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

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13

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

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23 **Abstract**

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

33 **Keywords**

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

35

## 36            **Introduction**

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

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

57    The analyses of the  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios can be more complicated. First,  
58    weak signals close to the detection limit make accurate measurements difficult. The most  
59    commonly used detector for isotopic analysis by TIMS is the Faraday cup coupled to a  
60     $10^{11} \Omega$  current amplifier. This detector is highly stable helping reaching a high accuracy  
61    measurement (*i.e.* measurement trueness and precision). However, this detection system  
62    is not adapted for weak signals. The development of the  $10^{12}$  and  $10^{13} \Omega$  current  
63    amplifiers helps improving the Faraday cup sensitivity [1,9]. When the isotope  
64    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  $^{235}\text{U}$  or  $^{238}\text{U}$ ) to the minor isotope detection (*i.e.*  $^{234}\text{U}$  or  $^{236}\text{U}$ ). 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

95        **Experimental**

96        **Materials, reagents and certified reference materials**

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

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

107       **Sample preparation**

108       Each participant of the “2017 Nuclear Material Round Robin” received a uranium oxide  
109       pellet (UO<sub>2</sub>) of about 5 g in a 20 mL HDPE vial (hereafter referred to as RTT sample).  
110       The RTT sample is a uranium fuel pellet fabricated in Brazil with a uranium isotope  
111       composition close to a low enrichment uranium oxide pellet before irradiation in  
112       Pressurized Water Reactor [11]. The TIMS requires working with liquid samples. Thus,  
113       the first preparation step was the dissolution of the pellet. It was weighed and about  
114       15 mL of 8 mol L<sup>-1</sup> nitric acid was added. This solution (pellet + nitric acid) was heated  
115       at 135 °C in a PFA vial until complete dissolution. The pellet dissolution solution  
116       (hereafter referred to as RRT solution), which had a uranium concentration about  
117       250 µg µL<sup>-1</sup>, was diluted with 3 mol L<sup>-1</sup> in order to obtain solutions of concentration  
118       suitable for isotopic analysis: about 4 µg µL<sup>-1</sup> and 1 µg µL<sup>-1</sup>.

119

## 120 Thermal Ionization Mass Spectrometer

121 The Thermo Fisher Triton TIMS used for the experiments and the deposit technique were  
122 previously described in detail [12]. The TIMS is equipped with 9 Faraday cups (all are  
123 movable except the central denoted C) which can be coupled to  $10^{11}$   $\Omega$  current amplifiers  
124 (9 are available and hereafter Faraday cups coupled with  $10^{11}$   $\Omega$  amplifiers are referred to  
125 as FC 11) or a  $10^{12}$   $\Omega$  current amplifier (1 is available and hereafter a Faraday cup  
126 coupled with a  $10^{12}$   $\Omega$  amplifier is referred to as FC 12). 4 Faraday cups are positioned in  
127 low masses (noted L1 to L4) and 4 Faraday cups are positioned in high masses (noted H1  
128 to H4). The TIMS is also equipped with one fixed discrete dynode Secondary Electron  
129 Multiplier located behind the central Faraday cup (hereafter referred to as SEM). The  
130 SEM is combined with a high abundance filter (RPQ for Retarding Potential  
131 Quadrupole). The SEM calibration was performed using the method described in [12].

## 132 Isotopic analysis methods

### 133 *The total evaporation method*

134 The TE method applied in the present study was described in details in previous work for  
135 the  $^{235}\text{U}/^{238}\text{U}$  major isotope ratio measurement [1,2,8,12]. The quantity of uranium  
136 deposit was 1  $\mu\text{g}$ . This uranium amount allows the accurate determination of the  
137  $^{235}\text{U}/^{238}\text{U}$  isotope ratio in compliance with the International Target Value (ITV) [1,2]. The  
138  $^{238}\text{U}^+$  ion beam target intensity was measured using the FC 11 exclusively that was fixed  
139 at 15 V whereas the  $^{235}\text{U}^+$  ion beam was measured either by FC 11 or FC 12.

