



## On the application of ICP-MS techniques for measuring uranium and plutonium: a Nordic inter-laboratory comparison exercise

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## **Title page**

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21 **On the application of ICP-MS techniques for measuring**  
22 **uranium and plutonium: a Nordic inter-laboratory**  
23 **comparison exercise**

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38 **Abstract**

39 Inductively coupled plasma mass spectrometry (ICP-MS) techniques are widely used for  
40 determination of long-lived radionuclides and their isotopic ratios in the nuclear fields.  
41 Uranium (U) and Pu (Pu) isotopes have been determined by many researchers with ICP-  
42 MS due to its relatively high sensitivity and short measurement time. In this work, an

43 inter-laboratory comparison exercise among the Nordic countries was performed,  
44 focusing on the measurement of U and Pu isotopes in certified reference materials by  
45 ICP-MS. The performance and characters of different ICP-MS instruments are evaluated  
46 and discussed in this paper.

## 47 **Keywords**

48 ICP-MS, Pu, U, NBL CRM-103A, IAEA-384

## 49 **Introduction**

50 Inductively coupled plasma mass spectrometry (ICP-MS) was developed by combing an  
51 inductively coupled plasma source at atmospheric pressure with mass spectrometry. ICP-  
52 MS has advantages of relatively low operational cost, easy sample introduction and high  
53 sample throughput. Since its first commercial introduction in 1983, ICP-MS has become  
54 widely used for determination of radionuclides (e.g., actinides) and their isotopic ratios in  
55 the fields related to environmental monitoring, nuclear waste disposal and management,  
56 radioecology and tracer studies, nuclear forensics and nuclear emergency  
57 preparedness.[1–13] Many researchers have applied ICP-MS for the determination of  
58 uranium (U) and plutonium (Pu) isotopes, because of its relatively high sensitivity and  
59 high sample throughput due to the short measurement time needed compared to  
60 traditional radiometric techniques.[14–23]

61 There are several types of ICP-MS instruments commercially available, including  
62 quadrupole ICP-MS (ICP-QMS), single- or double-focusing sector field ICP-MS (ICP-  
63 SFMS), multi-collector ICP-MS (MC-ICP-MS), and recently introduced triple  
64 quadrupole ICP-MS (ICP-QQQ). Each type of instrument has advantages and drawbacks  
65 with respect to the determination of U and Pu isotopes. ICP-QMS, ICP-SFMS and ICP-  
66 QQQ are single collector inductively coupled mass spectrometers based on different  
67 technical principles. The basic difference between operating principles of single collector  
68 and multi-collector ICP-MS instruments is the sequential measurement of multiple

69 isotopes by one detector vs. the simultaneous measurement of isotopes at multiple  
70 detectors, respectively. Owing to its possibility of simultaneous detection, multi-collector  
71 ICP-MS is outstanding regarding expanded uncertainty of isotope ratio determination.  
72 However, depending on the application and the need of precision, single collector or  
73 quadrupole ICP-MS may give sufficiently good results [24].

74 Among the Nordic countries, there are probably 20 ICP-MS facilities, which are currently  
75 applied for measuring radionuclides and their isotopic ratios. With different application  
76 purposes and technical background of the analysts, each ICP-MS laboratory has different  
77 set-ups and experiences in instrumental operation. Aiming to prompt knowledge sharing  
78 among different ICP-MS laboratories, and thus achieve more efficient application of ICP-  
79 MS techniques, an inter-laboratory comparison exercise was performed during 2016. The  
80 exercise focused on the determination of U and Pu isotopes in certified reference  
81 materials with the application of different ICP-MS instruments. It consisted of two  
82 aspects: 1) ICP-MS measurement for U isotopic ratios ( $^{234}\text{U}/^{235}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$  and  
83  $^{234}\text{U}/^{238}\text{U}$ ); 2) ICP-MS measurement for Pu isotopes ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ) concentrations and  
84 isotopic ratio. The inter-comparison results were evaluated and discussed to shed some  
85 light on the analytical feature of different ICP-MS instruments and the effect of  
86 operational conditions/auxiliary devices on the ICP-MS performance.

## 87 **Experimental**

### 88 ***Materials***

89 A certified reference material NBL CRM 103-A Pitchblende Ore – Silica Mixture  
90 Uranium Standard (U  $0.04992 \pm 0.00078$  Wt.%) from New Brunswick Laboratory (NBL)  
91 was used in the inter-comparison exercise to perform the U isotopic ratios ( $^{234}\text{U}/^{235}\text{U}$ ,  
92  $^{235}\text{U}/^{238}\text{U}$ ,  $^{234}\text{U}/^{238}\text{U}$ ) measurement. According to the certificate, the material was  
93 prepared by milling and blending NBL CRM 6-A Pitchblende Ore ( $67.91 \pm 0.05$  Wt.%  
94  $\text{U}_3\text{O}_8$ ) with silica (99.9%  $\text{SiO}_2$ ) to obtain a uniform mixture of desired U concentration.  
95 NBL CRM 103-A is not certified for U isotope ratios, but the material has natural U

96 isotopic composition, hence the IUPAC observed range of natural variations for U [25]  
97 has been used in this inter-comparison.

98 Another certified reference material IAEA-384 Fangataufa Lagoon sediment was used for  
99 the determination of the concentrations of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  and their isotopic ratio. This  
100 material was collected by IAEA-MEL in July 1996 in Fangataufa Lagoon (French  
101 Polynesia), where nuclear weapon testing had been carried out.

### 102 ***Sample preparation for measuring U isotope ratios***

103 Details of the sample preparation procedure for U isotopic ratios measurement are  
104 summarized below. Generally, a certain amount of NBL CRM 103-A reference material  
105 was dissolved using mineral acids (i.e., HF,  $\text{HNO}_3$  and HCl). After suitable dilution with  
106 diluted  $\text{HNO}_3$ , the sample was measured by different ICP-MS instruments in each  
107 laboratory.

108 At Lab A, 50-100 mg of NBL CRM 103-A reference material was dissolved using about  
109 2 ml of concentrated HF and 2 ml of concentrated  $\text{HNO}_3$  with addition of 200  $\mu\text{l}$  of  
110 concentrated HCl. Thereafter the sample solution was diluted with 0.3-0.5 M  $\text{HNO}_3$  to an  
111 appropriate concentration.

112 At Lab B, 100 mg of NBL CRM 103-A reference material was dissolved in 2 ml of  
113 concentrated HF, 2 ml concentrated  $\text{HNO}_3$  and 200  $\mu\text{l}$  of concentrated HCl. Thereafter  
114 the sample solution was diluted in 0.28 M  $\text{HNO}_3$  to appropriate concentration.

115 At Lab C, 50 mg of NBL CRM 103-A reference material was dissolved using a  
116 microwave-assisted digestion system with 2 ml of concentrated HF and 2 ml of  
117 concentrated  $\text{HNO}_3$  in closed Teflon vessels at 600 W RF power for 25 minutes. Digests  
118 were evaporated to dryness and re-dissolved in 0.3 M  $\text{HNO}_3$ . Thereafter the sample  
119 solution was diluted in 1.4 M  $\text{HNO}_3$  to appropriate concentration.

120 At Lab D, 2 mg of NBL CRM 103-A reference material was weighed to a Teflon beaker  
121 and 5 ml of concentrated  $\text{HNO}_3$  (super pure) was added. The mixture was nearly boiled

122 for 2 hours. The solution was filtered through a membrane filter (Acrodisc® Syringe  
123 Filter, 0.2 µm Supor® Membrane, Pall Life Sciences) and diluted to 100 ml with H<sub>2</sub>O.

124 At Lab E, the sample was dissolved only with 0.1 M HNO<sub>3</sub> in the preliminary test.  
125 However, the sample solution obtained was not clear, and analytical result was very  
126 unstable with high deviation, indicating that the solution was inhomogeneous.  
127 Afterwards, the sample was dissolved with 0.5 M HNO<sub>3</sub> + 0.25% (v/v) HF, wherein clear  
128 solutions were obtained.

129 At Lab F, 80 mg of NBL CRM 103-A reference material was digested in PTFE tubes  
130 with 2.5 ml of concentrated HNO<sub>3</sub> for 40 minutes at 260 °C in an UltraWave from  
131 Milestone. The samples were diluted to 25 ml with de-ionized water after digestion.

### 132 ***Sample preparation for measuring Pu isotopes***

133 For <sup>239</sup>Pu and <sup>240</sup>Pu concentration and isotopic ratio measurement, two approaches were  
134 used for the sample preparation: 1) centralized sample preparation and dispatching the  
135 purified Pu solution to each laboratory for direct ICP-MS measurement; 2) dispatching  
136 the raw reference material IAEA-384 and performing independent sample preparation in  
137 individual laboratory. In general, the radiochemical methods used for the determination  
138 of Pu in the raw IAEA-384 material were based on sample pre-treatment followed by  
139 extraction chromatographic separation (two labs used TEVA, one used tandem UTEVA +  
140 TRU and one used UTEVA column) and ICP-MS measurement.

141 **Pre-purification of IAEA-384 for Pu measurement.** Pu contained in IAEA-384  
142 material was pre-separated at Lab A and distributed to participating institutes for  
143 measurement. The chemical separation procedure for purification of Pu at Lab A is  
144 summarized as follows. 2 g of IAEA-384 sediment was spiked with 0.2528g of 0.1037  
145 Bq/kg <sup>242</sup>Pu tracer and dissolved directly with 20 ml of 8 M HNO<sub>3</sub>. A 4 ml of anion  
146 exchange column (AG 1×4, 50-100 mesh) was packed and preconditioned with 20 ml of  
147 8 M HNO<sub>3</sub>. The dissolved sample solution was loaded onto the column, and the column  
148 was washed with 60 ml of 8 M HNO<sub>3</sub> followed by 40 ml of 9 M HCl. The Pu was eluted  
149 with 50 ml of 0.5 M HCl and the eluate was evaporated to dryness. The Pu residue was

150 dissolved with 12 ml of 0.5 M HNO<sub>3</sub>, and each 2 ml of aliquot was transferred to a  
151 scintillation vial and delivered to ICP-MS measurement in each laboratory.

