 3, especially for the FC 12 which has the longest response time. Then, Faraday cups used in sequence 3 had an inaction time of 26 s before restarting measurement. This time corresponds to the idle time of the sequence 3 (5 s) and the sequence 2 total measurement time when the Faraday cups used in sequences 1 and 3 were not collecting any signal (we recall that the idle time of sequence 2 is 1 s and measurement time of sequence 2 is 4×5 s).

In the fourth sequence, the magnetic field was modified to collect at the central detector mass 236.4, corresponding to $^{236}\text{U} + 0.35$ ($\approx 236.05 + 0.35$). This step measured the tailing contribution at mass $^{234}\text{U} + 0.35$ and $^{236}\text{U} + 0.35$. The measurement of sequence 3

202 and 4 was performed with 2 integrations of 4 s, which is sufficient to have a good
203 estimation of the peak tailing contribution.

204 While using the CMD method, the uranium deposit quantity was about 4 µg. After
205 introducing the filaments inside the TIMS source, the beginning of the method was
206 identical to the TE method: ionization and evaporation filament heating, peak centering,
207 ion focusing and electronic baselines measurements prior to data acquisition. Contrary to
208 the TE method, where the sequence started straight after the electronic baselines, the
209 CMD sequences started when the desired intensity for the $^{234}\text{U}^+$ ion beam (between 10
210 and 50 mV on the FC 12 in sequence 1) was obtained. These intensities were chosen in
211 order to perform the SEM/FC inter-calibration with a good accuracy: a minimum $^{234}\text{U}^+$
212 ion beam intensity of 1×10^{-14} A was reached, corresponding to a significant signal of
213 10 mV or higher on the FC 12 (sequence 1). This signal also corresponded to about
214 62 500 cps on the SEM (sequence 2), which is low enough for the ^{234}U isotope intensity
215 to not saturate the detector and reduce significantly its lifespan (the recommended signal
216 in the SEM is $< 1\,000\,000$ cps). The evaporation filament temperature was controlled to
217 keep the ion beam intensity constant during the measurement, by increasing the
218 evaporation current when necessary. Each measurement corresponded to 6 blocks of 10
219 cycles. Each cycle corresponded to the acquisition of the 4 measurement sequences
220 presented in the Table 1. The baseline, the “peak center” and the lens optimization were
221 performed every 2 blocks. After each block, the amplifiers $10^{11} \Omega$ connected to the
222 Faraday cups rotated for permitting each Faraday cups to connect to each used amplifier
223 during the analysis.

224 Among the different fractionation laws (linear law, power law, exponential law or
225 Rayleigh law), the exponential law was found to be the best approach for many elements
226 [10,13,14]. It was then used for the isotope fractionation correction (Eq. (1)).

$$R_{corr} = R_{meas} \times \left(\frac{M_i}{M_j} \right)^p \quad (1)$$

Where p is the normalization factor. R_{corr} is the $^{234}\text{U}/^{238}\text{U}$ or $^{236}\text{U}/^{238}\text{U}$ corrected isotope ratio. R_{meas} is the $^{234}\text{U}/^{238}\text{U}$ or $^{236}\text{U}/^{238}\text{U}$ measured isotope ratio in the sequence 1 and M_i and M_j are the molar masses of the isotope involved in the isotope ratio.

The normalization factor was obtained using Eq. (2):

$$p = \frac{\ln \left(\frac{\left(\frac{^{235}\text{U}}{^{238}\text{U}} \right)_{cert}}{\left(\frac{^{235}\text{U}}{^{238}\text{U}} \right)_{meas}} \right)}{\ln \left(\frac{M_{^{235}\text{U}}}{M_{^{238}\text{U}}} \right)} \quad (2)$$

Where $(^{235}\text{U}/^{238}\text{U})_{cert}$ is the $^{235}\text{U}/^{238}\text{U}$ certified isotope ratio for the U015 CRM or the ratio measured using the TE method for the RRT sample. $(^{235}\text{U}/^{238}\text{U})_{meas}$ is the $^{235}\text{U}/^{238}\text{U}$ isotope ratio measured in sequence 1. $M_{^{235}\text{U}}$ and $M_{^{238}\text{U}}$ are the molar masses of the ^{235}U and ^{238}U isotopes.

