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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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► **To cite this version:**

Alexandre Quemet, A. Ruas, V. Dalier, C. Rivier. Development and comparison of high accuracy thermal ionization methods for uranium isotope ratios determination in nuclear fuel. *International Journal of Mass Spectrometry*, 2019, 438, 10.1016/j.ijms.2019.01.008 . cea-02339918

HAL Id: cea-02339918

<https://cea.hal.science/cea-02339918v1>

Submitted on 21 Oct 2021

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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}U isotope abundance
44 indicates the enrichment level of the nuclear material, the ^{234}U isotope abundance
45 determination provides information on the material origin and finally, the ^{236}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}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

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⁻¹ and 8 mol L⁻¹ 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, WXTF 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 ²³⁴U/²³⁸U (0.00008634(92), k = 2),
106 ²³⁵U/²³⁸U (0.015565(16), k = 2) and ²³⁶U/²³⁸U (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 (UO₂) 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⁻¹ 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⁻¹, was diluted with 3 mol L⁻¹ in order to obtain solutions of concentration
118 suitable for isotopic analysis: about 4 µg µL⁻¹ and 1 µg µL⁻¹.

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} Ω current amplifiers
124 (9 are available and hereafter Faraday cups coupled with 10^{11} Ω amplifiers are referred to
125 as FC 11) or a 10^{12} Ω current amplifier (1 is available and hereafter a Faraday cup
126 coupled with a 10^{12} Ω 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 μg . 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}U and ^{238}U isotopes, and 5 analyses were performed using the FC 12
144 to collect ^{235}U and the FC 11 to collect ^{238}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}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 $^{235}\text{U}/^{238}\text{U}$ 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}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 $^{234}\text{U}/^{235}\text{U}$ 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}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 4×5 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 1×10^{-14} A was reached, corresponding to a significant signal of
213 10 mV or higher on the FC 12 (sequence 1). This signal also corresponded to about
214 62 500 cps on the SEM (sequence 2), which is low enough for the ^{234}U isotope intensity
215 to not saturate the detector and reduce significantly its lifespan (the recommended signal
216 in the SEM is $< 1\,000\,000$ cps). The evaporation filament temperature was controlled to
217 keep the ion beam intensity constant during the measurement, by increasing the
218 evaporation current when necessary. Each measurement corresponded to 6 blocks of 10
219 cycles. Each cycle corresponded to the acquisition of the 4 measurement sequences
220 presented in the Table 1. The baseline, the “peak center” and the lens optimization were
221 performed every 2 blocks. After each block, the amplifiers $10^{11} \Omega$ connected to the
222 Faraday cups rotated for permitting each Faraday cups to connect to each used amplifier
223 during the analysis.

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

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

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}U
 234 and ^{238}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}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 $M_{234\text{U}}$ and $M_{238\text{U}}$ are the molar masses of the ^{234}U and ^{238}U isotopes. p is the
 242 normalization factor obtained from Eq. (2).

243 The $^{236}\text{U}/^{238}\text{U}$ 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}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. $M_{236\text{U}}$ and $M_{238\text{U}}$ 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 $^{235}\text{U}^+$ 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}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 $^{234}\text{U}/^{238}\text{U}$ 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}U intensity (25 mV) compared to the
302 ^{234}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}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 $^{234}\text{U}/^{238}\text{U}$ 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}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 $^{234}\text{U}/^{238}\text{U}$ 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}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}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 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 $^{235}\text{U}/^{238}\text{U}$ 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 2×10^{-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 $^{234}\text{U}/^{238}\text{U}$ 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}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}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.

476 **Acknowledgements**

477 We are grateful to Dr. S. Baghdadi (IRSN/PSN-EXP/SSRD/BTE) for her precious advice
478 on the present paper. We would like to thank the entire IAEA staff who organized the
479 round robin test (Seibersdorf-Austria).

480 **Table**

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

Cups	L2	L1	C	H1	H2	Number of integrations	Measurement time (s)	Idle time (s)
Detectors	FC 12	FC 11	SEM	FC 11	FC 11			
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 ²³⁴U/²³⁸U and
 485 ²³⁶U/²³⁸U 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 ²³⁵U/²³⁸U 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	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$
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

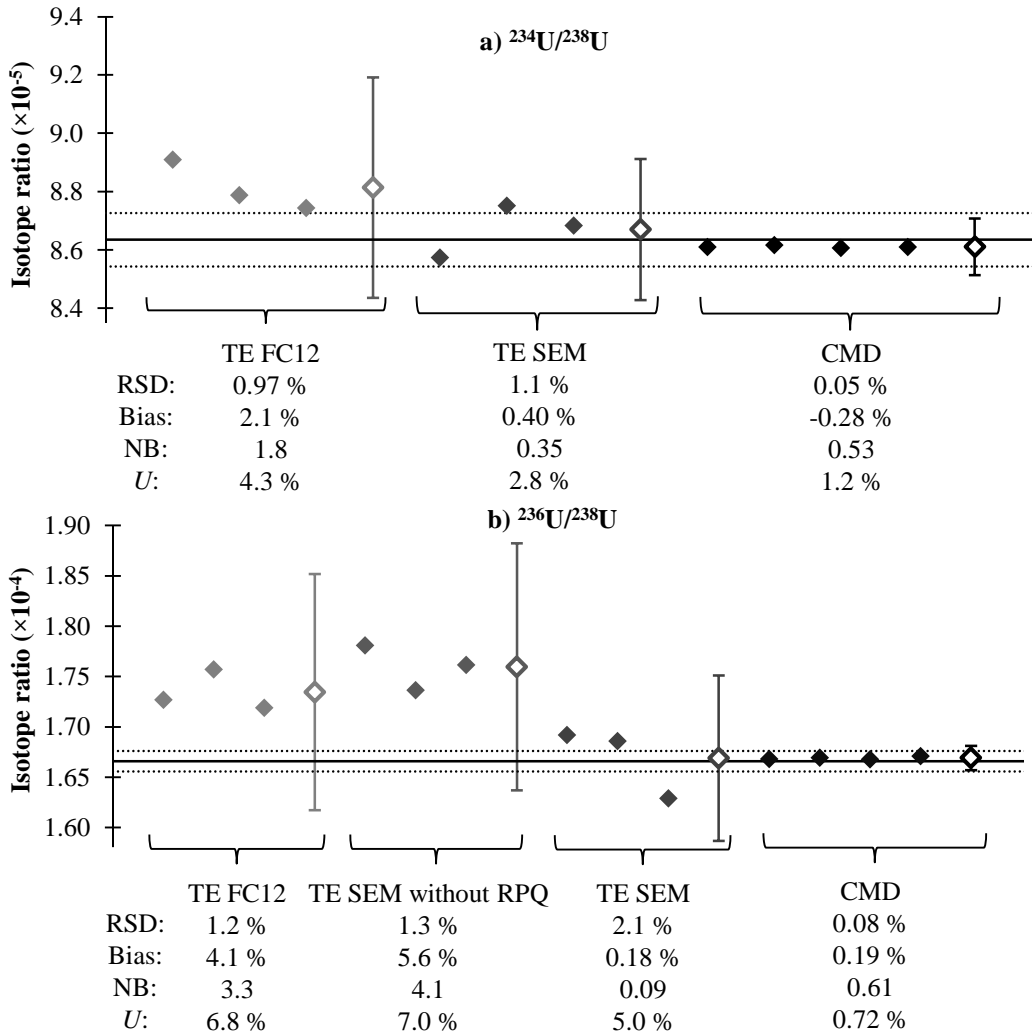
495

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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