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1 **Determination of $^{144}\text{Ce}/^{238}\text{U}$ atom ratio in spent nuclear fuel using double**
2 **spike isotope dilution mass spectrometry**

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16 **Abstract**

17 The low abundant cerium-144 radionuclide is one of the significant contributors to the decay
18 heat from spent nuclear fuel for cooling times of less than ten years after nuclear reactor
19 discharge. The accurate quantification of the ^{144}Ce content (or $^{144}\text{Ce}/^{238}\text{U}$) in irradiated nuclear
20 fuel is necessary to validate and extend the neutronic calculation codes as well as to improve
21 the short-term nuclear waste management strategies. In order to quantify $^{144}\text{Ce}/^{238}\text{U}$ atom ratios
22 at low uncertainty, we developed a new analytical technique based on double spike isotope
23 dilution associated with mass spectrometry. This includes 1) the chemical elimination of the
24 major neodymium-144 isobaric interference by two steps of liquid chromatography prior to
25 isotope analysis by Thermal Ionization Mass Spectrometry (TIMS) using both total
26 evaporation and sequential methods, and 2) the preparation and use of an in-house double spike
27 solution, using a mixture of a natural Ce solution with a ^{233}U -enriched solution. This new
28 approach was applied for the first time on two Mixed Oxide (MOx) spent nuclear fuel samples
29 and allowed the determination of $^{144}\text{Ce}/^{238}\text{U}$ atomic ratios ranging from 35×10^{-6} to 59×10^{-6} with
30 a relative expanded uncertainty of measurement of around 1 % at a 95 % confidence level.

31

32 **1 Introduction**

33 During the irradiation of fuels in a reactor, two types of nuclear reactions occur, i.e., (1) fission
34 of fertile isotopes (^{235}U and ^{239}Pu) that lead to the formation of lighter fission products (e.g. Cs,
35 Sr, lanthanides including Ce and Nd, and platinum group elements) and (2) neutron capture
36 giving rise to heavier products (i.e., actinides). Among the nuclides produced, some of them
37 are radioactive. The precise knowledge of the energy released by radioactive decay, known as
38 decay heat, is mandatory for radiological safety and the management of spent nuclear fuels.
39 Among these radionuclides, the ^{144}Ce isotope is a fission product that significantly participates
40 (including its short-lived product ^{144}Pr) to the decay heat for cooling times below 10 years.
41 Accurate quantification of this low abundance isotope in cooled spent nuclear fuels is thus
42 required for two reasons: (1) to bring new constraints on neutronic calculation codes that
43 predict the evolution of the fuel composition through time and (2) to improve the short-term
44 management of irradiated fuels.¹

45 Cerium is the second element of the lanthanide series. While most of the lanthanides are found
46 in solution at the oxidation state +3, cerium can form Ce(III) or Ce(IV) depending on the
47 oxidizing conditions. Naturally occurring cerium has 4 stable isotopes: ^{136}Ce (0.19%), ^{138}Ce
48 (0.25%), ^{140}Ce (88.45%) and ^{142}Ce (11.11%), whereas in irradiated fuels, it has two main stable
49 isotopes, ^{140}Ce and ^{142}Ce , and one low abundance radioactive isotope, ^{144}Ce (β^- , half-life:
50 284.89 ± 0.04 days), that decay to form ^{144}Pr (β^- , half-life: 17.29 ± 0.06 min) and ultimately
51 ^{144}Nd .² The ^{144}Ce content in spent fuel depends mainly on the initial amount of fissile isotopes
52 (enrichment) and the burn-up experienced by the fuel in the nuclear reactor (^{144}Ce production)
53 as well as on the cooling time since the discharge of the fuel (^{144}Ce radioactive decay).

54 The analysis of ^{144}Ce content in spent fuel is usually performed by gamma-ray spectrometry
55 using an aliquot of dissolved spent fuel solutions without extensive sample preparation.
56 However, the measurement uncertainty obtained with this technique remains around 3 percent

57 or more at a 95% confidence level.¹ Isotope dilution mass spectrometry is a method that can
58 provide the most accurate quantification of trace element content.^{3,4} In order to reduce the
59 measurement uncertainty of ^{144}Ce content (through $^{144}\text{Ce}/^{238}\text{U}$) in spent nuclear fuels, a novel
60 approach combining a two-step liquid chromatography, thermal ionization mass spectrometry
61 technique and high-accuracy double spike isotope dilution method has been developed.

62 Double spike isotope dilution mass spectrometry has previously been applied for the accurate
63 and precise determination of (1) radionuclide ratios in nuclear fuels before irradiation, such as
64 $^{166}\text{Er}/^{238}\text{U}$ ⁵ or in irradiated materials, such as $^{241}\text{Am}/^{238}\text{U}$, $^{244}\text{Cm}/^{238}\text{U}$, $^{90}\text{Sr}/^{238}\text{U}$, $^{166}\text{Er}/^{238}\text{U}$,
65 $^{152}\text{Sm}/^{153}\text{Eu}$ ⁶⁻⁸ and (2) U and Pu content in irradiated materials using large-size dried spikes⁹.

66 Moreover, high-precision Ce isotope measurements have been carried out for years by mass
67 spectrometry using TIMS as an elemental (Ce^+) or an oxide (CeO^-) species¹⁰⁻¹⁶ and by MC-
68 ICPMS^{11,17} on various types of geological samples not containing ^{144}Ce . Prior to mass
69 spectrometry analysis by TIMS and MC-ICPMS, in order to remove the spectral and non-
70 spectral interferences, an efficient separation of cerium from the other elements must be
71 performed. Overall, matrix elements first need to be eliminated from the lanthanide fraction
72 using ion exchange¹⁸ or extracting¹⁹ chromatography. Then Ce purification from the other
73 lanthanides, especially with respect to the interfering Nd, was carried out using oxidative
74 extraction,²⁰⁻²³ capillary electrophoresis,^{24,25} and liquid ion exchange or extraction
75 chromatography^{26,27}.

