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226Ra and 137Cs determination by inductively coupled plasma mass spectrometry: state of the art and perspectives including sample pretreatment and separation steps

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1 ²²⁶Ra and ¹³⁷Cs determination by inductively coupled plasma mass
2 spectrometry: state of the art and perspectives including sample
3 pretreatment and separation steps
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11 **Keywords**

12 Radium; Cesium; Sample handling; Inductively Coupled Plasma – Mass Spectrometry; Solid Phase
13 Extraction; Separation.
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31 **Abbreviations**

32 AMP: Ammonium molybdophosphate; AMS: Accelerator Mass Spectrometry; CDTA: 1,2-
33 diaminocyclohexanetetraacetic acid; CRC: Collision Reaction Cell; CRM: Certified Reference Materials;
34 DF: Decontamination Factors; DHC: Diammonium hydrogen citrate; DIHEN: Direct Injection High
35 Efficiency Nebulizer; dSPE: dispersive Solid Phase Extraction; EF: Enrichment Factor; ETV:
36 ElectroThermal Vaporization; FI: Flow-Injection; HR-ICP-MS: High Resolution ICP-MS; IAEA:
37 International Atomic Energy Agency; ICP-Q-MS: Single Quadrupole ICP-MS; ICP-QQQ-MS: Triple
38 Quadrupole ICP-MS; IDL: Instrumental Detection Limit; IIP: Ion-Imprinted Polymers; KED: Kinetic
39 Energy Discrimination; LA: Laser Ablation; LLE: Liquid-Liquid Extraction; LOV: lab-on-valve; MC-ICP-
40 MS: Multicollector-Inductively Coupled Plasma-Mass Spectrometer; MDL: Method Detection Limit;
41 MOF: Metal-Organic Framework; MRT: Molecular Recognition Technology; MSFIA: Multi-Syringe
42 Flow Injection Analysis; NORM: Naturally Occurring Radioactive Material; NTA: Nitilotriacetic acid;
43 PAN: Polyacrylonitrile; SF-ICP-MS: Sector Field Mass Spectrometer; STD: Standard configuration; TDS:
44 Total Dissolved Solids; US EPA: United States Environmental Protection Agency; WHO: World Health
45 Organization.

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65 **1. Introduction**

66 Among all existing radionuclides, interest in accurate determination of ^{226}Ra and ^{137}Cs is strongly
67 related to radiological protection issues and to their use as contamination tracers, for the reasons
68 given below. Indeed, over the past decades, human activities contributed to their release in the
69 environment at different concentration levels and *via* different sources, thereby increasing potential
70 risks of ionizing radiation exposure to human and his environment. In the case of ^{226}Ra which is a
71 Naturally Occurring Radioactive Material (NORM), release sources namely include uranium, coal and
72 phosphate mining, and fracking (International Atomic Energy Agency, 2014). For the anthropogenic
73 isotope ^{137}Cs , main releases come from global fallout, nuclear accidents (Chernobyl, Fukushima), and
74 to a lesser extent from regulated releases from nuclear facilities (Burger and Lichtscheidl, 2018;
75 Gupta, 2016). Since Ra^{2+} and Cs^+ share similar properties with respectively Ca^{2+} and K^+ , once released
76 to the environment, they are likely to replace them in biological and physico-chemical processes,
77 thus promoting their accumulation in living organisms and consequently increasing the internal dose.
78 By taking into account their high specific activities and the type of radiations they induce, their
79 tracing from contamination sources constitutes a major concern in radiological environmental
80 monitoring (Jia and Jia, 2012; Russell et al., 2015). However, current challenges are related to the
81 understanding of the geochemical behavior and more specifically of the transport mechanisms of
82 these radionuclides in the environment and between environment and humans, which implies being
83 able to precisely measure their concentration at ultra-trace level in complex matrices and sometimes
84 in small sample volumes.

85 As many radionuclides, both ^{226}Ra and ^{137}Cs are still often measured by radiometric techniques
86 according to their emission properties. Hence, the determination of ^{226}Ra can be performed with
87 alpha (Song et al., 2017; Straub et al., 2018) and gamma spectrometry (van Beek et al., 2010; Molina
88 Porras et al., 2017), or through the determination of its daughter nuclides namely by ^{222}Rn emanation
89 (Perrier et al., 2016) and liquid scintillation (Godoy et al., 2016; Idoeta et al., 2018). About ^{137}Cs ,
90 gamma-spectrometry and beta-counting techniques are commonly employed but gamma
91 spectrometry remains by far the current preferred detection method (Haller et al., 1967). Indeed,
92 gamma rays are slightly attenuated by the sample matrix contrary to alpha and beta particles
93 meaning that direct measurement can be carried out (Lariviere et al., 2006; Zheng et al., 2013).
94 Moreover, since alpha and beta counting techniques require long equilibration and counting times to
95 achieve low detection limits, they are not well adapted to process a large number of samples, and
96 they may also not be efficient for applications targeting samples of low activities and small volumes
97 (Abbasi, 2018).

98 For some years now, mass spectrometric techniques have also proven their worth in the
99 quantification of radionuclides (Hou and Roos, 2008; Zheng et al., 2013). Among them, Inductively
100 Coupled Plasma Mass Spectrometry (ICP-MS) is the most widely used analytical technique, especially
101 for ^{226}Ra , but other techniques such as Thermal Ionization Mass Spectrometry (TIMS) and Accelerator
102 Mass Spectrometry (AMS) have also been employed (Zheng et al., 2013; International Atomic Energy
103 Agency, 2010; Lehto and Hou, 2011; Bu et al., 2016; Croudace et al., 2017; Thakur et al., 2021). ICP-
104 MS is indeed more accessible than the other two techniques cited and continuous progresses in
105 instrumentation regularly enlarge the panel of applications and issues it can help to address. Initially,
106 this analytical technique focused on longer-lived radionuclides (^{238}U , ^{232}Th , etc.) whose low specific
107 activities favor atom-counting over radiometric techniques (Croudace et al., 2017; Lariviere et al.,
108 2006). In the past few decades, improvements in instrument sensitivity achieved through advances in
109 sample introduction systems, mass spectrometer configuration, and vacuum pump technologies
110 have opened up the possibility of using ICP-MS for quantification of shorter-lived radionuclides,
111 including ^{137}Cs (half-life, 30 years) (Amr et al., 2016; Bu et al., 2016; Cao et al., 2016; Ohno and
112 Muramatsu, 2014; Yang et al., 2016; Zheng et al., 2014b, 2014a). Indeed, ICP-MS offers multiple
113 advantages such as measurement of the $^{137}\text{Cs}/^{135}\text{Cs}$ isotope ratio enabling to identify the origin of
114 radioactive cesium (Bu et al., 2016; Russell et al., 2015) and simultaneous determination of the stable
115 ^{133}Cs isotope allowing to assess extraction yield of the sample pretreatment step.

116 However, to reach low detection limits and perform accurate and precise measurements of radium
117 and cesium by ICP-MS, removing spectral and non-spectral interferences is mandatory. As far as we
118 know, direct analysis remains limited and rare studies manage to overcome those interference issues
119 using only artifacts related to advances in instrumentation such as Collision Reaction Cell (CRC) or
120 tandem mass spectrometry (MS/MS) (Ben Yaala et al., 2019; Epov et al., 2003; Ohno and Muramatsu,
121 2014; Wærsted et al., 2018; Xiao et al., 2020). If such a methodology can be applied on a case-by-
122 case basis to certain samples, depending on the matrix and concentrations targeted as well as on the
123 instrument, it is far from being generalizable to any kind of samples and applications yet. This is why
124 sample pretreatment is an essential stage of the analytical process. Several methods and strategies
125 have been employed in the past decades with the aim of extracting and preconcentrating radium and
126 cesium and/or eliminating elements causing major interferences, notably the most abundant alkali
127 and alkaline-earth cations in nature (Na^+ , Ba^{2+} , Ca^{2+} , and Mg^{2+}). These methods include sample
128 pretreatment techniques (Liquid-Liquid Extraction (LLE) (Beklemishev et al., 1994; van Leeuwen et al.,
129 2005; Wang and Zhuang, 2019a), precipitation, and Solid Phase Extraction (SPE)), but also separation
130 techniques (Liquid Chromatography (LC) and Capillary Electrophoresis (CE)), or a combination of
131 these different possibilities. It is sometimes possible to hyphenate them with ICP-MS to perform a so-
132 called on-line analysis, which usually results in a substantial saving of time and enhanced

133 repeatability. Among the abovementioned techniques, SPE is the most widely used due to its easy
134 handling, the variety of sorbents available and the selectivity of which is constantly increasing.
135 Furthermore, it is worth mentioning its automation ability and high design flexibility that allow it to
136 meet the diverse application requirements. Nevertheless, some application fields need to push
137 current sample pretreatment and detection methods over the edge in order to achieve the lowest
138 detection limits.

