



HAL
open science

Development and comparison of two high accuracy methods for uranium concentration in nuclear fuel: ID-TIMS and K-edge densitometry

Alexandre Quemet, Alexandre Ruas, Eric Esbelin, Vincent Dalier, Cédric Rivier

► To cite this version:

Alexandre Quemet, Alexandre Ruas, Eric Esbelin, Vincent Dalier, Cédric Rivier. Development and comparison of two high accuracy methods for uranium concentration in nuclear fuel: ID-TIMS and K-edge densitometry. *Journal of Radioanalytical and Nuclear Chemistry*, 2019, 321 (3), pp.997-1004. 10.1007/s10967-019-06670-y . cea-03470768

HAL Id: cea-03470768

<https://cea.hal.science/cea-03470768>

Submitted on 8 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1

Title

2 Names of the authors: Alexandre Quemet¹, Alexandre Ruas², Eric Esbelin¹, Vincent
3 Dalier¹ and Cédric Rivier¹

4 Title: Development and comparison of two high accuracy methods for uranium
5 concentration in nuclear fuel: ID-TIMS and K-edge densitometry

6 Affiliation(s) and address(es) of the author(s):

7 - ¹ CEA, DEN, DMRC, SA2I, L2AT, BP17171, 30207 Bagnols sur Cèze, France

8 - ² Onsite Laboratory Team, Nuclear Material Laboratory, Office of Safeguards
9 Analytical Services, Department of Safeguards, International Atomic Energy
10 Agency, Tokyo Regional Office, Seibunkan Bldg, 9F, 1-5-9 Iidabashi, Chiyoda-ku,
11 Tokyo 102-0072, Japan

12 E-mail address of the corresponding author: alexandre.quemet@cea.fr

13

14 **Development and comparison of two high accuracy**
15 **methods for uranium concentration in nuclear fuel:**
16 **ID-TIMS and K-edge densitometry**

17 Alexandre Quemet¹, Alexandre Ruas², Eric Esbelin¹, Vincent Dalier¹ and Cédric Rivier¹

18 ¹*CEA, DEN, DMRC, SA2I, L2AT, BP17171, 30207 Bagnols sur Cèze, France*

19 ²*Onsite Laboratory Team, Nuclear Material Laboratory, Office of Safeguards Analytical*
20 *Services, Department of Safeguards, International Atomic Energy Agency, Tokyo*

21 *Regional Office, Seibunkan Bldg, 9F, 1-5-9 Iidabashi, Chiyoda-ku, Tokyo 102-0072,*

22 *Japan*

23 **Abstract**

24 This study compares the two analytical methods for uranium concentration determination
25 with high accuracy in uranium pellet: K-edge densitometer (KED) and the isotope dilution
26 with Thermal Ionisation Mass Spectrometry measurements (ID-TIMS). Both techniques
27 are compared in terms of time, generated radioactive effluent, simplicity, uncertainty
28 estimation and detection limit. ID-TIMS shows lower detection limit and uncertainties than
29 KED. However, the KED analysis time is shorter and generates less effluent. Both
30 techniques were used for metrological analysis of uranium concentration in nuclear
31 materials. The optimization of sample spike mixture isotope ratio for ID-TIMS to decrease
32 uncertainties is also discussed.

33 **Keywords**

34 Uranium concentration; TIMS; K-edge densitometer; isotope dilution

35

36 **Introduction**

37 Uranium detailed accountancy is of prime interest in the nuclear industry, at various stages
38 of the nuclear fuel cycle and for safeguards purposes [1–3]. ATALANTE is a nuclear
39 facility of the French Alternative Energies and Atomic Energy Commission (CEA) and
40 dedicated to the research on the nuclear spent fuel reprocessing. Studies such as nuclear
41 fuel dissolution, actinides separation and precipitation are performed, requiring to
42 determine the uranium concentration with high accuracy.

43 Among the specific analytical techniques available in such facility, K-edge densitometry
44 (KED) is an effective technique to determine uranium assay in nuclear fuel dissolution
45 solution [4, 5]. KED is an X-ray absorbance spectrometry technique based on the Beer-
46 Lambert's law. The uranium concentration in solution is proportional to the X-ray
47 attenuation. High uranium concentrations, typically above 50 g L⁻¹, can be measured with
48 high accuracy. For lower concentration, spectral discontinuities make the spectrum process
49 difficult and uncertainties increase significantly. K-edge spectrometry is a nondestructive,
50 non-invasive, relatively fast technique and requires little sample preparation.

51 Isotope Dilution (ID) is a well-known method for quantification based on internal
52 calibration [6, 7]. The ID principle is to mix a known amount of sample containing a known
53 isotope composition with a spike solution containing a known concentration and isotope
54 composition. The spike solution contains the same analyte as the sample with a different
55 isotope composition. The isotope ratio of the sample – spike mixture reflects the sample
56 analyte concentration. The ID methodology requires only isotope ratio measurements and
57 knowing masses involved in the sample – spike mixture. As it is based on isotope ratio
58 determination, an accurate technique for isotope ratio measurements must be preferred.
59 Thermal-Ionization Mass Spectrometry (TIMS) is the reference technique for the accurate
60 determination of uranium isotope ratios [8–13]. The ID methodology coupled to TIMS for
61 the isotope ratio measurements (ID-TIMS) is then a powerful combination for the uranium
62 concentration determination.