76 In this study, different separation techniques were developed to purify the cerium fraction and
77 remove both the dominant matrix elements (e.g. U, Pu) and the interfering isotopes (e.g. ^{142}Nd ,
78 ^{144}Nd). Cerium purification was achieved in two steps: (1) U and Pu were separated from the
79 fission products and minor actinides through gravity column liquid chromatography using a
80 strong anion exchange resin and HCl as the mobile phase, and (2) the separation of the fission
81 products and minor actinides was performed by high performance liquid chromatography

82 (HPLC) using a strong cation exchange resin and 2-hydroxy-2-methylbutyric acid (HMB) as
83 the mobile phase^{28,29}. Purification yields, decontamination factors of each separated fraction,
84 as well as procedural blank levels were carried out on a quadrupole ICP-MS. Then, thermal
85 ionization mass spectrometry (TIMS) was used to measure the Ce isotope ratios at high
86 precision by a sequential method (i.e., sequential heating steps of the filaments before the
87 proper isotopic measurement sequence) and a total evaporation method, both of which are
88 commonly performed for the isotopic analysis of nuclear samples.³⁰⁻³³ Finally, a $^{140}\text{Ce}/^{233}\text{U}$
89 double spike was prepared in our laboratory using certified reference materials (a ^{233}U solution
90 certified for its U content and isotopic composition, and a Ce solution that had a natural isotopic
91 composition certified only for its Ce content) in order to determine the atomic ratio $^{144}\text{Ce}/^{238}\text{U}$
92 at low uncertainties (around or lower than 1%) in a dissolved spent nuclear fuel solution using
93 the double isotope dilution method. Accurate and precise isotopic compositions of both the Ce
94 solution and the fuel sample are required to determine the atomic ratio $^{144}\text{Ce}/^{238}\text{U}$ by the double
95 isotope dilution method and were determined by TIMS.

96

97 **2 Materials and methods**

98 **2.1 Materials**

99 **2.1.1 Reagents**

100 High purity 67-70% nitric acid and/or 33-36% hydrochloric acid (PlasmaPURE, from SCP
101 Science, Baie d'Urfé, Canada) and ultrapure water with a resistivity of 18.2 M Ω (Milli-Q
102 system, Millipore, Milford, USA) were mixed to obtain diluted solutions used as eluents for
103 gravity column liquid chromatography and for ICP-MS analysis (2% HNO₃). These reagents
104 were also utilized to clean materials before use, including all SavillexTM (Teflon® PFA) vials

105 containing the spent fuel samples and all Nalgene™ (Teflon™ FEP) bottles hosting the
106 chromatographic eluents and the double spike solution.

107 The chromatographic eluent used for separating fission products and minor actinides (Am, Cm)
108 from major actinides (U and Pu) was 10M HCl. The reducing agent HI 57% (VWR, Fontenay
109 sous bois, France) was utilized to prepare the chromatographic eluent 10M HCl/0.1M HI for
110 Pu elution. Finally, U was eluted using 3M HCl.

111 The chromatographic eluent for lanthanide separation using HPLC was prepared freshly by
112 dissolution of 2-hydroxy-2-methylbutyric acid, HMB (Sigma-Aldrich, Saint-Quentin-
113 Fallavier, France) in ultrapure water. The pH of the mobile phase was adjusted with a 25%
114 ammonia solution (Suprapur, Merck, Darmstadt, Germany) to respectively 3.6 and 4.5 for the
115 0.1M HMB and 0.2M HMB solutions. A 0.13mM Arsenazo III solution (analytical grade,
116 Sigma Aldrich, Saint-Quentin-Fallavier, France), prepared in acetic acid (Suprapur, Merck,
117 Darmstadt, Germany) buffer solution, was taken as the post-column complexing agent for
118 lanthanides and actinides permitting the detection of these complexes with an UV detector.

119

120 **2.1.2 Reference materials**

121 To date, no certified isotopic reference material for natural Ce is available. Therefore, a mono-
122 elemental solution of Ce NIST3110 (NIST, Gaithersburg, USA) certified at 9.971 ± 0.015 mg
123 (Ce) · g⁻¹ of 10% HNO₃ solution, (*u_c*), with natural isotopic abundances (¹³⁶Ce (0.25%), ¹³⁸Ce
124 (0.19%), ¹⁴⁰Ce (88.45%), ¹⁴²Ce (11.11%))³⁴ was chosen for this study.

125 The uranium spike employed for the double spike solution consisted of an isotopic certified
126 reference material ²³³U IRMM 040a (JRC, Geel, Belgium), approved for its ²³³U content
127 (4.0278 ± 0.0036 mol of ²³³U · kg⁻¹ of 5M HNO₃ solution, (*u_c*) and for its isotopic abundance

128 $(n(^{233}\text{U})/n(\text{U}) = 0.980430 \pm 0.000029, u_c)$. The U standard solution used in this study to
129 evaluate the TIMS performances (internal precision, external reproducibility, accuracy) was a
130 NIST SRM U-500 standard certified for its isotopic composition ($^{235}\text{U}/^{238}\text{U} = 0.9997 \pm 0.0007,$
131 u_c).

132 Solutions to optimize the chromatographic elution and analytical conditions as well as to
133 simulate a spent fuel sample (the elemental proportions of the fuel were simulated to verify the
134 yield of purification of the chromatographic elution) were freshly prepared by appropriate
135 dilution and mixture of the 1000 mg/mL individual stock standard solutions of U, Sm, Nd, Pr,
136 Ce in 2% HNO_3 (SPEX CertiPrep, Metuchen, USA), certified for elemental content.

137

138 **2.1.3 Spent fuel samples**

139 Two uranium and plutonium mixed oxide (MOx) spent nuclear fuel samples were analyzed.
140 After an irradiation period in a nuclear reactor and a cooling period of less than 10 years,
141 targeted sections of irradiated fuel rods were cut, extracted and dissolved in hot cell facilities
142 (ATALANTE, CEA Marcoule). Then, aliquots of diluted solutions of two spent nuclear MOx
143 fuels were supplied to the Laboratory of Analytical development for Nuclear, Isotopic and
144 Elemental Analysis (LANIE, CEA Saclay, France) for both elemental and isotopic
145 characterization. The analyzed elements included actinides and fission products, and one of the
146 challenges was to determine the $^{144}\text{Ce}/^{238}\text{U}$ ratio in these samples using the double spike isotope
147 dilution technique.