152 **Radiochemical separation for IAEA-384.** Raw IAEA-384 reference material was also  
153 processed in participating laboratories to perform the inter-comparison of radiochemical  
154 analysis for Pu determination. The radiochemical separation procedures used in this inter-  
155 comparison are summarized below.

156 At Lab A, 0.2 g of IAEA-384 reference material was spiked with 0.1g of 0.1037 Bq/kg  
157 <sup>242</sup>Pu tracer and digested with 40 ml *aqua regia* at 200 °C for 2 hours. After filtration, 1  
158 mg of Fe was added to form Fe(OH)<sub>3</sub> co-precipitation with the addition of NH<sub>3</sub> to pH 8-  
159 9. After centrifugation, the residue was dissolved with 2 ml concentrated HCl and diluted  
160 to 100 ml. In total of 300 mg of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added with stirring for 20 min. to reduce Pu  
161 to Pu(III). NH<sub>3</sub>·H<sub>2</sub>O was added to adjust the sample to pH 8-9 and the precipitate was  
162 centrifuged. 3 ml of concentrated HNO<sub>3</sub> was added to dissolve the residue and the sample  
163 was finally adjusted to 3 M HNO<sub>3</sub> for chromatographic purification. 2 ml of TEVA (100-  
164 150 μm) column was packed and preconditioned with 20 ml of 3 M HNO<sub>3</sub>. The dissolved  
165 sample solution was loaded onto the TEVA column, and the column was washed with 60  
166 ml of 8 M HNO<sub>3</sub> followed by 40 ml of 9 M HCl. The Pu was eluted with 50 ml of 0.5 M  
167 HCl and the eluate was evaporated to dryness. The Pu residue was dissolved with 5 ml of  
168 0.5 M HNO<sub>3</sub> and measured with an ICP-QQQ instrument.

169 At Lab B, the reference material IAEA-384 was first checked for moisture content. 1 g of  
170 IAEA-384 sediment was mixed with 3 g lithium metaborate (LiBO<sub>2</sub>, Claisse, ultra-pure  
171 grade, Gammadata, Uppsala, Sweden) and thereafter spiked with about 10 pg of <sup>242</sup>Pu  
172 (NIST SRM 4334G). The sample mixture was first pre-oxidized at 650°C for 1 hour prior  
173 to fusion for 15 minutes at 1050°C. The melt was allowed to cool before mixing with 100  
174 ml of 1.4 M HNO<sub>3</sub> and thereafter the melt was dissolved under stirring and heat. When  
175 dissolved, PEG2000 was added to a concentration of 0.0002 M and thereafter the sample  
176 volume was evaporated to half the volume, leading to a sample matrix of 2.8 M HNO<sub>3</sub>.  
177 The sample was left over night to allow silica to flocculate and thereafter the sample was  
178 filtrated using filter paper (Munktell filter paper No. 00M). The sample filtrate was



179 heated to 90°C and thereafter 375 mg of NH<sub>2</sub>OH·HCl was added. After cooling, 900 mg  
180 of NaNO<sub>2</sub> was added to assure that all Pu was oxidized to Pu(IV). 2 ml TEVA (Triskem)  
181 columns were packed in-house in 3 ml cartridges (Isolute reservoir 3 ml, Biotage,  
182 Uppsala, Sweden). 20 µm polyethene frits (Biotage) were used to keep the TEVA resin in  
183 the reservoir. The column was pre-conditioned with 5 ml of 3 M HNO<sub>3</sub> and then the  
184 sample was added. The column was rinsed with 10 ml of 3 M HNO<sub>3</sub>, followed by 10 ml  
185 of 9 M HCl and 20 ml 3 M HNO<sub>3</sub>. Pu was eluted in 5 ml of 0.01% hydroxyethylidene  
186 diphosphonic acid (HEDPA, purum, Merck Millipore, Stockholm, Sweden) and  
187 measured with an ICP-SFMS instrument.

188 At Lab C, 0.25 g of IAEA-384 reference material was digested with a microwave-  
189 assisted digestion system using HNO<sub>3</sub>+HF mixture as described earlier for pre-treatment  
190 of NBL CRM 103-A. After evaporation, the sample was re-dissolved in 3M HNO<sub>3</sub> and  
191 then loaded on a pre-packed 2 ml UTEVA column for Pu separation from matrix. The  
192 UTEVA column was washed by 12 ml of 3 M HNO<sub>3</sub> and 4 ml of 9.6 M HCl followed by  
193 Pu elution in 8 ml of 5 M HCl+0.05M oxalic acid. <sup>242</sup>Pu spike (NIST SRM 4334G) was  
194 used as a tracer of the entire procedure.

195 At Lab D, 1 g of IAEA-384 reference material was spiked with 26 mBq (177 pg) of <sup>242</sup>Pu  
196 as a tracer. The sample was dissolved with the mixture of concentrated HNO<sub>3</sub> (30 ml) and  
197 concentrated HCl (10 ml) on a hotplate for 6 hours. The sample solution was filtrated and  
198 evaporated to dryness. Radiochemical separation of Pu from the disturbing matrix and  
199 other radionuclides was performed according to the method described elsewhere [26]. In  
200 general, after dissolving the sample in 10 ml of 1 M Al(NO<sub>3</sub>)<sub>3</sub> + 3 M HNO<sub>3</sub>, 2 ml of 0.6  
201 M ferrous sulfamate solution and 150 mg of ascorbic acid were added. After 15 minutes,  
202 the sample solution was loaded into an UTEVA column (preconditioned with 5 ml of 3  
203 M HNO<sub>3</sub>). The UTEVA column was washed with 10 ml of 3 M HNO<sub>3</sub>. The effluent of  
204 the sample loading and washing solution were loaded onto a TRU column  
205 (preconditioned with 5 ml of 2 M HNO<sub>3</sub>). The TRU column was washed with 5 ml of 2  
206 M HNO<sub>3</sub>, 5 ml of 0.1 M NaNO<sub>2</sub> + 2 M HNO<sub>3</sub>, 3 ml of 0.5 M HNO<sub>3</sub>, 2 ml of 9 M HCl, 20  
207 ml of 4 M HCl and 10 ml of 0.1 M HF + 4 M HCl, respectively. Pu was finally eluted  
208 with 10 ml of 0.1 M NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> and evaporated to dryness. 2 ml of conc. HNO<sub>3</sub> was

209 added to the residue and re-evaporated into dryness. The separation procedure with  
210 UTEVA and TRU columns was repeated. After elution from TRU column, the  
211 ammonium oxalate solution containing Pu was evaporated into dryness with addition of a  
212 few drops of H<sub>2</sub>O<sub>2</sub> and concentrated HNO<sub>3</sub>. The residue was dissolved to 10 ml of 5 %  
213 HNO<sub>3</sub> and filtered through a membrane filter (Acrodisc® Syringe Filter, 0.2 µm Supor®  
214 Membrane, Pall Life Sciences). Blank samples were processed similarly with the  
215 sediment samples. Blank samples and acid blank of 5% HNO<sub>3</sub> were included to the  
216 measurement sample set.

217 At Lab F, 1 g of IAEA 384 was weighed directly in to a PTFE digestion tube and 12 mL  
218 of concentrated HNO<sub>3</sub> and 4 mL of 48 % (w/w) HF were added. 24.1 pg of <sup>242</sup>Pu was  
219 added as a yield tracer. The samples were digested (UltraClave IV, Milestone Ltd) at a  
220 temperature of 260 °C for 40 minutes. After digestion, the samples were transferred to  
221 PTFE beakers and left to evaporate to dryness on a sand-bath. Matrix separation was  
222 performed according to the method described in [27]. The eluate from the separation was  
223 evaporated to dryness, and taken up in 7 ml of 0.8 M HNO<sub>3</sub> + 0.2 M HF for analysis. The  
224 pre-purified Pu sample was diluted in a ratio of 1:3 with 0.8 M HNO<sub>3</sub> + 0.2 M HF before  
225 analysis.

## 226 ***Instrumentation, measurement and calculations***

227 Within this work, six Nordic laboratories participated in the inter-comparison exercise,  
228 where two ICP-QQQ, one MC-ICPMS and four ICP-SFMS instruments were employed  
229 for the U and Pu measurement. Table 1 summarizes the instrumentation conditions used  
230 in each laboratory.

231 Lab A: The instrumentation used throughout the work was an ICP-QQQ (Agilent 8800).  
232 Both U and Pu measurements, standard introduction system consisted of MicroMist  
233 nebulizer and Scott-type double pass spray chamber, together with Ni skimmer cone and  
234 x-lens were used. Typical sensitivity of the instrument is about 0.7 cps per ppq for <sup>238</sup>U.  
235 The uptake of the sample was performed at a flow rate of 20 µL/min with a standard  
236 peristaltic pump equipped in the ICP-QQQ instrument. A <sup>242</sup>Pu standard solution was  
237 diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL, USA). A 1000

238 ppm standard solution of U (Scientific Standards) was diluted to different levels of  
239 concentrations and used for calibration purposes. All standard solutions and samples were  
240 diluted to appropriate concentrations using high purity water and concentrated nitric acid.