63 The present study was performed in the context of the “2017 Nuclear Material Round
64 Robin” organized by the International Atomic Energy Agency (IAEA) which aims at
65 determining the uranium isotope ratio and mass fraction in nuclear materials. The isotope
66 ratios determination was presented in a previous paper [10]. This paper presents a
67 comparison between the ID-TIMS and the K-edge densitometry for the uranium
68 concentration determination with high accuracy in a uranium pellet.

69 **Experimental**

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

71 All solutions were prepared in polypropylene vials, except for uranium solutions, which
72 were prepared in PFA vials. 1 mol L⁻¹, 3 mol L⁻¹ and 8 mol L⁻¹ nitric acid solutions were
73 prepared by diluting high purity nitric acid (Merck, Suprapur) in deionized water
74 (resistivity: 18.2 MΩ.cm). A high accuracy scale (Mettler-Toledo, WXTP 205) was used
75 to prepare all solutions.

76 The spike solution used in the ID methodology was the IRMM 054 certified reference
77 material (CRM) provided by the Joint Research Centre of the European Commission
78 (EC-JRC). This CRM contains high amounts of the ²³⁵U isotope and is certified for the
79 concentration and the isotope ratios. This solution was diluted gravimetrically in order to
80 obtain a uranium concentration near 10 μg g⁻¹.

81 **Sample preparation**

82 The inter-laboratory comparison (ILC) sample is a low enrichment uranium oxide pellet.
83 The K-edge densitometer available in the laboratory and the TIMS require working with
84 solutions. The ILC uranium pellet was dissolved in hot nitric acid (8 mol L⁻¹). This solution
85 (pellet + nitric acid) was heated to 135 °C in a PFA vial until complete dissolution. The
86 dissolution solution had about 250 g L⁻¹ uranium concentration [10].

87 Instrumental

88 *Thermal Ionization Mass Spectrometer*

89 The Thermo Fisher Triton and VG Sector 54 TIMS used for the experiments and the
90 deposit technique were previously described in detail [14]. The measurements were
91 performed using Faraday cups coupled to $10^{11} \Omega$ current amplifiers (hereafter referred to
92 as FC 11). All the isotope ratio measurements were performed with the total evaporation
93 method (TE method) described previously [10]. The $^{238}\text{U}^+$ ion beam target intensity was
94 set at 1 V and 2.2 V for the VG Sector 54 and for the Triton TIMS, respectively.

95 The uranium concentration ($[\text{U}]_S$) was determined using isotope dilution according to Eq.
96 (1):

$$[\text{U}]_S = [\text{U}]_T \cdot \frac{m_T}{m_S} \cdot \frac{M_S}{M_T} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \quad (1)$$

97 Where T refers to the spike (or tracer), Mix refers to the sample - spike mixture and S refers
98 to the sample; m are the masses involved in the mixture, M are the atomic weights, (235)
99 and (238) are the isotope abundances. R_{mix} and R_T correspond to the $^{238}\text{U}/^{235}\text{U}$ mixture and
100 spike isotope ratio, respectively. R_S corresponds to the $^{235}\text{U}/^{238}\text{U}$ sample isotope ratio. The
101 isotopic composition of the pellet (needed for the $[\text{U}]_S$ calculation by ID-TIMS) was
102 determined with high accuracy measurements in the previous study [10].

103 The uranium mass fraction determination by ID-TIMS was performed using the two TIMS
104 available in the laboratory with 3 different determinations. First, 3 diluted dissolution
105 solutions ($[\text{U}] \approx 10 \mu\text{g g}^{-1}$ and hereafter referred to as diluted solution 1, 2 or 3) were
106 prepared gravimetrically from the initial dissolution solution ($[\text{U}]_i \approx 250 \text{ g.L}^{-1}$). Then, 5
107 (diluted solution 1 – spike) mixtures, 3 (diluted solution 2 – spike) mixtures and 2 (diluted
108 solution 3 – spike) mixtures were prepared gravimetrically. Each mixture was evaporated
109 after preparation, and then dissolved again in $10 \mu\text{L}$ of 1 mol L^{-1} nitric acid. $1 \mu\text{L}$ (about
110 400 ng of U) of this final solution was deposited onto a filament for each individual

111 measurement. The $^{238}\text{U}/^{235}\text{U}$ isotope ratio of each mixture was analyzed using the TE
112 method. The $^{238}\text{U}/^{235}\text{U}$ ratios ranged from 1.08 to 1.23. The 5 (diluted solution 1 – spike)
113 mixtures were analyzed using the VG Sector 54 TIMS. The uranium concentration was the
114 average of the 5 individual measurements. The (diluted solution 2 and 3 – spike) mixtures
115 were analyzed using the Triton TIMS and the respective uranium concentrations were
116 determined by computing the average of each respective individual measurements. Finally,
117 the uranium mass fraction of the pellet was the average of the 3 groups of determination.