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

146 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  
147 TE method at the same time as the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio measurements. 3 analyses were  
148 performed using the FC 12 to collect the  $^{234}\text{U}$  isotope and the SEM to collect the  $^{236}\text{U}$   
149 isotope and 3 analyses were performed using the FC 12 to collect the  $^{236}\text{U}$  isotope and the  
150 SEM to collect the  $^{234}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$  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.*  $^{234}\text{U}/^{238}\text{U}$  and  
158  $^{236}\text{U}/^{238}\text{U}$  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.*  $^{235}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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  $^{236}\text{U}$  isotope on the SEM.  
170 The other detectors (Faraday cups) were positioned to collect all of the other uranium  
171 isotopes: the  $^{234}\text{U}$  isotope was collected on the FC 12 (L2 cup), the  $^{235}\text{U}$  (L1 cup) and  
172  $^{238}\text{U}$  (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  $^{234}\text{U}$  isotope on the  
177 SEM. The H1 cup, not used in sequence 1, was positioned to collect the  $^{235}\text{U}$  on a FC 11.  
178 This step was dedicated to the real-time SEM/FC inter-calibration. It was calculated  
179 using the  $^{234}\text{U}/^{235}\text{U}$  isotope ratio in order to avoid any signal fluctuation and decrease the  
180 uncertainty. The inter-calibration was performed by comparing the  $^{234}\text{U}/^{235}\text{U}$  isotope ratio  
181 measured in sequence 1 using FC 12 and FC 11 with the  $^{234}\text{U}/^{235}\text{U}$  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.*  $^{236}\text{U} - 0.35$ ,  $^{236}\text{U}$  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  $^{234}\text{U} - 0.35$ . 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  $^{236}\text{U} + 0.35$  ( $\approx 236.05 + 0.35$ ). This step measured the  
201 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  $1 \times 10^{-14}$  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  $^{234}\text{U}$  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)).

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

227 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  
 228 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  $M_i$   
 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):

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

231 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  
 232 measured using the TE method for the RRT sample.  $(^{235}\text{U}/^{238}\text{U})_{meas}$  is the  $^{235}\text{U}/^{238}\text{U}$   
 233 isotope ratio measured in sequence 1.  $M_{^{235}\text{U}}$  and  $M_{^{238}\text{U}}$  are the molar masses of the  $^{235}\text{U}$   
 234 and  $^{238}\text{U}$  isotopes.

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

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

237 The  $(234/238)_{meas}$  isotope ratio is the  $^{234}\text{U}/^{238}\text{U}$  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  $^{238}\text{U}$  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  $^{238}\text{U}$  in sequence 1.  
 241  $M_{^{234}\text{U}}$  and  $M_{^{238}\text{U}}$  are the molar masses of the  $^{234}\text{U}$  and  $^{238}\text{U}$  isotopes.  $p$  is the  
 242 normalization factor obtained from Eq. (2).

243 The  $^{236}\text{U}/^{238}\text{U}$  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).

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

245 Where  $G$  is the SEM/FC inter-calibration gain. The  $(236/238)_{\text{meas}}$  isotope ratio is the  
 246  $^{236}\text{U}/^{238}\text{U}$  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  $^{238}\text{U}$  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  $^{238}\text{U}$  in sequence 1.  $M_{236\text{U}}$  and  $M_{238\text{U}}$  are the molar masses of the  $^{234}\text{U}$  and  $^{238}\text{U}$   
 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  $^{235}\text{U}^+$  and  $^{238}\text{U}^+$  ion beams to the  $^{234}\text{U}^+$  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].

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

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  $^{238}\text{U}$  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  $^{238}\text{U}$  in sequence 1.

259 The  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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).

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

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).

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

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

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  $^{234}\text{U}/^{238}\text{U}$  and  
292  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}^+$  and  
295 25 mV for  $^{236}\text{U}^+$ . These intensities are very weak in comparison to the signal measured  
296 for  $^{238}\text{U}^+$  (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  $^{234}\text{U}^+$ ) and 60 times (for the  $^{236}\text{U}^+$ ) 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  $^{234}\text{U}/^{238}\text{U}$  and  
301  $^{236}\text{U}/^{238}\text{U}$  ratios, respectively. Despite the higher  $^{236}\text{U}$  intensity (25 mV) compared to the  
302  $^{234}\text{U}$  intensity (13 mV), the bias for the  $^{236}\text{U}/^{238}\text{U}$  (4.1 %) is significantly higher than the  
303  $^{234}\text{U}/^{238}\text{U}$  (2.1 %). The low signal intensity is therefore not the only reason for a higher  
304 bias. The presence of the  $^{238}\text{U}$  major isotope, closer to the  $^{236}\text{U}$  than to the  $^{234}\text{U}$  isotope,  
305 explains the bias difference because of peak tailing issues. The RSD for the  $^{234}\text{U}/^{238}\text{U}$  and  
306  $^{236}\text{U}/^{238}\text{U}$  isotope ratios were similar and about 1 %. Unlike the normalized bias observed  
307 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

