

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
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38 Abstract

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

inter-laboratory comparison exercise among the Nordic countries was performed,
focusing on the measurement of U and Pu isotopes in certified reference materials by
ICP-MS. The performance and characters of different ICP-MS instruments are evaluated
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-SFMS), multi-collector ICP-MS (MC-ICP-MS), and recently introduced triple 63 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

isotopes by one detector vs. the simultaneous measurement of isotopes at multiple
detectors, respectively. Owing to its possibility of simultaneous detection, multi-collector
ICP-MS is outstanding regarding expanded uncertainty of isotope ratio determination.
However, depending on the application and the need of precision, single collector or
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 aspects: 1) ICP-MS measurement for U isotopic ratios (234U/235U, 235U/238U and 82 ²³⁴U/²³⁸U); 2) ICP-MS measurement for Pu isotopes (²³⁹Pu and ²⁴⁰Pu) concentrations and 83 isotopic ratio. The inter-comparison results were evaluated and discussed to shed some 84 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*

A certified reference material NBL CRM 103-A Pitchblende Ore – Silica Mixture Uranium Standard (U 0.04992 \pm 0.00078 Wt.%) from New Brunswick Laboratory (NBL) was used in the inter-comparison exercise to perform the U isotopic ratios (²³⁴U/²³⁵U, ²³⁵U/²³⁸U, ²³⁴U/²³⁸U) measurement. According to the certificate, the material was prepared by milling and blending NBL CRM 6-A Pitchblende Ore (67.91 \pm 0.05 Wt.% U₃O₈) with silica (99.9% SiO₂) to obtain a uniform mixture of desired U concentration. 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 ²³⁹Pu and ²⁴⁰Pu 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, HNO₃ and HCl). After suitable dilution with 106 diluted HNO₃, 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 HNO₃ with addition of 200 µl of

110 concentrated HCl. Thereafter the sample solution was diluted with 0.3-0.5 M HNO₃ 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 HNO₃ and 200 µl of concentrated HCl. Thereafter
- 114 the sample solution was diluted in 0.28 M HNO₃ 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 HNO₃ 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 HNO₃. Thereafter the sample

solution was diluted in 1.4 M HNO₃ 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 HNO₃ (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 H₂O.

124 At Lab E, the sample was dissolved only with 0.1 M HNO₃in 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 $0.5 \text{ M HNO}_3 + 0.25\%$ (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 HNO₃ 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

For ²³⁹Pu and ²⁴⁰Pu concentration and isotopic ratio measurement, two approaches were 133 134 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

summarized as follows. 2 g of IAEA-384 sediment was spiked with 0.2528g of 0.1037

- 145 Bq/kg ²⁴²Pu tracer and dissolved directly with 20 ml of 8 M HNO₃. 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 HNO₃. The dissolved sample solution was loaded onto the column, and the column
- 148 was washed with 60 ml of 8 M HNO₃ 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 HNO₃, and each 2 ml of aliquot was transferred to a

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

²⁴²Pu tracer and digested with 40 ml *aqua regia* at 200 °C for 2 hours. After filtration, 1

mg of Fe was added to form $Fe(OH)_3$ co-precipitation with the addition of NH₃ 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 $K_2S_2O_5$ was added with stirring for 20 min. to reduce Pu

161 to Pu(III). NH₃·H₂O was added to adjust the sample to pH 8-9 and the precipitate was

162 centrifuged. 3 ml of concentrated HNO₃ was added to dissolve the residue and the sample

163 was finally adjusted to 3 M HNO₃ for chromatographic purification. 2 ml of TEVA (100-

164 150 μ m) column was packed and preconditioned with 20 ml of 3 M HNO₃. The dissolved

165 sample solution was loaded onto the TEVA column, and the column was washed with 60

166 ml of 8 M HNO₃ 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 HNO₃ 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 (LiBO₂, Claisse, ultra-pure

171 grade, Gammadata, Uppsala, Sweden) and thereafter spiked with about 10 pg of ²⁴²Pu

172 (NIST SRM 4334G). The sample mixture was first pre-oxidized at 650°C for 1 hour prior

to fusion for 15 minutes at 1050°C. The melt was allowed to cool before mixing with 100

174 ml of 1.4 M HNO₃ and thereafter the melt was dissolved under stirring and heat. When

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 HNO₃.

