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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 $^{235}$U/$^{238}$U [1,2,7].

The analyses of the $^{234}$U/$^{238}$U and $^{236}$U/$^{238}$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 $10^{11}$ Ω 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 $10^{13}$ Ω 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: $18.2 \, M\Omega.cm$). 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 $^{234}U/^{238}U$ (0.00008634(92), k = 2), $^{235}U/^{238}U$ (0.015565(16), k = 2) and $^{236}U/^{238}U$ (0.0001666(10), k = 2) isotope ratios.

### Sample preparation

Each participant of the "2017 Nuclear Material Round Robin" received a uranium oxide pellet ($UO_2$) 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 $250 \, \mu g \, \mu L^{-1}$, was diluted with $3 \, mol \, L^{-1}$ in order to obtain solutions of concentration suitable for isotopic analysis: about $4 \, \mu g \, \mu L^{-1}$ and $1 \, \mu g \, \mu L^{-1}$.

## 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 $10^{11}$ Ω current amplifiers (9 are available and hereafter Faraday cups coupled with $10^{11}$ Ω amplifiers are referred to as FC 11) or a $10^{12}$ Ω current amplifier (1 is available and hereafter a Faraday cup coupled with a $10^{12}$ Ω 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 $^{235}U/^{238}U$ 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 $^{235}U/^{238}U$ isotope ratio in compliance with the International Target Value (ITV) [1,2]. The $^{238}U^+$ ion beam target intensity was measured using the FC 11 exclusively that was fixed at 15 V whereas the $^{235}U^+$ 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 $^{235}U/^{238}U$ 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.

146     The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios were also acquired on the U015 CRM with the

147     TE method at the same time as the $^{235}U/^{238}U$ isotope ratio measurements. 3 analyses were

148     performed using the FC 12 to collect the $^{234}U$ isotope and the SEM to collect the $^{236}U$

149     isotope and 3 analyses were performed using the FC 12 to collect the $^{236}U$ isotope and the

150     SEM to collect the $^{234}U$ isotope.


151     *Classical method with multi-dynamic sequences*


152     The TE method is an accurate and simple analytical method for major isotope ratio

153     measurements (typically $^{235}U/^{238}U$ isotope ratio) [7]. However, the TE method has

154     limitations for the minor isotope ratios measurements because these measurements

155     require other corrections such as: the SEM calibration, changes in the peak centering and

156     focusing during the filament heating, or peak tailing corrections [6]. Hence, the classical

157     method is more adapted for minor isotope ratios determination (*e.g.* $^{234}U/^{238}U$ and

158     $^{236}U/^{238}U$ isotope ratios) because it allows the application of corrections through different

159     measurement sequences [2]. On the other hand, the classical method is affected by

160     isotope fractionation, as it is its main cause of the measurement bias, and requires another

161     mathematical correction. In the present study, when applying the classical method, the

162     isotope fractionation was corrected using an internal normalization established from the

163     major uranium isotope ratio. This isotope ratio (*e.g.* $^{235}U/^{238}U$ isotope ratio) was

164     previously determined using the TE method for major isotope ratio determination.

165     A classical multi-dynamic method (hereafter referred to as CMD method) was developed

166     to measure the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios. This method includes 4

167     measurement sequences performed one after the other in order to apply several

168     corrections and collect all of the uranium isotopes (Table 1).

169     In the first sequence, the magnetic field was set to collect the $^{236}U$ isotope on the SEM.

170     The other detectors (Faraday cups) were positioned to collect all of the other uranium

171     isotopes: the $^{234}U$ isotope was collected on the FC 12 (L2 cup), the $^{235}U$ (L1 cup) and

172     $^{238}U$ (H2 cup) isotopes were collected on a FC 11. An idle time of 1 s was applied and the

173     measurement was performed with 5 integrations of 4 s. The idle time is necessary to