148 Diluted solutions of irradiated MOx fuel samples contain mainly U (≈ 90 wt.%), where ^{238}U is
149 the dominant isotope, and to a lesser extent Pu (≈ 5 wt.%) and fission products (≈ 4 wt.%)
150 including lanthanides and minor actinides (≈ 1 wt.%) such as Am and Cm. As discussed above,
151 Ce has two dominant and stable isotopes in such samples, ^{140}Ce and ^{142}Ce with abundances

152 close to 50% each ($^{142}\text{Ce}/^{140}\text{Ce} \approx 0.9$), and one minor and radioactive isotope ^{144}Ce with a low
153 abundance $<1\%$ ($^{144}\text{Ce}/^{142}\text{Ce} \approx 0.02$). Spent fuel composition models (SPRC, CEA Cadarache,
154 France) suggest that at the time of the isotopic analysis in the LANIE lab, the MOx fuels had
155 $^{144}\text{Ce}/^{238}\text{U}$ ratios of around 50 ppm (at./at.). The stable ^{144}Nd was the major isobaric
156 interference with respect to ^{144}Ce , with a $^{144}\text{Nd}/^{144}\text{Ce}$ ratio around 20, while the lanthanide ^{144}Pr
157 (short-lived nuclides) contribution was negligible ($^{144}\text{Pr}/^{144}\text{Ce}$ below 5×10^{-5}).
158 The handling of radioactive samples (e.g., spent fuel) was carried out carefully in a dedicated
159 laboratory using negative pressure glove-boxes equipped with leaded glass in order to
160 minimize the analyst's exposure to radiation. All analysts systematically used active and
161 passive radiation dosimeters in order to record and control their exposure to radiations.

162

163 **2.1.4 Double spike solution**

164 A double spike is a mixture of a Ce solution that has natural isotopic abundances and a ^{233}U -
165 enriched solution has been prepared in order to determine the $^{144}\text{Ce}/^{238}\text{U}$ ratio in the spent fuels
166 using the double spike isotope dilution method. The ^{233}U was chosen as the ^{233}U abundance in
167 the samples was negligible ($^{233}\text{U}/^{238}\text{U}$ lower than 10^{-9}). The in-house double spike ^{140}Ce - ^{233}U
168 was gravimetrically prepared using a weight scale in a negative-pressure glove-box from Ce
169 NIST3110 and ^{233}U IRMM 040a (JRC, Geel, Belgium) solutions that were diluted with 4M
170 HNO_3 prepared from high-purity 69% nitric acid PlasmaPure and ultrapure water at LANIE
171 (CEA Saclay, France). The U content and the isotopic composition of the ^{233}U IRMM-040a
172 solution were certified, while for the Ce NIST 3110 solution, this was the case only for the Ce
173 content (Table 1). As no certified values were available, the value from the IUPAC report
174 ($^{142}\text{Ce}/^{140}\text{Ce} = 0.12565 \pm 0.00029$; u_c) representing the isotopic composition of chemical or
175 natural materials that are likely to be encountered in the laboratory was used in this study.³⁴

176 The accurate knowledge of the isotopic composition (Ce and U) of the double spike, or the
177 $^{140}\text{Ce}/^{233}\text{U}$ atom ratio, is required for the accurate determination of the $^{144}\text{Ce}/^{238}\text{U}$ ratio of a
178 spent fuel sample using the double spike isotope dilution – mass spectrometry technique. The
179 $^{140}\text{Ce}/^{233}\text{U}$ atom ratio of the double spike was determined at 0.01082 ± 0.00002 (u_c) from (1)
180 the weighted masses of each spike solution, (2) the Ce and U content in each solution, and (3)
181 the isotopic composition of Ce and U in the Ce NIST3110 and ^{233}U IRMM040a solutions,
182 respectively. The atomic and isotopic ratios of the double spike required for the double spike
183 isotope dilution – mass spectrometry technique are presented in the Table 1.

184

185 **2.1.5 Mass spectrometers**

186 A quadrupole ICP-MS “X series” mass spectrometer from Thermo Electron (Winsford, UK)
187 was used for the elemental analysis (e.g., purification yields, blank levels). This ICP-MS is the
188 first X series modified, with the ICP source in a glove-box, in order to handle radioactive
189 samples as previously described.³⁵

190 A thermal ionization mass spectrometer Sector 54 from GV Instruments (Manchester, UK) was
191 used to perform cerium and uranium isotope ratio measurements. The source of the instrument
192 is placed inside a glove-box to handle radioactive samples, as described previously.^{6,7} The
193 source is equipped with a turret of 20 positions, where removable triple filament arrangements
194 (side internal, central and side external) are available. Sector 54 instrument is equipped with
195 seven Faraday cups associated with amplifiers fitted with $10^{11} \Omega$ positive feedback resistors.
196 The Faraday amplifier gains were calibrated daily before the analytical sessions.
197 Reproducibility of the electronic gains was better than 20 ppm day⁻¹.

198

199 **2.2 Methods**

200 **2.2.1 Double spike isotope dilution method**

201 The double spike isotope dilution technique made it possible to directly and very accurately
 202 find out the atomic ratio of two isotopes from two elements present in a sample. ^{6,7} The
 203 ¹⁴⁴Ce/²³⁸U ratio was determined for each spent fuel (1) from two aliquots of the sample (A and
 204 B), and (2) from two aliquots of the mixture of the spent fuel sample with the ¹⁴⁰Ce/²³³U double
 205 spike (blends A and B). Finally, the ¹⁴⁴Ce/²³⁸U ratio in the sample can be determined according
 206 to the isotopic balance equation:

$$207 \quad \left(\frac{^{144}\text{Ce}}{^{238}\text{U}}\right)_S = \left(\frac{^{144}\text{Ce}}{^{142}\text{Ce}}\right)_S \times \left(\frac{^{140}\text{Ce}}{^{233}\text{U}}\right)_{Sp} \times \frac{\left(\frac{^{142}\text{Ce}}{^{140}\text{Ce}}\right)_M}{\left(\frac{^{238}\text{U}}{^{233}\text{U}}\right)_M} \times \frac{1 - \frac{\left(\frac{^{142}\text{Ce}}{^{140}\text{Ce}}\right)_{Sp}}{\left(\frac{^{142}\text{Ce}}{^{140}\text{Ce}}\right)_M}}{1 - \frac{\left(\frac{^{238}\text{U}}{^{233}\text{U}}\right)_{Sp}}{\left(\frac{^{238}\text{U}}{^{233}\text{U}}\right)_M}} \times \frac{1}{1 - \frac{\left(\frac{^{142}\text{Ce}}{^{140}\text{Ce}}\right)_M}{\left(\frac{^{142}\text{Ce}}{^{140}\text{Ce}}\right)_S}}$$