139 In our knowledge, to this date, literature reports only four reviews dealing with radium or cesium
140 isotopes determination, but none of them is dedicated specifically to their detection by ICP-MS. A
141 first short review on ^{226}Ra and ^{228}Ra that briefly describes some preconcentration methods and
142 radiometric or mass spectrometric techniques available for their detection was published in 2018
143 (Abbasi, 2018). In 2021, a comprehensive review has been focused on depicting and comparing the
144 efficiency of various analytical techniques used to collect, pretreat, and analyze radium isotopes both
145 by radiometry and mass spectrometry (Thakur et al., 2021). It has also pointed out challenges arising
146 from the analysis of Ra in gas and oil waste from hydraulic fracking processes. Russell *et al.* have
147 published in 2015 a review only focused on the determination of ^{135}Cs , ^{137}Cs and their isotopic ratio in
148 environmental samples (Russell et al., 2015). They detail some general information on radiocesium
149 (source, variation and behavior in environment), and provide the common methods to separate it
150 from the sample matrix before performing measurements by neutron activation analysis or mass
151 spectrometry. In 2016, another group made a review on the determination of fission products ^{135}Cs
152 and ^{137}Cs in combination with ^{90}Sr , summarizing strategies available for eliminating interferences by
153 chemical separation and mass spectrometry with a special focus on application of $^{135}\text{Cs}/^{137}\text{Cs}$
154 measurement in real samples (Bu et al., 2016). Through this review, we contribute to a complete and
155 detailed state of the art of preconcentration and separation approaches based on SPE and
156 alternative procedures associated with ICP-MS analysis of radium and cesium over the last 30 years,
157 providing a critical overview of the performances of the different approaches applied either to
158 environmental or biological matrices. Since total chemical purification is never fully achieved,
159 solutions to improve ^{226}Ra and ^{137}Cs signal detection and quantification taking advantage of ICP-MS
160 instrumentation are in turn discussed. After a quick outline of current limitations and future outlooks
161 of the different analytical process steps, the last section makes an overview of applications involving
162 the determination of ^{226}Ra and ^{137}Cs .

163

164 **2. Sample handling: a critical stage of the analytical methodology**

165 The term “sample handling” can be used to refer to all steps between sampling and separation by
166 chromatographic methods or detection (e.g. sample drying, grinding, sieving, ashing, matrix

167 decomposition, extraction, purification, and preconcentration). Here, we will however restrict its use
168 to the process step enabling analyte(s) extraction, matrix cleaning (i.e. purification), and/or
169 enrichment. Indeed, the purpose of a sample handling step preceding an ICP-MS analysis is two-fold:
170 eliminate fully or partly major elements in order to prevent matrix effects but also elements that can
171 lead to formation of isobaric or polyatomic interferences, as illustrated in Table 1 for ^{137}Cs and ^{226}Ra
172 ICP-MS detection.

173

174 **2.1. Solid phase extraction: the most spread technique**

175 SPE is nowadays a well-established technique for radionuclides as for many other application fields,
176 and its working principle which is similar to the one of chromatography, and related terminology
177 have been well described by the community (Buszewski and Szultka, 2012; Poole et al., 2016; Poole,
178 2019). The usual SPE protocol includes an initial conditioning step of the sorbent followed by
179 percolation of the sample, washing of the non-retained components and finally elution of the target.
180 It has in particular replaced traditional LLE processes which were time-consuming, poorly
181 automatable, generally consumed large amounts of organic reagents, and therefore didn't meet the
182 requirements of green chemistry. Moreover, LLE is not well suited upstream to ICP-MS detection
183 since in the final stage, ions stand in the organic phase jointly with the chelating agent. SPE
184 overcomes the abovementioned drawbacks.

185

186 **2.1.1. Ra and Cs extraction using variety of SPE supports**

187 The choice of the SPE support is usually driven by its specificity towards the targeted ions or towards
188 interfering ions which need to be removed prior to analysis. Table 2 gathers characteristics of SPE
189 sorbents encountered in Ra and Cs sample preparation protocols followed by ICP-MS detection
190 which are expanded in Table 3 (an extended form of this table is available in supplementary
191 information) and whose performances will be discussed in next sections. SPE sorbents can be
192 classified according to many possible criteria such as the nature of the phase, the specificity, and
193 interaction mechanism(s) between analytes and sorbent. In Table 2, we chose to classify them
194 according to the retention mechanism involved (ion-exchange or surface complexation), exemplifying
195 the chemical structure of the interaction site(s) when known. Looking then on the right hand column
196 of each category, readers can get a general idea of their specificity. The goal of this section is to
197 understand and discuss sorbent popularity in light of current knowledge about their application
198 through years: specificity, cost, and limitations.

199 The most used resins in Ra SPE procedures are the cation-exchange resin AG50W-X8 alone (Bonin et
200 al., 2020; Dalencourt et al., 2018; Hodge and Laing, 1994; Park et al., 1999; E.M. van Es et al., 2017;
201 Yang et al., 2020) or in combination with an Sr-spec resin (Copia et al., 2015; Evans et al., 2015;
202 Lagacé et al., 2017; Larivière et al., 2007, 2005; Zhang et al., 2015) containing a crown ether chelating
203 agent, both not being designed to specifically extract Ra. Ra-specific sorbents include MnO₂-based
204 resins, Radium specific disks named RAD disks and resin AnaLig Ra-01. Historically, the affinity of Ra²⁺
205 for Mn-based resins (MnO₂ resin (Moon et al., 2003; Varga, 2007, 2008), Mn-fibers (Bourquin et al.,
206 2008), MnO₂-Polyacrylonitrile (PAN) (Dulanská et al., 2015), and MnO₂-SiO₂ (Dulanská et al., 2018))
207 was exploited extensively for its determination in water samples owing to their low price, high
208 adsorption coefficient and the possibility to be prepared homemade. Nevertheless, experience has
209 shown that extraction efficiency can be greatly affected by factors such as extreme pH values, salt
210 concentrations, or use in reducing environment that leads to destruction of the support, making Mn-
211 based resins not sufficiently robust for radium pre-concentration in complex matrices (International
212 Atomic Energy Agency, 2010; Varga, 2007). The other two sorbents stated, RAD disks and AnaLig Ra-
213 01, contain macrocyclic ligands whose structures are undisclosed by the supplier and which can
214 selectively entrap Ra²⁺ based on the Molecular Recognition Technology (MRT), i.e. the ion is
215 selectively recognized related to the cavity size, the nature and number of chemical functions and
216 charges present, as well as the ligand conformation (Dalencourt et al., 2020; Joannon and Pin, 2001;
217 Schettler et al., 2015; Verlinde et al., 2019). To the best of our knowledge, the AnaLig Ra-01 resin is
218 the only specific resin towards Ra that is currently available on the market and deserves thus to be
219 better known and employed in the future despite its substantial cost (price excluding tax: 1940 € for
220 10 g) (Dalencourt et al., 2020; Verlinde et al., 2019). Indeed, since Pedersen's early observations on
221 the ability of crown ethers to complex alkali and alkaline earth ions (Izatt, 2007; Pedersen, 1988),
222 great efforts have been made to increase the stability and selectivity of cation-ligand complexes (van
223 Leeuwen et al., 2005) giving rise to molecules such as highly substituted crown ethers (Chiarizia et al.,
224 1999; Dietz et al., 1997), calixarenes (AlHaddad et al., 2020) or calixarene-crown ethers (Chen et al.,
225 n.d.) whose syntheses are in return costly and time-consuming. This research of selectivity is all the
226 more challenging in case of Ra²⁺ since from the alkaline earth cations, it has the lowest tendency to
227 form complexes (van Leeuwen et al., 2005) and behave the same way as Ba²⁺, main competitor for
228 interaction sites. Recently, a new calixarene-based ligand called macropa (18-membered
229 bispicolinate diazacrown macrocycle) proved to be an efficient Ra²⁺ chelator for nuclear medicine
230 applications (Abou et al., 2021).

231 For Cs⁺ extraction, inorganic ion-exchange resins constituted of pure ammonium molybdophosphate
232 (AMP) or AMP-PAN were mainly employed, followed by subsequent extraction on resin AG50W-X8
233 functionalized with sulfonate moieties (Amr et al., 2016; Epov et al., 2004; Zhu et al., 2021a, 2020).