241 For the measurement of U at Lab A, the instrument was controlled for mass bias using  
242 the standard solution NBL-112a with a concentration of 0.5 ppb. The major isotope ratio  
243  $n(^{235}\text{U})/n(^{238}\text{U})$  was determined in a sample diluted to achieve a maximum intensity of  $1$   
244  $\times 10^6$  counts/s at  $m/z$  238. The minor isotope ratio  $n(^{234}\text{U})/n(^{235}\text{U})$  was measured in a  
245 sample diluted to achieve an intensity of about  $1 \times 10^6$  counts/s at  $m/z$  235 and thereafter  
246 the  $n(^{234}\text{U})/n(^{238}\text{U})$  ratio was calculated from the ratios of  $n(^{235}\text{U})/n(^{238}\text{U})$  and  
247  $n(^{234}\text{U})/n(^{235}\text{U})$ . For the measurement of Pu, a 0.5 M  $\text{HNO}_3$  as a blank,  $^{242}\text{Pu}$  (4.09 ppt)  
248 standard and  $^{238}\text{U}$  (1ppb) standard was measured in parallel with the purified Pu fraction  
249 (in 0.5 M  $\text{HNO}_3$ ). 1 ppb In (as  $\text{InCl}_3$ ) was added into each sample and used as an internal  
250 standard to calibrate the efficiency of instrument. The signals at  $m/z$  240 and 242 were  
251 corrected for contributions from blank levels and the signal at  $m/z$  239 was corrected for  
252 contributions both from blank and  $^{238}\text{U}$ . Mass bias correction was not performed for  
253  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , whereas average isotope ratios ( $n=5$ ) of  $n(^{239}\text{Pu})/n(^{242}\text{Pu})$  and  
254  $n(^{240}\text{Pu})/n(^{242}\text{Pu})$  were calculated based on the intensities measured by ICP-MS.  
255 Thereafter the activity concentrations of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in the raw sample were  
256 calculated by multiplying the total amount of  $^{242}\text{Pu}$  tracer spiked in the sample with  
257  $^{239}\text{Pu}/^{242}\text{Pu}$  and  $^{240}\text{Pu}/^{242}\text{Pu}$  isotopic ratios, respectively.

258 Lab B: The instrumentation used throughout the work was an ICP-SFMS (Element XR,  
259 Thermo Scientific, Bremen, Germany). For the Pu measurement, the retarding potential  
260 quadrupole lens of the ICP-SFMS was activated to reduce the peak tailing of the  
261 instrument, whilst for the U measurement the RPQ lens was inactivated. The instrument  
262 was tuned for maximum U intensity meanwhile keeping the U oxide formation as low as  
263 possible. The typical sensitivity is about 2 cps per ppq for  $^{238}\text{U}$  with the RPQ lens  
264 inactivated. When using the instrument with the RPQ lens activated, the typical  
265 sensitivity is decreased by about 10%, see Table 1. The automatic dead time correction  
266 was disconnected as this correction was performed post-acquisition. The sample

267 introduction systems used consisted of a Conikal nebulizer, a Twister spray chamber, a  
268 standard torch and nickel cones (all from GlassExpansion, Melbourne, Australia).

269 For the determination of U and Pu at Lab B, the instrument was controlled for mass bias  
270 and spectral interference at  $m/z$  239 from  $^{238}\text{U}$  using the certified reference material  
271 IRMM-073/7 (IRMM, Institute for Reference Materials and Measurements, Geel,  
272 Belgium). IRMM-184 was used as a quality control sample. The raw data was extracted  
273 from the instrument to avoid non-linearity effects as published earlier [28] and data  
274 reduction thereafter was done off-line in order to correct detector dead time of the  
275 individual, averaged signal intensities. The detector dead time and its associated  
276 uncertainty, was determined to be  $73.1 \pm 1.4$  ns, with the 70 ns nominal dead time setting  
277 on the ion detection board using IRMM-073/5 (IRMM, Institute for Reference Materials  
278 and Measurements, Geel, Belgium) by a method described by Appelblad and Baxter [29].  
279 Following the dead time correction, the intensities were corrected for contributions from  
280 blank levels, and thereafter mass bias corrected ratios for  $n(^{234}\text{U})/n(^{238}\text{U})$ ,  $n(^{235}\text{U})/n(^{238}\text{U})$ ,  
281  $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ ,  $n(^{239}\text{Pu})/n(^{242}\text{Pu})$  and  $n(^{240}\text{Pu})/n(^{242}\text{Pu})$  were calculated using the Russell  
282 equation [30]. For the separated Pu sample, the signal at  $m/z$  239 was also corrected for  
283 contributions from  $^{238}\text{UH}$  and peak tailing from  $^{238}\text{U}$  prior to mass bias correction. All  
284 uncertainties were evaluated in accordance with ISO/GUM (1995) using the software  
285 GUM Workbench [32].

286 Lab C: An ICP-SF-MS (ELEMENT XR, Thermo Scientific) was used for both Pu and U  
287 measurement in this work. For the U ratio measurement, a dual spray chamber for signal  
288 stability improvement together with a Micromist nebulizer and standard cones were used.  
289 RPQ (Retarding Potential Quadrupole) lenses were activated to improve abundance  
290 sensitivity. This set-up offers a typical sensitivity of 1.2 cps per ppq for  $^{238}\text{U}$  and  
291  $^{238}\text{U}/^{238}\text{U}^1\text{H}$  ratio of >60000. For the Pu isotope measurement, a desolvation sample  
292 introduction system (APEX) equipped with a PFA nebulizer and high efficiency  
293 skimmer cone was used. RPQ was also activated with a typical sensitivity of > 6 cps per  
294 ppq for  $^{238}\text{U}$ . Standard solutions of U0002 CRM, IRMM-184, CRM130 and 1000-ppm U  
295 standard (Scientific Standards) were used for tailing and spectral interference corrections  
296 as well as for calibration purposes.

297 Mathematical corrections for  $^{238}\text{U}^{\text{H}^+}$  and tailings were performed based on experimental  
298 factors deduced by analyzing U0002 CRM. Mass bias was assessed using IRMM-184  
299 (natural U). Concentration was determined using external calibration with diluted  
300 CRM130 (Pu) and Scientific Standards 1000 ppm U solutions.

301 Lab D: Two ICP-MS instruments, a Nu Plasma Multi-Collector ICP-MS and a Nu AttoM  
302 Single-Collector ICP-MS (Nu Instruments Ltd., Wrexham, UK), were used in this inter-  
303 comparison. Limit of detection (LOD) was  $< 20$  ppq for Pu and U before the sample  
304 measurements.

305 The analyses of U isotopes were carried out by using a Nu Plasma Multi-Collector ICP-  
306 MS at low mass resolution ( $\Delta m/m = 400$ ). The U measurements were performed in  
307 dynamic mode and consists of 1 block of 12 integrations of 15s (2 cycles for the two  
308 isotopes ratio) and 1s (3 cycles for the tail corrections). A 5 min wash using  $\text{HNO}_3$  (2%)  
309 has been used between U isotopes measurements. Two Faraday detectors have been used  
310 for  $^{238}\text{U}$  and  $^{235}\text{U}$  and one ion counter has been used for  $^{234}\text{U}$ ,  $^{233}\text{U}$  and tail corrections in  
311 U isotope measurements. The samples have been standard bracketed using the NBL112a  
312 standard [33] in order to correct for mass fractionation and Faraday cup to ion counter  
313 gain. Peak tailing has been corrected using an exponential function after dynamic  
314 measurements at three different half-masses 232.5, 233.5 and 234.5 on the same ion  
315 counter used for the determination of  $^{234}\text{U}$  and  $^{233}\text{U}$ . The international U standard UO10  
316 has been used for quality control at the beginning and at the end of each run. The  
317 measured  $^{234}\text{U}/^{238}\text{U}$  and  $^{235}\text{U}/^{238}\text{U}$  ratios for that standard during analytical sessions were  
318  $0.00005436 \pm 35$  and  $0.010149 \pm 8$  ( $n = 4$ ), compared to respective values  $0.00005448 \pm$   
319  $4$  (reference value from [34]) and  $0.010140 \pm 10$  (certified value).

320 The Nu AttoM Single-Collector ICP-MS instrument was used for the determination of  
321  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . The sample introduction system consisted of an autosampler, a peristaltic  
322 pump, a Meinhard nebulizer, nickel and sampler cones and a cyclonic spray chamber  
323 without cooling. In determination of  $^{240}\text{Pu}$  and  $^{239}\text{Pu}$ , the samples were bracketed using a  
324 CPI<sup>TM</sup> single element solution of 1 ppb of U in 2%  $\text{HNO}_3$ , meaning that the U standard  
325 solution was measured between every sample measurement. A blank has been measured

326 before every sample and standard. Analyses were performed in deflector jump mode  
327 using 80 sweeps of 500 cycles at low resolution. The isotopes of  $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  
328 and  $^{242}\text{Pu}$ , as well as half masses at 239.5 and 240.5 were measured. The dwell time was  
329 1ms for each isotope. Washing time was 120 s and a further 60 s of sample uptake was  
330 allowed before measurement started. The results have been calculated using an in house  
331 excel data reduction program. The natural ratio of  $^{238}\text{U}/^{235}\text{U}$  has been used to calculate  
332 the mass bias and apply a correction for  $^{240}\text{Pu}/^{239}\text{Pu}$ . The fractionation factor, which was  
333 used to correct for the mass bias on  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio, was calculated based on the  
334  $^{235}\text{U}/^{238}\text{U}$  ratio (set at 0.0072527). After an acid blank correction, a linear regression  
335 through the half mass 239.5 and 240.5 was also made, to calculate the tailing on  $^{239}\text{Pu}$   
336 and  $^{240}\text{Pu}$ .