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 NH₂OH·HCl was added. After cooling, 900 mg

180 of NaNO₂ 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

the reservoir. The column was pre-conditioned with 5 ml of 3 M HNO₃ and then the

184 sample was added. The column was rinsed with 10 ml of 3 M HNO₃, followed by 10 ml

185 of 9 M HCl and 20 ml 3 M HNO₃. Pu was eluted in 5 ml of 0.01% hydroxylethylidene

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-

assisted digestion system using HNO₃+HF mixture as described earlier for pre-treatment

190 of NBL CRM 103-A. After evaporation, the sample was re-dissolved in 3M HNO₃ 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 HNO₃ and 4 ml of 9.6 M HCl followed by

193 Pu elution in 8 ml of 5 M HCl+0.05M oxalic acid. ²⁴²Pu 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 ²⁴²Pu 196 as a tracer. The sample was dissolved with the mixture of concentrated HNO₃ (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(NO₃)₃ + 3 M HNO₃, 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 HNO₃). The UTEVA column was washed with 10 ml of 3 M HNO₃. The effluent of 204 the sample loading and washing solution were loaded onto a TRU column 205 (preconditioned with 5 ml of 2 M HNO₃). The TRU column was washed with 5 ml of 2

206 M HNO₃, 5 ml of 0.1 M NaNO₂ + 2 M HNO₃, 3 ml of 0.5 M HNO₃, 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

with 10 ml of 0.1 M NH₄HC₂O₄ and evaporated to dryness. 2 ml of conc. HNO₃ 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

ammonium oxalate solution containing Pu was evaporated into dryness with addition of a

few drops of H₂O₂ and concentrated HNO₃. The residue was dissolved to 10 ml of 5 %

213 HNO₃ 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% HNO₃ 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

of concentrated HNO₃ and 4 mL of 48 % (w/w) HF were added. 24.1 pg of ²⁴²Pu was

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

evaporated to dryness, and taken up in 7 ml of $0.8 \text{ M HNO}_3 + 0.2 \text{ M HF}$ for analysis. The

pre-purified Pu sample was diluted in a ratio of 1:3 with 0.8 M HNO₃ + 0.2 M HF before
analysis.

226 Instrumentation, measurement and calculations

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

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

ppm standard solution of U (Scientific Standards) was diluted to different levels of concentrations and used for calibration purposes. All standard solutions and samples were 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 the standard solution NBL-112a with a concentration of 0.5 ppb. The major isotope ratio 242 $n(^{235}\text{U})/n(^{238}\text{U})$ was determined in a sample diluted to achieve a maximum intensity of 1 243 $\times 10^6$ counts/s at m/z 238. The minor isotope ratio $n(^{234}\text{U})/n(^{235}\text{U})$ was measured in a 244 sample diluted to achieve an intensity of about 1×10^6 counts/s at m/z 235 and thereafter 245 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 246 $n(^{234}\text{U})/n(^{235}\text{U})$. For the measurement of Pu, a 0.5 M HNO₃ as a blank, ²⁴²Pu (4.09 ppt) 247 standard and ²³⁸U (1ppb) standard was measured in parallel with the purified Pu fraction 248 249 (in 0.5 M HNO₃). 1 ppb In (as InCl₃) 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 contributions both from blank and ²³⁸UH. Mass bias correction was not performed for 252 ²³⁹Pu and ²⁴⁰Pu, whereas average isotope ratios (n=5) of $n(^{239}Pu)/n(^{242}Pu)$ and 253 $n(^{240}\text{Pu})/n(^{242}\text{Pu})$ were calculated based on the intensities measured by ICP-MS. 254 Thereafter the activity concentrations of ²³⁹Pu and ²⁴⁰Pu in the raw sample were 255 calculated by multiplying the total amount of ²⁴²Pu tracer spiked in the sample with 256 ²³⁹Pu/²⁴²Pu and ²⁴⁰Pu/²⁴²Pu isotopic ratios, respectively. 257