The $^{234}\text{U}/^{238}\text{U}$ isotope ratio $((234/238)_{corr})$, corrected from the peak tailing and the isotope fractionation, is then given by Eq. (3):

$$\left(\frac{234}{238} \right)_{corr} = \left(\left(\frac{234}{238} \right)_{meas} - \frac{1}{2} \left(\frac{233.7}{238} + \frac{234.4}{238} \right) \right) \left(\frac{M_{^{234}\text{U}}}{M_{^{238}\text{U}}} \right)^p \quad (3)$$

The $(234/238)_{meas}$ isotope ratio is the $^{234}\text{U}/^{238}\text{U}$ isotope ratio measured in sequence 1. The 233.7/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 3 over the signal of ^{238}U in sequence 1. The 234.4/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 4 over the signal of ^{238}U in sequence 1. $M_{^{234}\text{U}}$ and $M_{^{238}\text{U}}$ are the molar masses of the ^{234}U and ^{238}U isotopes. p is the normalization factor obtained from Eq. (2).

The $^{236}\text{U}/^{238}\text{U}$ isotope ratio $((236/238)_{corr})$ corrected from the peak tailing, the SEM/FC inter-calibration gain and the isotope fractionation is given by Eq. (4).

$$\left(\frac{236}{238} \right)_{corr} = \frac{1}{G} \left(\left(\frac{236}{238} \right)_{meas} - \frac{1}{2} \left(\frac{235.7}{238} + \frac{236.4}{238} \right) \right) \left(\frac{M_{^{236}\text{U}}}{M_{^{238}\text{U}}} \right)^p \quad (4)$$

Where G is the SEM/FC inter-calibration gain. The $(236/238)_{\text{meas}}$ isotope ratio is the $^{236}\text{U}/^{238}\text{U}$ isotope ratio measured in sequence 1. The 235.7/238 ratio corresponds to the signal measured on the SEM in sequence 3 over the signal of ^{238}U in sequence 1. The 236.4/238 ratio corresponds to the signal measured on the SEM in sequence 4 over the signal of ^{238}U in sequence 1. $M_{236\text{U}}$ and $M_{238\text{U}}$ are the molar masses of the ^{234}U and ^{238}U isotopes. p is the normalization factor obtained from Eq. (2).

The SEM/FC inter-calibration gain was calculated using Eq. (5). It includes the peak tailing correction from the $^{235}\text{U}^+$ and $^{238}\text{U}^+$ ion beams to the $^{234}\text{U}^+$ beam detection on the FC 12. No peak tailing correction was applied to the SEM since the RPQ energy filter helps decreasing the peak tailing by 2 orders of magnitude [4,10].

$$G = \left(\frac{\left(\frac{234}{235} \right)_{s2}}{\left(\frac{234}{235} \right)_{s1}} \right) \times \frac{\left(\frac{234}{238} \right)_{s1}}{\left(\frac{234}{238} \right)_{s1} - \frac{1}{2} \left(\frac{233.7}{238} + \frac{234.4}{238} \right)} \quad (5)$$

Where $S1$ and $S2$ are isotope ratio measured in sequence 1 or 2, respectively. The 233.7/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 3 over the signal of ^{238}U in sequence 1. The 234.4/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 4 over the signal of ^{238}U in sequence 1.

The $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ corrected isotope ratios were calculated during each measurement cycle. After the end of the measurement (*i.e.* after the 6 blocks of 10 cycles) a statistical test rejecting the values outside the average plus or minus twice the standard deviation was applied twice for both isotope ratios. Around 7 % of the values were rejected. The $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ corrected isotope ratios were obtained by the average of the non-rejected values.