337 Lab E: An ICP-SFMS (Element 2, Thermo) was used only for U isotopic ratio  
338 measurement. The sample introduction system included an SC2 DX auto sampler  
339 (Elemental Scientific) with prepFAST 400 online dilution system, PFA nebulizer, PFA  
340 cyclonic spray chamber with Peltier cooling from ESI, and sapphire demountable torch.  
341 Al skimmer and sample cones were used for the measurement. The typical sensitivity was  
342 approx. 0.8 cps per ppq for  $^{238}\text{U}$ .  $^{235}\text{U}$  and  $^{238}\text{U}$  were measured in analog mode, and  $^{234}\text{U}$   
343 was measured in counting mode. The  $\text{UH}^+$  formation at  $m/z=236$  from  $^{235}\text{U}$  was approx.  
344 0.01%. For mass bias correction, IRMM-184 was used with appropriate concentrations  
345 versus tested sample.

346 Lab F: An ICP-QQQ (Agilent 8800) with a quartz Micromist nebulizer and a Peltier  
347 cooled ( $2\text{ }^\circ\text{C}$ ) Scott double pass spray chamber was used for the analysis of both Pu and  
348 U. Because there was still U present in the sample solution after the single step extraction  
349 chromatography, mass was shifted to  $m+16$  and  $m+32$  through reaction with 0.32  
350 mL/min  $\text{CO}_2$  in the reaction cell, allowing for unreacted Pu to be analysed on mass (here:  
351 239, 240, 242) with negligible remaining  $^{238}\text{UH}^+$  interference. The concentrations of U  
352 are, in all samples, estimated at  $m+16$  for control of the  $^{238}\text{UH}^+$  interference. No  
353 correction equation was applied to the results, as the concentrations of U were low. The  
354 octapole bias was kept close to zero ( $-1\text{ V}$ ) to prevent increased formation of  $\text{PuO}^+$ . For  
355 increased sensitivity, an s-lens was used and the mass balance of the quadrupoles was set

356 to 92 % (240 amu/260 amu). Typical sensitivity in no-gas mode is about 1.5 cps per ppq  
357 for  $^{238}\text{U}$ . Due to bureaucratic difficulties, it proved impossible to obtain an isotopic Pu  
358 standard for isotope calibration and mass bias determination. Therefore IAEA 135  
359 certified reference material was chosen to be used as an isotopic standard material for  
360 mass bias correction based on the average  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio (n=47) published in  
361 literature. The concentrations of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  were calculated from  $^{240}\text{Pu}/^{242}\text{Pu}$  and  
362  $^{239}\text{Pu}/^{242}\text{Pu}$  multiplied by total amount of  $^{242}\text{Pu}$  spiked.

363 Due to high concentrations of U in the sample, the instrument was run in low sensitivity  
364 mode and with x-lens installed. The samples were analyzed in MS-MS mode, where  
365 Q1=Q2, and with no gas present in the reaction cell. NBL CRM 129A was used for mass  
366 bias correction for the uranium atom ratios.

### 367 ***Quality control***

368 The six laboratories in this inter-comparison exercise are leading Nordic laboratories with  
369 respect to ICP-MS and radiochemistry. Each lab in this inter-comparison exercise has  
370 well-established quality assurance program, as well as substantial experiences in  
371 operating ICP-MS measurement and relevant radiochemical separation for Pu and U. All  
372 the laboratories regularly participate into intentional inter-comparison exercise arranged  
373 by IAEA, NPL, IRMM and other organisations, and carry out internal performance  
374 evaluation by measuring certified reference materials. Most labs also perform U and Pu  
375 determination on a routine base and receive internal/external inspection for their quality  
376 control program.

### 377 **Individual laboratory performance evaluation and scoring**

378 Based on the ISO 13528 (ISO 13528) and IUPAC-CITAC recommendation [35], two  
379 tests including z-score and zeta-score were used to evaluate the individual performance of  
380 individual laboratory. z-score is calculated according to the following equation:

$$381 \quad z = \frac{x - \bar{x}}{\sigma_t} \times 100\% \quad (1)$$

382 where  $x$  is the participant's result,  $X$  is the assigned value,  $\sigma_i$  is the standard deviation set  
383 externally for the performance assessment. The standard deviations ( $\sigma_i$ ) were set to be  
384  $0.05X$  for  $^{234}\text{U}/^{235}\text{U}$  and  $^{235}\text{U}/^{238}\text{U}$ ,  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratios,  $0.005X$  for  $^{235}\text{U}/^{238}\text{U}$  atomic  
385 ratio and  $0.2X$  for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activity. According to the IUPAC-CITAC  
386 recommendation [35], the performance is considered to be acceptable if  $|z| \leq 2$ . A  $|z|$  from  
387 2 to 3 indicates that the results are of questionable quality. If  $|z| > 3$ , the analysis was  
388 considered to be out of control.

389 Optimally, according to the ISO 13528 standard for profession testing [35, 36], the *zeta*-  
390 score methodology should be used in evaluation of results in an inter-comparison. The  
391 *zeta*-score is calculated according to:

$$392 \quad \text{zeta} = \frac{x - X}{\sqrt{u_x^2 + u_X^2}} \quad (2)$$

393 where  $x$  is the participant's result,  $X$  is the assigned value,  $u_x$  is the standard uncertainty  
394 of a participant's result, and  $u_X$  is the standard uncertainty of the assigned value. The  
395 performance is considered to be acceptable if  $|\text{zeta}| \leq 2$ . A  $|\text{zeta}|$  from 2 to 3 indicates that  
396 the results are of questionable quality. If  $|\text{zeta}| > 3$ , the analysis was considered to be out  
397 of control.

398 Besides *z*-score and *zeta*-score, the relative bias was also calculated for evaluation of the  
399 analytical accuracy:

$$\text{Bias} = \frac{x - X}{X} \times 100\% \quad (3)$$

400 where  $x$  is the participant's result,  $X$  is the assigned value.  
401

402 The criteria for accuracy evaluation is according to IAEA recommendation [37]. If the  
403  $|\text{Bias}| < \text{MARB}$  (Maximum Acceptable Relative Bias) the result will be 'Acceptable' for  
404 accuracy. In this inter-comparison, The MARB value was set to 10% for U isotopic ratios  
405 and 20% for  $^{239,240}\text{Pu}$  activities and  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio analysis, respectively.



406 **Results and discussion**

407 The results achieved from the inter-comparison exercise are presented in Table 2 for U  
408 isotopic ratios ( $^{234}\text{U}/^{235}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$ ) in the NBL CRM 103-A reference  
409 material, and in Table 3 for Pu isotopes ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ) massic activity and  $^{240}\text{Pu}/^{239}\text{Pu}$   
410 atomic ratio in the reference material IAEA-384. The value of  $n$  in bracket is the number  
411 of replicates for the individual ICP-MS measurement. All uncertainties for the results  
412 obtained in this work are expanded uncertainties as obtained after uncertainty  
413 propagation with a coverage factor  $k=1$ .

414 ***U isotopic ratio***

415 Six results were reported for U isotopic ratios in NBL CRM 103-A. However, as the  
416 reference material used for this inter-comparison is not certified, there is no value  
417 available, either for  $X$  or  $u_x$ . As the reference material used is of natural U composition,  
418 the IUPAC observed range of natural variations for U could be used (0.00725-0.00726  
419 molar ratio) [25]. Because the number of participants in this inter-comparison is very  
420 small, we used the average of the IUPAC observed range of natural variations given in  
421 the publication, and the standard deviation for the upper and lower level of the range.

422  ***$^{234}\text{U}/^{235}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  atomic ratios:*** As depicted in Fig. 1 and 2, it can be seen that all  
423 the  $^{234}\text{U}/^{235}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  atomic ratios obtained in this inter-comparison are within the  
424 range of natural variation of natural U. The absolute values of  $z$ -score and  $zeta$ -score  
425 obtained for all results are less than 2, indicating the reported values and uncertainties are  
426 acceptable. All the laboratories achieved satisfactory accuracy both  $^{234}\text{U}/^{235}\text{U}$  and  
427  $^{234}\text{U}/^{238}\text{U}$  atomic ratios with relative bias ranging from -1.0% to 1.6% (except Lab E  
428 obtained relative bias of about -6%).

429  ***$^{235}\text{U}/^{238}\text{U}$  atomic ratio:*** The recommended range of natural U is relatively narrow  
430 (0.00725-0.00726 molar ratio), some of the reported results (Lab C and Lab D) deviated  
431 from that range (Fig. 3(a)). All the  $z$ -score values are within  $\pm 2$  (Fig. 3(b)), indicating  
432 that all results meet the quantitative requirement ( $\sigma_t$ ) set for this inter-comparison.  
433 However, in the  $zeta$ -score test, two values of  $|zeta|$  are in between of 2 and 3 (Lab

434 C=2.68, Lab D=2.28). This may be due to some bias was not taken into consideration  
435 when calculating the isotope ratio or the uncertainty. Nevertheless, high accuracy was  
436 obtained in all laboratories for  $^{235}\text{U}/^{238}\text{U}$  atomic ratio with relative bias varying from -  
437 0.9% to 0.5%.

### 438 ***Pu concentration and isotopic ratio***

439 Five results were reported for the Pu isotopes results for both pre-purified and the raw  
440 IAEA-384 material. In the pre-purification of Pu from IAEA-384 for direct measurement  
441 by ICP-MS by participating Labs, removal of U was deliberately retained insufficient  
442 (decontamination factor < 1000), in order to evaluate the performance of each laboratory  
443 in correcting for the polyatomic ions and tailing effect of  $^{238}\text{U}$  at  $m/z=239$  and 240.