118 *K-edge densitometry*

119 The nuclearized KED used for the experiments was previously described in details [4]. The
120 X-ray generator and X-ray tube (W anode, MG165) are marketed by Yxlon. The tube
121 configuration used in the laboratory is 150 kV and 10 mA for assay sample measurements,
122 or 5 mA for blank reference solution measurements. The detectors are hyper-pure Ge
123 crystals (Canberra EGX 200-10, active area 200 mm²) cooled with liquid nitrogen. The
124 acquisition electronics are Canberra DSA-1000 coupled with Genie 2000 software. The
125 spectral data were processed using a CEA developed software using standardless
126 algorithms [4]. Measurements are performed without any calibration except for energy.
127 The typical counting time was 1000 s.

128 This device is located in the back area of the analysis hot cell line of ATALANTE. The
129 sample, packaged in small polypropylene vials, is transferred *via* a pneumatic line from the
130 hot cell to the KED. The minimum volume required to ensure the X-rays are absorbed by
131 the sample in this system is about 1.5 mL.

132 The dissolution solution was analyzed by KED without any further preparation except vial
133 transfer. The result was obtained from the average of 5 individual measurements of the
134 same vial containing the dissolution solution. Between each individual measurement, the
135 vial was returned to the hot cell line before a new transfer back to the KED in order to take
136 into account the uncertainties due to the vial position in the KED. The concentration
137 determined using the KED system was in g L⁻¹. In order to obtain the uranium mass fraction

138 in the pellet, the dissolution solution density is necessary and was performed with an
139 Anton-Paar DMA 58 density meter.

140 Results evaluation and uncertainties estimation

141 *Results evaluation*

142 The bias was calculated using Eq. (2).

$$\text{Bias (\%)} = \frac{[\text{U}] - \text{cert}}{\text{cert}} \cdot 100 \quad (2)$$

143 Where [U] is the uranium concentration determined by ID-TIMS or KED and *cert* is the
144 ILC assigned value.

145 The precision was evaluated by computing the Relative Standard Deviation (RSD) of all
146 the measurements.

147 Eq. (3) was used to determine if the analytical method has a statistically significant bias
148 [15]. If the normalized bias (*NB*) was lower than 2, the method was considered having no
149 statistically significant bias.

$$\text{NB} = \frac{|[\text{U}] - \text{cert}|}{\sqrt{u^2([\text{U}]) + u_{\text{cert}}^2}} \quad (3)$$

150 Where $u([\text{U}])$ is the uranium concentration uncertainty determined by ID-TIMS or KED at
151 $k = 1$ and u_{cert} is the assigned value uncertainty at $k = 1$.

152

153

154 Uranium concentration uncertainty using ID-TIMS

155 The uranium concentration uncertainty ($u([U]_s)$, at $k = 1$), determined by ID-TIMS shown
 156 in Eq. (4), was estimated by combining the uncertainties from each term of Eq. (1). The
 157 terms of Eq. (1) were considered as not correlated.

$$\begin{aligned}
 u^2([U]_s) = & \left(\frac{m_T}{m_S} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2([U]_T) \\
 & + \left([U]_T \cdot \frac{1}{m_S} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2(m_T) \\
 & + \left(-[U]_T \cdot \frac{m_T}{m_S^2} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2(m_S) \\
 & + \left([U]_T \cdot \frac{m_T}{m_S} \cdot \frac{1}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2((235)_T) \\
 & + \left(-[U]_T \cdot \frac{m_T}{m_S} \cdot \frac{(235)_T}{(238)_S^2} \cdot \frac{M_S}{M_T} \cdot \frac{R_{\text{Mix}} - R_T}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2((238)_S) \\
 & + \left([U]_T \cdot \frac{m_T}{m_S} \times \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{(R_{\text{Mix}} - R_T) \cdot R_{\text{Mix}}}{(1 - R_{\text{Mix}} \cdot R_S)^2} \right)^2 \cdot u^2(R_S) \\
 & + \left(-[U]_T \cdot \frac{m_T}{m_S} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{1}{1 - R_{\text{Mix}} \cdot R_S} \right)^2 \cdot u^2(R_T) \\
 & + \left([U]_T \cdot \frac{m_T}{m_S} \cdot \frac{(235)_T}{(238)_S} \cdot \frac{M_S}{M_T} \cdot \frac{1 - R_T \cdot R_S}{(1 - R_S \cdot R_{\text{Mix}})^2} \right)^2 \cdot u^2(R_{\text{Mix}}) + u^2(\text{dilution}) \\
 & + u^2(\text{precision})
 \end{aligned} \tag{4}$$

158 In Eq. (4), the molar masses uncertainties were considered negligible and were not taken
 159 into account for the final uncertainty computation. The term $u(\text{precision})$ is the method
 160 precision, corresponding to the standard deviation of the 3 groups of determination. The
 161 term $u(\text{dilution})$ is the sample dilution uncertainty. The concentration ($[U]_T$), isotope ratio
 162 (R_T) and isotope abundance ($(235)_T$) related to the spike solution and their respective
 163 uncertainties were given in the CRM certificate (Table 1). The sample isotope ratio (R_S)
 164 and isotope abundance ($(238)_S$) were estimated in a previous study by the TE method for

165 the $^{235}\text{U}/^{238}\text{U}$ isotope ratio and the classical method with multi-dynamic sequences for the
166 $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios (required to compute the ^{238}U isotope abundance)
167 [10].