308 was equal to 3.3 showing that the method has a significant bias for the  $^{236}\text{U}/^{238}\text{U}$  ratio.  
309 The uncertainties were estimated to 4.3 % for the  $^{234}\text{U}/^{238}\text{U}$  ratio and 6.8 % for the  
310  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}$  isotope and 150000 cps for the  $^{236}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  ratio and 0.18 %  
316 for the  $^{236}\text{U}/^{238}\text{U}$  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  $^{236}\text{U}$  (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 ( $\text{NB} > 2$ ). The  $^{236}\text{U}/^{238}\text{U}$  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  $^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  obtained with the TE method  
333 using the SEM and the RPQ filter (Fig. 1) are high (1.1 % for the  $^{234}\text{U}/^{238}\text{U}$  ratio and  
334 2.1 % for the  $^{236}\text{U}/^{238}\text{U}$  ratio). The poor repeatability is explained by the SEM instability  
335 during the measurement. The SEM calibration can vary significantly during an analysis

336 without any predictable trend [1]. Despite the SEM instability, the estimated uncertainty  
337 (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  
338 compared to the TE FC 12 method (4.3 % for the  $^{234}\text{U}/^{238}\text{U}$  ratio and 6.8 % for the  
339  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$   
341 ratio and 71 % for the  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  ratio  
345 and 0.19 % for the  $^{236}\text{U}/^{238}\text{U}$  ratio (Fig. 1 and Table 3). The observed RSD on the  
346  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  ratio and 0.72 % for the  $^{236}\text{U}/^{238}\text{U}$  ratio. The main  
356 sources of uncertainty for  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  ratio and 23 % for  
359 the  $^{236}\text{U}/^{238}\text{U}$  ratio) and precision (1 % for the  $^{234}\text{U}/^{238}\text{U}$  ratio and 5 % for the  $^{236}\text{U}/^{238}\text{U}$   
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  $^{234}\text{U}/^{238}\text{U}$  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  $^{236}\text{U}/^{238}\text{U}$  isotope ratio using TE FC 12, TE SEM and CMD methods, respectively.

365 *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  $^{234}\text{U}/^{238}\text{U}$  and  
383  $^{236}\text{U}/^{238}\text{U}$  ratios computation is created, the method can be easily used put in routine  
384 analysis. The method requires bigger sample amount (about 4  $\mu\text{g}$ ) than the TE method  
385 (less than 1  $\mu\text{g}$ ) 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  $^{235}\text{U}/^{238}\text{U}$  isotope  
387 ratio determination with a high accuracy method, like the TE method, is needed to  
388 perform the isotope fractionation correction of the  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  isotope ratio is  
392 generally too low to perform both the measurement of the  $^{234}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  isotope ratios are below  $2 \times 10^{-5}$ , the signal with FC 11 for the  $^{238}\text{U}$   
396 isotope measurement would exceed its maximum limit (50 V). So, for depleted uranium  
397 using the CMD method, the  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios are not directly  
398 accessible. These minor ratios could be obtained indirectly using the measurements of the  
399  $^{234}\text{U}/^{235}\text{U}$  and  $^{236}\text{U}/^{235}\text{U}$  isotope ratios and by knowing the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio. In this  
400 case, the CMD method would need adjustment: the internal normalization would be  
401 performed with the measurement of the  $^{234}\text{U}/^{235}\text{U}$  as the  $^{238}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios measurements. The CMD method

422 displayed no significant bias (normalized bias below to 2). These results validate the  
423  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios determination using the CMD method.

424 The result obtained for the  $^{235}\text{U}/^{238}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$   
439 ratio measurements with the FC 11 or the FC 12 for the  $^{235}\text{U}$  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  $^{234}\text{U}/^{238}\text{U}$  (bias = 0.27 %),  $^{235}\text{U}/^{238}\text{U}$  (bias = 0.07 %) and  
444  $^{236}\text{U}/^{238}\text{U}$  (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  $^{234}\text{U}/^{238}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$   
447 and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios, respectively. The  $^{235}\text{U}/^{238}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$  isotope ratio determination  
452 have a similar contribution: U015 CRM certified isotope ratio (41 %), precision (31 %)  
453 and method trueness (28 %). The  $^{234}\text{U}/^{238}\text{U}$  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  $^{236}\text{U}/^{238}\text{U}$  isotope ratio uncertainty is estimated at 0.72 % ( $k = 2$ ). In the  
458 same way as the  $^{234}\text{U}/^{238}\text{U}$ , 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.