444  ***$^{239}\text{Pu}$  and  $^{240}\text{Pu}$  massic activity:*** All the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  values obtained for the pre-  
445 purified material in this inter-comparison are higher than the reference value, with  
446 relative bias within 8-17% (except  $^{240}\text{Pu}$  results in Lab C, D and F with 31%, 187% and  
447 26%, respectively) and most of them are even above the upper limit of the 95%  
448 confidential interval (Fig. 4(a) and 5(a)). All the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  results obtained for the  
449 raw material are lower than the reference value, but well within the 95% confidential  
450 interval with relative bias of -13% to 8%. This indicates satisfactory accuracy for  $^{239}\text{Pu}$   
451 and  $^{240}\text{Pu}$  massic activities was achieved in all the laboratories for the raw IAEA-384  
452 material, while most results (except  $^{240}\text{Pu}$  values reported by Lab C, D and F) for the pre-  
453 purified material have satisfactory accuracy.

454 From the results presented, it is expected that  $z$ -score and  $zeta$ -score tests (Fig.4 and 5)  
455 would result in positive values for the purified material, while tests for the raw material  
456 would result in negative values. All the results passed the  $z$ -score and  $zeta$ -score tests for  
457  $^{239}\text{Pu}$  massic activity, indicating acceptable values and uncertainty (Fig. 4(b) and 4(c)). It  
458 can be seen from Fig. 5(b) that, except the Lab D result (9.37) for the pre-purified  
459 material which fails the  $z$ -score test, all the other  $z$ -score values for  $^{240}\text{Pu}$  are distributed  
460 within the acceptance criteria. In the  $zeta$ -score test (Fig. 5(c)), the  $zeta$ -score for the Lab  
461 C result in pre-purified material is 2.87, indicating the  $^{240}\text{Pu}$  value obtained is of  
462 questionable quality. This might be a consequence of the relatively low uncertainty for

463 the reported results. The *zeta*-score of the result of  $^{240}\text{Pu}$  in pre-purified material reported  
464 by Lab D is 3.29, indicating that the analysis is considered to be out of control.

465 The difference in the overall results between pre-purified and raw IAEA-384 could be  
466 potentially due to the uncertainties existed in the concentrations of  $^{242}\text{Pu}$  tracers and/or  
467 the inhomogeneity of the reference material. Another possible explanation to the  
468 consistent positive bias of the results for the pre-purified Pu samples could be due to the  
469 interferences (e.g., lanthanides [38]) present in the solution due to insufficient chemical  
470 separation. However, this explanation needs to be confirmed by further studies.

471  **$^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio:** The reference value for the  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio for IAEA-  
472 384 is  $0.049\pm 0.001$  [39]. All the reported values in this inter-comparison (except the  
473 result for the raw IAEA-384 material in Lab D with an exceptionally high relative bias  
474 (144.9%)) meet the criteria for accuracy evaluation with relative bias from -10% to 8%.  
475 For the raw material, except Lab D that obtained a *z*-score of -2.04, all the other *z*-score  
476 and *zeta*-score values obtained by each individual lab meet the criteria of the acceptable  
477 performance (Fig. 6). However, for the purified material, results indicate some deviation:  
478 in the *z*-score test, one value (Lab F=2.45) is questionable and two values (Lab C=3.67  
479 and Lab D=28.98) are unacceptable; in the *zeta*-score test, the Lab C and Lab D results  
480 (6.36 and 4.72, respectively) could be considered to be out of control. The high *zeta*-score  
481 obtained by Lab C for purified material might be related to the relative lower uncertainty  
482 in the reported results. The Lab D result of the  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio for the pre-  
483 purified material that was out of control might be due to unexpectedly high tailing in the  
484 spectra from  $^{238}\text{U}$ . The positive deviation from the reference value may be a result from  
485 not having control of the correction of the tailing at  $m/z=240$  from  $^{238}\text{U}$ . In this work, Lab  
486 D used a linear regression model for explaining the tailing from  $^{238}\text{U}$  on the masses  
487 above. However, this model might not explain the tailing properly, thus under-correction  
488 of the spectral interference is plausible [40].

489 **Uncertainty:** Noteworthy is that the uncertainties for the Pu results, especially for  $^{239}\text{Pu}$ ,  
490 in the raw material for all laboratories are lower than for the pre-purified materials. This  
491 is most likely due to the fact that the pre-purified material was deliberately not

492 completely cleaned up so larger uncertainties in corrections for hydrides, tailing and  
493 various matrix effects could play a role. It might also be due to the limited amount of  
494 material distributed to each lab contains relatively low quantity of Pu in the solution,  
495 therefore the total count rate in ICP-MS would be lower than for the raw material  
496 prepared by individually.

#### 497 ***Performance of different ICP-MS instruments***

498 In this inter-comparison exercise, three ICP-SFMS, two ICP-QQQ and one MC-ICPMS  
499 instrument were used for the U isotopic ratio measurement. For the Pu concentration and  
500 isotopic ratio measurement, four ICP-SFMS and two ICP-QQQ were used for the inter-  
501 comparison exercise.

#### 502 ***Precision for U isotopic ratio measurement***

503 For U isotopic ratios measurement, Element XR ICP-SFMS at Lab C and MC-ICP-MS at  
504 Lab D obtained comparably high precision with the expanded relative uncertainties of  
505 0.1-0.3%. The Lab B, Lab E and Lab F results are generally comparable within the range  
506 of 0.3-1.0%. Highest uncertainties were reported by Lab A ranging within 1.3-2.2%. It  
507 should be noted that for uncertainty estimation among all the laboratories in this work,  
508 the measurement precision of the sample as a main contributor, and the precision of the  
509 calibrator used for the correction of mass bias, the effect of dead time and the background  
510 have been taken into account.

511 In this work, all measurements using ICP-SFMS were done at low-resolution with  
512 maximum transmission and flat topped peaks to allow the best peak jumping conditions.  
513 The typical statistical precision for isotopic ratio measurement by double focusing ICP-  
514 SFMS instruments with single ion detection was reported to be about 0.1% [41], which is  
515 generally in line with the value reported by the ICP-SFMS at Lab C. Besides counting  
516 statistics, the measurement precision is affected by sample introduction and plasma  
517 fluctuation in the ICP source. The different introduction systems employed by ICP-SFMS  
518 instruments at Lab E (PFA-ST nebulizer) and Lab B (self-aspired nebulization with

519 conical nebulizer) could explain the difference in uncertainties obtained by the  
520 laboratories B, C and E.

521 ICP-SFMS and MC-ICP-MS are both sector field mass spectrometers with the  
522 application of single and multi-collector, respectively. The MC-ICP-MS has been  
523 reported in literature superior to the other instruments used with respect to isotope ratio  
524 measurements, provided that contribution from counting statistics is negligible.  
525 According to literature, one order magnitude higher precision can be achieved by MC-  
526 ICP-MS compared to ICP-SFMS [41]. The MC-ICP-MS enables flat-topped peaks even  
527 at higher resolution but drops in sensitivity. In this work, the MC-ICP-MS analysis was  
528 operated at low resolution mode with flat topped peaks at maximum transmission,  
529 therefore the relative uncertainty of the U isotope ratios measurement were superior (0.1-  
530 0.3%) to most single detector-ICP-MS results for U isotope ratios measurement in this  
531 work. The most likely reason for the relatively high uncertainty of U isotopic ratio  
532 measurement at Lab A relative Lab F (identical instrument with only the skimmer cone,  
533 Ni vs Pt, differs) is the daily performance.

#### 534 *Sensitivity and abundance sensitivity*

535 Sensitivities for different ICP-MS instruments used in this work vary within 0.7-6  
536 cps/ppq, with ICP-SFMS instruments (single or multi-collector) generally showing better  
537 transmission due to higher extraction voltage. Differences in sensitivity among different  
538 instrument types can be explained by different transmission efficiency, caused by  
539 differences in interface construction (e.g., ion deflection by ICP-QMS), acceleration  
540 voltages and electrostatic lens systems, vacuum systems, measurement strategies  
541 (reaction/collision mode) or mass resolution mode applied. Instruments equipped with  
542 improved interface design have yet an order of magnitude better transmission due to both  
543 geometry factors and the increased pumping rate. It is evident that the application of  
544 desolvation system APEX-Q at Lab C enhanced the sensitivity of ICP-SFMS instruments  
545 by 5 times (from 1.2 cps/ppq to 6 cps/ppq). The use of a high performance Pt cone and s-  
546 lens for ICP-QQQ at Lab F vs. Ni cone and x-lens at Lab A, led to a twofold increase in  
547 sensitivity.

548 The main problem in determination of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  by ICP-MS is the occurrence of  
549 interferences, including peak tailing or abundance sensitivity effects of neighboring  $^{238}\text{U}$ ,  
550 and the formation of polyatomic ions. The pronounced polyatomic interferences are the  
551 formation of U hydrides ( $^{238}\text{U}^1\text{H}^+$  and  $^{238}\text{U}^2\text{H}^+$ ) as the concentration of  $^{238}\text{U}$  in most  
552 environmental samples is more than five orders of magnitude higher than that of  $^{239}\text{Pu}$   
553 and  $^{240}\text{Pu}$ . Other nuclides in the sample matrix can also form polyatomic ions (e.g.,  
554  $^{204}\text{Pb}^{35}\text{Cl}^+$ ,  $^{207}\text{Pb}^{16}\text{O}_2^+$ ,  $^{202}\text{Hg}^{37}\text{Cl}^+$ ,  $^{208}\text{Pb}^{16}\text{O}_2^+$ ,  $^{208}\text{Pb}^{16}\text{O}^{14}\text{N}^1\text{H}_2^+$ ,  $^{194}\text{Pt}^{14}\text{N}^{16}\text{O}_2^+$  ) which  
555 hamper the accurate detection of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  [5, 42]. Therefore, careful chemical  
556 separation is necessary to eliminate these interferences, especially U, to ensure the  
557 reliability of the measurement.