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 was tuned for maximum U intensity meanwhile keeping the U oxide formation as low as 262 possible. The typical sensitivity is about 2 cps per ppq for ²³⁸U with the RPQ lens 263 264 inactivated. When using the instrument with the RPQ lens activated, the typical sensitivity is decreased by about 10%, see Table 1. The automatic dead time correction 265 266 was disconnected as this correction was performed post-acquisition. The sample

introduction systems used consisted of a Conikal nebulizer, a Twister spray chamber, a
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 and spectral interference at m/z 239 from ²³⁸U using the certified reference material 270 271 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 individual, averaged signal intensities. The detector dead time and its associated 275 276 uncertainty, was determined to be 73.1 ± 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 blank levels, and thereafter mass bias corrected ratios for $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$, 280 $n(^{240})$ Pu/ $n(^{239})$, $n(^{239})$ Pu/ $n(^{242})$ and $n(^{240})$ Pu/ $n(^{242})$ Pu were calculated using the Russell 281 equation [30]. For the separated Pu sample, the signal at m/z 239 was also corrected for 282 contributions from ²³⁸UH and peak tailing from ²³⁸U prior to mass bias correction. All 283 284 uncertainties were evaluated in accordance with ISO/GUM (1995) using the software 285 GUM Workbench [32].

Lab C: An ICP-SF-MS (ELEMENT XR, Thermo Scientific) was used for both Pu and U 286 287 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 sensitivity. This set-up offers a typical sensitivity of 1.2 cps per ppg for ²³⁸U and 290 291 238 U/ 238 U¹H ratio of >60000. For the Pu isotope measurement, a desolvation sample 292 introduction system (APEX) equipped with a PFA nebulizer and high efficiency skimmer cone was used. RPO was also activated with a typical sensitivity of > 6 cps per 293 ppq for ²³⁸U. Standard solutions of U0002 CRM, IRMM-184, CRM130 and 1000-ppm U 294 295 standard (Scientific Standards) were used for tailing and spectral interference corrections 296 as well as for calibration purposes.

Mathematical corrections for ²³⁸UH⁺ and tailings were performed based on experimental factors deduced by analyzing U0002 CRM. Mass bias was assessed using IRMM-184 (natural U). Concentration was determined using external calibration with diluted 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 HNO₃ (2%) 309 has been used between U isotopes measurements. Two Faraday detectors have been used for ²³⁸U and ²³⁵U and one ion counter has been used for ²³⁴U, ²³³U and tail corrections in 310 311 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 counter used for the determination of ²³⁴U and ²³³U. The international U standard UO10 315 316 has been used for quality control at the beginning and at the end of each run. The measured ²³⁴U/²³⁸U and ²³⁵U/²³⁸U ratios for that standard during analytical sessions were 317 318 0.00005436 ± 35 and 0.010149 ± 8 (n = 4), compared to respective values $0.00005448 \pm$ 319 4 (reference value from [34]) and 0.010140 ± 10 (certified value).

