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Title

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

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Abstract

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

Keywords

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

Introduction

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

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

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

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

Experimental

Materials, reagents and certified reference materials

All solutions were prepared in polypropylene vials, except for uranium solutions, which were prepared in PFA vials. 1 mol L⁻¹, 3 mol L⁻¹ and 8 mol L⁻¹ nitric acid solutions were prepared by diluting high purity nitric acid (Merck, Suprapur) in deionized water (resistivity: 18 2 MΩ.cm). A high accurated scale (Mettler-Toledo, WXTP 205) was used to prepare all solutions.

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

Sample preparation

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

Instrumental

Thermal Ionization Mass Spectrometer

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

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

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

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

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

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

K-edge densitometry

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

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

The dissolution solution was analyzed by KED without any further preparation except vial transfer. The result was obtained from the average of 5 individual measurements of the same vial containing the dissolution solution. Between each individual measurement, the vial was returned to the hot cell line before a new transfer back to the KED in order to take into account the uncertainties due to the vial position in the KED. The concentration 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).

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

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.

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

150 Where $u([U])$ 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 ($[U]_T$, m_T ,
187 m_S , $(235)_T$, $(238)_S$, R_S or R_T) depend only on the sample and spike characteristics and on

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

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

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

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

Uranium concentration uncertainty using KED analysis

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

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

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

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

Results and discussion

ID-TIMS

The results are presented in Table 2. The RSD of the 3 groups of determinations is equal to 0.12 %. The result obtained for the uranium mass fraction of the pellet is $0.8835 \pm 0.0028 \text{ g g}^{-1}$ ($k = 2$). The bias is equal to 0.30 %. The relative uncertainty, computed with Eq. (4), is estimated at 0.32 % and is in compliance with the safeguard ITV (0.36 %, $k = 2$) [17]. The relative contribution study (expressed in percent) of the main uncertainty sources for the uranium mass fraction is given in Fig. 2. The spike concentration uncertainty (0.04 %) has a very low contribution and is a minor source of uncertainty (4.2 % of the total budget). The main uncertainty sources are the precision (59.4 % of the total budget), the dilution to obtain a sample concentration of about $10 \mu\text{g g}^{-1}$ (19.7 % of the total budget) and the $^{238}\text{U}/^{235}\text{U}$ sample - spike mixture isotope ratio determination (14.1 % of the total budget).

KED

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

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

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

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

Conclusions

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

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

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

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Table

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

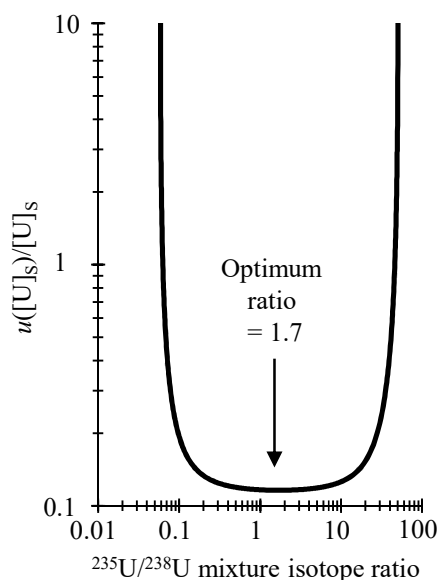
Parameters	Value	Uncertainty (k=1)
$[U]_T$	9.5044	0.0039
m_T	0.246555	0.000059
m_S	0.218465	0.000059
M_S	237.992	-
M_T	235.201	-
$(235)_T$	93.1760	0.0034
$(238)_S$	98.053	0.010
R_S	0.019658	0.000015
R_T	0.058065	0.000017
Parameters	Value	Relative Uncertainty (k=1)
R_{Mix}	Between 0.0586 and 50.87	0.07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

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

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

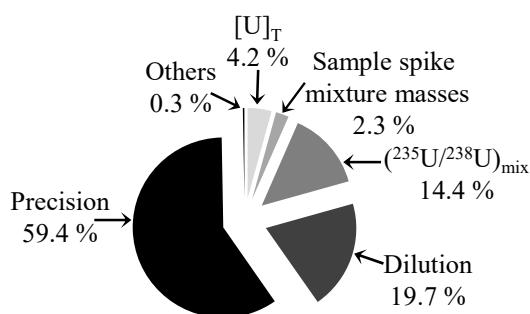
378 **Figure**



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

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