558 Although most U in the sample can be removed effectively through several stages of  
559 chemical separation, a minor amount of U may always remain in the final solution before  
560 ICP-MS measurement. Application of proper sample introduction system in ICP-MS  
561 measurement for Pu measurement can efficiently reduce the  $\text{UH}^+/\text{U}^+$  ratio. Cao et al. [42]  
562 summarized the interference effect from  $^{238}\text{UH}^+$  by ICP-MS with different introduction  
563 systems reported in literature with  $\text{UH}^+/\text{U}^+$  ratios varying from  $1.5 \times 10^{-3}$  to  $7.2 \times 10^{-6}$ .  
564 APEX-Q was reported to have one order of magnitude lower  $\text{UH}^+/\text{U}^+$  ratio than  
565 pneumatic nebulizers such as MicroMist and PFA. In this work, however, APEX-Q  
566 system employed in combination with PFA nebulizer for ICP-SFMS at Lab C, indicated  
567 no better  $\text{UH}^+/\text{U}^+$  ratio ( $10^{-5}$ ) compared with the ICP-QQQ at Lab A and ICP-SFMS at  
568 Lab B (equipped with Conical nebulizer through self-aspired nebulization).

569 The quadrupole instruments have their main advantage in superior abundance sensitivity,  
570 which in particular is valid for the ICP-QQQ instrument using two quadrupoles thus  
571 enabling abundance sensitivities in the order of  $10^{-14}$ . The ICP-QQQ further has a gas  
572 reaction cell enabling active removal of polyatomic interferences but at a cost in ion-  
573 transmission. In this work, a reaction cell was applied to the ICP-QQQ at Lab F to  
574 eliminate the  $^{238}\text{U}$  interferences by highly efficient reaction of  $\text{U}^+$  and  $\text{UH}^+$  with  $\text{CO}_2$ , but  
575 no reaction with  $\text{Pu}^+$ .

576 It should be noted that even though this work focus much on the performance of different  
577 ICP-MS instruments in the intercom-prison exercise, the difference in the analytical  
578 accuracy and precision among the participating labs could also be related to different  
579 sample processing procedure prior to the ICP-MS measurement, for example, whether a  
580 microwave digestion procedure, filtering or a fusion melt was utilized in the sample pre-  
581 treatment.

582 **Table 1** Instrumentation conditions used in each laboratory for the inter-comparison exercise

	Lab A	Lab B		Lab C		Lab D		Lab E	Lab F
<b>Instrument model</b>	Agilent 8800 ICP-QQQ	Element XR ICP-SFMS		Element XR ICP-SFMS		Nu Plasma MC-ICP-MS	AttoM double-focusing ICP-SFMS	Element 2 ICP-SFMS	Agilent 8800 ICP-QQQ
<b>Radionuclides measured</b>	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$ , $^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$	$^{238}\text{U}$ , $^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$ , $^{238}\text{U}$	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$ , $^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$	$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$ , $^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{242}\text{Pu}$
<b>Auto-sampler</b>	AS X-520 (CETAC))	No	No			ASX110	ASX260	SC2 DX	AS X-520 (CETAC))
<b>Sample uptake</b>	Peristaltic pump	Self-aspired nebulization	Self-aspired nebulization	Peristaltic pump	APEX-Q	Peristaltic pump	Peristaltic pump	PrepFast system	ISIS 2
<b>Nebulizer</b>	MicroMist (Borosilicate glass)	Conikal nebulizer	Conikal nebulizer	MicroMist nebulizer	PFA nebulizer	Meinhard and Desolvating nebulizer (DSN)	Meinhard nebulizer	PFA-ST	MicroMist quartz
<b>Spray chamber</b>	Quartz, , Scott-type double-pass	Twister spray chamber	Twister spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic double pass spray chamber	Quartz baffled micro cyclonic with dual gas inlet	Quartz, Scott-type double-pass
<b>Cooling</b>	Peltier cooling system	No cooling	No cooling	No cooling	No cooling	No cooling	No cooling	PC <sup>3x</sup> -Peltier cooling system	PC <sup>3x</sup> -Peltier cooling system
<b>Sample cone</b>	1 mm diameter orifice, Ni sample cone	Ni sampler, TF1001-Ni	Ni sampler, TF1001-Ni	Ni sample cone	Ni sample cone	Ni sample cone	Ni skimmer cone	Alunium ES-3000-18032	1 mm Pt cone
<b>Skimmer cone</b>	0.4 mm diameter orifice, stainless steel base with Ni tip	Ni skimmer, TF-1002A-Ni	Ni skimmer, TF-1002A-Ni	X skimmer cone	X skimmer cone	Ni skimmer cone	Ni skimmer cone	Alunium type X-Skimmer ES-3000-1805X	0.4 mm Ni skimmer cone,
<b>RF generator</b>	1500 W	1200 W	1200 W	1400 W	1400 W	1300 W	1300W	1350 W Power	1550 W
<b>Typical sensitivity, cps/ppq <math>^{238}\text{U}</math></b>	0.7	2	1.8	1.2	6	2	2	0.8	1.5 with s-lens (s-lens for Pu and x-lens for U)
<b><math>^{238}\text{UH}^+/\text{U}^+</math></b>	1/14892	1/104000	1/104000		1/100000		3/100000		None



583 **Table 2.** Results of U isotopic ratios for NBL CRM 103-A from each laboratory for the inter-comparison exercise ( $U$  is the expanded  
584 relative uncertainty with a coverage factor of  $k=1$ )

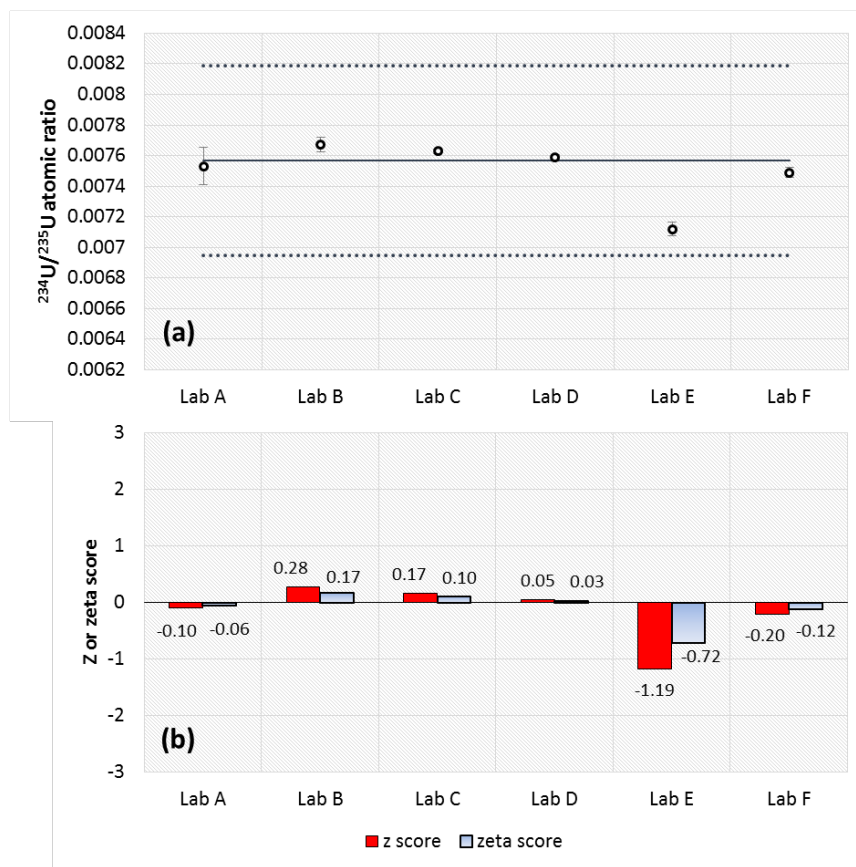
Atom ratio		Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Ref. value
$^{234}\text{U}/^{235}\text{U}$	<b>Average</b>	0.007530 (n=10)	0.007672 (n=6)	0.007630 (n=6)	0.007587 (n=2)	0.007119 (n=6)	0.007490 (n=10)	0.007567
	<b><math>U</math> (<math>k=1</math>), %</b>	1.63	0.64	0.20	0.22	0.64	0.47	8.20
	<b>Bias, %</b>	-0.49	1.38	0.83	0.26	-5.93	-1.02	
$^{235}\text{U}/^{238}\text{U}$	<b>Average</b>	0.007193 (n=10)	0.007268 (n=6)	0.007225 (n=6)	0.007278 (n=2)	0.007288 (n=6)	0.00727 (n=10)	0.007255
	<b><math>U</math> (<math>k=1</math>), %</b>	1.36	0.30	0.14	0.12	0.36	0.37	0.07
	<b>Bias, %</b>	-0.85	0.18	-0.41	0.31	0.45	0.21	
$^{234}\text{U}/^{238}\text{U}$	<b>Average</b>	0.0000542 (n=10)	0.0000558 (n=6)	0.0000551 (n=6)	0.0000551 (n=2)	0.0000519 (n=6)	0.0000544 (n=1)	0.0000549
	<b><math>U</math> (<math>k=1</math>), %</b>	2.21	0.72	0.18	0.31	0.96	0.55	8.20
	<b>Bias, %</b>	-1.28	1.64	0.36	0.55	-5.56	0.91	