234 However, it is worthwhile to notice that pure AMP was preferentially used in batch mode (see
235 section 2.2.1) than in cartridge because the material consists of fine particles, leading to AMP leakage
236 from the cartridge and limiting the loading flow rate ($< 1 \text{ mL min}^{-1}$) to avoid back pressure (Epov et
237 al., 2004). To solve these issues, Epov *et al.* tried to load AMP on different kind of supports (glass
238 wool, Teflon beads or silica gel) (Epov et al., 2004). Small particle size of the silica gel prevented them
239 to work at flow rates greater than 1 mL min^{-1} and they found out that in addition to the flow rate
240 value, Cs recovery was also highly dependent on the amount of support material. The best
241 compromise was achieved using 100 to 250 mg of glass wool plus 25 mg of AMP since recoveries
242 between 95% and 99% could be reached working at flow rates in the range 1 to 8 mL min^{-1} . More
243 recent papers rather use AMP-PAN sorbents (Zhu et al., 2021a, 2020). Potassium nickel ferrocyanate
244 (KNiFC) is another inorganic material known to possess high affinity for Cs but it is less used because
245 less selective than AMP-based sorbent. Zheng *et al.* effectively observed that KNiFC-PAN adsorbed
246 circa two times more Ba (21.1%) and three times more Sn (60%) than AMP-PAN (Zheng et al., 2014a),
247 elements that are source of isobaric and polyatomic interferences, respectively. Valuable research on
248 the design of specific macrocyclic chelating agent has also been carried out in case of Cs^+ (Dozol et
249 al., 1999; Frensdorff, 1971; Simonnet et al., 2018; Wang and Zhuang, 2019a), but contrary to Ra^{2+} , no
250 commercial sorbent containing Cs specific macrocyclic extractants exists at this time. To take
251 advantage of the great potential of these molecules, one group however solubilized the commercial
252 ligand MacroLig 209R in octanol and loaded it onto a commercial Amberchrom CG-71 resin (Russell
253 et al., 2014b). Bearing two crown-6 groups, one MacroLig 209R ligand can in theory binds two Cs^+
254 ions (Cs coordination number being 6) but comparison between theoretical and experimental
255 capacities rather revealed a 1:1 stoichiometry. Thus, the capacity of the resin could be improved by
256 increasing the calixarene concentration into the impregnated resin but this solution may be limited
257 by the high cost of the molecule.

258 One can finally notice that apart from rare authors that make their resins themselves (Russell et al.,
259 2014b), sorbents used for Ra and Cs SPE are commercial. They can be purchased already packed in
260 cartridges, with different options, or even in powder form enabling users to develop custom
261 applications: adaptation of the amount of phase and cartridge format (e.g. AnaLig Ra-01 resin packed
262 into a 2 x 40 mm tube (Verlinde et al., 2019) or AG50W-X8 resin loaded into a 10 mL Eppendorf
263 pipette tip (Yang et al., 2020)) or modification of the initial phase to design tailor-made sorbents
264 (Russell et al., 2014b).

265

266 2.1.2. Key parameters for an optimal SPE

267 SPE procedure development must be guided by the objective of removing a maximum of interfering
268 elements while minimizing at most the number of manipulations and the sample processing time. As
269 a proof of efficiency, a common practice consists in exhibiting the decontamination factor (DF) values
270 (Figure 1) or the elution profiles obtained with the optimized method. Basically, the minimum DF to
271 reach is dictated by the ICP-MS instrument, and more precisely by concentrations from which
272 spectral interferences induce an overestimation of the targeted radionuclide signal. For example,
273 measurement of the DF of multiple elements (solutions at 100 ng L^{-1}) from a cartridge containing
274 0.02 M of calixarene ligand (MacroLig 209R) demonstrated the high specificity of the resin: apart
275 from Cs (1), Rb (30) led to the lowest DF among the alkali metals (K (1,100), Na (2,100), and Li
276 (7,100)) and all other elements tested including Ba, which is responsible for isobaric interferences (DF
277 values ranging from 880 to 12,000). DF can also be used to compare efficiency of different methods,
278 so long as they are applied on similar sample matrices.

279 As a first step, one need to know the affinity, maximum capacity, and breakthrough volumes of the
280 supports that will be used. These parameters may be provided by the supplier, found in previous
281 papers or have to be estimated former in the lab. The support affinity is most of the time evaluated
282 by batch experiments to avoid collecting several fractions at this stage of development. For instance,
283 a valuable set of data on distribution coefficients (K_d) of Ra and a large panel of elements (alkali,
284 alkaline-earth, poor, and transition metals, lanthanides, and actinides) for the resin AnaLig Ra-01 in
285 acidic medium (HNO_3 and HCl concentrated from 0.01 to 10 M) was determined by batch
286 experiments (50 mg of resin, 20 h of contact time under stirring) by Gourgiotis *and coll.* while until
287 now, poor knowledge about this resin was available (Verlinde et al., 2019). Also knowing the matrix
288 composition and the order of magnitude of the concentration of targeted radionuclides in the
289 sample, the parameters aforementioned constrain the amount of sorbent and the sample loading
290 volume required. Usually, the optimization is carried out using simulated samples, sometimes also
291 called artificial or synthetic samples, which refer as pure solutions mimicking the matrix composition
292 of the targeted real samples and spiked with the radionuclides of interest.

293 Then the most important part of the procedure development is based on determining the best
294 conditions for fixing ions and next their desorption, playing essentially on the nature of solutions and
295 the volumes used. Adding one or more washings before elution can greatly improve the selectivity of
296 the extraction protocol by eliminating some interfering elements also retained during sample
297 loading. Obviously, when more than one resin is used (e.g. need to improve the decontamination
298 factors depending on the concentration targeted, or several targeted elements with different
299 chemical properties to extract and measure), new constraints may result. In the best case, elution
300 fraction from a resin can directly be percolated on the next one, as realized for instance with
301 successive extractions on AG50W-X8 and Sr-spec resins (Copia et al., 2015; Lagacé et al., 2017). But

302 this is far from being always the case since the elution solution is generally not a suitable medium for
303 fixing ions on the following resin; an evaporation to dryness is thus often needed before re-
304 dissolution in the appropriate medium (Larivière et al., 2005, 2003; Pietruszka et al., 2002; Zhang et
305 al., 2015). This increases the risk of contaminations and losses and the total analysis time. It is worth
306 noting that most of the time, authors only adapt a procedure from an existing one so that it meets
307 the requirements of their samples and application, but uncommon are papers in which an advanced
308 optimization is conducted. Hereafter, you will find some developments or facts that deserve to be
309 pointed out.

310 The first SPE procedure on AnaLig Ra-01 resin was established from K_d values in different media
311 which allowed to select the nature of solutions to apply as well as their order (Verlinde et al., 2019).
312 Since apart from Ra and Ba, the most retained elements, Pb and Tl, were weakly adsorbed at 6 M HCl,
313 and Sr at 0.1 M HCl, the SPE procedure was thus realized by loading the sample in 0.1 M HCl to
314 minimize Sr retention and washing the cartridge with 0.1 M HCl and 6 M HCl, therefore achieving to
315 purify the sample from more than 70% of Sr and 80% of Tl and Pb before elution of Ra and Ba with
316 0.12 M of nitrilotriacetic acid (NTA) adjusted to pH 10. Residual amounts of Sr and Ba in the elution
317 fraction did not induce formation of polyatomic interference $^{88}\text{Sr}^{138}\text{Ba}$, even with solution containing
318 circa $300 \mu\text{g L}^{-1}$ of each element, thus making this procedure that requires only one resin quite simple
319 to implement. Though in that case, selective Ra elution was achieved with the help of a chelating
320 agent, sometimes element affinity to the support is so strong that finding a competitive stripping
321 agent is not easy. For instance, Ra elution from RAD disks prior to radiometric detection (application
322 for which these disks have first been conceived) involve the use of ethylenediaminetetraacetic acid
323 (EDTA) (Fons-Castells et al., 2016; Purkl and Eisenhauer, 2003) or diammonium hydrogen citrate
324 (DHC) (Ďurecová, 1997). However, to reach quantitative Ra recovery, it requires high concentrations
325 and large volumes of these reagents. Thus rather than performing a tough elution step that could
326 degrade the procedure blank, one group decided to recover Ra by digesting the resin with strong
327 acids (hydrofluoric acid, aqua regia containing H_2O_2 and HClO_4) (Joannon and Pin, 2001). Although
328 specific to Ra and attractive for radiochemical analyses, RAD disks appear rather a burden prior to
329 ICP-MS introduction, due to the use of chelating agents, which probably explains why they occur only
330 twice in Table 3 (Joannon and Pin, 2001; Schettler et al., 2015). Concerning procedures on other kind
331 of sorbents, most of the groups applied HCl or HNO_3 solutions at various molarities to separate Ra^{2+}
332 or Cs^+ from interfering elements (Bi et al., 2016; Granet et al., 2008; Hodge and Laing, 1994; Kim et
333 al., 1999; Park et al., 1999; Russell et al., 2014b; Tsai et al., 2010; E.M. van Es et al., 2017; E. M. van Es
334 et al., 2017; Yang et al., 2020). Working with the resin AG50W-X8, Larivière *et coll.* were the first ones
335 who exclusively employed complexing agents (EDTA, NTA, and 1,2-diaminocyclohexanetetraacetic
336 acid (CDTA)) all along their procedure, thus taking advantage of the different complexation

337 properties of these agents to compensate the lack of resin selectivity (Dalencourt et al., 2018).
338 Nevertheless, some elements competitors for interaction sites (Na, Cs, Ca, Ba, Cr, Zn, and Th) were
339 still present, up to 40% of their initial amount, in the radium fraction. Note that if chelating agent
340 may be useful to perform selective elution, their presence in the elution fraction may cause
341 important matrix effects in ICP-MS. Gourgiotis *et coll.* observed the presence of NTA entailed a
342 decrease of the signal, but they were able to take into account the derive by the use of ^{103}Rh as
343 internal standard (Verlinde et al., 2019). Another group noticed that apparent signal generated at
344 m/z 226 by the presence of the polyatomic interferences $^{88}\text{Sr}^{138}\text{Ba}^+$ was 7 to 22-fold higher in NTA
345 solution than in HNO_3 , reinforcing the need to remove those elements before elution to avoid
346 mistakes during quantification (Dalencourt et al., 2018). Using the same resin, Yang *et al.* (Yang et al.,
347 2020) managed for their part to remove Na, K, Mg, Ca, and Sr elements using a low amount of
348 organic solvent (20% ethanol) in 4 M HCl as washing solution. These conditions were selected to
349 make a compromise between cation exchange distribution coefficients for Ba and Sr in mixtures of
350 HCl with variable percentage of solvents (methanol, ethanol, acetone, and dioxane) (Strelow, 1968),
351 and the fact that the presence of solvent can slow down the flow rate and rate of exchange between
352 solution and resin, and also induce Ba precipitation as chlorides.