## 462 **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  $^{235}\text{U}/^{238}\text{U}$  major isotope ratio. One of the methods for the  $^{234}\text{U}/^{238}\text{U}$   
466 and  $^{236}\text{U}/^{238}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$  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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479        round robin test (Seibersdorf-Austria).

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	$^{234}\text{U}$	$^{235}\text{U}$	$^{236}\text{U}$		$^{238}\text{U}$	5	4	1
Sequence 2			$^{234}\text{U}$	$^{235}\text{U}$		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  $^{234}\text{U}/^{238}\text{U}$  and  
 485  $^{236}\text{U}/^{238}\text{U}$  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  $^{235}\text{U}/^{238}\text{U}$  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.
$^{234}\text{U}/^{238}\text{U}$	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

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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	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
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

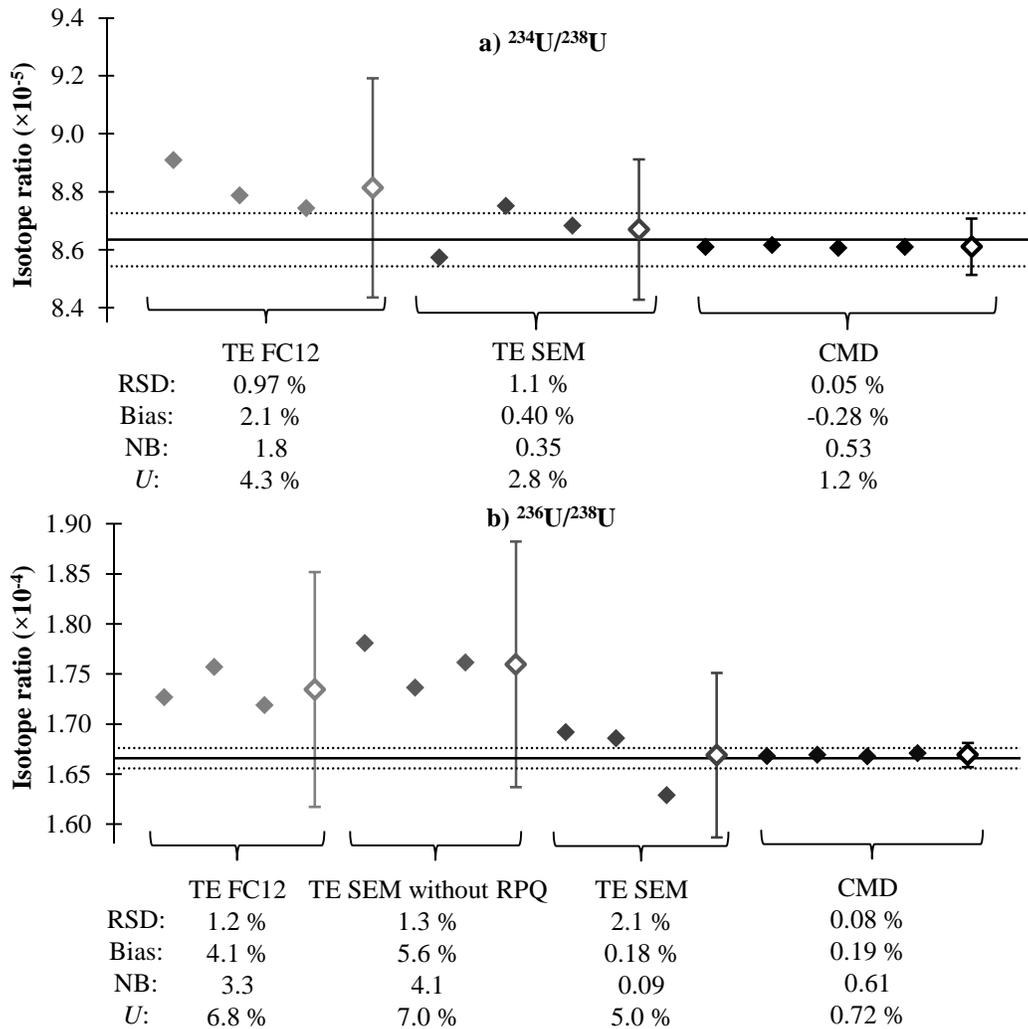
495

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	$^{234}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$		
			TE FC 11	TE FC 12	TE Average
Method	CMD	CMD			
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

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**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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