208 where S stands for sample, Sp for double spike and M for sample-double spike mixture (i.e.,
 209 blend). The ratios (¹⁴⁰Ce/¹⁴²Ce)_S and (¹⁴⁴Ce/¹⁴²Ce)_S of the spent fuel samples were measured
 210 by TIMS using the sequential method, while the ratios (¹⁴⁰Ce/¹⁴²Ce)_M and (²³⁸U/²³³U)_M of the
 211 blends were measured by TIMS using the total evaporation method. The determination of the
 212 (¹⁴⁰Ce/¹⁴²Ce)_{SP}, (²³⁸U/²³³U)_{SP} and (¹⁴⁰Ce/²³³U)_{SP} ratios of the double spike is described in
 213 Section 2.1.4. The procedural flowchart for the double spike isotope dilution method is
 214 presented in Figure 1. Ultimately, the absolute ¹⁴⁴Ce content in the spent fuel diluted solution
 215 was deduced from the U content determined by single isotope dilution mass spectrometry
 216 techniques with a relative expanded uncertainty of around 0.4% at *k* = 2 (not shown in this
 217 article).

218

219 **2.2.2 Elemental purification**

220 Elemental purification of Ce and U is required to eliminate the matrix and the interfering
221 elements before isotopic analysis by mass spectrometry. In spent nuclear fuel samples, uranium
222 is the dominant matrix element, while ^{142}Nd , ^{144}Nd and ^{238}Pu are respectively the main isobaric
223 interferences for ^{142}Ce , ^{144}Ce and ^{238}U that are involved in isotope ratios measured by mass
224 spectrometry. In this particular study, the main challenge was to remove the high amount of
225 ^{144}Nd from the very low amount of ^{144}Ce ($^{144}\text{Nd}/^{144}\text{Ce} \approx 20$).

226

227 *2.2.2.1 Separation U/Pu/Fission products + minor actinides*

228 Chemical separations of U/Pu/Fission products + minor actinides from spent fuels were
229 performed in a glove-box following a procedure adapted from Huntley (2001)³⁶ using
230 gravitational chromatographic columns filled with a strong anionic resin AG1-X8 200-400
231 mesh (BioRad, Hercules, CA, USA) in a hydrochloric medium. The elution conditions (acid
232 molarity, eluted volume) were optimized using a synthetic mixture of mono-elemental
233 solutions of U and lanthanides (Spex, CertiPrep, Metuchen, NJ, USA) simulating the
234 composition of the spent fuel.

235 For this procedure, aliquots of spent fuel solutions dissolved in 8M HNO_3 were evaporated to
236 dryness at 90°C on a hot plate in a glove-box, and dissolved in 10M HCl. Then, the samples
237 were loaded into the gravitational column and the “fission products + minor actinides” fraction
238 (including Ce and Nd) was eluted using 5 mL of 10M HCl, while anionic chloro-complexes of
239 U(VI) and Pu(VI) were fixed on this quaternary ammonium-type resin. The Pu was then
240 reduced and discarded with 5 mL 10M HCl/0.1M HI, as Pu(III) cationic chloro-complexes
241 (Huntley, 2001). Finally, U was collected using 3 mL of 1M HCl.

242

243 *2.2.2.2 Ce purification from “fission products + minor actinides” fraction*

244 The Ce purification of the “fission products + minor actinides” fraction of spent fuels (Figure
245 2) was performed using high-performance liquid chromatography (HPLC). A DIONEX
246 (Sunnyvale, CA, USA) ICS 3000 gradual dual pump was used with a LUNA SCX (Strong
247 Cation Exchange) analytical column (250 mm of length, internal diameter of 4.6 mm) protected
248 by a 3-mm long security guard column system positioned just in front (Phenomenex, Torrance,
249 CA, USA). The stationary phase was silica-based and bonded with benzene sulfonic acid, with
250 a particle size of 5 μm and having a 100 \AA pore size. The eluent flow rate was 1 mL min^{-1} and
251 the Rheodyne injection valve (9725 i) was equipped with a 50- μl sample loop. The HPLC was
252 hyphenated to a UV-visible detector (654 nm, Jasco UV-2070) with post-column reaction with
253 Arsenazo III (0.1 mL min^{-1}) in order to detect the separated lanthanides, as previously
254 described (Goutelard et al., 2009). The addition of a flow rate split in the system between the
255 column outlet and the Arsenazo III inlet, allowed the detection of lanthanides only from 10%
256 of the flow rate and the simultaneous collection (90% of the flow rate) of the pure fractions of
257 each of the lanthanides for isotopic analysis. The columns, injection valve, split, UV-visible
258 detector were located inside the glove-box. Chromatographic pumps and eluents were placed
259 outside the glove-box. Tubing and connections from the pump to the injection valve were in
260 polyether-ether ketone (PEEK). Flow rate control of the HPLC pumps and integration of the
261 transient UV peaks were performed with the Chromeleon Software.

262 At the time of sample injection into the HPLC system via a syringe into the Rheodyne valve,
263 the elution of fission products started with an isocratic mode using 0.1M HMB at pH 3.6 to
264 elute the heavier lanthanides (Gd-Eu-Sm) during 30 min, followed by a gradient step which
265 involved the linear replacement during 45 min of the first eluent by a second one (0.2M HMB,
266 pH 4.5) with a higher ligand concentration and a higher pH in order to separately elute Nd, Pr,
267 and Ce in that order.^{29,37} The elution conditions (HMB concentration, pH, isocratic and gradient
268 elution mode) were previously optimized using a synthetic mixture of mono-elemental

269 solutions of lanthanides (Spex, CertiPrep, Metuchen, NJ, USA) simulating the lanthanide
270 content of spent fuels. With this method, a Ce peak apex appeared more than 6 min after the
271 Nd peak and more than 2 min after the Pr peak (Fig. 2). An aliquot of the collected Ce fractions
272 was analyzed using a Q-ICPMS in order to check the yields of Ce and the absence of residual
273 Nd.