353 Considering Cs extraction on AMP support, Cs elution is most of the time achieved by applying an
354 alkaline solution but this one also entails decomposition of the AMP support, which results in
355 contaminations of Mo coming from the resin in the elution fraction, as well as varying amounts of Sn,
356 Sb, and Ba coming from the sample and retained to some extent during percolation. Since some of
357 those elements may interfere with detection of ^{135}Cs and ^{137}Cs forming polyatomic interferences
358 ($^{119}\text{Sb}^{16}\text{O}^+$, $^{121}\text{Sb}^{16}\text{O}^+$, $^{120}\text{Sn}^{17}\text{O}^+$, $^{95}\text{Mo}^{40}\text{Ar}^+$, and $^{97}\text{Mo}^{40}\text{Ar}^+$) or leading to the presence of isobaric
359 interferences (stable ^{135}Ba and ^{137}Ba isotopes), this explains why, further purification on AG50W-X8
360 was made (Amr et al., 2016; Epov et al., 2004). Rather than dissolving the AMP-PAN resin and
361 introducing high amount of interfering elements in the sample, Zhu *et al.* achieved to elute Cs with 4
362 M NH_4Cl (Zhu et al., 2020). But, since presence of large amount of NH_4^+ could compete with Cs^+ for
363 interaction sites on AG50W-X8 resin, a sublimation step was introduced to remove NH_4Cl (heating at
364 350°C for 1-2 h in presence of 60 mg of LiCl as protective agent to prevent loss of Cs) before
365 proceeding further in sample purification.

366 When the final elution volume does not allow sufficient Ra or Cs enrichment or if the elution medium
367 is not suitable for introduction in ICP-MS, a final evaporation/re-dissolution step can be applied
368 (Granet et al., 2008; Hodge and Laing, 1994; Joannon and Pin, 2001; Kim et al., 1999; Park et al.,
369 1999; Tsai et al., 2010; E.M. van Es et al., 2017; Verlinde et al., 2019; Yang et al., 2020). Sometimes, it
370 is also preceded by treatments with oxidizing agents to remove any residual organic matter present
371 prior to analysis (Hodge and Laing, 1994; Tsai et al., 2010; Verlinde et al., 2019). In complement to

372 the optimization of volume and nature of solutions, it can be useful to evaluate the impact of the
373 flow-rate on the recovery (minimum contact time necessary between sample-support so that
374 interactions can occur) in order to increase the sample handling throughput. This is however not
375 much studied in literature.

376 Reliable manners to quantify possible loss during sample handling, concentrations of radionuclides of
377 interest, and to estimate the method detection limit must be used, especially when a complex
378 procedure is realized. The best approach for precise yield calculation remains isotopic dilution. For
379 ^{226}Ra , a radiochemical tracer such as ^{228}Ra (Kayzar and Williams, 2016; Kim et al., 1999; Larivière et
380 al., 2007; Pietruszka et al., 2002; Scott et al., 2019), which is the most used, or ^{225}Ra (Schettler et al.,
381 2015), is added before starting the procedure. The use of ^{228}Ra demands to remove its daughter ^{228}Th
382 just before the analysis to avoid isobaric interference. This often involves addition of an extra TRU
383 cartridge at the end of the extraction procedure. Due to the short half-life of ^{225}Ra ($T_{1/2} \sim 14.9$ days),
384 Schettler *et al.* determined the recoveries by gamma spectrometry, requiring a wait of about 12 days
385 after SPE and analysis of ^{226}Ra by ICP-MS (Schettler et al., 2015). It is however worth noting that such
386 tracers cannot be bought as pure solution, they always contain ^{226}Ra to some extent, and nowadays
387 there is still no Ra source certified in isotopic ratio available on the market. Thus, the main difficulties
388 lie first of all in finding a source with a high 228/226 ratio to avoid adding uncertainty during
389 determination of ^{226}Ra concentration in the sample. Secondly, in characterizing precisely the
390 composition of the spike, and determining the ideal amount of spike to add in the sample to
391 minimize uncertainties. In-house spikes may for instance been prepared from an old thorium salt
392 (Chabaux et al., 1994) or commercial Th standard solution (Vieira et al., 2021). An alternative to
393 isotopic dilution is based on measuring the level of ^{133}Ba before and after sample purification (Tsai et
394 al., 2010; Yang et al., 2020). In the case of ^{135}Cs and ^{137}Cs , common practice consists in using the
395 stable isotope ^{133}Cs (Amr et al., 2016; Zhu et al., 2021a). Isotopic dilution was also used to determine
396 low concentrations of ^{135}Cs in soil samples based on gamma spectrometry measurements of ^{137}Cs
397 already present in the sample (Zhu et al., 2020). In that case, except for the tracer, the principal
398 analysis of the target radionuclide was made by ICP-MS.

399 In many cases, the instrumental detection limit (IDL) was determined by measuring the signal of the
400 target analyte in clean blanks (diluted HNO_3 solutions) (Table 3), which does not take into account
401 the matrix composition (eluent solution and presence of remaining interfering elements) of the
402 fraction injected in ICP-MS after sample purification. This results in an overestimated IDL. Though not
403 perfect, the following approach was used by Wang and coworkers to take into account matrix
404 effects: they quantified ^{226}Ra in several matrices with the standard addition methods and used the
405 different slopes of the curves to estimate impact of the amount of total dissolved solids (TDS) on the
406 IDL, which ranged from 0.12 to 2.2 pg L^{-1} for matrix containing up to 12% of TDS (W. Wang et al.,

2021). Sometimes, IDL calculation is also based only on three times the standard deviation of the blank solution, omitting thus the non-negligible contribution of the mean of the blank, which is not acceptable since it leads to overestimation. Comparison of data from literature is thus a bit biased by the lack of homogeneity of practices and the different analyzers used. The overall Method Detection Limit (MDL) can be either experimentally determined applying the sample preparation method before ICP-MS analysis, or calculated (theoretical MDL) by dividing the IDL by the theoretical enrichment factor. Though an experimental MDL is closer to the real value, it remains an overestimation because it is difficult to make a solution truly representative of the composition of the real sample for its determination; none of the published studies has attempted to reconstitute the sample matrix. As it can be seen, for many of the values presented in Table 3, the nature of the solution used was not specified in articles. In addition, when only an MDL value was provided by authors, it is not always clear to know if they correspond to theoretical or experimental data since too little information about detection limit estimation was given. From all these data, the lowest MDL reached for ^{226}Ra is 0.009 pg L^{-1} (Bonin et al., 2020). It was assessed by applying their SPE procedure on 500 mL of a 0.25 M HCl solution adjusted to pH 2, taking thus into account only background noise that can arise from residual contaminants coming from the resin and reagents used. This value is five times higher than the calculated theoretical MDL (0.002 pg L^{-1}) although it still does not consider matrix effects.

Once the method is optimized, the last step is to determine whether it is robust by applying it to different kind of matrices allowing thus to identify the limits of the proposed methodology and assess improvement options. As an example, Lagacé *et al.* attained the limit of their procedure trying to percolate increasing volumes of spiked seawaters (from 10 to 90 mL and containing from 0.26 to 2.34 g of salts on 1 g AG50W-X8 + 1 g Sr-spec) (Lagacé et al., 2017). They indeed managed to recover $99 \pm 4\%$ ($n=3$) of Ra when loading 10 mL of seawater, but when treating larger volumes, the Ra-recovery gradually decreased from $85 \pm 9\%$ ($n=3$) for 30 mL to $57 \pm 8\%$ ($n=3$) for 90 mL, showing that either the capacity of the resin or the breakthrough volume were exceeded with such kind of matrix. From all the sorbents, the AnaLig Ra-01 resin is the only one that presents a very high affinity for Ra since only 50 mg of the resin was enough to recover up to 73% of Ra by loading 100 mL of spiked seawater, with no dependence of the matrix composition on the efficiency of the procedure (Verlinde et al., 2019).