The Nu AttoM Single-Collector ICP-MS instrument was used for the determination of ²³⁹Pu and ²⁴⁰Pu. The sample introduction system consisted of an autosampler, a peristaltic pump, a Meinhard nebulizer, nickel and sampler cones and a cyclonic spray chamber without cooling. In determination of ²⁴⁰Pu and ²³⁹Pu, the samples were bracketed using a CPITM single element solution of 1 ppb of U in 2% HNO₃, meaning that the U standard 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 using 80 sweeps of 500 cycles at low resolution. The isotopes of ²³⁸U, ²³⁵U, ²³⁹Pu, ²⁴⁰Pu, 327 and ²⁴²Pu, as well as half masses at 239.5 and 240.5 were measured:. The dwell time was 328 1ms for each isotope. Washing time was 120 s and a further 60 s of sample uptake was 329 330 allowed before measurement started. The results have been calculated using an in house excel data reduction program. The natural ratio of $^{238}U/^{235}U$ has been used to calculate 331 the mass bias and apply a correction for ${}^{240}Pu/{}^{239}Pu$. The fractionation factor, which was 332 used to correct for the mass bias on ²⁴⁰Pu/²³⁹Pu ratio, was calculated based on the 333 334 ²³⁵U/²³⁸U ratio (set at 0.0072527). After an acid blank correction, a linear regression through the half mass 239.5 and 240.5 was also made, to calculate the tailing on ²³⁹Pu 335 and ²⁴⁰Pu. 336

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 approx. 0.8 cps per ppq for ²³⁸U. ²³⁵U and ²³⁸U were measured in analog mode, and ²³⁴U 342 was measured in counting mode. The UH⁺ formation at m/z=236 from ²³⁵U was approx. 343 344 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 °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 CO₂ in the reaction cell, allowing for unreacted Pu to be analysed on mass (here: 239, 240, 242) with negligible remaining ²³⁸UH⁺ interference. The concentrations of U 351 are, in all samples, estimated at m+16 for control of the ²³⁸UH⁺ interference. No 352 353 correction equation was applied to the results, as the concentrations of U were low. The 354 octapole bias was kept close to zero (-1 V) to prevent increased formation of PuO⁺. For 355 increased sensitivity, an s-lens was used and the mass balance of the quadrupoles was set to 92 % (240 amu/260 amu). Typical sensitivity in no-gas mode is about 1.5 cps per ppq for 238 U. Due to bureaucratic difficulties, it proved impossible to obtain an isotopic Pu standard for isotope calibration and mass bias determination. Therefore IAEA 135 certified reference material was chosen to be used as an isotopic standard material for mass bias correction based on the average 240 Pu/ 239 Pu atom ratio (n=47) published in literature. The concentrations of 239 Pu and 240 Pu were calculated from 240 Pu/ 242 Pu and 239 Pu/ 242 Pu multiplied by total amount of 242 Pu spiked.

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

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

$$z = \frac{x - \overline{x}}{\sigma_t} \times 100\% \tag{1}$$

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

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

$$zeta = \frac{x - \overline{x}}{\sqrt{u_x^2 + u_X^2}}$$
(2)

where *x* is the participant's result, *X* is the assigned value, u_x is the standard uncertainty of a participant's result, and u_x is the standard uncertainty of the assigned value. The performance is considered to be acceptable if $|zeta| \le 2$. A |zeta| from 2 to 3 indicates that the results are of questionable quality. If |zeta| > 3, the analysis was considered to be out of control.

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

$$Bias = \frac{x - X}{X} \times 100\% \tag{3}$$

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

392

400

402 The criteria for accuracy evaluation is according to IAEA recommendation [37]. If the 403 |Bias| < 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}Pu activities and ²⁴⁰Pu/²³⁹Pu 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 ($^{234}U/^{235}U$, $^{235}U/^{238}U$ and $^{234}U/^{238}U$) in the NBL CRM 103-A reference 409 material, and in Table 3 for Pu isotopes (239 Pu and 240 Pu) massic activity and 240 Pu/ 239 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 ${}^{234}U/{}^{235}U$ and ${}^{234}U/{}^{238}U$ atomic ratios: As depicted in Fig. 1 and 2, it can be seen that all 423 the ${}^{234}U/{}^{235}U$ and ${}^{234}U/{}^{238}U$ 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 ${}^{234}U/{}^{235}U$ and 427 ${}^{234}U/{}^{238}U$ atomic ratios with relative bias ranging from -1.0% to 1.6% (except Lab E 428 obtained relative bias of about -6%).