274

275 **2.2.3 Mass spectrometry measurements**

276 *2.2.3.1 Q-ICPMS*

277 The elemental analysis, including the screening of the purified fractions to verify the
278 purification yields, decontamination factors and measurement of blank levels, were carried out
279 on a quadrupole ICP-MS “X series” (Thermo Electron, Winsford, UK). Sample introduction
280 in the plasma was performed with a quartz bead impact spray chamber and a quartz concentric
281 nebulizer (1.0 mL min⁻¹). Tuning parameters were optimized daily with a 1-ppb multi-element
282 test solution in order to obtain the maximum count rates and stability for the ¹¹⁵In and ²³⁸U
283 signals and the lowest oxide rate and doubly-charged ion rate.

284

285 *2.2.3.2 TIMS*

286 Cerium and uranium isotope ratio measurements were performed on a thermal ionization mass
287 spectrometer Sector 54 from GV Instruments (Manchester, UK). One of the main bias factors
288 impairing accuracy in TIMS is isotope fractionation occurring during the evaporation
289 process.³⁸ An accurate analysis of the isotopic composition of non-natural samples by TIMS
290 can be performed with both the sequential method (i.e., comparison with a reference sample)
291 or with the total evaporation method.³¹ The so-called “sequential” method was based on a
292 procedure of sequential heating steps of the filaments, prior to the proper isotopic measurement,
293 and these steps were pre-calibrated for a given element using a reference material with a known

294 isotopic composition in order to obtain the isotopic reference value. The calibrated operating
295 procedure was then carefully applied to the unknown samples assuming that there is a
296 minimum isotope fractionation during the acquisition. The total evaporation method, based on
297 the integration of all the ions formed during analysis, was considered to be more accurate than
298 the sequential method since the effects of isotope fractionation on the final results were
299 minimized.^{30-33, 39} However, the total evaporation method become less accurate for the
300 quantification of isotope ratios involving a minor isotope (e.g., $^{144}\text{Ce}/^{142}\text{Ce}$ of the spent fuel),
301 due to the lower precision associated with low quantity of accumulated signal recorded for the
302 minor isotopes.

303 As a consequence, the Ce and U isotopic data were acquired in static multicollection mode
304 with Faraday cups, using (1) the total evaporation method ^{30-33, 39} for the determination of
305 $^{142}\text{Ce}/^{140}\text{Ce}$ and $^{238}\text{U}/^{235}\text{U}$ ratios in the blends and for the qualification of the $^{142}\text{Ce}/^{140}\text{Ce}$ ratios
306 in the reference material (Ce NIST3110), and (2) the sequential method for the determination
307 of the Ce isotopic composition (that involved the ^{144}Ce minor isotope) in the spent fuel samples.
308 Due to the lack of an isotopic reference material for Ce, the Ce NIST 3110 solution was used
309 as a reference material to calibrate the sequential method and the IUPAC Ce isotopic
310 composition value was taken as a reference.³⁴

311 When using the sequential method to measure Ce in spent fuel samples and the NIST3110
312 solution, 150 ng of Ce diluted in 2% HNO_3 was deposited on the evaporating rhenium filament
313 (located in the external side position of the turret). The heating process corresponded to a
314 succession of current increases applied to the filaments until the sum of the $^{140}\text{Ce}^+$ and $^{142}\text{Ce}^+$
315 ion beams reached target voltages, followed by periods of acquisition used to control the
316 evolution of the isotope fractionation. The acquisition method applied for the isotope ratio
317 measurements included 4 blocks of 10 cycles, when the sum of the $^{140}\text{Ce}^+$ and $^{142}\text{Ce}^+$ ion beams
318 reached 2 V. Faraday cup configurations for the Ce isotope ratio measurements are reported in

319 Table 2. For the Ce measurements using the total evaporation method of NIST3110 solution
320 and blends, only 50 ng of Ce diluted in 2% HNO₃ was loaded on the evaporating filament. The
321 total ion current measured on masses 140 and 142 with this methods was higher than 2×10^{-11}
322 A.

323 Approximately 50 ng of U diluted in 2% HNO₃ was deposited on the evaporating rhenium
324 filament for U measurements of U-500 and blends performed by the total evaporation method.
325 Faraday cup configurations for the U isotope ratio measurements are reported in Table 3. The
326 total ion current measured on 238 and 235 (U-500) or 233 (blend) with this method was found
327 to be higher than 10^{-11} A for each mass.

328

329 **3 Results and discussion**

330 **3.1 Ce and U purification**

331 In the “fission products + minor actinides” fraction collected during the U/Pu/fission products
332 separation on AG1-X8 resin, the Ce and Nd yields were determined by Q-ICPMS to be around
333 90%. In the collected uranium fraction, the U yield reached 90% and the residual Pu was found
334 to be negligible. The level of U blanks was also checked by Q-ICPMS and was determined to
335 be negligible.

336 In the Ce fraction collected after the fission product separation step using HPLC (Fig. 2), Ce
337 yields reached at least 90%. Residual Nd in the Ce fraction could be neglected. The total level
338 of procedural blanks at m/z=144 was very low, less than 1 ng, compared with the amount of
339 ¹⁴⁴Ce recovered after the elemental purification steps (a few μg) and was therefore negligible
340 with respect to the ¹⁴⁴Ce/¹⁴²Ce ratio measurements.

341

3.2 Ce and U isotope ratios determination by TIMS

3.2.1 Ce and U isotope ratios of reference materials

The $^{142}\text{Ce}/^{140}\text{Ce}$ ratios of the Ce NIST3110 solution were measured by a TIMS Sector 54 using both total evaporation and sequential methods. The average $^{142}\text{Ce}/^{140}\text{Ce}$ ratio for Ce NIST3110 solution was found to be 0.125911 ± 0.000040 ($n=8$, 1σ) by the total evaporation method, and 0.125690 ± 0.000055 ($n=7$, 1σ) for 7 independent measurements using the sequential technique (Table 4). The respective relative external reproducibility was 0.03 % (RSD, 1σ) for the total evaporation method and 0.04% (RSD, 1σ) for the sequential technique. The averages of the $^{142}\text{Ce}/^{140}\text{Ce}$ ratios obtained with both methods were in good agreement with the IUPAC reference value ($^{142}\text{Ce}/^{140}\text{Ce} = 0.12565 \pm 0.00029$; u_c).³⁴ The average $^{142}\text{Ce}/^{140}\text{Ce}$ ratio obtained using the sequential method was very close to the IUPAC reference value (bias of 0.03%) as the analytical procedure was designed to reach this value. The average $^{142}\text{Ce}/^{140}\text{Ce}$ ratio obtained using the total evaporation method was slightly higher (bias of 0.21%) but still remained consistent with the uncertainty of the IUPAC reference value.