2.1.3. Figures of merit of SPE procedures for Ra and Cs in literature

It can be seen from Table 3 that despite the complexity of some of the procedures, most of the time, global recoveries greater than 70% were obtained. Therefore, the recovery yield is not a pertinent

440 criterion to distinguish a method from another. In addition, when no standard deviation or relative
441 standard deviation is specified, the question of the repeatability remains unanswered.

442 So far, large sample amounts are still needed to succeed in accurately measuring ^{226}Ra or ^{137}Cs ,
443 especially in water samples where radionuclides concentrations are known to be lower. Apart from
444 two groups which were able to perform Ra extraction from well waters and wastewater from shale
445 gas extraction with volumes as low as 2 mL (Larivière et al., 2005; Zhang et al., 2015), Ra or Cs single
446 and sequential SPE procedures were mainly applied to liquid samples between 0.01 and 1 L
447 (Benkhedda et al., 2005; Bi et al., 2016; Copia et al., 2017, 2015; Dalencourt et al., 2020, 2018; Epov
448 et al., 2004; Evans et al., 2015; Hodge and Laing, 1994; Joannon and Pin, 2001; Lagacé et al., 2017;
449 Larivière et al., 2003; Park et al., 1999; Schettler et al., 2015; E. M. van Es et al., 2017; E.M. van Es et
450 al., 2017; Verlinde et al., 2019; W. Wang et al., 2021; Yang et al., 2020), and sometimes even several
451 L (Kim et al., 1999; Tsai et al., 2010); as well as on solid samples (between 0.004 and 100 g) after
452 digestion and re-dissolution in different volumes of percolation solution (between 1 and 500 mL)
453 (Amr et al., 2016; Bonin et al., 2020; Dalencourt et al., 2018; Granet et al., 2008; Kim et al., 1999;
454 Larivière et al., 2007, 2003; Pietruszka et al., 2002; Russell et al., 2014b; Tsai et al., 2010; Zhu et al.,
455 2020). Hence, significant discrepancies in terms of theoretical enrichment factors (EF, ratio of
456 percolated volume to elution or re-dissolution volume calculated for a maximum recovery of 100%)
457 between methods can be noticed, values ranging from several tens to several hundreds. Though
458 starting from a high sample volume is comfortable to exceed the IDL, it is not always a feasible
459 option. Indeed, the lack of protocols adapted to small volumes makes currently difficult, if not
460 impossible, the determination of these two radionuclides in samples whose volumes are intrinsically
461 limited (e.g. pore water, biological samples), and thus is a barrier to progresses on understanding
462 their geochemical behavior or health impact. In addition, the price to pay when loading such sample
463 volumes is the use of large amounts of resins (up to 10 or 25 mL or g sometimes (Bi et al., 2016; Kim
464 et al., 1999; Larivière et al., 2007; Pietruszka et al., 2002; Tsai et al., 2010; Yang et al., 2020)) and
465 reagents to accomplish purification and elution, which can be detrimental to the chemical procedure
466 blank and often induce addition of extra purification or enrichment steps. As illustration, 100 mL of
467 solution were required to recover Ra after percolation of 5 L of geothermal water on 10 g of AG50W-
468 X12 resin. But as the EF was not enough, an additional evaporation/re-dissolution step was
469 performed to increase it to 1,000, which of course was time-consuming in view of the volume to
470 treat. Other cases can be found in supplementary information in the extended form of Table 3 where
471 more details on the procedures are available.

472 Those last years, groups working on Ra and Cs have more and more tended to develop rapid and
473 straightforward SPE procedures, thus avoiding as far as possible the association of several resins.
474 Single resin extraction procedures represent almost 50% of the works presented in Table 3 (Bi et al.,

475 2016; Bonin et al., 2020; Dalencourt et al., 2018; Granet et al., 2008; Hodge and Laing, 1994; Joannon
476 and Pin, 2001; Kim et al., 1999; Park et al., 1999; Russell et al., 2014b; Tsai et al., 2010; E.M. van Es et
477 al., 2017; E. M. van Es et al., 2017; Verlinde et al., 2019; Yang et al., 2020). Note however that among
478 them, rare are papers which trialed their final method to aqueous samples highly charged in salts
479 such as seawater (Verlinde et al., 2019), or to solid extracts (Bonin et al., 2020; Russell et al., 2014b),
480 and even more to both solid extracts and liquid samples (Dalencourt et al., 2018); which makes quite
481 limited comparison between methods in terms of robustness. Labor-intensive protocols that employ
482 2 to 5 different sorbents were in particular developed to extract Ra from aqueous samples with high
483 level of TDS (e.g. seawater, fracking or mine waters (Dalencourt et al., 2020; Epov et al., 2004; Evans
484 et al., 2015; Lagacé et al., 2017; W. Wang et al., 2021; Zhang et al., 2015)) and from complex solid
485 matrices (e.g. soils and sediments (Amr et al., 2016; Larivière et al., 2007; Zhu et al., 2020), rocks and
486 ores (Larivière et al., 2003; Pietruszka et al., 2002; Scott et al., 2019), or biological solid samples
487 (spruce twigs and needles) (Larivière et al., 2003)), or when other radionuclides than ^{226}Ra needed to
488 be measured: determination of uranium and thorium series nuclides (Dalencourt et al., 2020; Scott et
489 al., 2019), of ^{226}Ra and ^{227}Ac to establish model age of nuclear materials (Kayzar and Williams, 2016),
490 or of ^{226}Ra – ^{230}Th – ^{238}U disequilibria in volcanic rocks (Pietruszka et al., 2002). In the case of multi-SPE
491 procedures, we observed these last years some effort being made on better thinking the procedures
492 to reduce the sample preparation time, and to facilitate the treatment of several samples
493 simultaneously or else procedure automation. Though in the past, each SPE could be intersected by
494 an evaporation step (Larivière et al., 2007, 2005, 2003; Pietruszka et al., 2002; Schettler et al., 2015;
495 Zhang et al., 2015), nowadays some authors manage to do fully without any evaporation step, even
496 combining 3 different sorbents (Dalencourt et al., 2020; W. Wang et al., 2021). The following smart
497 trick was also implemented by Larivière *et coll.* in order to minimize the sample pretreatment time: a
498 common sample matrix was loaded on 3 cartridges connected in series and containing a total of 4
499 resins in the order TRU (for selective U and Th extraction), Sr resin (for selective Pb and Po
500 separation) and a mixture of AnaLig Ra-01 and AG50W-X8 resins (for selective Ra extraction)
501 (Dalencourt et al., 2020). After applying a common washing step, cartridges were separated to
502 perform specific elution steps on each one. Comparing all procedures from Table 3, the sample
503 processing time ranges, when it is specified, from several minutes (Benkhedda et al., 2005; Evans et
504 al., 2015; Larivière et al., 2003) to several hours (<3 h in (Dalencourt et al., 2020, 2018; Epov et al.,
505 2004; Larivière et al., 2005; Verlinde et al., 2019) and >7 h in (Lagacé et al., 2017; Park et al., 1999;
506 Zhang et al., 2015)), and even days (Hodge and Laing, 1994; Larivière et al., 2007; Zhu et al., 2020),
507 showing that many of the procedures are still very time-consuming, even when only one or two
508 resins are employed.

509 Considering all the performance criteria available (see Table 3 and extended form of Table 3:
510 recovery yield, enrichment factor, procedure complexity, sample preparation time, and suitability to
511 diverse matrices), we believe that SPE procedures developed by Larivière *et coll.* (Dalencourt et al.,
512 2018) and Amr *et al.* (Amr et al., 2016) (first developed by Epov *et al.* (Epov et al., 2004)), respectively
513 for targeted Ra and Cs extraction, are to this day the most performing. In addition, they have both
514 the potential to be automated to perform on-line SPE, which refers to the introduction of SPE
515 support(s) into column(s) whose outputs are directly connected to ICP-MS. Such automated systems
516 for on-line purification, preconcentration, and detection are advantageous in many ways: they can
517 avoid time-consuming laboratory bench work and reduce risks of exposition to ionizing radiations,
518 which is all the more important when extracting Cs from samples containing ^{134}Cs and ^{137}Cs isotopes
519 that are short-lived gamma ray radionuclides (half-lives of 2.1 and 30 years, respectively).