585

586 **Table 3.** Results of Pu isotopes for IAEA-384 from each laboratory for the inter-comparison exercise (U is the expanded relative  
587 uncertainty with a coverage factor of  $k=1$ )

Institute		Lab A		Lab B		Lab C		Lab D		Lab F		Ref. value
Sample name		Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=3)	Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=1)	Pre-purified Pu (n=3)	Raw material (n=2)	Raw material
<sup>239</sup> Pu, Bq/kg	<b>Average</b>	106.0	89.4	107.3	85.4	108.6	86.3	115.4	96.6	110.0	95.0	98 (85-105)
	<b>U (k=1), %</b>	2.1	0.8	1.6	0.8	1.5	1.3	16.5	5.3	6.1	2.0	
	<b>Bias, %</b>	8.2	-8.8	9.5	-12.9	10.8	-11.9	17.8	-1.4	12.2	-3.1	
<sup>240</sup> Pu, Bq/kg	<b>Average</b>	20.3	16.6	20.5	15.8	22.9	15.8	50.3	15.9	22.0	18.3	17.5 (15.1-18.7)
	<b>U (k=1), %</b>	15.8	3.0	2.0	1.3	3.1	2.5	19.5	21.4	8.2	1.6	
	<b>Bias, %</b>	16.0	-5.1	17.0	-9.7	30.9	-9.7	187.4	-9.1	25.7	4.6	
<sup>240</sup> Pu/ <sup>239</sup> Pu atom ratio	<b>Average</b>	0.053	0.051	0.052	0.050	0.058	0.050	0.120	0.044	0.055	0.053	0.049
	<b>U (k=1), %</b>	13.2	3.9	13.5	10.0	1.7	2.0	12.5	11.4	5.5	3.8	2.0
	<b>Bias, %</b>	8.2	4.1	6.1	2.0	18.4	2.0	144.9	-10.2	12.2	8.2	

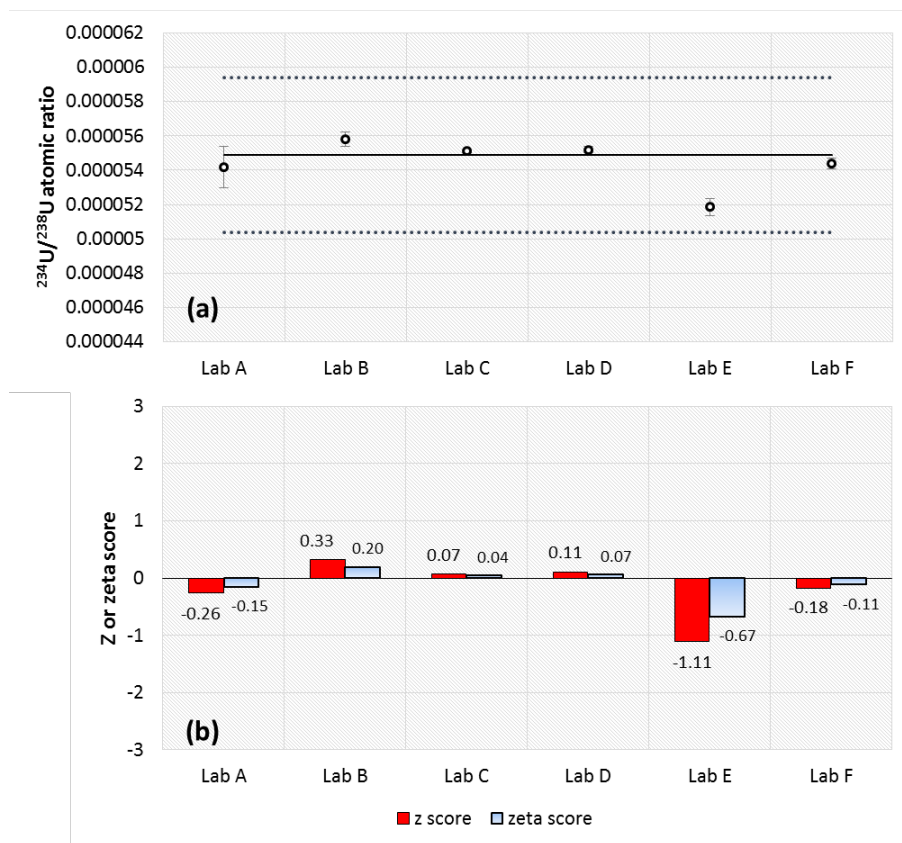
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589

590 **Fig. 1**  $^{234}\text{U}/^{235}\text{U}$  isotope ratio (a) and z-score and zeta-score (b) calculated from the  
 591 measurement of the reference material NBL CRM 103-A. The solid and dotted lines  
 592 represent the observed average and variation of natural U (given by IUPAC), respectively  
 593 [25]. The error bars of the results represent the expanded uncertainty with a coverage  
 594 factor,  $k=1$ .

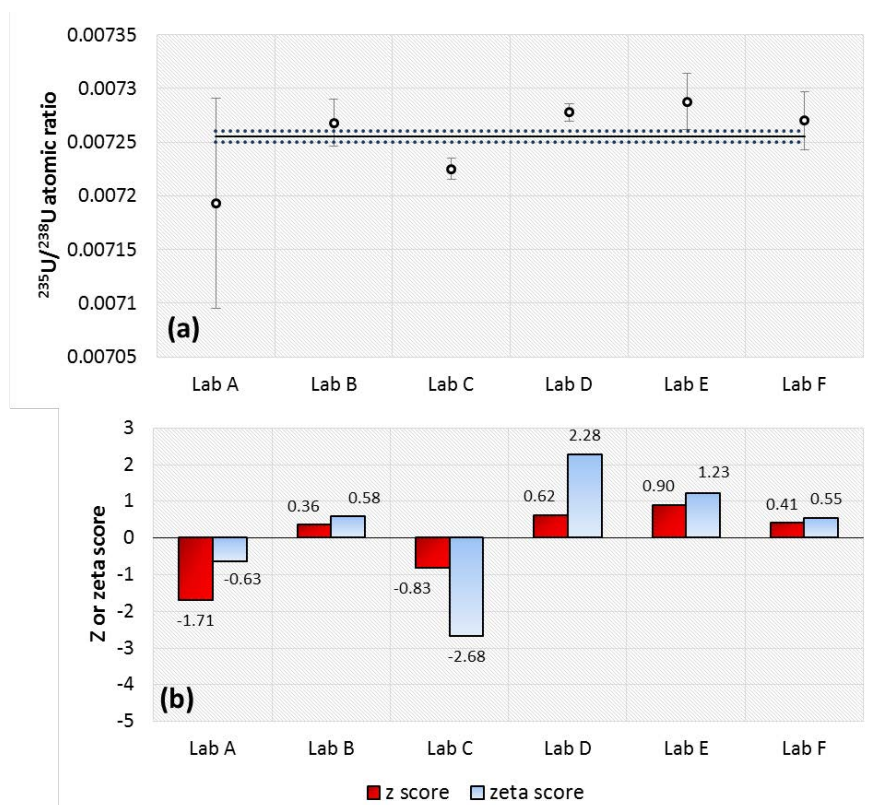
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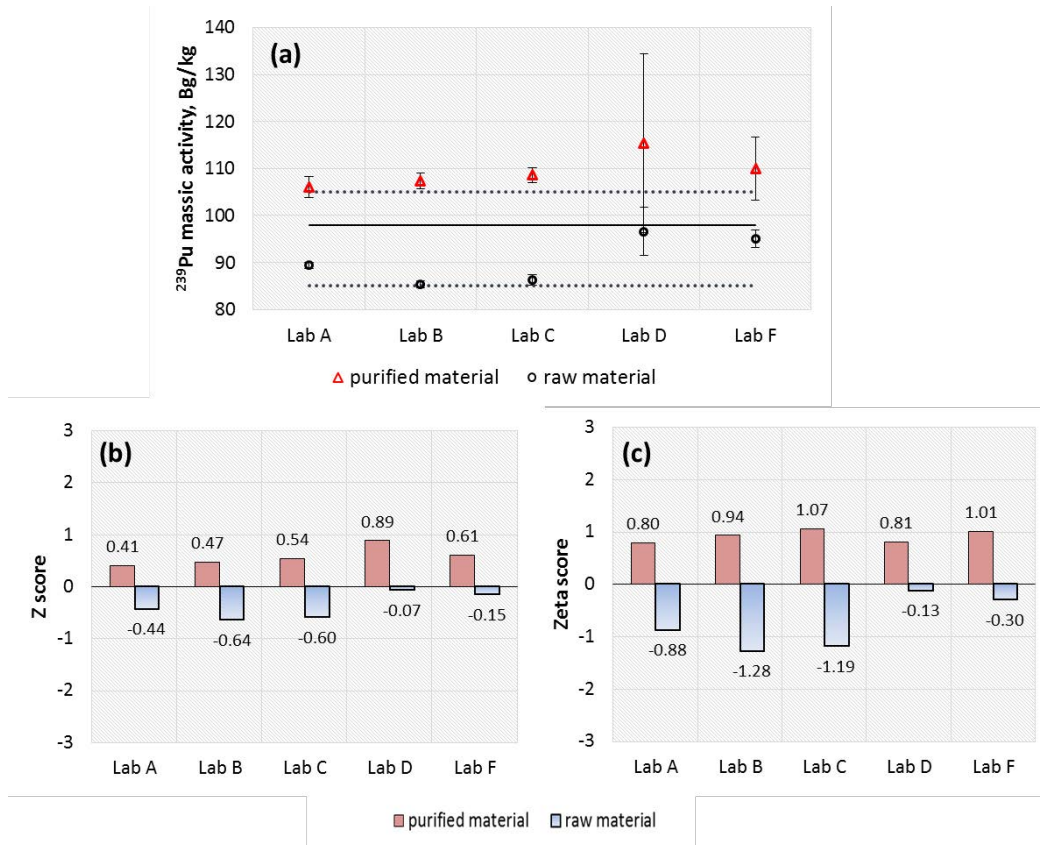
597 **Fig. 2**  $^{234}\text{U}/^{238}\text{U}$  isotope ratio (a) and  $z$ -score and  $zeta$ -score (b) calculated from the  
 598 measurement of the reference material NBL CRM 103-A. The solid and dotted lines  
 599 represent the observed average and variation of natural U (given by IUPAC), respectively  
 600 [25]. The error bars of the results represent the expanded uncertainty with a coverage  
 601 factor,  $k=1$ .