For the method validation, 4 analyses were performed on the U015 CRM. For the RRT sample determination, 5 analyses were performed.

269 Results evaluation and uncertainties estimation

270 Bias, or trueness, was calculated using Eq. (6).

$$Bias (\%) = \frac{Z - cert}{cert} \times 100 \quad (6)$$

271 Where Z is the experimental value and cert is the reference value of the CRM used to
272 evaluate the method trueness or the RRT assigned value.

273 According to the NF T 90-210 norm, Eq. (7) was used to determine if the analytical
274 method has a statistically significant bias [15]. If the normalized bias (NB) is lower than
275 2, the method is considered having no statistically significant bias.

$$NB = \frac{|Z - cert|}{\sqrt{s^2 + u_{cert}^2}} \quad (7)$$

276 Where s is the standard deviation of the different measurements and u_{cert} is the CRM or
277 assigned value uncertainty with a coverage factor at $k = 1$.

278 The precision of the different methods was evaluated by calculating the Relative Standard
279 Deviation (RSD) of all the measurements.

280 The isotope ratio measurement uncertainties estimation was described in previous work
281 [12]. The isotope ratio (R) uncertainty (u) at $k = 1$ was estimated using Eq. (8).

$$\frac{u^2(R)}{(R)^2} = \frac{u^2(\bar{x})}{\bar{x}^2} + \frac{u^2(trueness)}{(trueness)^2} + \frac{u^2(cert)}{(cert)^2} \quad (8)$$

$$\frac{u(trueness)}{trueness} = \frac{Maximum\ bias\ on\ CRM}{\sqrt{3}} \quad (9)$$

The first term of Eq. (8) includes the uncertainty from the random effects and is given by the RSD of all the measurements (*i.e.* the precision). The second and third terms take into account the systematic effects (*i.e.* the measurement trueness of the method). The measurement trueness is calculated using Eq. (9) and is determined with the U015 CRM because of its isotopic properties close to the RRT sample.

Results and discussion

Comparison of isotope measurement methods for minor isotope ratio determination

The CMD method was compared to the TE method using the FC 12 (“TE FC 12”) as well as the TE method using the SEM (“TE SEM”) for the determination of the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ minor isotope ratios of the U015 CRM. The results are presented in Fig. 1.

TE method using FC 12

Using the TE method, the signals measured on the FC 12 were 13 mV for $^{234}\text{U}^+$ and 25 mV for $^{236}\text{U}^+$. These intensities are very weak in comparison to the signal measured for $^{238}\text{U}^+$ (15 V). The theoretical Faraday cup detection limit can be estimated as 3 times the quadratic sum of the standard deviation of the Johnson Nyquist noise and the Poisson-noise (about 0.4 mV for a FC 12) [16,17]. The minor isotope signals are about 30 times (for the $^{234}\text{U}^+$) and 60 times (for the $^{236}\text{U}^+$) higher than the estimated detection limit of the FC 12. The TE FC 12 method showed a bias of 2.08 % and 4.11 % for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios, respectively. Despite the higher ^{236}U intensity (25 mV) compared to the ^{234}U intensity (13 mV), the bias for the $^{236}\text{U}/^{238}\text{U}$ (4.1 %) is significantly higher than the $^{234}\text{U}/^{238}\text{U}$ (2.1 %). The low signal intensity is therefore not the only reason for a higher bias. The presence of the ^{238}U major isotope, closer to the ^{236}U than to the ^{234}U isotope, explains the bias difference because of peak tailing issues. The RSD for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios were similar and about 1 %. Unlike the normalized bias observed for the $^{234}\text{U}/^{238}\text{U}$ isotope ratio (1.8), the normalized bias for the $^{236}\text{U}/^{238}\text{U}$ isotope ratio

was equal to 3.3 showing that the method has a significant bias for the $^{236}\text{U}/^{238}\text{U}$ ratio. The uncertainties were estimated to 4.3 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 6.8 % for the $^{236}\text{U}/^{238}\text{U}$ ratio, with a major contribution from the systematic error (Table 2).