520 To the best of our knowledge, only three groups developed on-line SPE coupled to ICP-MS for
521 measurement of ^{226}Ra , performing a fast sequential extraction (< 30 min) on two to three different
522 sorbents by the use of a flow-injection (FI) introduction system (Benkhedda et al., 2005; Evans et al.,
523 2015) or a lab-on-valve (LOV) and multi-syringe flow injection analysis system (LOV-MSFIA) (W. Wang
524 et al., 2021). In the latter case, we are not convinced that the term LOV used by authors is
525 appropriate since no monolithic structure comprising channels (including incorporation of sorbent
526 phase in microconduits) is shown on the setup, and reagents are used above the milliliter levels
527 contrary to definitions on that technology available in literature since its invention by J. Ruzicka
528 (Luque de Castro, 2014; Ruzicka, 2000; Yu et al., 2011). It is rather also a FI system since sorbents
529 seem to be in cartridges linked to several valves and syringes. Currently, the great majority of Ra and
530 Cs extraction procedures are still performed off-line (Table 3), with flow rates generally ranging
531 between 1 and 4 mL min⁻¹ with cartridges (Bi et al., 2016; Bonin et al., 2020; Dalencourt et al., 2020;
532 Lagacé et al., 2017; Larivière et al., 2005; E. M. van Es et al., 2017; Yang et al., 2020) and up to 50 mL
533 min⁻¹ on Radium RAD specific disks (Joannon and Pin, 2001; Schettler et al., 2015). Ra extraction at a
534 lower flow rate (0.1 mL min⁻¹) was also applied off-line on 50 mg of AnaLig Ra-01 resin packed into a
535 2 x 40 mm column and the use of a peristaltic pump in order to minimize back pressure and increase
536 the interaction time with the sorbent (Verlinde et al., 2019). Since flow rates up to about 1 mL min⁻¹
537 can be compatible with ICP-MS inlet and since the tendency is to move toward procedures
538 simplification, the on-line SPE approach should spread in next years. Note however that the main
539 constrain during on-line SPE is to introduce only compatible effluents to the plasma. This implies
540 being able to elute target elements with sufficiently low HNO₃ molarities from the last support, or
541 alternatively choose to dilute the elution solution and consequently decrease the enrichment factor.
542 As seen in extended form of Table 3, few elution media from the off-line procedures would be
543 compatible without modification for direct analysis, which explain why an evaporation step stands as

544 final step. Procedures need also to be better thought in that way. And contrary to traditional
545 introduction system, the use of an on-line SPE system generates transient signals the duration of
546 which depends on the loop size, meaning that when carrying a multielement analysis, more
547 compromises have to be taken during selection of measurements parameters.

548 As a final remark, the reuse of resins is not common in articles, mainly for two reasons (Russell et al.,
549 2014b; W. Wang et al., 2021). For many application fields such as precise isotopic ratio measurement
550 for dating purpose, any memory effect of sorbents is not tolerated and sorbent washing to remove
551 residual traces of elements may be very time-consuming and may also consume lots of reagents. In a
552 study, a kind of reuse was made reprocessing the separation of Ra from Ba two times on the same Sr-
553 spec resin to improve the decontamination factor. But no contamination issues, neither extensive
554 cleaning are involved in that case since it concerns the same sample. The only true reuse example
555 refers to a calixarene impregnated resin (Russell et al., 2014b). Due to the high cost of the MacroLig
556 209R ligand impregnated, Russell *et al.* investigated the possibility to regenerate (with 20 mL of 0.5
557 mM HNO₃) and reuse their custom made cartridge, demonstrating that about 2% of Cs remained on
558 the cartridge after extraction of Cs from leached sediments. This could be solved by further washing
559 but obviously, a compromise must be found between cost of regeneration and cost of using a new
560 sorbent.

561

562 **2.2. Other purification techniques**

563 2.2.1. Dispersive solid phase extraction alone or associated with SPE

564 Unlike conventional SPE, in dispersive solid phase extraction (dSPE), also named batch extraction,
565 sorbent particles are not packed in a cartridge but dispersed in the sample. This implies to separate
566 particles from the sample solution before changing the solution for next extraction steps (washing
567 and desorption). For this purpose, three approaches may be implemented: filtration through a
568 syringe filter (Cao et al., 2016; Russell et al., 2014a; Varga, 2008; Yang et al., 2016; Zheng et al., 2016,
569 2014b, 2014a), centrifugation, or use of a magnetic field when sorbent particles have magnetic
570 properties. In any case, it requires a lot of manipulations and increases the risk of loss of the target
571 analyte as encountered by Zhu *et al.* (AMP powdered adsorbed on the flask walls and thus impacting
572 the Cs recovery yield) (Zhu et al., 2021b). The main parameter influencing the dSPE recovery yield,
573 and that should therefore be optimized, is the contact time between sorbent and sample to reach an
574 equilibrium state. Generally, adsorption times of 1 (Cao et al., 2016; Russell et al., 2014a; Varga,
575 2008; Yang et al., 2016; Zheng et al., 2016, 2014b, 2014a; Zhu et al., 2021b; Zok et al., 2021) or 2 h
576 (Asai et al., 2020) were applied by authors, meaning that sorption kinetics is quite fast. This was

577 proved by Russell *et al.* who specified that under 30 min, Cs ions were still detected in solution while
578 Cs uptake was maximum after 60 min and remained unchanged after 24 h (Russell *et al.*, 2014a).
579 dSPE was mainly applied for Cs extraction and only inorganic resins were employed, namely AMP
580 (Cao *et al.*, 2016; Yang *et al.*, 2016; Zheng *et al.*, 2016, 2014b, 2014a; Zhu *et al.*, 2021b; Zok *et al.*,
581 2021), AMP loaded on silica gel (Russell *et al.*, 2014a), or KNiFC embedded in a PAN matrix (Cs resin)
582 (Asai *et al.*, 2020) in case of Cs, and MnO₂ resin (Varga, 2008) for Ra. Adsorption is generally
583 performed under stirring to favor ion diffusion towards sorbent. Mass transfer is also facilitated with
584 small sorbent's particles (nanoparticles being the best) that have a high surface-to-volume ratio
585 (Poole, 2019) and depends on temperature. Asai *et al.* used Cs resin with particle size distribution of
586 100-600 µm and realized extraction at room temperature but in other articles, temperature is not
587 given, meaning the effects of temperature was not explored in any paper though it could result in a
588 further decrease of the procedure time (Asai *et al.*, 2020).

589 It can be seen from Table 4 (an extended form of this table is available in supplementary
590 information) that except in one paper, dSPE was combined to conventional SPE for further sample
591 purification, resulting in the use of a total number of 1 to 4 different sorbents (Asai *et al.*, 2020; Cao
592 *et al.*, 2016; Russell *et al.*, 2014a; Varga, 2008; Yang *et al.*, 2016; Zheng *et al.*, 2016, 2014b, 2014a;
593 Zok *et al.*, 2021). As mentioned previously, the use of AMP in dSPE prior to other purification steps
594 often demand to dissolve the AMP sorbent to recover Cs, which also leads to introduction of
595 interfering elements such as Mo, in the sample. As an alternative, Zhu *et al.* did not dissolve the AMP
596 sorbent with a conventional strong basis solution, but with Sr(OH)₂, which allowed to recover free Cs⁺
597 in solution while MoO₄²⁻ and PO₄³⁻ were precipitated in the forms SrMoO₄ and Sr₃(PO₄)₂ (Zhu *et al.*,
598 2021b).

599 Zheng *et al.* developed a method enabling to measure ¹³⁵Cs and ¹³⁵Cs/¹³⁷Cs isotope ratio in highly
600 radioactive samples (¹³⁷Cs activity more than 1,000 Bq kg⁻¹) requiring the use of 3 steps (one in dSPE
601 followed by two in SPE) and 3 sorbents (35 mg of AMP + AGMP-1M and AG50W-X8 in the form of 2
602 mL cartridges) for 2 to 10 g of sample (Zheng *et al.*, 2014a). However, they demonstrated 2 years
603 later that the same method was not suitable when treating low radioactive samples (20 < ¹³⁷Cs
604 activity < 1,000 Bq kg⁻¹) (Zheng *et al.*, 2016). To compensate the low activities, they were indeed
605 forced to increase the sample amount up to 40 g sometimes, inducing the presence of main matrix
606 elements (Al, Ca, K, Mg, and Na) in the final fraction at concentrations up to 70 mg L⁻¹ which would
607 cause severe matrix effects in ICP-MS. The purification was improved by replacing the 2 mL AG50W-
608 X8 cartridge by a bigger one (10.5 mL) and by adding also an extra Sr-spec resin (concentrations of
609 matrix elements in the analyzed fraction were reduced from 0.02 to 2.3 mg L⁻¹ this way), making this
610 extensive but powerful purification method in combination with an APEX-Q-ACM and ICP-MS/MS
611 detection system, one of the most sensitive of Table 4 (MDL of 2 pg L⁻¹), and even of Table 3 and 5,

612 for the determination of ^{135}Cs , ^{137}Cs , and $^{135}\text{Cs}/^{137}\text{Cs}$. The method was well validated by measuring Cs
613 isotopes and 135/137 isotopic ratio in 7 CRM and comparing values obtained by TIMS measurements
614 of the same samples available in literature. The lowest MDL ($1.5 \times 10^{-4} \text{ pg L}^{-1}$) was however recently
615 achieved by a procedure also involving 3 steps (one in dSPE followed by two in SPE) with 3 sorbents
616 (10 g of AMP + 2 mL AMP-PAN cartridge + 10 mL AG50W-X8 cartridge) and enabling to assess both
617 ^{135}Cs and $^{135}\text{Cs}/^{137}\text{Cs}$ in large volumes of seawater (40-50 mL) by ICP-MS/MS (Zhu et al., 2021b).