429 $^{235}U/^{238}U$ 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 ± 2 (Fig. 3(b)), indicating 432 that all results meet the quantitative requirement (σ_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**

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

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

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 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 material which fails the z-score test, all the other z-score values for ²⁴⁰Pu are distributed 459 within the acceptance criteria. In the *zeta*-score test (Fig. 5(c)), the *zeta*-score for the Lab 460 C result in pre-purified material is 2.87, indicating the ²⁴⁰Pu value obtained is of 461 462 questionable quality. This might be a consequence of the relatively low uncertainty for

the reported results. The *zeta*-score of the result of ²⁴⁰Pu in pre-purified material reported
by Lab D is 3.29, indicating that the analysis is considered to be out of control.

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

²⁴⁰Pu/²³⁹Pu atom ratio: The reference value for the ²⁴⁰Pu/²³⁹Pu atomic ratio for IAEA-471 472 384 is 0.049±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%. For the raw material, except Lab D that obtained a z-score of -2.04, all the other z-score 475 476 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=3.67479 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 in the reported results. The Lab D result of the ²⁴⁰Pu/²³⁹Pu atomic ratio for the pre-482 483 purified material that was out of control might be due to unexpectedly high tailing in the spectra from ²³⁸U. The positive deviation from the reference value may be a result from 484 485 not having control of the correction of the tailing at m/z=240 from ²³⁸U. In this work, Lab D used a linear regression model for explaining the tailing from 238 U on the masses 486 487 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 ²³⁹Pu, 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**

In this inter-comparison exercise, three ICP-SFMS, two ICP-QQQ and one MC-ICPMS instrument were used for the U isotopic ratio measurement. For the Pu concentration and isotopic ratio measurement, four ICP-SFMS and two ICP-QQQ were used for the intercomparison 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 application of single and multi-collector, respectively. The MC-ICP-MS has been 522 523 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-ICP-MS compared to ICP-SFMS [41]. The MC-ICP-MS enables flat-topped peaks even 526 527 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.

The main problem in determination of ²³⁹Pu and ²⁴⁰Pu by ICP-MS is the occurrence of 548 549 interferences, including peak tailing or abundance sensitivity effects of neighboring ²³⁸U, 550 and the formation of polyatomic ions. The pronounced polyatomic interferences are the formation of U hydrides ($^{238}U^{1}H^{+}$ and $^{238}U^{2}H^{+}$) as the concentration of ^{238}U in most 551 environmental samples is more than five orders of magnitude higher than that of ²³⁹Pu 552 and ²⁴⁰Pu. Other nuclides in the sample matrix can also form polyatomic ions (e.g., 553 ${}^{204}Pb{}^{35}Cl^+, \ {}^{207}Pb{}^{16}O_2{}^+, \ {}^{202}Hg{}^{37}Cl^+, \ {}^{208}Pb{}^{16}O_2{}^+, \ {}^{208}Pb{}^{16}O{}^{14}N{}^1H_2{}^+, \ {}^{194}Pt{}^{14}N{}^{16}O_2{}^+ \) \ which$ 554 hamper the accurate detection of ²³⁹Pu and ²⁴⁰Pu [5, 42]. Therefore, careful chemical 555 556 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 ICP-MS measurement. Application of proper sample introduction system in ICP-MS 560 561 measurement for Pu measurement can efficiently reduce the UH⁺/U⁺ ratio. Cao et al. [42] summarized the interference effect from ²³⁸UH⁺ by ICP-MS with different introduction 562 systems reported in literature with UH⁺/U⁺ ratios varying from 1.5×10^{-3} to 7.2×10^{-6} . 563 APEX-Q was reported to have one order of magnitude lower UH⁺/U⁺ ratio than 564 565 pneumatic nebulizers such as MicroMist and PFA. In this work, however, APEX-Q system employed in combination with PFA nebulizer for ICP-SFMS at Lab C, indicated 566 no better UH⁺/U⁺ ratio (10⁻⁵) compared with the ICP-QQQ at Lab A and ICP-SFMS at 567 Lab B (equipped with Conical nebulizer through self-aspired nebulization). 568