168 The sample (m_S) and spike (m_T) masses uncertainties involved in the mixture were
169 estimated by taking into account the trueness, drift and resolution of the scale and the
170 method precision (Eq. (5)) [16]. The scale trueness and drift were estimated with a type B
171 evaluation and a uniform law (first term in Eq. (5)). This term corresponds to the maximum
172 permissible errors (MPE) fixed by the laboratory divided by square root of 3. The scale
173 resolution (q) uncertainty was also estimated using a type B evaluation and a uniform law
174 (second term in Eq. (5)). The method precision, including scale precision and operator
175 effect, corresponds to the experimental standard deviation obtained from a series of n
176 measurements divided by the square root of n and was a type A evaluation (third term in
177 Eq. (5)). The air buoyancy (Archimedes' principle) was taken into account for the masses
178 correction and its uncertainty was considered negligible.

$$u^2(m) = \left(\frac{MPE}{\sqrt{3}}\right)^2 + \left(\sqrt{\frac{q^2}{12}}\right)^2 + \left(\frac{s}{\sqrt{n}}\right)^2 \quad (5)$$

179 The mixture isotope ratio uncertainty was estimated at 0.14 % ($k = 2$), corresponding to
180 the International Target Value (ITV) for a $^{235}\text{U}/^{238}\text{U}$ isotope ratio of about 1 [17]. A similar
181 uncertainty was previously estimated for a $^{235}\text{U}/^{238}\text{U}$ isotope ratio close to 1 in these
182 working condition using the TE method with FC 11 [14].

183 *Investigation on the optimum isotope ratio of the mixture for the* 184 *ID-TIMS*

185 The ID-TIMS require an optimum mixture isotope ratio (R_{Mix}), which can be determined
186 theoretically [18]. The ID-TIMS parameters other than the mixture isotope ratio ($[\text{U}]_T$, m_T ,
187 m_S , $(235)_T$, $(238)_S$, R_S or R_T) depend only on the sample and spike characteristics and on

188 the mixture masses. These parameters were assumed constant for the theoretical study
189 hereafter described and equal to the values presented in Table 1.

190 Using Eq. (1) and the fixed parameters given in the Table 1, it is possible to compute using
191 a spreadsheet the sample concentration for a given mixture isotope ratio. This $^{238}\text{U}/^{235}\text{U}$
192 mixture isotope ratio is between the sample (0.0581) and spike (50.87) isotope ratios.

193 Likewise, the sample concentration uncertainty can be computed using Eq. (4) for each
194 mixture isotope ratio included between the $^{238}\text{U}/^{235}\text{U}$ sample and spike isotope ratios. The
195 $u(\textit{precision})$ and $u(\textit{dilution})$ terms were assumed to be constant in this theoretical study.
196 The $u(\textit{precision})$ term was set at 0.06 % ($k = 1$), which is a value previously obtained in
197 our laboratory for actinide concentration determination by ID-TIMS [14]. The $u(\textit{dilution})$
198 term was set at 0.034 %, which is an arbitrary value commonly observed in our laboratory
199 for this type of dilution. These 2 set values are not function of the mixture isotope ratio and
200 do not change the optimum determination. By combining Eq. (1) and (4), the concentration
201 relative uncertainty ($u([\text{U}]/[\text{U}], k = 1)$), as a function of the mixture isotope ratio, can be
202 drawn from the spreadsheet (Fig. 1). The optimum mixture isotope ratio is obtained when
203 the function reaches its minimum.

204 In our analysis conditions, the optimum mixture isotope ratio is obtained for a $^{238}\text{U}/^{235}\text{U}$
205 isotope ratio of 1.7 (Fig. 1). Experimentally, it is possible to adjust the sample and spike
206 solution amount in the mixture to be closer to the optimum mixture isotope ratio. In
207 addition, this theoretical study shows that the sample concentration relative uncertainty is
208 almost stable around the optimum isotope ratio. It shows that the uncertainty increases
209 large when the mixture isotope ratio approaches the spike or sample isotope ratios. The
210 mixture isotope ratios from 1.08 to 1.23 (which are the ratios measured in this study),
211 increase the concentration uncertainty only by 0.09 % to 0.18 % compared to the best
212 theoretically achievable uncertainty.