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

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

185 In the third sequence, the magnetic field of the sector field was modified so that the SEM
186 was set at 235.7 amu (*i.e.* $^{236}$U - 0.35, $^{236}$U mass being about 236.05 amu) for tailing
187 contribution measurement. It was measured closer to the peak in order to make the linear
188 interpolation more accurate. This step measured in parallel the tailing contribution at
189 mass $^{234}$U – 0.35. The Faraday cups used in this sequence were the same as in sequence
190 1. The signal intensities measured during sequence 3 were weak compared to the signal
191 intensities in sequence 1. An idle time is necessary to ensure that the Faraday cups
192 response return to their background level before the measurement in sequence 3,
193 especially for the FC 12 which has the longest response time. Then, Faraday cups used in
194 sequence 3 had an inaction time of 26 s before restarting measurement. This time
195 corresponds to the idle time of the sequence 3 (5 s) and the sequence 2 total measurement
196 time when the Faraday cups used in sequences 1 and 3 were not collecting any signal (we
197 recall that the idle time of sequence 2 is 1 s and measurement time of sequence 2 is
198 $4 \times 5$ s).

199 In the fourth sequence, the magnetic field was modified to collect at the central detector
200 mass 236.4, corresponding to $^{236}$U + 0.35 ($\approx$ 236.05 + 0.35). This step measured the
201 tailing contribution at mass $^{234}$U + 0.35 and $^{236}$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 $^{234}U^+$ 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 $^{234}U^+$
212 ion beam intensity of $1 \times 10^{-14}$ 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)).

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

9

227 Where p is the normalization factor. $R_{corr}$ is the $^{234}U/^{238}U$ or $^{236}U/^{238}U$ corrected isotope

228 ratio. $R_{meas}$ is the $^{234}U/^{238}U$ or $^{236}U/^{238}U$ measured isotope ratio in the sequence 1 and $M_i$

229 and $M_j$ are the molar masses of the isotope involved in the isotope ratio.

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

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

231 Where $(^{235}U/^{238}U)_{cert}$ is the $^{235}U/^{238}U$ certified isotope ratio for the U015 CRM or the ratio

232 measured using the TE method for the RRT sample. $(^{235}U/^{238}U)_{meas}$ is the $^{235}U/^{238}U$

233 isotope ratio measured in sequence 1. $M_{235_U}$ and $M_{238_U}$ are the molar masses of the $^{235}U$

234 and $^{238}U$ isotopes.

235 The $^{234}U/^{238}U$ isotope ratio $((234/238)_{corr})$, corrected from the peak tailing and the isotope

236 fractionation, is then given by Eq. (3):

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

237 The $(234/238)_{meas}$ isotope ratio is the $^{234}U/^{238}U$ isotope ratio measured in sequence 1. The

238 233.7/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 3

239 over the signal of $^{238}U$ in sequence 1. The 234.4/238 ratio corresponds to the signal

240 measured on the L2 Faraday cup in sequence 4 over the signal of $^{238}U$ in sequence 1.

241 $M_{234_U}$ and $M_{238_U}$ are the molar masses of the $^{234}U$ and $^{238}U$ isotopes. p is the

242 normalization factor obtained from Eq. (2).

243 The $^{236}U/^{238}U$ isotope ratio $((236/238)_{corr})$ corrected from the peak tailing, the SEM/FC

244 inter-calibration gain and the isotope fractionation is given by Eq. (4).

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

245   Where G is the SEM/FC inter-calibration gain. The $(236/238)_{meas}$ isotope ratio is the

246   $^{236}U/^{238}U$ isotope ratio measured in sequence 1. The 235.7/238 ratio corresponds to the

247   signal measured on the SEM in sequence 3 over the signal of $^{238}U$ in sequence 1. The

248   236.4/238 ratio corresponds to the signal measured on the SEM in sequence 4 over the

249   signal of $^{238}U$ in sequence 1. $M_{236_U}$ and $M_{238_U}$ are the molar masses of the $^{234}U$ and $^{238}U$

250   isotopes. p is the normalization factor obtained from Eq. (2).