The quadrupole instruments have their main advantage in superior abundance sensitivity, which in particular is valid for the ICP-QQQ instrument using two quadrupoles thus enabling abundance sensitivities in the order of 10^{-14} . The ICP-QQQ further has a gas reaction cell enabling active removal of polyatomic interferences but at a cost in iontransmission. In this work, a reaction cell was applied to the ICP-QQQ at Lab F to eliminate the ²³⁸U interferences by highly efficient reaction of U⁺ and UH⁺ with CO₂, but no reaction with 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.

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

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

- 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 U/ ²³⁵ U	Average	0.007530	0.007672	0.007630	0.007587 (n=2)	0.007119	0.007490 (n=10)	0.007567
		(n=10)	(n=6)	(n=6)		(n=6)		
	U (k=1), %	1.63	0.64	0.20	0.22	0.64	0.47	8.20
	Bias, %	-0.49	1.38	0.83	0.26	-5.93	-1.02	
²³⁵ U/ ²³⁸ U	Average	0.007193	0.007268	0.007225	0.007278 (n=2)	0.007288	0.00727 (n=10)	0.007255
		(n=10)	(n=6)	(n=6)		(n=6)		
	U (k=1), %	1.36	0.30	0.14	0.12	0.36	0.37	0.07
	Bias, %	-0.85	0.18	-0.41	0.31	0.45	0.21	
²³⁴ U/ ²³⁸ U	Average	0.0000542	0.0000558	0.0000551	0.0000551	0.0000519	0.0000544	0.0000549
		(n=10)	(n=6)	(n=6)	(n=2)	(n=6)	(n=1)	
	U (k=1), %	2.21	0.72	0.18	0.31	0.96	0.55	8.20
	Bias, %	-1.28	1.64	0.36	0.55	-5.56	0.91	

586 **Table 3**. Results of Pu isotopes for IAEA-384 from each laboratory for the inter-comparison exercise (U is the expanded relative

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

587 uncertainty with a coverage factor of k = 1)



589

590Fig. 1 234 U/ 235 U isotope ratio (a) and *z*-score and *zeta*-score (b) calculated from the591measurement of the reference material NBL CRM 103-A. The solid and dotted lines592represent the observed average and variation of natural U (given by IUPAC), respectively593[25]. The error bars of the results represent the expanded uncertainty with a coverage594factor, *k*=1.



596

597Fig. 2 234 U/ 238 U isotope ratio (a) and *z*-score and *zeta*-score (b) calculated from the598measurement of the reference material NBL CRM 103-A. The solid and dotted lines599represent the observed average and variation of natural U (given by IUPAC), respectively600[25]. The error bars of the results represent the expanded uncertainty with a coverage601factor, *k*=1.



604Fig. 3 235 U/ 238 U isotope ratio (a) and z-score and zeta-score (b) calculated from the605measurement of the reference material NBL CRM 103-A. The solid and dotted lines606represent the observed average and variation of natural U (given by IUPAC), respectively607[25]. The error bars of the results represent the expanded uncertainty with a coverage608factor, k=1.



610 **Fig. 4** ²³⁹Pu massic activities (a), *Z*-score (b) and *Zeta*-score (c) for the reference material 14EA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [39]. The error bars of the results represent the expanded 13 uncertainty with a coverage factor, k=1.

614



616 **Fig. 5** ²⁴⁰Pu 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.



621

622 **Fig. 6** 240 Pu/ 239 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.

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, while few ²⁴⁰Pu values for the pre-purified material indicate high relatively bias. This 634 emphasizes the importance of the purity of Pu fraction with respect to the analytical 635 636 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.

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

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