618 In order to limit radiation dose arising from treatment of liquid wastes containing ^{137}Cs , Asai *et al.*
619 (Asai et al., 2020) only performed a dSPE procedure with a Cs resin (10-30 mg) and including two
620 steps (Cs accumulation and washing), on a very low sample volume (0.03-0.3 mL) before subsequent
621 Cs analysis by Laser Ablation ICP-MS (LA-ICP-MS) directly on the resin. In all other dSPE procedures,
622 no washing step was realized prior to desorption (often on the top of a SPE cartridge by passing an
623 eluent solution from the syringe filter used to collect sorbent particles), probably to minimize ion loss
624 and extraction procedure duration.

625 Due to a lack of data related to extraction and re-dissolution volumes, only two high theoretical EF
626 values of 300 and 25,000, were estimated, respectively for procedures involving Ra and Cs extraction
627 from seawater, where activities are much lower than in other matrices (Varga, 2008; Zhu et al.,
628 2021b). Recoveries of generally more than 70% were achieved using either dSPE alone or combined
629 to SPE. However, except when highly specific sorbents towards Ra and Cs will exist and will enable to
630 reach high enough DF by only performing an adsorption and a desorption step, dSPE could not be
631 used as a stand-alone technique and in any case, will remain less convenient than cartridge-based
632 SPE with the same sorbent. It should be noted that the direct analysis by LA-ICP-MS on the resin after
633 dSPE can be as well an interesting alternative when difficulties for eluting the target analyte from the
634 sorbent are encountered. In such a case, enrichment is indeed no longer possible if large volumes of
635 eluents are necessary, and matrix effects may occur during ICP-MS analysis when exotic and
636 concentrated chelating agents are used.

637

638 2.2.2. Precipitation/co-precipitation associated with SPE

639 Precipitation consists in the conversion of the analyte in solution into an insoluble form by addition
640 of a carrier that drives the formation of the so-called precipitate (Table 4). Since Ra abundance in
641 environment is too low to overcome the solubility limit of any Ra solid compounds, co-precipitation
642 of Ra is induced by the presence of other elements, such as Ba, Ca or Pb (International Atomic Energy
643 Agency, 2010). Addition of a sulfate or a carbonate carrier therefore entails formation of respectively
644 BaSO_4 , PbSO_4 or CaCO_3 mineral phases, which incorporate Ra (and other elements) during
645 precipitation process. Co-precipitation with manganese dioxide constitutes another alternative and

646 was mostly used by authors (Bourquin et al., 2011; Cozzella et al., 2011; Sharabi et al., 2010; Zoriy et
647 al., 2005). This technique consists in mixing the sample with potassium permanganate and
648 manganese dichloride. The formation of the MnO₂ precipitate is then driven by adjustment of the pH
649 to 8-9 (Sharabi et al., 2010; Vieira et al., 2021). Above 9 precipitation of Mg may occur (Vieira et al.,
650 2021).

651 Since MnO₂ can enclosed a variety of elements other than Ra (e.g. Th, U, Po, Ac, and Pb), procedures
652 include further purification by SPE using 1 (Cozzella et al., 2011; Zoriy et al., 2005) and up to 3
653 (Bourquin et al., 2011) or 4 (Sharabi et al., 2010) resins. According to Cozzella *et al.*, supernatant
654 contained most of Ca and part of Sr and subsequent SPE using AG50W-X8 resin was thus essentially
655 made to separate Mn, and Ba from Ra (Cozzella et al., 2011). Dissolution of the MnO₂ precipitate
656 prior to SPE was performed using HCl from 6 M (Bourquin et al., 2011; Sharabi et al., 2010; Vieira et
657 al., 2021) to 9 M (Cozzella et al., 2011). A representative and low experimental MDL of 0.17 pg L⁻¹ was
658 obtained by applying this procedure on six urine samples from unexposed workers of a research site
659 (Cozzella et al., 2011). The proposed method was also able to reach mean recoveries of up to 76%
660 with only 5% RSD (n=6), requiring a global time of 2 days for sample preparation and analysis of a
661 batch of 4 samples. The limiting step is co-precipitation since it requires one night to fully form the
662 precipitate and let it decant.

663 For the purification of digested soil samples, some groups opted for lead-sulphate co-precipitation
664 followed by additional extraction on AG50W-X12 resin (Kim et al., 1999; Tsai et al., 2010). The
665 Pb(Ra)SO₄ co-precipitate obtained was then dissolved in a mixture of 0.1 M EDTA and 5 M
666 ammonium acetate adjusted to pH 4.5-5 before loading on the AG50W-X12 cation exchange resin to
667 eliminate other cations also entrapped in the precipitate and including Pb whose presence may lead
668 to the formation of hydride (²⁰⁸Pb¹⁶O¹H₂⁺) and oxide (²⁰⁸Pb¹⁸O⁺) at *m/z* 226 in the ICP plasma. The
669 carbonate co-precipitation method was employed twice, by addition of a NaCO₃ carrier resulting in
670 the formation of Ca(Ra)CO₃ (Foster et al., 2004; Hsieh and Henderson, 2011). This method is however
671 not recommended for very large sample volumes since carbonates are known to be more soluble
672 than sulphate-compounds (International Atomic Energy Agency, 2010).

673 In case of Cs, Ba removal by precipitation of Ba(OH)₂ was employed only once without performing
674 other purification technique (Meeks et al., 1998). No conclusion on the efficiency of this one-stage
675 approach can however be drawn since no recoveries are mentioned.

676 Precipitation or co-precipitation are in particular well suited to preconcentrate analytes from large
677 sample volumes by the use of common reagents. This cannot always be achieved by conventional
678 SPE since sorbent capacity and/or breakthrough volume can be outreached when loading samples of
679 several hundreds of mL. Ra preconcentration from diverse sample matrices (mineral and ground
680 water (Zoriy et al., 2005), natural and saline water (Sharabi et al., 2010), seawater (Bourquin et al.,

681 2011; Foster et al., 2004; Hsieh and Henderson, 2011), urine (Cozzella et al., 2011) but also sediments
682 and soils (Kim et al., 1999; Tsai et al., 2010)) of volumes of sample or extract ranging from 20 mL to
683 60 L was accomplished using this technique combined to SPE, leading sometimes to extremely high
684 theoretical enrichment factors (between 4 and 20,000). However, as dSPE, precipitation and co-
685 precipitation techniques require lots of manipulations and thus cannot be automatized; and
686 moreover, cannot be used as stand-alone techniques as they do not sufficiently purify the sample.

687

688 **2.3. Research on emerging sorbents to improve extraction techniques**

689 As previously mentioned, extraction of ^{226}Ra and ^{137}Cs at ultra-trace level in complex matrices is at
690 the moment limited by the lack of capacity and specificity of available commercial sorbents. This
691 results in the implementation of complex and time-consuming multi-steps and multi-SPE procedures.
692 New developments are therefore focusing on the design of innovative sorbents, on the one hand
693 playing on the nature of the material to increase the reactive surface and thus the capacity (e.g.
694 nanostructured materials or composite sorbents), and on the other hand, playing on the binding site
695 to make the support more specific (e.g. ion-imprinted polymers (IIPs)). Note that sorbents presented
696 below may not have been specifically designed for purification prior to analysis by ICP-MS but it is
697 interesting to spend a little time examining these new trends which could help improving SPE
698 extraction techniques and open-up new application perspectives.

699 Nanometer-sized materials are particularly interesting as they exhibit large surface area. Depending
700 on the preparation method, they can be prepared in different forms including nanoparticles,
701 nanofibers, nanoribbons or nanowires. Recently, Alby *et al.* (Alby et al., 2018) published a
702 comprehensive review in which they compare different inorganic nanostructured materials, namely
703 titanate, vanadate, tungsten, manganese oxides, hexacyanoferrates, metal sulfides, and ammonium
704 molybdophosphates in order to fix Cs. Though the coefficient distribution values did not seem to vary
705 significantly from one family to another, due to their structures, the sorption capacities were really
706 different, vanadate oxides and metal sulfides-based materials presenting the best ones (i.e. 4.00
707 mmol g^{-1} for a potassium metal sulfide framework $\text{K}_{2x}\text{Mg}_x\text{Sn}_{3-x}\text{S}_6$ ($x = 0.5-1$) also known as KMS-2
708 (Mertz et al., 2013) and 3.29 mmol g^{-1} for vanadate nanofibers (Sarina et al., 2014)). Nevertheless,
709 some of them can only be used over a limited pH range otherwise their sorption capacities are
710 altered (e.g. pH 1 for vanadosilicates, pH 6 for vanadate nanotubes and pH 7-9 for titanate
711 nanotubes and silicotitanates). This may constitute a limit for some applications. In a more general
712 review about radionuclides trapping, a state of the art of progress in synthesis and application for
713 other types of nanomaterials was done: Metal-Organic Frameworks (MOFs, formed by a network of
714 coordination bonds between metal ions and organic ligands) and covalent organic frameworks,

715 graphene oxides, carbon nanomaterials, nanoscale zerovalent iron, MXene and polymer brushes
716 (Wang et al., 2019). Authors also provide insight of advantages and disadvantages of each material as
717 well as limitations that make them currently available for laboratory applications rather than large
718 scale studies (e.g. pollution management).