251   The SEM/FC inter-calibration gain was calculated using Eq. (5). It includes the peak

252   tailing correction from the $^{235}U^+$ and $^{238}U^+$ ion beams to the $^{234}U^+$ beam detection on the

253   FC 12. No peak tailing correction was applied to the SEM since the RPQ energy filter

254   helps decreasing the peak tailing by 2 orders of magnitude [4,10].

$$G = \left( \frac{\left(\frac{234}{235}\right)_{S2}}{\left(\frac{234}{235}\right)_{S1}} \right) \times \frac{\left(\frac{234}{238}\right)_{S1}}{\left(\frac{234}{238}\right)_{S1} - \frac{1}{2}\left(\frac{233.7}{238} + \frac{234.4}{238}\right)} \tag{5}$$

255   Where S1 and S2 are isotope ratio measured in sequence 1 or 2, respectively. The

256   233.7/238 ratio corresponds to the signal measured on the L2 Faraday cup in sequence 3

257   over the signal of $^{238}U$ in sequence 1. The 234.4/238 ratio corresponds to the signal

258   measured on the L2 Faraday cup in sequence 4 over the signal of $^{238}U$ in sequence 1.

259   The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ corrected isotope ratios were calculated during each

260   measurement cycle. After the end of the measurement (*i.e.* after the 6 blocks of 10 cycles)

261   a statistical test rejecting the values outside the average plus or minus twice the standard

262   deviation was applied twice for both isotope ratios. Around 7 % of the values were

263   rejected. The $^{234}U/^{238}U$ and $^{236}U/^{238}U$ corrected isotope ratios were obtained by the

264   average of the non-rejected values.

265   For the method validation, 4 analyses were performed on the U015 CRM. For the RRT

266   sample determination, 5 analyses were performed.

267

268

269      Results evaluation and uncertainties estimation

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

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

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.

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

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).

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

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

282    The first term of Eq. (8) includes the uncertainty from the random effects and is given by

283    the RSD of all the measurements (*i.e.* the precision). The second and third terms take into

284    account the systematic effects (*i.e.* the measurement trueness of the method). The

285    measurement trueness is calculated using Eq. (9) and is determined with the U015 CRM

286    because of its isotopic properties close to the RRT sample.


287    **Results and discussion**


288    Comparison of isotope measurement methods for minor isotope ratio

289    determination


290    The CMD method was compared to the TE method using the FC 12 ("TE FC 12") as well

291    as the TE method using the SEM ("TE SEM") for the determination of the $^{234}$U/238U and

292    $^{236}$U/$^{238}$U minor isotope ratios of the U015 CRM. The results are presented in Fig. 1.


293    *TE method using FC 12*


294    Using the TE method, the signals measured on the FC 12 were 13 mV for $^{234}$U$^+$ and

295    25 mV for $^{236}$U$^+$. These intensities are very weak in comparison to the signal measured

296    for $^{238}$U$^+$ (15 V). The theoretical Faraday cup detection limit can be estimated as 3 times

297    the quadratic sum of the standard deviation of the Johnson Nyquist noise and the Poisson-

298    noise (about 0.4 mV for a FC 12) [16,17]. The minor isotope signals are about 30 times

299    (for the $^{234}$U$^+$) and 60 times (for the $^{236}$U$^+$) higher than the estimated detection limit of the

300    FC 12. The TE FC 12 method showed a bias of 2.08 % and 4.11 % for the $^{234}$U/$^{238}$U and

301    $^{236}$U/$^{238}$U ratios, respectively. Despite the higher $^{236}$U intensity (25 mV) compared to the

302    $^{234}$U intensity (13 mV), the bias for the $^{236}$U/$^{238}$U (4.1 %) is significantly higher than the

303    $^{234}$U/$^{238}$U (2.1 %). The low signal intensity is therefore not the only reason for a higher

304    bias. The presence of the $^{238}$U major isotope, closer to the $^{236}$U than to the $^{234}$U isotope,

305    explains the bias difference because of peak tailing issues. The RSD for the $^{234}$U/$^{238}$U and

306    $^{236}$U/$^{238}$U isotope ratios were similar and about 1 %. Unlike the normalized bias observed

307    for the $^{234}$U/$^{238}$U isotope ratio (1.8), the normalized bias for the $^{236}$U/$^{238}$U isotope ratio

308     was equal to 3.3 showing that the method has a significant bias for the $^{236}$U/$^{238}$U ratio.