TE method using SEM

The SEM improves the sensitivity in comparison to the FC 12: the measured signals were 78000 cps for the ^{234}U isotope and 150000 cps for the ^{236}U isotope. These intensities are much higher than the SEM dark noise (below 10 counts per minute). In comparison to the TE FC 12 method, the bias greatly decreased (0.40 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 0.18 % for the $^{236}\text{U}/^{238}\text{U}$ ratio). This improvement can be due to the better detector sensitivity and to the fact that the SEM is equipped with a RPQ filter that provides a bias reduction for the minor isotope ratio determination. In order to find the best contributor to the improvement of the measurement trueness, 3 additional analyses under the same analytical conditions except that the RPQ filter was not used were performed using the TE method with the SEM to collect the ^{236}U (Fig. 1.b). The measurement trueness was degraded without the RPQ filter: the bias was higher than 5 %, while a bias below 0.2 % is obtained with the RPQ filter. The normalized bias computed without RPQ filter shows the method has a significant bias ($\text{NB} > 2$). The $^{236}\text{U}/^{238}\text{U}$ ratios determined using the TE FC 12 method and the TE SEM method without RPQ filter were all higher than the certified values (Fig. 1). This is obviously due to the peak tailing effect of ^{238}U as the abundance sensitivity is about 10^{-6} without RPQ filter for the Triton TIMS. These observations show when reducing the peak tailing contribution using the RPQ energy filter is the main cause of the measurement trueness improvement. On the other hand, it can be noticed that the use of the RPQ filter reduces the ions intensity by about 5 %. This loss is negligible compared to the benefit obtained on the measurement trueness.

However, the observed RSD for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ obtained with the TE method using the SEM and the RPQ filter (Fig. 1) are high (1.1 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 2.1 % for the $^{236}\text{U}/^{238}\text{U}$ ratio). The poor repeatability is explained by the SEM instability during the measurement. The SEM calibration can vary significantly during an analysis

without any predictable trend [1]. Despite the SEM instability, the estimated uncertainty (2.8 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 5.0 % for the $^{236}\text{U}/^{238}\text{U}$ ratio) slightly decreased compared to the TE FC 12 method (4.3 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 6.8 % for the $^{236}\text{U}/^{238}\text{U}$ ratio). The relative contribution of the main uncertainty sources (Table 3) shows that the total uncertainties are mainly due to the precision (55 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 71 % for the $^{236}\text{U}/^{238}\text{U}$ ratio). The method shows no significant bias for both isotope ratios: the normalized biases are below 2.

CMD method

The biases obtained using the CMD method are equal to -0.28 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 0.19 % for the $^{236}\text{U}/^{238}\text{U}$ ratio (Fig. 1 and Table 3). The observed RSD on the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ are equal to 0.05 % and 0.08 %, respectively. The normalized bias calculated for both isotope ratios were below 2, showing the method has no significant bias. The CMD method improves the measurement trueness by decreasing the abundance sensitivity influence using the RPQ filter combined with a mathematical correction. The CMD method also improves the precision due to a “real time” SEM calibration. The impact of the SEM fluctuation is then minimized. The method’s internal normalization helps maintaining a good measurement accuracy and correct the isotope fractionation. Different parameters influencing the isotope fractionation, such as the deposit quality, are compensated by the internal normalization. The uncertainties were estimated to 1.2 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 0.72 % for the $^{236}\text{U}/^{238}\text{U}$ ratio. The main sources of uncertainty for $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios confirm the significant improvement of the precision and the measurement trueness when applying the CMD method (Table 2): the measurement trueness (11 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 23 % for the $^{236}\text{U}/^{238}\text{U}$ ratio) and precision (1 % for the $^{234}\text{U}/^{238}\text{U}$ ratio and 5 % for the $^{236}\text{U}/^{238}\text{U}$ ratio) are minor contributors to the total uncertainty. The main contribution is the CRM uncertainty. The lowest uncertainties are obtained with the CMD method: $U(k=2) = 4.3\%$, 2.8% and 1.2% for the $^{234}\text{U}/^{238}\text{U}$ isotope ratio using TE FC 12, TE SEM and CMD methods, respectively, and $U(k=2) = 6.8\%$, 5.0% and 0.72% for the $^{236}\text{U}/^{238}\text{U}$ isotope ratio using TE FC 12, TE SEM and CMD methods, respectively.