213 *Uranium concentration uncertainty using KED analysis*

214 The main parameters to take into account for the concentration uncertainty by KED
215 measurement are: the instrument variability (X-ray tube, detector), the vial position, the
216 counting time precision, the vial length, the sample matrix and the theoretical values of
217 mass attenuation coefficients. The uranium concentration relative uncertainty $u([U])/[U]$
218 ($k = 1$) was estimated using Eq. (6). The first three terms correspond to the KED
219 measurement uncertainty. The fourth term is the density uncertainty of the dissolution
220 solution at $k = 1$ and also includes the density difference between the density and KED
221 measurements as the two measurements were not performed at the exact same temperature.
222 The first term of Eq. (6) takes into account the measurement precision component. It
223 includes the uncertainty from random effects (instrument variability, vial position and
224 counting time precision) and is given by the RSD of all the measurements. The second and
225 third terms take into account the systematic error components (vial length, sample matrix
226 and theoretical values of mass attenuation coefficients). The measurement trueness
227 ($u^2(\text{trueness})/(\text{trueness})^2$) is calculated with Eq. (7). The CRM were chosen so that they
228 respected different criteria: same element, similar analyte concentration and matrix. The
229 EQRAIN solutions, provided by the CEA/CETAMA during ILC were used [4]. They were
230 chosen because: the analyte is the same, the uranium concentrations are close (about 250
231 and 360 g L⁻¹ for the EQRAIN solutions and about 280 g L⁻¹ for the dissolution sample)
232 and the matrix is the same (uranium only in HNO₃ media). Only the EQRAIN solutions
233 analyzed using the same configuration and the same detector as the dissolution sample (as
234 the detector was changed in 2016) were used to compute the trueness term.

235 The term $u^2(\text{ref})/(\text{ref})^2$ corresponds to the CRM (EQRAIN U) concentration relative
236 uncertainty at $k = 1$.

$$\frac{u^2([U])}{([U])^2} = \frac{u^2(\bar{x})}{\bar{x}^2} + \frac{u^2(\text{trueness})}{(\text{trueness})^2} + \frac{u^2(\text{ref})}{(\text{ref})^2} + \frac{u^2(\text{density})}{(\text{density})^2} \quad (6)$$

$$\frac{u(\text{trueness})}{\text{trueness}} = \frac{\text{Maximum bias on CRM}}{\sqrt{3}} \quad (7)$$

237 **Results and discussion**

238 ID-TIMS

239 The results are presented in Table 2. The RSD of the 3 groups of determinations is equal
240 to 0.12 %. The result obtained for the uranium mass fraction of the pellet is
241 $0.8835 \pm 0.0028 \text{ g g}^{-1}$ ($k = 2$). The bias is equal to 0.30 %. The relative uncertainty,
242 computed with Eq. (4), is estimated at 0.32 % and is in compliance with the safeguard ITV
243 (0.36 %, $k = 2$) [17]. The relative contribution study (expressed in percent) of the main
244 uncertainty sources for the uranium mass fraction is given in Fig. 2. The spike
245 concentration uncertainty (0.04 %) has a very low contribution and is a minor source of
246 uncertainty (4.2 % of the total budget). The main uncertainty sources are the precision
247 (59.4 % of the total budget), the dilution to obtain a sample concentration of about $10 \mu\text{g g}^{-1}$
248 ($^{238}\text{U}/^{235}\text{U}$ sample - spike mixture isotope ratio
249 determination (14.1 % of the total budget).

250 KED

251 A uranium concentration of $278.4 \pm 2.1 \text{ g L}^{-1}$ ($k = 2$) was found for the dissolution solution.
252 Considering the dissolution solution density and the mass of the initial pellet before
253 dissolution, the uranium mass fraction of the pellet is estimated to $0.8807 \pm 0.0067 \text{ g g}^{-1}$
254 ($k = 2$, Table 2). The RSD of the 5 individual determinations is 0.33 %. The bias is below
255 0.1 %. The uranium mass fraction determined using the KED system is in compliance with
256 the assigned value provided by the IAEA: the normalized bias is equal to 0.09. The relative
257 uncertainty is estimated to 0.76 % and is slightly higher than the ITV (0.56 %, $k = 2$) [17].
258 The study of the main uncertainty sources shows the total uncertainty is mainly due to the
259 precision (76 % of the total uncertainty). The trueness component (18 % of the total
260 uncertainty) and the CRM reference uncertainty component (6 % of the total uncertainty)
261 have a minor contribution to the total uncertainty. The density uncertainty contribution is
262 negligible: below 0.2 % of the total uncertainty.

263 ID-TIMS and KED comparison

264 The ID-TIMS and the KED perform uranium assay with high accuracy. However, in terms
265 of analytical performance, implementation, analysis time and generated radioactive
266 effluent, they have different assets (Table 3).

267 The KED requires high uranium concentration solution in order to obtain the lowest
268 uncertainties: uranium concentration higher than 50 g L^{-1} is needed to get relative expanded
269 uncertainties ($k = 2$) lower than 1%. The TIMS analyses require a lower uranium amount
270 than the KED: less than $1 \mu\text{g}$ of uranium is required for TIMS analyses. Solutions
271 containing less than 1 mg L^{-1} of uranium can be analyzed by ID-TIMS and the ITV can
272 still be achieved (0.36 %, $k = 2$). The ID-TIMS gives directly the uranium mass fraction in
273 the nuclear materials, whereas the density determination for the KED system is required
274 beforehand. Both techniques showed no significant bias compared to the assigned value:
275 the normalized biases are below 2. The ID-TIMS uncertainty estimation (0.32 %, $k = 2$)
276 was in compliance with the ITV and was lower than the KED uncertainty estimation
277 (0.76 %, $k = 2$).