309     The uncertainties were estimated to 4.3 % for the $^{234}$U/$^{238}$U ratio and 6.8 % for the

310     $^{236}$U/$^{238}$U ratio, with a major contribution from the systematic error (Table 2).

311     *TE method using SEM*

312     The SEM improves the sensitivity in comparison to the FC 12: the measured signals were

313     78000 cps for the $^{234}$U isotope and 150000 cps for the $^{236}$U isotope. These intensities are

314     much higher than the SEM dark noise (below 10 counts per minute). In comparison to the

315     TE FC 12 method, the bias greatly decreased (0.40 % for the $^{234}$U/$^{238}$U ratio and 0.18 %

316     for the $^{236}$U/$^{238}$U ratio). This improvement can be due to the better detector sensitivity and

317     to the fact that the SEM is equipped with a RPQ filter that provides a bias reduction for

318     the minor isotope ratio determination. In order to find the best contributor to the

319     improvement of the measurement trueness, 3 additional analyses under the same

320     analytical conditions except that the RPQ filter was not used were performed using the

321     TE method with the SEM to collect the $^{236}$U (Fig. 1.b). The measurement trueness was

322     degraded without the RPQ filter: the bias was higher than 5 %, while a bias below 0.2 %

323     is obtained with the RPQ filter. The normalized bias computed without RPQ filter shows

324     the method has a significant bias (NB > 2). The $^{236}$U/$^{238}$U ratios determined using the TE

325     FC 12 method and the TE SEM method without RPQ filter were all higher than the

326     certified values (Fig. 1). This is obviously due to the peak tailing effect of $^{238}$U as the

327     abundance sensitivity is about $10^{-6}$ without RPQ filter for the Triton TIMS. These

328     observations show when reducing the peak tailing contribution using the RPQ energy

329     filter is the main cause of the measurement trueness improvement. On the other hand, it

330     can be noticed that the use of the RPQ filter reduces the ions intensity by about 5 %. This

331     loss is negligible compared to the benefit obtained on the measurement trueness.

332     However, the observed RSD for the $^{234}$U/$^{238}$U and $^{236}$U/$^{238}$U obtained with the TE method

333     using the SEM and the RPQ filter (Fig. 1) are high (1.1 % for the $^{234}$U/$^{238}$U ratio and

334     2.1 % for the $^{236}$U/$^{238}$U ratio). The poor repeatability is explained by the SEM instability

335     during the measurement. The SEM calibration can vary significantly during an analysis

14

336     without any predictable trend [1]. Despite the SEM instability, the estimated uncertainty

337     (2.8 % for the $^{234}$U/$^{238}$U ratio and 5.0 % for the $^{236}$U/$^{238}$U ratio) slightly decreased

338     compared to the TE FC 12 method (4.3 % for the $^{234}$U/$^{238}$U ratio and 6.8 % for the

339     $^{236}$U/$^{238}$U ratio). The relative contribution of the main uncertainty sources (Table 3)

340     shows that the total uncertainties are mainly due to the precision (55 % for the $^{234}$U/$^{238}$U

341     ratio and 71 % for the $^{236}$U/$^{238}$U ratio). The method shows no significant bias for both

342     isotope ratios: the normalized biases are below 2.