Methods comparison

These 3 methods have different assets in terms of analysis time, simplicity, trueness and repeatability. The TE FC 12 method is the simplest and the most straightforward method: no inter-calibration gain is required between two sample analyses as the Faraday cups are very stable and all the isotope ratios of an element (major and minor isotope) are directly obtained. However, this method needs to take into account the method bias in the uncertainty calculation. The application of this method is easily transposable to another element assuming that the number of minor isotopes do not exceed the number of FC 12. An analysis using the FC 12 takes generally between 20 to 60 minutes.

The TE SEM method is rather simple also. The sample analysis itself has the same duration as the TE method with FC 12 (between 20 to 60 minutes). However, the SEM/FC inter-calibration gain is required before and after each sample analysis. This explains the longer total analysis time (each inter-calibration gain takes about 20 minutes). The method gives directly all the isotope ratios of an element (major and minor isotope). Depending on the number of SEM detectors available in the instrument, the analysis might require several runs. Also, this method can be easily transposable to another element.

The CMD method is the most complex one. However, once the file for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios computation is created, the method can be easily used put in routine analysis. The method requires bigger sample amount (about 4 μg) than the TE method (less than 1 μg) in order to keep a high signal during the entire analysis that lasts about 90 minutes. Also, this method requires the results of others analyses: the $^{235}\text{U}/^{238}\text{U}$ isotope ratio determination with a high accuracy method, like the TE method, is needed to perform the isotope fractionation correction of the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios, which increases the overall analysis time. This method is dedicated to the situation where high accuracy minor isotope ratio determination is necessary. The method can be transposable to enriched uranium. However, for depleted uranium, the $^{234}\text{U}/^{238}\text{U}$ isotope ratio is generally too low to perform both the measurement of the $^{234}\text{U}/^{238}\text{U}$ isotope ratio and the SEM/FC inter-calibration in the same method. Indeed, the SEM/FC inter-calibration

requires a minimum signal of 10 mV with the FC 12. Considering that for depleted uranium, the $^{234}\text{U}/^{238}\text{U}$ isotope ratios are below 2×10^{-5} , the signal with FC 11 for the ^{238}U isotope measurement would exceed its maximum limit (50 V). So, for depleted uranium using the CMD method, the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios are not directly accessible. These minor ratios could be obtained indirectly using the measurements of the $^{234}\text{U}/^{235}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ isotope ratios and by knowing the $^{235}\text{U}/^{238}\text{U}$ isotope ratio. In this case, the CMD method would need adjustment: the internal normalization would be performed with the measurement of the $^{234}\text{U}/^{235}\text{U}$ as the ^{238}U isotope would not be collected. In a more general point of view, the CMD method needs adjustments for each element to be measured. The analyzed element needs to have a minimum of 3 isotopes: one major isotope, one minor isotope needing a measurement with the SEM and an “intermediate” isotope allowing the in situ SEM/FC inter-calibration. This last isotope needs a significantly lower abundance compared to the major isotope and a significantly higher abundance compared to the minor isotope.

The CMD method shows also some similarities with the measurement sequence of the MTE method [10]. The main difference between the MTE and the CMD methods comes from the isotope fractionation correction: total evaporation for the MTE method or internal normalization for the CMD method. The MTE method is the reference method in order to have the lowest uncertainties. However, the CMD method presents some advantages compared to the MTE method. The principal advantages is a shorter analysis time: the CMD method take about 90 min compared to the 3-5 hours for the MTE method. The CMD method is also simpler to configure in the TIMS software. The CMD method is directly configurable in the TIMS software without the requirement of an external script [10].