The $^{235}\text{U}/^{238}\text{U}$ ratios of the NIST U-500 standard solution were measured by TIMS Sector54 using the total evaporation and the average $^{235}\text{U}/^{238}\text{U}$ ratio obtained (0.9999 ± 0.0004 , SD, 1σ , $n=22$), corresponding to an external reproducibility of 0.04% (RSD, 1σ), and were found to be in good agreement with the reference value 0.9997 ± 0.0007 (1σ) (Table 4).

3.2.2 Ce isotopic compositions of spent fuels

The measurement of $^{142}\text{Ce}/^{140}\text{Ce}$ and the $^{144}\text{Ce}/^{142}\text{Ce}$ ratios were determined by TIMS for each aliquot (A and B) of the spent fuel samples using the sequential method due to the low abundance of ^{144}Ce (Table 5). A minimum of one analysis was performed for each aliquot. The

366 average $^{142}\text{Ce}/^{140}\text{Ce}$ and $^{144}\text{Ce}/^{142}\text{Ce}$ ratios were measured respectively at 0.88602 ± 0.00580
367 and 0.001411 ± 0.00011 for MOx 1 and at 0.87200 ± 0.00571 and 0.01828 ± 0.00014 for MOx
368 2 ($U, k = 2$). The relative differences between the two aliquots A and B were 0.16%
369 ($^{142}\text{Ce}/^{140}\text{Ce}$) and 0.19% ($^{144}\text{Ce}/^{142}\text{Ce}$) of MOx 1 and 0.01% for both ratios of MOx 2. The
370 relative standard deviation (1σ) of $^{142}\text{Ce}/^{140}\text{Ce}$ and $^{144}\text{Ce}/^{142}\text{Ce}$ obtained from three TIMS
371 measurements on MOx 1 were 0.11% and 0.38%, respectively. The relative standard deviation
372 was higher for $^{144}\text{Ce}/^{142}\text{Ce}$ compared with $^{142}\text{Ce}/^{140}\text{Ce}$, because the signal for the 144 ion beam
373 (15 mV) was lower compared to the signals recorded for the 142 and 140 ion beams (around
374 1V each).

375 The relative uncertainty ($k = 1$) of the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio of MOx 1 was evaluated at 0.33% using
376 a quadratic combination of (1) the relative standard deviation (0.11%) of the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio
377 of the MOx 1, (2) the relative combined uncertainty of the IUPAC reference value (0.23%)
378 used to set up the sequential method, and (3) the relative difference between the IUPAC
379 reference value and the total evaporation result (0.21%). The relative uncertainty ($k = 1$) of the
380 $^{144}\text{Ce}/^{142}\text{Ce}$ ratio of MOx 1 was evaluated at 0.38% using only the relative standard deviation
381 (1σ) of three TIMS measurements, as neither reference value nor total evaporation results were
382 available.

383 These relative uncertainties were then assigned to the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio and the $^{144}\text{Ce}/^{142}\text{Ce}$ ratio
384 of MOx 2 as the ratios were of the same magnitude. These uncertainty values encompassed the
385 relative difference observed on the measured isotope ratios between each aliquot of the two
386 fuels and were therefore representative.

387

388 **3.2.3 Ce and U isotope ratios of blends**

389 The measurement of the $^{142}\text{Ce}/^{140}\text{Ce}$ and $^{233}\text{U}/^{238}\text{U}$ ratios was performed twice on two different
390 mixtures (blends A and B with varying amounts of sample and spike) by TIMS using the total
391 evaporation method. The relative difference with regard to the $^{142}\text{Ce}/^{140}\text{Ce}$ and $^{233}\text{U}/^{238}\text{U}$ ratios
392 obtained from the repeated measurements of the same blend was less than 0.2% which was
393 consistent with the typical combined uncertainties found for total evaporation measurements
394 in our lab (0.2%, $k=2$). Then, the average of the 2 analyses obtained for each of the blends A
395 or B for each isotope ratio was separately taken into account to solve the double spike isotope
396 dilution equation.

397

398 **3.3 $^{144}\text{Ce}/^{238}\text{U}$ atom ratio in spent fuels by double spike isotope dilution**

399 **- mass spectrometry**

400 The $^{144}\text{Ce}/^{238}\text{U}$ atom ratio of the dissolved solutions of spent fuel was determined from the
401 double spike isotope dilution equation and the associated expanded combined uncertainty was
402 evaluated by the error propagation of each contributing term following a Kragten approach
403 (Table 6).⁴⁰ The average $^{144}\text{Ce}/^{238}\text{U}$ atom ratios of dissolved fuel solutions were quantified at
404 58.8 ± 0.7 ppm (at./at.) ($U, k=2$) for MOx 1, and 34.7 ± 0.4 ppm (at./at.) ($U, k=2$) for MOx 2,
405 corresponding to a relative expanded combined uncertainty of 1.1 % each. The results obtained
406 on the final $^{144}\text{Ce}/^{238}\text{U}$ atom ratios of dissolved fuel solutions using the two different blends (A
407 and B) presented a relative difference lower than 0.3% for both MOx fuels thus confirming the
408 consistency of the uncertainty estimation.

409 The relative contributions of the main sources of uncertainty were determined (Fig. 3) and it
410 appeared that the main uncertainty contribution to the $^{144}\text{Ce}/^{238}\text{U}$ atom ratio came from the
411 uncertainty of the low $^{144}\text{Ce}/^{142}\text{Ce}$ ratio measured in the spent fuel sample which accounted for
412 approximately 50% of the expanded combined uncertainty. Among the other main uncertainty

413 contributors of the expanded combined uncertainty, the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio measured by TIMS
414 using the sequential method in the fuel made up 10-15%, the $^{142}\text{Ce}/^{140}\text{Ce}$ ratio measured by
415 TIMS using the total evaporation method in the blend represented 16-19%, while the $^{140}\text{Ce}/^{233}\text{U}$
416 and $^{142}\text{Ce}/^{140}\text{Ce}$ ratios in the double spike accounted for respectively 9-10% and 6-9%.

417 This study demonstrates that our new method allows the determination of $^{144}\text{Ce}/^{238}\text{U}$ ratios at
418 a few tens of ppm with expanded combined uncertainty of around 1% ($k=2$) in MOx samples,
419 which represents a significant improvement compared with the measurement uncertainty of
420 several percent at a 95% confidence level obtained for ^{144}Ce content with gamma-ray
421 spectrometry.