278 Both techniques require an identical pellet dissolution step. KED analysis can be performed
279 directly on the dissolution solution (matrix $8 \text{ mol L}^{-1} \text{ HNO}_3$). No solution treatment, no
280 dilution and no calibration are required [4]. Cross contamination is then limited. As the
281 KED system is a nondestructive technique, the same aliquot can be used to measure
282 uranium with the KED system and be used for others analyses like isotopic, radiometric or
283 density measurements (in some situations, taking into account evaporation loss is
284 necessary). High activity solution can be analyzed with the KED system as it is installed
285 in a shielded line. The TIMS can be installed in glove box environment but not in a hot
286 cell: high activity solutions require a dilution step in order to be suitable for working in
287 glove box. The dilution step is also required in order not to consume too much of the
288 solution spike. Indeed, for spiking the dissolution solution directly would have a
289 prohibitive cost as the spike solution quantity would be important. For very irradiating
290 samples such as high active liquid waste, the spiking step must be done in the hot cell
291 before the sample transfers.

292 As the analytical protocol is very different, both techniques present different analysis time.
293 For KED, about 5 minutes are required to prepare the sample in the analytical vial. The
294 analysis time is about 1 h 15 for 5 analysis of the same sample (about 15 min for 1
295 determination). Considering the fast analysis time of the KED system; the dissolution
296 solution density determination is the most critical step to the total analysis time (about
297 5 h 20). The ID-TIMS analysis overall process takes longer than the KED analysis. The
298 dilution step is performed in 1 h. The sample preparation, including sample - spike mixture
299 preparation, sample - spike mixture evaporation, deposit onto the filament, filament
300 loading inside the TIMS source take about 8 h in total. Then, the vacuum must be drawn
301 inside the source (about 4 h). This step is generally not critical in terms of operator working
302 time as the filament loading can be done at the end of a working day and the vacuum inside
303 the source can be obtain overnight. The analysis time of the 10 sample - spike mixtures
304 with the TE method requires about 9 h of work: Faraday cups calibration duration is about
305 10 min per day of use, heating filament about 10 min per analysis, signal optimization
306 about 5 min per analysis, the analysis time duration is about 30 min and the shutdown is
307 about 2 min per analysis. The ID-TIMS methodology requires also the sample isotope
308 determination. In total, we have calculated the analysis time for the sample isotope
309 determination with TIMS at 19 h [10]. The total ID-TIMS analysis time is estimated at
310 41 h, thus about 8 times higher for the ID-TIMS than KED.

311 The KED system does not consume the sample solution as it is a nondestructive technique
312 and generates no effluent as there is no dilution step. However, this technique consumes
313 sample solution indirectly as the density determination requires about 2 mL that cannot be
314 reused due to possible cross-contamination. The effluent generated for cleaning the density
315 meter represents about 10 mL. The total effluent generated was 12 mL, only due to density
316 determination. Moreover, the used KED system requires at least 1.5 mL of solution, which
317 can be a disadvantage when the available sample volume is low. The TIMS analyses need
318 a dilution step as uranium concentration is high (higher than 1 g.L^{-1}). In this study, 600 μL
319 of the dissolution solution was used, corresponding to $3 \times 200 \mu\text{L}$ for the 3 determinations
320 by ID-TIMS. 200 μL of solution (about 300 mg of uranium) is enough to obtain an accurate
321 weight without generating too much nuclear effluent. The generated effluent was estimated
322 at 60 mL for one determination. In this study, the 3 determinations generated 180 mL of

323 effluent, only due to the dilution step. The ID-TIMS (0.6 mL) consumes less sample than
324 the KED system (2 mL required only for the density determination). However, the KED
325 system generates 15 times less volume of radioactive effluent.

326 **Conclusions**

327 This study presents a comparison between the ID-TIMS and the KED system for uranium
328 concentration determination with high accuracy. The results obtained with both techniques
329 are in compliance with the assigned value. Both techniques can be used for metrological
330 analysis of high uranium concentration while having different assets. The minimal
331 measurable concentration with ID-TIMS is lower than the KED's. The analysis time is
332 about 8 time higher for the ID-TIMS than for the KED. The ID-TIMS generates about 15
333 times more radioactive effluent. However, in our studies, only the estimated uncertainties
334 obtained with ID-TIMS are in compliance with the ITV. The estimated uncertainties
335 obtained with the KED are slightly higher.