Method validation

The results for the method validation on the U015 CRM are summarized in Table 2. The CMD method shows lower bias, better repeatability and uncertainty compared to the TE method for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios measurements. The CMD method

displayed no significant bias (normalized bias below to 2). These results validate the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios determination using the CMD method.

The result obtained for the $^{235}\text{U}/^{238}\text{U}$ is in good agreement with the certified value. The bias obtained is equal to 0.03 % and the RSD is 0.02 %. The normalized bias is equal to 0.62, showing that the method leads to no significant bias. The uncertainty is estimated to 0.16 % ($k = 2$) and is in compliance with the safeguard requirements given by the ITV (0.28 %, $k = 2$) on this range of uranium isotopic composition [18]. It should be noticed that the first five experiments were performed before the RRT sample isotope measurement and the last one after the RRT sample isotope measurement (see next section), ensuring that the instrumental performance is satisfactory during the whole measurement series. These results validate the $^{235}\text{U}/^{238}\text{U}$ isotope ratio determination using the TE method.

Isotope ratio measurement in the uranium pellet

The RRT sample was analyzed as an unknown sample. However, at the end of the study, the results were compared to the RRT assigned values in order to evaluate the developed methodology.

The method developed and validated using the U015 CRM was applied. The $^{235}\text{U}/^{238}\text{U}$ ratio measurements with the FC 11 or the FC 12 for the ^{235}U detection show no significant bias: biases are below 0.1 % and the normalized biases are below 2 (Table 4). The measurements seem to demonstrate that the precision is slightly better using the FC 12 (RSD = 0.03 %) than using the FC 11 (RSD = 0.06 %).

The results obtained for the $^{234}\text{U}/^{238}\text{U}$ (bias = 0.27 %), $^{235}\text{U}/^{238}\text{U}$ (bias = 0.07 %) and $^{236}\text{U}/^{238}\text{U}$ (bias = 0.93 %) isotope ratios are in good agreement with the assigned values provided by IAEA (Table 4). The RSD are similar to the ones obtained for the U015 CRM and are lower than 0.1 %: 0.07 %, 0.04 % and 0.08 % for the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios, respectively. The $^{235}\text{U}/^{238}\text{U}$ isotope ratio uncertainty is estimated at 0.15 % ($k = 2$) and is in compliance with the ITV (0.28 %, $k = 2$) for this

type of enriched uranium [18]. The relative contribution, expressed in percent, of the main uncertainty sources for the uranium isotope ratios determination is given in Table 2. The three uncertainty sources considered for the $^{235}\text{U}/^{238}\text{U}$ isotope ratio determination have a similar contribution: U015 CRM certified isotope ratio (41 %), precision (31 %) and method trueness (28 %). The $^{234}\text{U}/^{238}\text{U}$ isotope ratio uncertainty is estimated at 1.13 % ($k = 2$). The uncertainty associated with the CRM isotope ratio is the main uncertainty source in the final uncertainty (87 %). The uncertainties associated with the method bias (11 %) and the precision (2 %) have a limited impact on the final uncertainty. The $^{236}\text{U}/^{238}\text{U}$ isotope ratio uncertainty is estimated at 0.72 % ($k = 2$). In the same way as the $^{234}\text{U}/^{238}\text{U}$, the final uncertainty mostly comes from the CRM isotope ratio uncertainty (72 %).

The methodology developed to perform uranium isotope ratio with high accuracy showed no significant bias: all the normalized biases are lower than 2.

Conclusions

This study shows the possibility of the TE and the CMD methods for determining uranium isotope ratios with low uncertainties. The TE method allows to reach the ITV requirements for the $^{235}\text{U}/^{238}\text{U}$ major isotope ratio. One of the methods for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ minor isotope ratios determination was the classical method using multi-dynamic sequences. This classical method allows mathematical correction of the abundance sensitivity and calibrating the SEM detector while the method is running. An internal normalization using the $^{235}\text{U}/^{238}\text{U}$ major isotope ratio was used to overcome the isotope fractionation. The CMD method decreases the bias, the repeatability and the estimated uncertainties compared to the TE method for uranium minor isotope ratios determination, which is also an interesting feature for forensic analysis applications.