422

423 **4 Conclusion**

424 A new double spike isotope dilution combined with the mass spectrometry method was
425 developed in order to determine the $^{144}\text{Ce}/^{238}\text{U}$ ratio at a few tens of ppm in spent nuclear fuel
426 (MOx) with a relative expanded uncertainty of around 1% at $k=2$. This was at least three times
427 lower compared to those obtained with the classical and well-established gamma-ray
428 spectrometry technique. This new method required (1) the use of a $^{140}\text{Ce}-^{233}\text{U}$ double spike
429 which was specifically developed at the LANIE laboratory, (2) the development of Ce
430 purification using two-step liquid chromatography, and (3) the development of Ce isotope
431 measurements by thermal ionization mass spectrometry using both the total evaporation
432 method for the qualification of Ce NIST3110 and blend analysis, as well as the sequential
433 method, calibrated with the IUPAC reference value, for spent nuclear fuel sample analysis.

434 The main issue in this study was how to quantify the low ^{144}Ce content, since the uncertainty
435 of the $^{144}\text{Ce}/^{142}\text{Ce}$ ratio measured in the spent fuel sample accounted for approximately half of
436 the final combined uncertainty associated with the $^{144}\text{Ce}/^{238}\text{U}$ ratio measurement. In order to

437 improve the uncertainties associated with this low-abundance isotope, the use of new-
438 generation mass spectrometers, especially ones equipped with high-ohm amplifiers (10^{12} or
439 10^{13} ohm instead of 10^{11} ohm amplifiers) can be considered.

440 This new technique is therefore a robust alternative to the classical methods. With reduced
441 uncertainties, it one that will better constrain the validation of neutronic calculations that
442 predict the evolution of the fuel composition with time. It should also improve the decay-heat
443 quantification and the short-term management of irradiated fuels.

444

445 **5 Conflicts of interest**

446 There are no conflicts to declare.

447

448 **6 Acknowledgements**

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450

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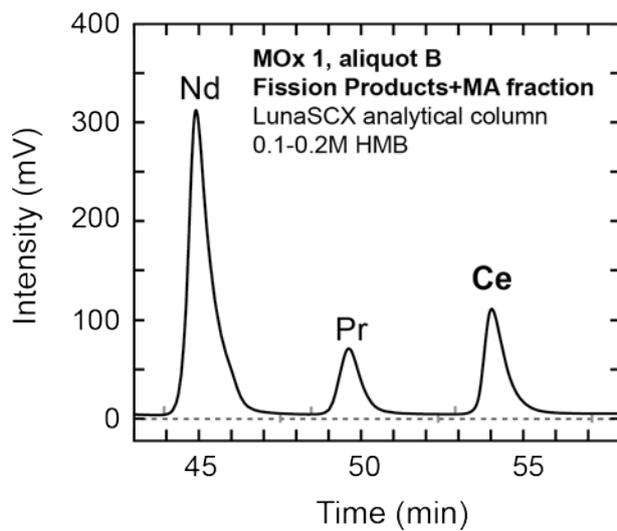
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568 **Figure 1:** Flow chart representing the analytical procedure performed for the determination of
 569 $^{144}\text{Ce}/^{238}\text{U}$ atom ratios in spent fuel samples. Abbreviations: S, for sample; M, for mixture (i.e.,
 570 blend); MA, for minor actinides; Seq., for the sequential method; TE, for the total evaporation
 571 method.

572

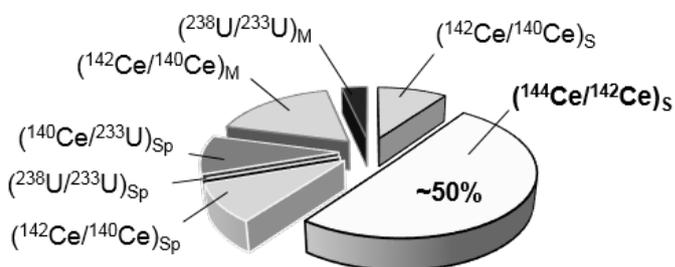
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574

575 **Figure 2:** Chromatogram illustrating the separation of Nd (and other fission products and
 576 minor actinides (MA)) from Ce in MOx spent fuels by HPLC.

577



578

579 **Figure 3:** Diagram representing the contribution of the uncertainty of each component
 580 involved in the combined standard uncertainty associated with the determination of the

581 $^{144}\text{Ce}/^{238}\text{U}$ ratio of aliquot A from MOx 1 spent fuel by the double spike isotope dilution-mass
 582 spectrometry technique. Abbreviations: S, for sample; Sp, for spike; M, for Mixture.

583

584

585 **9 Tables**

586

| Ratio | Value | Combined uncertainty | Relative combined uncertainty |
|-----------------------------------|---------|----------------------|-------------------------------|
| $^{140}\text{Ce}/^{233}\text{U}$ | 0.01082 | 0.00002 | 0.17% |
| $^{142}\text{Ce}/^{140}\text{Ce}$ | 0.12565 | 0.00029 | 0.23% |
| $^{238}\text{U}/^{233}\text{U}$ | 0.00820 | 0.00001 | 0.12% |

587

588 **Table 1:** In-house ^{140}Ce - ^{233}U double spike composition corresponding to a mixture of Ce
 589 NIST3110 solutions (certified for its Ce content) and ^{233}U spike IRMM 040a (certified for its
 590 U content and isotopic composition). The $^{142}\text{Ce}/^{140}\text{Ce}$ is the representative isotopic composition
 591 of a chemical or natural material that is likely to be encountered in the laboratory according to
 592 a IUPAC report (Berglund and Wieser, 2011). The description of how the $^{140}\text{Ce}/^{233}\text{U}$ atom ratio
 593 was determined can be found in the text.