343     *CMD method*


344     The biases obtained using the CMD method are equal to -0.28 % for the $^{234}$U/$^{238}$U ratio

345     and 0.19 % for the $^{236}$U/$^{238}$U ratio (Fig. 1 and Table 3). The observed RSD on the

346     $^{234}$U/$^{238}$U and $^{236}$U/$^{238}$U are equal to 0.05 % and 0.08 %, respectively. The normalized

347     bias calculated for both isotope ratios were below 2, showing the method has no

348     significant bias. The CMD method improves the measurement trueness by decreasing the

349     abundance sensitivity influence using the RPQ filter combined with a mathematical

350     correction. The CMD method also improves the precision due to a "real time" SEM

351     calibration. The impact of the SEM fluctuation is then minimized. The method's internal

352     normalization helps maintaining a good measurement accuracy and correct the isotope

353     fractionation. Different parameters influencing the isotope fractionation, such as the

354     deposit quality, are compensated by the internal normalization. The uncertainties were

355     estimated to 1.2 % for the $^{234}$U/$^{238}$U ratio and 0.72 % for the $^{236}$U/$^{238}$U ratio. The main

356     sources of uncertainty for $^{234}$U/$^{238}$U and $^{236}$U/$^{238}$U isotope ratios confirm the significant

357     improvement of the precision and the measurement trueness when applying the CMD

358     method (Table 2): the measurement trueness (11 % for the $^{234}$U/$^{238}$U ratio and 23 % for

359     the $^{236}$U/$^{238}$U ratio) and precision (1 % for the $^{234}$U/$^{238}$U ratio and 5 % for the $^{236}$U/$^{238}$U

360     ratio) are minor contributors to the total uncertainty. The main contribution is the CRM

361     uncertainty. The lowest uncertainties are obtained with the CMD method:

362     $U$ (k = 2) = 4.3 %, 2.8 % and 1.2 % for the $^{234}$U/$^{238}$U isotope ratio using TE FC 12, TE

363     SEM and CMD methods, respectively, and $U$ (k = 2)= 6.8 %, 5.0 % and 0.72 % for the

364     $^{236}$U/$^{238}$U isotope ratio using TE FC 12, TE SEM and CMD methods, respectively.

*Methods comparison*

366     These 3 methods have different assets in terms of analysis time, simplicity, trueness and

367     repeatability. The TE FC 12 method is the simplest and the most straightforward method:

368     no inter-calibration gain is required between two sample analyses as the Faraday cups are

369     very stable and all the isotope ratios of an element (major and minor isotope) are directly

370     obtained. However, this method needs to take into account the method bias in the

371     uncertainty calculation. The application of this method is easily transposable to another

372     element assuming that the number of minor isotopes do not exceed the number of FC 12.

373     An analysis using the FC 12 takes generally between 20 to 60 minutes.

374     The TE SEM method is rather simple also. The sample analysis itself has the same

375     duration as the TE method with FC 12 (between 20 to 60 minutes). However, the

376     SEM/FC inter-calibration gain is required before and after each sample analysis. This

377     explains the longer total analysis time (each inter-calibration gain takes about 20

378     minutes). The method gives directly all the isotope ratios of an element (major and minor

379     isotope). Depending on the number of SEM detectors available in the instrument, the

380     analysis might require several runs. Also, this method can be easily transposable to

381     another element.

382     The CMD method is the most complex one. However, once the file for the $^{234}U/^{238}U$ and

383     $^{236}U/^{238}U$ ratios computation is created, the method can be easily used put in routine

384     analysis. The method requires bigger sample amount (about 4 µg) than the TE method

385     (less than 1 µg) in order to keep a high signal during the entire analysis that lasts about 90

386     minutes. Also, this method requires the results of others analyses: the $^{235}U/^{238}U$ isotope

387     ratio determination with a high accuracy method, like the TE method, is needed to

388     perform the isotope fractionation correction of the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios, which

389     increases the overall analysis time. This method is dedicated to the situation where high

390     accuracy minor isotope ratio determination is necessary. The method can be transposable

391     to enriched uranium. However, for depleted uranium, the $^{234}U/^{238}U$ isotope ratio is

392     generally too low to perform both the measurement of the $^{234}U/^{238}U$ isotope ratio and the

393     SEM/FC inter-calibration in the same method. Indeed, the SEM/FC inter-calibration

394  requires a minimum signal of 10 mV with the FC 12. Considering that for depleted

395  uranium, the $^{234}U/^{238}U$ isotope ratios are below $2\times10^{-5}$, the signal with FC 11 for the $^{238}U$