Another application of the accurate determination of the pellet isotope composition is the uranium content determination with high accuracy using isotope dilution, a method that will be presented in future.

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Table

Table 1: Summarized description of one cycle of the CMD method

Cups	L2	L1	C	H1	H2	Number of	Measurement	Idle time
Detectors	FC 12	FC 11	SEM	FC 11	FC 11	integrations	time (s)	(s)
Sequence 1	^{234}U	^{235}U	^{236}U		^{238}U	5	4	1
Sequence 2			^{234}U	^{235}U		5	4	1
Sequence 3	233.7	234.7	235.7		237.7	2	4	5
Sequence 4	234.4	235.4	236.4		238.4	2	4	1

Table 2: Relative contribution (%) of the main uncertainty sources for the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios measurement with the TE method using the FC 12 (TE FC 12) or the SEM (TE SEM) and with the CMD method (CMD), and for the $^{235}\text{U}/^{238}\text{U}$ isotope ratio with the TE method (TE) for the U015 CRM and the RRT sample (RRT)

Isotope ratio	Sample	Method	Relative contribution (%)		
			Precision	Meas. trueness	Cert.
$^{234}\text{U}/^{238}\text{U}$	U015	TE FC 12	21	73	6
	U015	TE SEM	55	31	14
	U015	CMD	1	11	88
	RRT	CMD	2	11	87
$^{235}\text{U}/^{238}\text{U}$	U015	TE	13	36	51
	RRT	TE	29	29	42
$^{236}\text{U}/^{238}\text{U}$	U015	TE FC 12	12	87	1
	U015	TE SEM	71	27	2
	U015	CMD	5	23	72
	RRT	CMD	5	23	72

490

491 Table 3: Isotope ratios obtained on the U015 CRM with the TE method (TE) and the
 492 CMD method (CMD). Cert. corresponds to the CRM certified value, U_{cert} corresponds to
 493 the CRM certified value uncertainty ($k = 2$) and U corresponds to the total uncertainty
 494 ($k = 2$). NB corresponds to the normalized bias.

Isotope ratio	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
Method	CMD	TE	CMD
Cert.	0.00008634	0.015565	0.0001666
Results	0.00008610	0.015570	0.0001669
RSD (%)	0.05	0.02	0.08
Bias (%)	-0.28	0.03	0.19
NB	0.53	0.62	0.61
U_{cert} (%)	1.07	0.10	0.60
U (%)	1.13	0.16	0.72

495

496 Table 4: Isotope ratios obtained with the TE method using the FC 11 (TE FC 11) or the
 497 FC 12 (TE FC 12) and with the CMD method (CMD) on the RRT uranium pellet. $U_{ass_val.}$
 498 corresponds to the assigned value uncertainty ($k = 2$) and U corresponds to the total
 499 uncertainty ($k = 2$). NB corresponds to the normalized bias

Isotope ratio	$^{234}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$		
Method	CMD	CMD	TE FC 11	TE FC 12	TE Average
Assigned value	0.0001708	0.0000258	0.019645	0.019645	0.019645
Results	0.0001713	0.00002604	0.019658	0.019659	0.019658
RSD (%)	0.07	0.08	0.06	0.03	0.04
Bias (%)	0.27	0.93	0.06	0.07	0.07
NB	0.56	0.24	0.94	1.5	1.2
$U_{ass_val.}$ (%)	0.94	7.8	0.08	0.08	0.08
U (%)	1.13	0.72	0.18	0.15	0.15