336 The main approach to decrease the KED uncertainty, in order to be closer to the ITV, is to
337 improve the measurement precision as it is the main uncertainty source (76 % of the total
338 uncertainty budget). The vial position which may vary slightly from an analysis to another
339 in the KED system and the instrument variability (X-ray tube, detector) are the main
340 parameters influencing the method precision as well as the final uncertainty. An approach
341 to decrease the precision due to the instrument variability would be increasing the
342 measurement time. Even with a measurement time of 1 hour (15 min at present), the KED
343 would be faster than ID-TIMS. The precision due to the instrument variability would be
344 improved. However the precision due to the vial position would be the same whatever the
345 measurement time. The method used in the laboratory is a calibration free method, which
346 slightly increases the estimated uncertainties compared to methods using standard
347 calibration. A calibration would correct all physical phenomena including the ones that are
348 difficult to take into account in theoretical models. However, this correction would only
349 modify the method trueness. Therefore this would not change much the final uncertainty
350 as the trueness has a low contribution part in the final uncertainty (18 % of the total

351 uncertainty). The KED data were also processed using the algorithms with fitting windows
352 as proposed in [5] in order to show the influence on the repeatability. The repeatability
353 were similar for either the algorithms using fitting windows (RSD = 0.47 %) or our in-
354 house algorithm (RSD = 0.33 %). In addition, the KED system used for this study is
355 designed for dissolution or separation R&D studies that need quick results during the
356 experiments. Our KED system, implemented in hot-cell facility and used as a calibration
357 free method, is fully compatible for this type of application.

358 **Acknowledgements**

359 We are grateful to Dr. S. Baghdadi (IRSN/PSN-EXP/SSRD/BTE) for her precious advice
360 on the present paper. We would like to thank all of the IAEA staff (Seibersdorf-Austria)
361 who organized the interlaboratory comparison and all the KED staff for the KED
362 measurements.

363 **Table**

364 Table 1: Parameters used for the theoretical study of our studied case in order to find the
 365 optimum sample – spike mixture isotope ratio in the ID-TIMS

Parameters	Value	Uncertainty (k=1)
$[U]_T$	9.5044	0.0039
m_T	0.246555	0.000059
m_S	0.218465	0.000059
M_S	237.992	-
M_T	235.201	-
$(^{235})_T$	93.1760	0.0034
$(^{238})_S$	98.053	0.010
R_S	0.019658	0.000015
R_T	0.058065	0.000017
Parameters	Value	Relative Uncertainty (k=1)
R_{Mix}	Between 0.0586 and 50.87	0.07 %

366

367

368

369

370

371

372 Table 2: Uranium mass fraction determined by ID-TIMS and KED obtained on the
 373 uranium pellet. U_{ass_val} corresponds to the assigned value uncertainty ($k = 2$) and U
 374 corresponds to the total uncertainty ($k = 2$). NB corresponds to the normalized bias

Method	Uranium mass fraction	
	ID-TIMS	KED
Assigned value (g g^{-1})	0.88110	0.88110
Results (g g^{-1})	0.8835	0.8807
<i>RSD</i> (%)	0.12	0.33
<i>NB</i>	1.8	0.09
Bias (%)	0.28	-0.04
U_{ass_val} (% , $k = 2$)	0.05	0.05
U (% , $k = 2$)	0.32	0.76
<i>ITV</i> (% , $k = 2$)	0.36	0.56

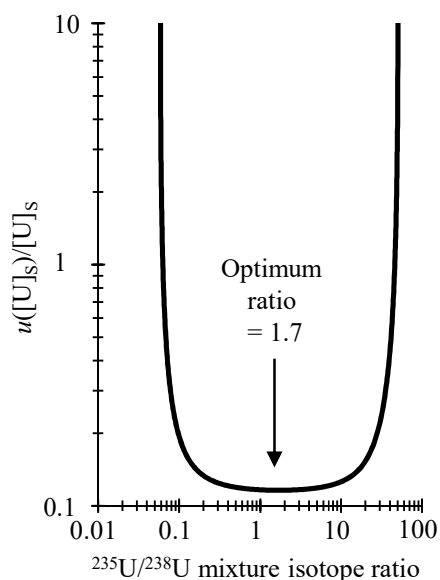
375

376 Table 3: Experimental duration and effluents

Technique	ID-TIMS	KED
		<u>Duration</u>
Dilution step	1 h	/
Sample preparation	12 h	5 min
Analysis	9 h	1 h 15 (5×15 min)
Density	/	4h
Isotope determination	19 h	/
Total	41 h	5h20
		<u>Waste management</u>
Sample solution consumption	600 μL	- 2 mL for the density determination - 0 mL for the KED analysis
Generated effluent	180 mL for the dilution step	10 mL for the density determination

377

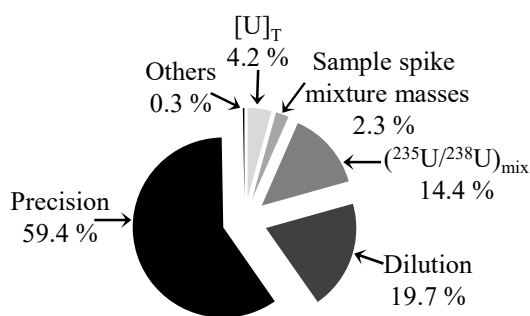
378 **Figure**



379

380 **Fig. 1:** Schematic of the uranium concentration relative uncertainty ($u([U]_s)/[U]_s$, %, $k = 1$) as a function of the mixture isotope ratio in order to find the optimum mixture
 381 isotope ratio in our studied case. The $[U]_s$ and $u([U]_s)$ terms were calculated using Eq.
 382 (1) and Eq. (4), respectively, considering all the isotope dilution terms constants (Table 1)
 383 except the mixture isotope ratio value
 384