396  isotope measurement would exceed its maximum limit (50 V). So, for depleted uranium

397  using the CMD method, the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios are not directly

398  accessible. These minor ratios could be obtained indirectly using the measurements of the

399  $^{234}U/^{235}U$ and $^{236}U/^{235}U$ isotope ratios and by knowing the $^{235}U/^{238}U$ isotope ratio. In this

400  case, the CMD method would need adjustment: the internal normalization would be

401  performed with the measurement of the $^{234}U/^{235}U$ as the $^{238}U$ isotope would not be

402  collected. In a more general point of view, the CMD method needs adjustments for each

403  element to be measured. The analyzed element needs to have a minimum of 3 isotopes:

404  one major isotope, one minor isotope needing a measurement with the SEM and an

405  "intermediate" isotope allowing the in situ SEM/FC inter-calibration. This last isotope

406  needs a significantly lower abundance compared to the major isotope and a significantly

407  higher abundance compared to the minor isotope.

408  The CMD method shows also some similarities with the measurement sequence of the

409  MTE method [10]. The main difference between the MTE and the CMD methods comes

410  from the isotope fractionation correction: total evaporation for the MTE method or

411  internal normalization for the CMD method. The MTE method is the reference method in

412  order to have the lowest uncertainties. However, the CMD method presents some

413  advantages compared to the MTE method. The principal advantages is a shorter analysis

414  time: the CMD method take about 90 min compared to the 3-5 hours for the MTE

415  method. The CMD method is also simpler to configure in the TIMS software. The CMD

416  method is directly configurable in the TIMS software without the requirement of an

417  external script [10].

418     Method validation

419  The results for the method validation on the U015 CRM are summarized in Table 2. The

420  CMD method shows lower bias, better repeatability and uncertainty compared to the TE

421  method for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios measurements. The CMD method

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422 displayed no significant bias (normalized bias below to 2). These results validate the

423 $^{234}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios determination using the CMD method.

424 The result obtained for the $^{235}U/^{238}U$ is in good agreement with the certified value. The

425 bias obtained is equal to 0.03 % and the RSD is 0.02 %. The normalized bias is equal to

426 0.62, showing that the method leads to no significant bias. The uncertainty is estimated to

427 0.16 % (k = 2) and is in compliance with the safeguard requirements given by the ITV

428 (0.28 %, k = 2) on this range of uranium isotopic composition [18]. It should be noticed

429 that the first five experiments were performed before the RRT sample isotope

430 measurement and the last one after the RRT sample isotope measurement (see next

431 section), ensuring that the instrumental performance is satisfactory during the whole

432 measurement series. These results validate the $^{235}U/^{238}U$ isotope ratio determination using

433 the TE method.

### 434  Isotope ratio measurement in the uranium pellet

435 The RRT sample was analyzed as an unknown sample. However, at the end of the study,

436 the results were compared to the RRT assigned values in order to evaluate the developed

437 methodology.

438 The method developed and validated using the U015 CRM was applied. The $^{235}U/^{238}U$

439 ratio measurements with the FC 11 or the FC 12 for the $^{235}U$ detection show no

440 significant bias: biases are below 0.1 % and the normalized biases are below 2 (Table 4).

441 The measurements seem to demonstrate that the precision is slightly better using the FC

442 12 (RSD = 0.03 %) than using the FC 11 (RSD = 0.06 %).

443 The results obtained for the $^{234}U/^{238}U$ (bias = 0.27 %), $^{235}U/^{238}U$ (bias = 0.07 %) and

444 $^{236}U/^{238}U$ (bias = 0.93 %) isotope ratios are in good agreement with the assigned values

445 provided by IAEA (Table 4). The RSD are similar to the ones obtained for the U015

446 CRM and are lower than 0.1 %: 0.07 %, 0.04 % and 0.08 % for the $^{234}U/^{238}U$, $^{235}U/^{238}U$

447 and $^{236}U/^{238}U$ isotope ratios, respectively. The $^{235}U/^{238}U$ isotope ratio uncertainty is

448 estimated at 0.15 % (k = 2) and is in compliance with the ITV (0.28 %, k = 2) for this

449    type of enriched uranium [18]. The relative contribution, expressed in percent, of the

450    main uncertainty sources for the uranium isotope ratios determination is given in Table 2.