500

501

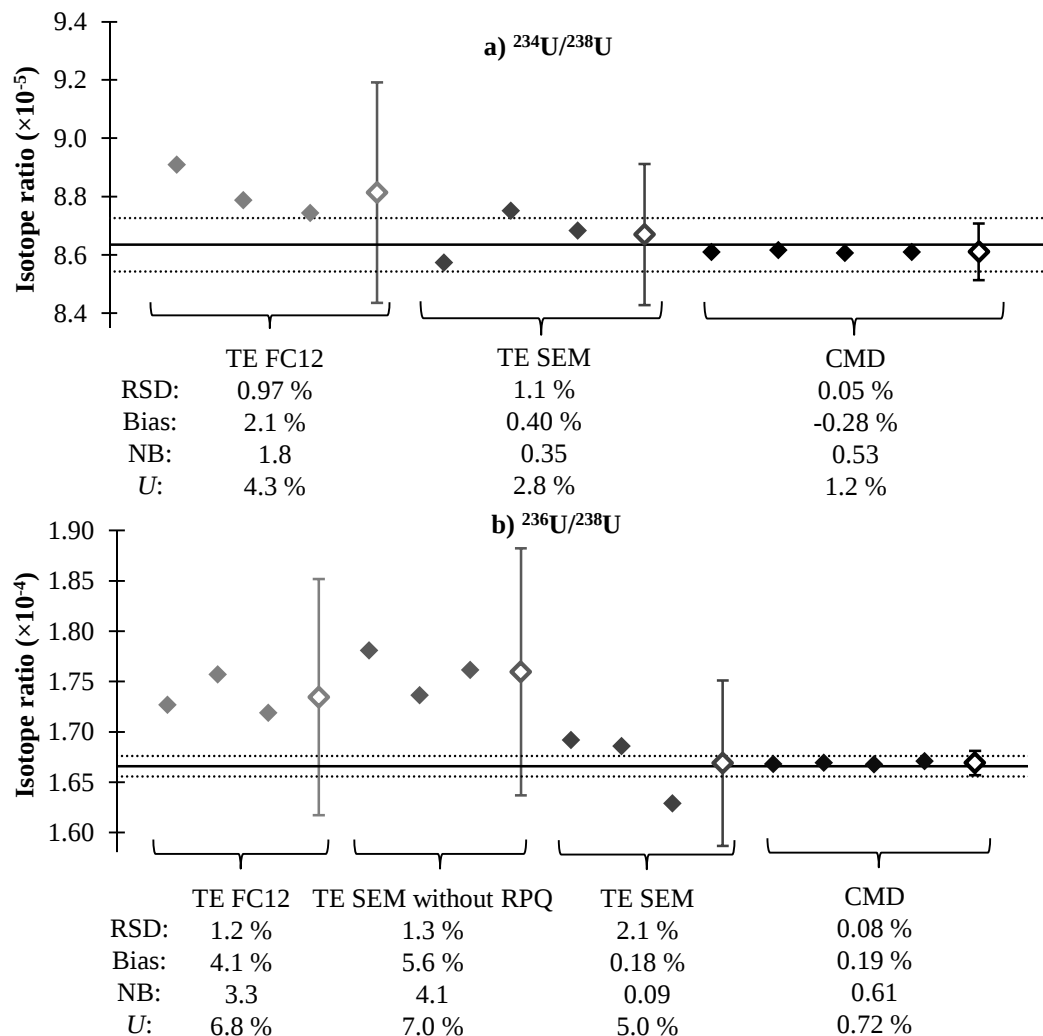


Fig. 1: $^{234}\text{U}/^{238}\text{U}$ (a) and $^{236}\text{U}/^{238}\text{U}$ (b) isotope ratios measurement on the U015 CRM (full diamonds) with the TE method using the FC 12 (TE FC 12) and the SEM (TE SEM) and with the CMD method (CMD). Empty diamonds with error bars represent the series average with its estimated uncertainties at $k = 2$. U corresponds to the total uncertainty ($k = 2$). NB corresponds to the normalized bias. The full line (-) corresponds to the certified value and the dotted line (...) represents its uncertainty at $k = 2$

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