594

595

| Faraday cups | L2 | L1 | Ax | H1 | H2 | H3 | H4 |
|---------------------------|-----|-----|------------|-----|------------|-----|-------------|
| Ion m/z | 136 | 138 | 140 | 141 | 142 | 143 | 144 |
| MOx fuel sample | | | | | | | |
| Analyzed element | | | Ce | | Ce | | Ce |
| Ce isotope abundances | | | 52% | | 47% | | 1.0% |
| Main interfering elements | | | | Pr | Nd | Nd | Nd, Pr |
| NIST3110 standard | | | | | | | |

| | | | | |
|-----------------------|-------|-------|--------------|--------------|
| Analyzed element | Ce | Ce | Ce | Ce |
| Ce isotope abundances | 0.19% | 0.25% | 88.5% | 11.1% |

596

597 **Table 2:** Collectors configuration of TIMS Sector 54 used for Ce isotope analyses of the spent
598 fuel samples and Ce NIST3110 solution. The Ce isotopic composition and the main isobaric
599 interfering elements are indicated. The Ce abundances were approximated for the MOx fuels
600 at the time of the analyses. The isotopes used for the analysed ratios are given in bold.

601

602

| | | | | | | | |
|---------------------------|-------------|-------|---------------|-------|---------------|----|----|
| Faraday cups | L2 | L1 | Ax | H1 | H2 | H3 | H4 |
| Ion m/z | 233 | 234 | 235 | 236 | 238 | | |
| Blend | | | | | | | |
| Analyzed element | U | U | U | U | U | | |
| U isotope abundances | ≈50% | <0.1% | <0.1% | <0.1% | ≈50% | | |
| Main interfering element | | | | | Pu | | |
| SRM U-500 standard | | | | | | | |
| Analyzed element | | U | U | U | U | | |
| U isotope abundances | | 0.52% | 49.70% | 0.08% | 49.71% | | |

603

604 Table 3: The collector configuration of the TIMS Sector 54 used for the $^{238}\text{U}/^{233}\text{U}$ isotope ratios
605 analyses of the blends and the $^{235}\text{U}/^{238}\text{U}$ isotope ratio analyses of the SRM U-500 standard
606 (certified for its isotopic composition) by the total evaporation method. The U isotopic
607 composition and the main isobaric interfering element are indicated. The isotopes used for the
608 analysed ratios are given in bold.

609

610

| Ratio | Value | Standard deviation (1σ) | Relative standard deviation (1σ) | Accuracy |
|--------------------|--------------|--------------------------------|---|-----------------|
| Ce NIST3110 | | | | |

| | | | | |
|---|----------|----------|-------|-------|
| $^{142}\text{Ce}/^{140}\text{Ce}$ TIMS TE (n=8) | 0.125911 | 0.000040 | 0.03% | 0.21% |
| $^{142}\text{Ce}/^{140}\text{Ce}$ TIMS Seq. (n=7) | 0.125690 | 0.000055 | 0.04% | 0.03% |
| $^{142}\text{Ce}/^{140}\text{Ce}$ IUPAC reference value | 0.12565 | 0.00029 | 0.23% | |
| NIST U-500 | | | | |
| $^{235}\text{U}/^{238}\text{U}$ TIMS TE (n=22) | 0.9999 | 0.0004 | 0.04% | 0.02% |
| $^{235}\text{U}/^{238}\text{U}$ certificate | 0.9997 | 0.0007 | 0.07% | |

611

612 **Table 4:** Average Ce and U isotope ratios determined for reference materials by thermal
613 ionization mass spectrometry (TIMS) in order to estimate the external reproducibility of the
614 total evaporation (TE) method and the sequential (seq.) method. Here, n is the number of
615 measurements performed. The IUPAC reference value for a natural Ce solution was used
616 (Berglund and Wieser, 2011). The isotope ratio (IR) accuracy was expressed as $100 \times (\text{IR}_{\text{measured}}$
617 $– \text{IR}_{\text{reference or certificate}}) / \text{IR}_{\text{reference or certificate}}$.

618

| | Average value | Expanded uncertainty $k = 2$ | Relative expanded uncertainty $k = 2$ | Relative standard deviation 1σ | Relative difference between aliquots A and B |
|---|---------------|---------------------------------|--|--|--|
| MOx 1 | | | | | |
| $^{142}\text{Ce}/^{140}\text{Ce}$ (n=3) | 0.88602 | 0.00580 | 0.65% | 0.11% | 0.16% |
| $^{144}\text{Ce}/^{142}\text{Ce}$ (n=3) | 0.01411 | 0.00011 | 0.76% | 0.38% | 0.19% |
| MOx 2 | | | | | |
| $^{142}\text{Ce}/^{140}\text{Ce}$ (n=2) | 0.87200 | 0.00571 | 0.65% | | 0.01% |
| $^{144}\text{Ce}/^{142}\text{Ce}$ (n=2) | 0.01828 | 0.00014 | 0.76% | | 0.01% |

619

620 **Table 5:** Average Ce isotope ratios of spent fuels determined from two aliquots (A and B) by
621 TIMS (Sector 54) according to the sequential method for the two different MOx samples. Here,
622 n is the number of measurements performed. The relative difference between the isotope ratios
623 (IR) of aliquots A and B is expressed as $100 \times (\text{IR}_A – \text{IR}_B) / \text{IR}_B$. The explanation for the
624 estimation of the expanded uncertainties (U) can be found in the text.

625

626

| Sample | $^{144}\text{Ce}/^{238}\text{U}$ | Expanded combined uncertainty $k=2$ | Relative expanded combined uncertainty $k=2$ |
|--------------|----------------------------------|--|---|
| MOx 1 | 34.7×10^{-6} | 0.4×10^{-6} | 1.1% |
| MOx 2 | 58.8×10^{-6} | 0.7×10^{-6} | 1.1% |

627

628 **Table 6:** $^{144}\text{Ce}/^{238}\text{U}$ atom ratios determined in spent fuel using the double spike isotope dilution
629 mass spectrometry technique. The expanded combined uncertainties (U) were expressed using
630 a coverage factor (k) of 2, providing an interval with a 95% confidence level. Expanded
631 combined uncertainties U were determined following a Kragten approach.

632

633

634 **Significance to JAAS**

635 We have developed a new method for the determination of $^{144}\text{Ce}/^{238}\text{U}$ atom ratio at a few tens
636 of ppm with expanded uncertainty of around 1% ($k=2$) in spent nuclear fuels using a double
637 spike isotope dilution technique associated with thermal ionization mass spectrometry
638 measurements employing both the total evaporation and the sequential methods. This
639 represents a significant improvement compared to measurement uncertainties obtained for
640 ^{144}Ce content at a level of several percent with gamma-ray spectrometry. The accurate
641 quantification of the ^{144}Ce content in spent nuclear fuel is necessary to validate the neutronic
642 calculations, in particular for decay heat purposes.