451    The three uncertainty sources considered for the $^{235}U/^{238}U$ isotope ratio determination

452    have a similar contribution: U015 CRM certified isotope ratio (41 %), precision (31 %)

453    and method trueness (28 %). The $^{234}U/^{238}U$ isotope ratio uncertainty is estimated at

454    1.13 % (k = 2). The uncertainty associated with the CRM isotope ratio is the main

455    uncertainty source in the final uncertainty (87 %). The uncertainties associated with the

456    method bias (11 %) and the precision (2 %) have a limited impact on the final

457    uncertainty. The $^{236}U/^{238}U$ isotope ratio uncertainty is estimated at 0.72 % (k = 2). In the

458    same way as the $^{234}U/^{238}U$, the final uncertainty mostly comes from the CRM isotope

459    ratio uncertainty (72 %).

460    The methodology developed to perform uranium isotope ratio with high accuracy showed

461    no significant bias: all the normalized biases are lower than 2.


## Conclusions

463    This study shows the possibility of the TE and the CMD methods for determining

464    uranium isotope ratios with low uncertainties. The TE method allows to reach the ITV

465    requirements for the $^{235}U/^{238}U$ major isotope ratio. One of the methods for the $^{234}U/^{238}U$

466    and $^{236}U/^{238}U$ minor isotope ratios determination was the classical method using multi-

467    dynamic sequences. This classical method allows mathematical correction of the

468    abundance sensitivity and calibrating the SEM detector while the method is running. An

469    internal normalization using the $^{235}U/^{238}U$ major isotope ratio was used to overcome the

470    isotope fractionation. The CMD method decreases the bias, the repeatability and the

471    estimated uncertainties compared to the TE method for uranium minor isotope ratios

472    determination, which is also an interesting feature for forensic analysis applications.

473    Another application of the accurate determination of the pellet isotope composition is the

474    uranium content determination with high accuracy using isotope dilution, a method that

475    will be presented in future.

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## Acknowledgements

480     **Table**

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

| Cups Detectors | L2 FC 12 | L1 FC 11 | C SEM | H1 FC 11 | H2 FC 11 | Number of integrations | Measurement time (s) | Idle time (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 |

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484     Table 2: Relative contribution (%) of the main uncertainty sources for the $^{234}$U/$^{238}$U and
485     $^{236}$U/$^{238}$U isotope ratios measurement with the TE method using the FC 12 (TE FC 12) or
486     the SEM (TE SEM) and with the CMD method (CMD), and for the $^{235}$U/$^{238}$U isotope
487     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. |
| $^{234}$U/$^{238}$U | U015 | TE FC 12 | 21 | 73 | 6 |
| | U015 | TE SEM | 55 | 31 | 14 |
| | U015 | CMD | 1 | 11 | 88 |
| | RRT | CMD | 2 | 11 | 87 |
| $^{235}$U/$^{238}$U | U015 | TE | 13 | 36 | 51 |
| | RRT | TE | 29 | 29 | 42 |
| $^{236}$U/$^{238}$U | U015 | TE FC 12 | 12 | 87 | 1 |
| | U015 | TE SEM | 71 | 27 | 2 |
| | U015 | CMD | 5 | 23 | 72 |
| | RRT | CMD | 5 | 23 | 72 |

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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 | $^{234}U/^{238}U$ | $^{235}U/^{238}U$ | $^{236}U/^{238}U$ |
|---|---|---|---|
| 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 |

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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 | $^{234}U/^{238}U$ | $^{236}U/^{238}U$ | $^{235}U/^{238}U$ | | |
|---|---|---|---|---|---|
| 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