385



386

387 **Fig. 2:** Relative contribution (%) of the main uncertainty sources for the uranium mass
 388 fraction determined by ID-TIMS

389

390 **References**

- 391 1. Godoy MLDP, Godoy JM, Roldão LA, Tauhata L (2009) Determination of total
392 content and isotopic compositions of plutonium and uranium in environmental
393 samples for safeguards purposes by ICP-QMS. *J Environ Radioact* 100:613–625.
394 doi: 10.1016/j.jenvrad.2009.04.012
- 395 2. Metzger SC, Ticknor BW, Rogers KT, Bostick DA, McBay EH, Hexel CR (2018)
396 Automated Separation of Uranium and Plutonium from Environmental Swipe
397 Samples for Multiple Collector Inductively Coupled Plasma Mass Spectrometry.
398 *Anal Chem* 90:9441–9448. doi: 10.1021/acs.analchem.8b02095
- 399 3. Boulyga S, Konegger-Kappel S, Richter S, Sangély L (2015) Mass spectrometric
400 analysis for nuclear safeguards. *J Anal At Spectrom* 30:1469–1489. doi:
401 10.1039/c4ja00491d
- 402 4. Esbelin E, Rivier C, Duhamel G (2018) High concentration measurements of U and
403 Pu with nondestructive and standardless K-edge densitometer device. *X-Ray*
404 *Spectrom* 47:22–33. doi: 10.1002/xrs.2802
- 405 5. Ottmar H, Eberle H (1991) The hybrid K-edge/K-XRF densitometer: Principles-
406 design-performance. KFK Rep. 4590, Karlsruhe
- 407 6. Quemet A, Maillard C, Ruas A (2015) Determination of zirconium isotope
408 composition and concentration for nuclear sample analysis using Thermal Ionization
409 Mass Spectrometry. *Int J Mass Spectrom* 392:34–40. doi:
410 10.1016/j.ijms.2015.08.023
- 411 7. Aggarwal SK (2016) Thermal ionisation mass spectrometry (TIMS) in nuclear
412 science and technology – a review. *Anal Methods* 8:942–957. doi:
413 10.1039/c5ay02816g
- 414 8. Quemet A, Maloubier M, Dalier V, Ruas A (2014) Development of an analysis
415 method of minor uranium isotope ratio measurements using electron multipliers in

- 416 thermal ionization mass spectrometry. *Int J Mass Spectrom* 374:26–32. doi:
417 10.1016/j.ijms.2014.10.008
- 418 9. Quemet A, Maloubier M, Ruas A (2016) Contribution of the Faraday cup coupled
419 to 1012 ohms current amplifier to uranium 235/238 and 234/238 isotope ratio
420 measurements by Thermal Ionization Mass Spectrometry. *Int J Mass Spectrom*
421 404:35–39. doi: 10.1016/j.ijms.2016.04.005
- 422 10. Quemet A, Ruas A, Dalier V, Rivier C (2019) Development and comparison of high
423 accuracy thermal ionization methods for uranium isotope ratios determination in
424 nuclear fuel. *Int J Mass Spectrom* 438:166–174. doi: 10.1016/j.ijms.2019.01.008
- 425 11. Richter S, Kühn H, Aregbe Y, Hedberg M, Horta-Domenech J, Mayer K, Zuleger
426 E, Bürger S, Boulyga S, Köpf A, Poths J, Mathew K (2011) Improvements in routine
427 uranium isotope ratio measurements using the modified total evaporation method
428 for multi-collector thermal ionization mass spectrometry. *J Anal At Spectrom*
429 26:550–564. doi: 10.1039/C0JA00173B
- 430 12. Wegener MR, Mathew KJ, Hasozbek A (2013) The direct total evaporation (DTE)
431 method for TIMS analysis. *J Radioanal Nucl Chem* 296:441–445. doi:
432 10.1007/s10967-012-2182-3
- 433 13. Mathew KJ, O'Connor G, Hasozbek A, Kraiem M (2013) Total evaporation method
434 for uranium isotope-amount ratio measurements. *J Anal At Spectrom* 28:866–876.
- 435 14. Quemet A, Ruas A, Dalier V, Rivier C (2018) Americium isotope analysis by
436 Thermal Ionization Mass Spectrometry using the Total Evaporation Method. *Int J*
437 *Mass Spectrom* 431:8–14. doi: 10.1016/j.ijms.2018.05.017
- 438 15. AFNOR (2009) NF T90-210 norm : Water quality - Protocol for the initial method
439 performance assesment in a laboratory.
- 440 16. Désenfant M, Priel M, Rivier C (2005) Evaluation des incertitudes des résultats
441 d'analyse. Ref P105 V1. Les Tech l'Ingénieur 1–17.

- 442 17. International Atomic Energy Agency (2010) International Target Values 2010 for
443 Measurement Uncertainties in Safeguarding Nuclear Materials - STR368. Vienna,
444 Austria
- 445 18. Irrgeher J, Vogl J, Santner J, Prohaska T (2015) Chapter 8 Measurement Strategies.
446 In: Sect. F. Mass Spectrom. Elem. Isot. Anal. The Royal Society of Chemistry, pp
447 126–151
- 448