602



603

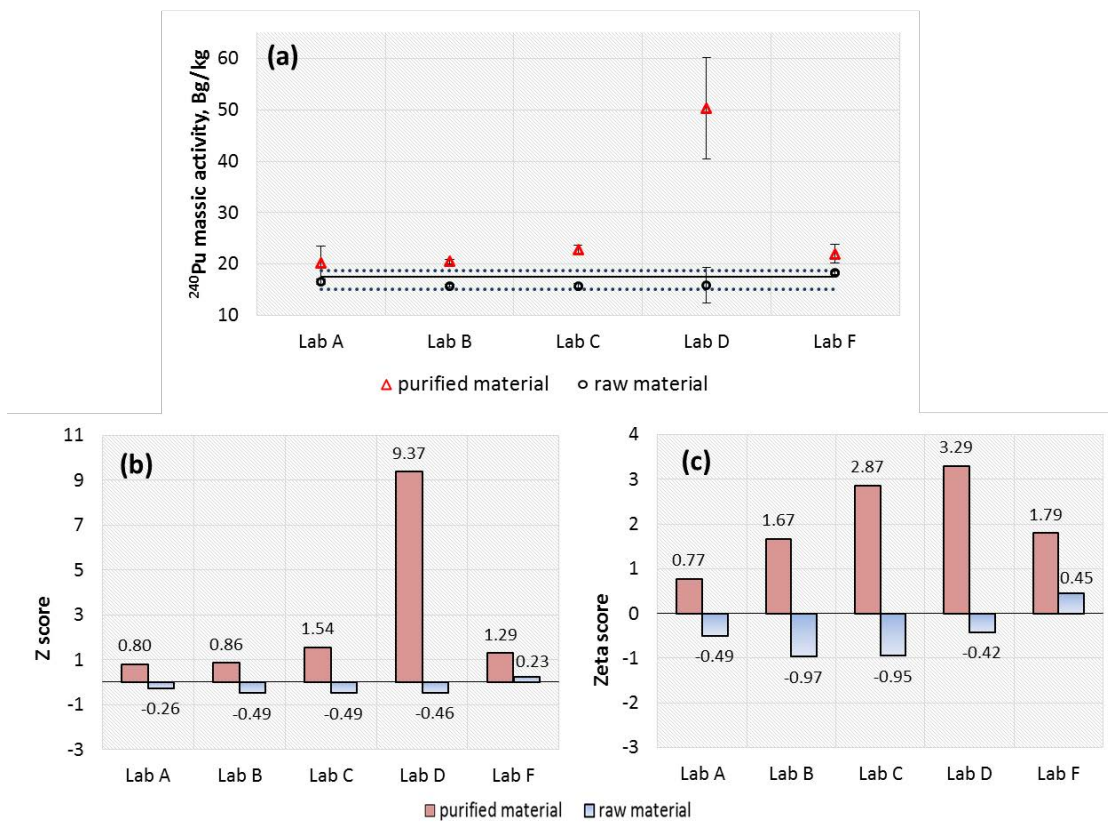
604 **Fig. 3**  $^{235}\text{U}/^{238}\text{U}$  isotope ratio (a) and  $z$ -score and  $zeta$ -score (b) calculated from the  
 605 measurement of the reference material NBL CRM 103-A. The solid and dotted lines  
 606 represent the observed average and variation of natural U (given by IUPAC), respectively  
 607 [25]. The error bars of the results represent the expanded uncertainty with a coverage  
 608 factor,  $k=1$ .



609

610 **Fig. 4**  $^{239}\text{Pu}$  massic activities (a), Z-score (b) and Zeta-score (c) for the reference material  
 611 IAEA-384. The solid line represents the reference value and dotted lines represent the  
 612 95% confidential interval [39]. The error bars of the results represent the expanded  
 613 uncertainty with a coverage factor,  $k=1$ .

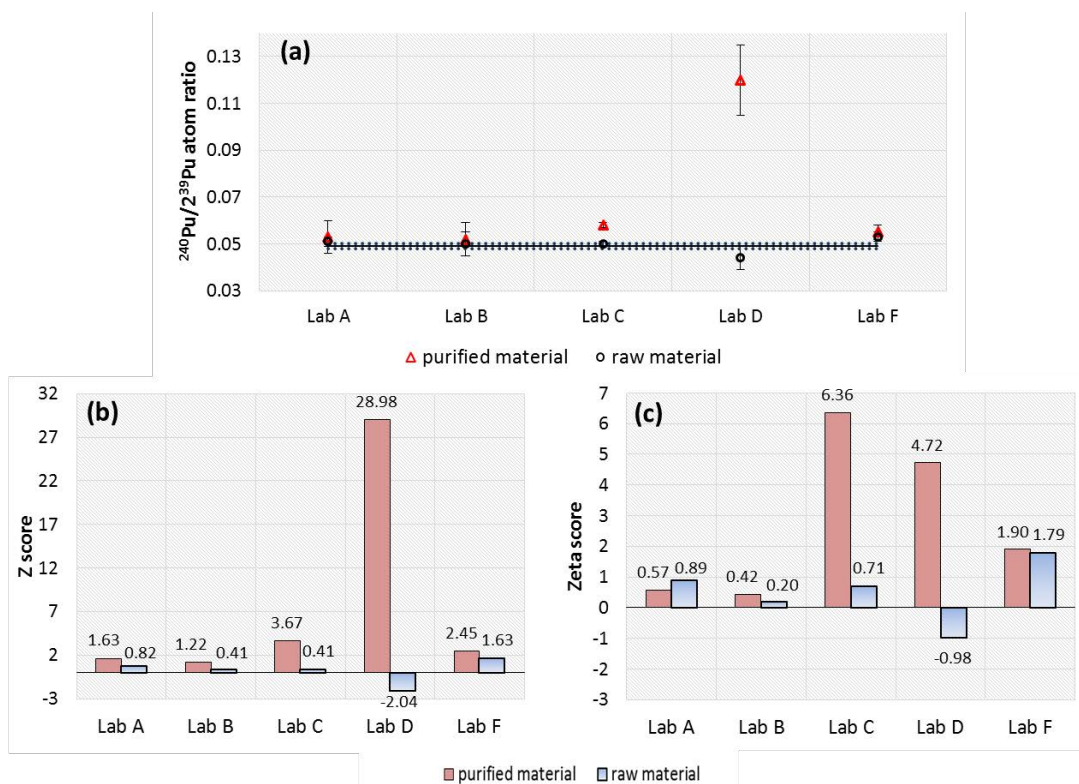
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615

616 **Fig. 5**  $^{240}\text{Pu}$  massic activities (a), Z-score (b) and Zeta-score (c) obtained for the reference  
 617 material IAEA-384. The solid line represents the reference value and dotted lines  
 618 represent the 95% confidential interval [39]. The error bars of the results represent the  
 619 expanded uncertainty with a coverage factor,  $k=1$ .

620



621

622 **Fig. 6**  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio (a), *Z*-score (b) and *Zeta*-score (c) obtained for the  
 623 reference material IAEA-384. The solid line represents the reference value and dotted  
 624 lines represent the 95% confidential interval [39]. The error bars of the results represent  
 625 the expanded uncertainty with a coverage factor,  $k=1$ .

626



627        **Conclusions**

628        Satisfactory accuracy was obtained in this inter-comparison exercise for all the U isotopic  
629        ratio measurement. High-resolution sector field ICP-MS is the preferred option to achieve  
630        high precision for U isotopic ratios. Although the U isotopic ratios measurement for  
631        NBL103 A was generally well performed in all labs, the measurement precision obtained  
632        in this work leaves room for improvement.

633        All the Pu results reported for the raw IAEA-384 material achieved satisfactory accuracy,  
634        while few  $^{240}\text{Pu}$  values for the pre-purified material indicate high relatively bias. This  
635        emphasizes the importance of the purity of Pu fraction with respect to the analytical  
636        accuracy and special care needs to be paid on the existence of interfering nuclides which  
637        could possibly induce large analytical error in the measurement. If the ICP-MS is  
638        sensitive to matrix effect or a solely calibration would not ensure the accuracy of the Pu  
639        result measured from a non-purified solution, an additional chemical purification of the  
640        Pu fraction might be needed.

641        It is believed that this inter-laboratory exercise is beneficial to share among different ICP-  
642        MS users and prompt more efficient application of ICP-MS. The fact of no satisfactory  
643        explanations on the lack of accuracy for some results obtained in this inter-comparison  
644        supports the idea that inter-comparisons should be conducted repeatedly to identify trends  
645        among laboratories.

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