502 **Figure**



503
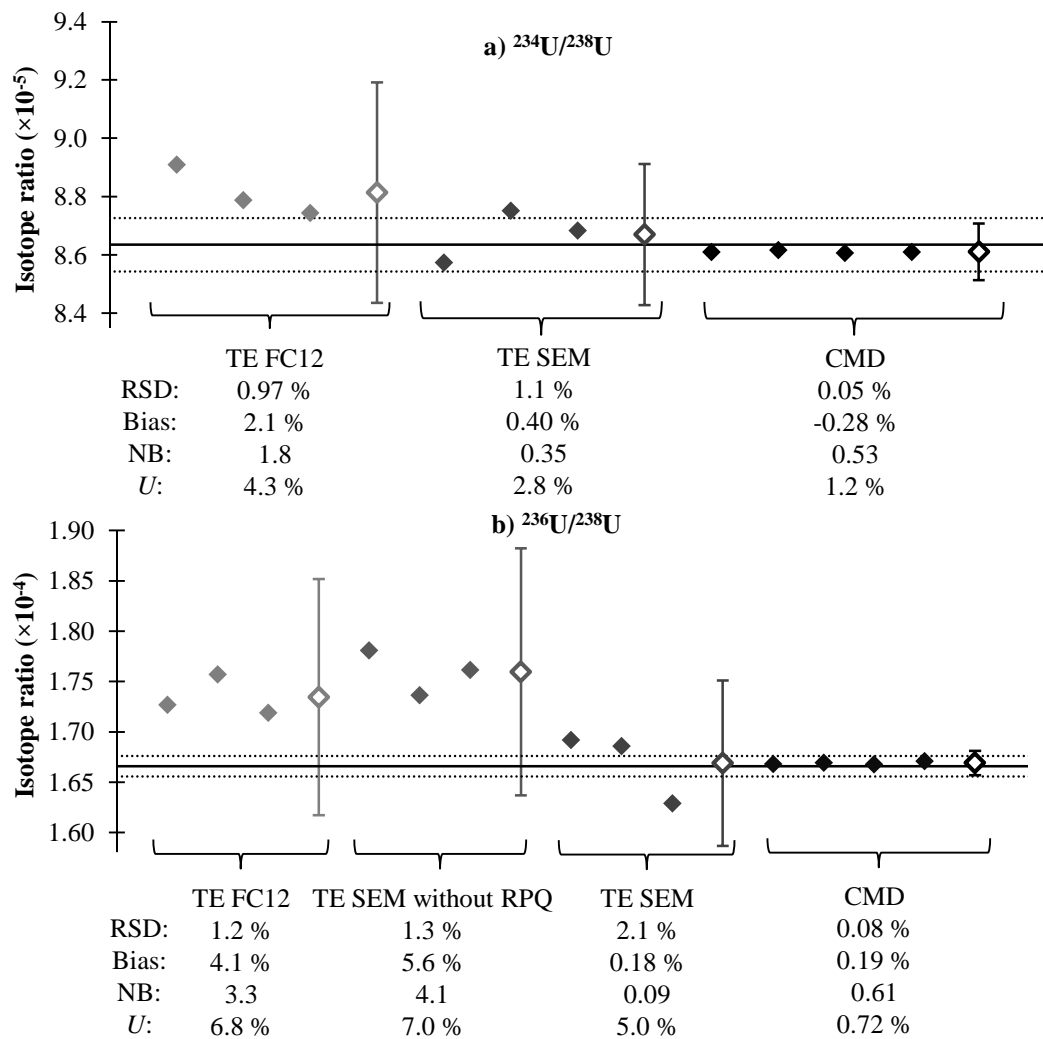504 **Fig. 1**: $^{234}U/^{238}U$ (a) and $^{236}U/^{238}U$ (b) isotope ratios measurement on the U015 CRM (full
505 diamonds) with the TE method using the FC 12 (TE FC 12) and the SEM (TE SEM) and
506 with the CMD method (CMD). Empty diamonds with error bars represent the series
507 average with its estimated uncertainties at k = 2. *U* corresponds to the total uncertainty
508 (k = 2). NB corresponds to the normalized bias. The full line (-) corresponds to the
509 certified value and the dotted line (…) represents its uncertainty at k = 2

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