719 Development of composite or hybrid sorbents was also investigated for Ra and Cs extraction, the
720 objective being to create a more performant solid support by taking advantage of the specific
721 properties of two different materials or more (synergic effect). Two Ra composite sorbents made of a
722 PAN polymer coated with MnO₂ (Dulanská et al., 2015) or of a silica gel and MnO₂ (Dulanská et al.,
723 2018) were studied for the determination of ²²⁶Ra in natural waters. Contrary to procedures
724 developed with previous commercial or self-prepared MnO₂ resins which often employ a mixture of
725 HCl/H₂O₂ to elute Ra that entails destruction of the resin and leaching of high amount of Mn in the
726 extract, they were able to elute Ra with HCl or HNO₃ solutions. In the study on MnO₂-PAN sorbent,
727 they only evaluated the effect of calcium concentration (from 70 to 2,070 mg L⁻¹) on Ba recovery
728 (analogue of Ra used during the optimization step) whereas experiments were done on a larger panel
729 of potential competitors (0.07-5.07 g L⁻¹ for Ca and Mg and 1-300 g L⁻¹ for K and Na) for MnO₂-SiO₂
730 sorbent. In both cases, salt content did not entail a significant decrease, Ba recovery being higher
731 than 95% for the whole concentration range tested, and above 77% in case of Ra extraction from
732 spiked mineral waters. No additional information on the sorption capacity was available.

733 In a review, Wang and Zhuang also mentioned the growing interest for cesium composite sorbents
734 made of a carbon substrate, including activated carbon, carbon nanotubes, graphene, and graphene
735 oxides (Wang and Zhuang, 2019b). As an example, a new Cs sorbent was prepared, which combined
736 the Cs-selective binding properties of potassium copper hexacyanoferrate with the intrinsic
737 advantages of a porous carbon activated substrate material (e.g. large surface area, high thermal and
738 mechanical stability, and strong resistance even in extreme chemical environment) (Wang et al.,
739 2009). In presence of interfering elements, the cesium capacity measured was 0.38 mmol g⁻¹ while
740 the support selectivity followed the order Cs >> Na > Co > Sr > Fe > Ni. No application on real samples
741 was however conducted. Additional chemical modification of the particles to provide them magnetic
742 properties was sometimes made (Kim et al., 2018; Xia et al., 2020). Magnetic particles can indeed be
743 of a great interest for dSPE applications since they can easily be collected using a magnetic field after
744 their immersion in the sample.

745 Due to their large specific surface area, adjustable pore size, and ease-of-functionalization, MOFs
746 have also been investigated for Cs removal (Asgari et al., 2019; Naeimi and Faghihian, 2017). A MOF
747 based on Nd-benzene tricarboxylic acid was designed to have high sorption capacities for Cs⁺ and Sr²⁺
748 and achieved maximum capacities around 0,7 mmol g⁻¹ for both ions (Asgari et al., 2019). Its
749 performances were not tested in presence of interfering elements nor on a real medium. Group of

750 Naeimi *et al.* even synthesized a composite porous magnetic sorbent, namely a magnetized Cu-
751 benzene tricarboxylic acid MOF (known as HKUST-1) impregnated with potassium nickel
752 hexacyanoferrate (Naeimi and Faghihian, 2017). It showed moderate sorption kinetics (adsorption
753 equilibrium reached in 45 min), high distribution coefficient for Cs^+ ($1,500 \text{ mL g}^{-1}$) and high adsorption
754 capacity (1.15 mmol g^{-1}) over a broad range of pH. They however noticed Cs^+ uptake was greatly
755 affected in the presence of high concentrations of K^+ and Na^+ ($> 50 \text{ mg L}^{-1}$ of interfering ions), thus
756 demonstrating a limited specificity in presence of these competitors that can be present with
757 concentrations in the range 10^4 mg kg^{-1} in the earth's crust (Darnley *et al.*, 1995). Here also, the
758 proposed adsorbent and adsorption conditions developed were not confronted to a real sample.
759 Note that most of these new materials are at the moment evaluated by dSPE, measuring the
760 distribution coefficients of various elements, but no elution step is performed. We thus have no idea
761 on how difficult it is to achieve elution of Ra or Cs, a necessary step to perform ICP-MS analysis by
762 classical solution nebulization rather than by laser ablation of the sorbent, nor if implementing flow
763 conditions affect the results. Consequently, even if some of them seem to have interesting features,
764 they are still far from an application on real samples, and characterizations need to be pushed
765 further.

766 To improve the specificity, some authors examined potential of ion-imprinted polymers, which
767 possess cavities designed to specifically recognize a target ion. IIP recognition capability is a result of
768 the synthesis process that uses the targeted ion or a chemical analogue as template. Cavities are
769 obtained by forming a complex between several molecules of one or more monomers of different
770 natures and the template ion, in a solvent. Then, in the presence of a cross-linking agent and a
771 polymerization initiator, polymerization occurs around the template ion, thus creating specific
772 cavities, complementary to the ion in terms of size, shape, and complexing groups. The template ion
773 is finally removed by washing to free the polymer matrix cavities. IIPs can be obtained in bulk or in
774 the form of (nano)particles according to the polymerization method employed. Though the use of
775 this technology has been previously reported in the field of radiochemistry such as for selective
776 uranium removal (Ahmadi *et al.*, 2010; Kusumkar *et al.*, 2021; Metilda *et al.*, 2007; Preetha *et al.*,
777 2006), nobody has yet investigated the possibility to design Ra-IIP and only a few groups synthesized
778 Cs-IIPs to use them either as sensor (Iwasaki and Yoshikawa, 2016; Z. Wang *et al.*, 2021) or as SPE
779 sorbents (Meng *et al.*, 2015; Shamsipur and Rajabi, 2013; Yang *et al.*, 2017; Zhang *et al.*, 2010), but
780 not for radiocesium determination purpose.

781 Shamsipur *et al.* (Shamsipur and Rajabi, 2013) synthesized for instance Cs-IIP nanoparticles (50-90
782 nm) by precipitation polymerization using dibenzo-24-crown-8 ether and methacrylic acid as
783 monomers, ethyleneglycol dimethacrylate as crosslinker, and a mixture of acetonitrile and
784 dimethylsulfoxide as solvent. In order to evaluate the specificity of the material, distribution

785 coefficients of several metal cations were measured in dSPE, therefore by batch experiments with 50
786 mg of IIP. K_d value was 1,534 mL g⁻¹ for Cs⁺ whereas it did not exceed 10 mL g⁻¹ for all other
787 interfering ions tested (Li⁺, Na⁺, K⁺, Rb⁺, NH⁴⁺, Ag⁺, Mg²⁺, Ca²⁺, and Sr²⁺), highlighting the presence of
788 specific cavities. Presence of specific recognition sites was also confirmed by the fact that the
789 corresponding non-imprinted polymer exhibited a K_d value for Cs⁺ around two times less than the
790 IIP. Batch measurements were conducted to estimate the IIP capacity (0.4 mmol g⁻¹). It was then
791 applied to the determination of Cs in spiked groundwater and tap water and the dSPE procedure
792 developed (200 mL of sample, adsorption at pH 9 for 20 min, and desorption with 2 mL HNO₃ 0.1 M
793 for 7 min) allowed to reach recoveries above 95% (n=3). Therefore, at first sight this approach seems
794 promising and it would be interesting in future years to inquire if it can be a viable alternative to
795 current sorbents.

796

797 **3. Use of separation techniques prior to ICP-MS detection**

798 Potential of separation techniques such as LC (Alonso et al., 1995; Granet et al., 2008; Isnard et al.,
799 2009; Liezers et al., 2009; Moreno et al., 1999, 1996; Plausinaitis et al., 2013; Taylor et al., 2008) and
800 CE (Pitois et al., 2008) were evaluated by a few groups to separate Cs from interfering elements but
801 not in case of Ra (Table 5). In particular, they were used to perform complete separation of Cs from
802 Ba whose natural isotopes 135 and 137 can interfere with accurate determination of ¹³⁵Cs, ¹³⁷Cs, as
803 well as ¹³⁵Cs/¹³⁷Cs atomic ratios. All of these studies made an application on real samples (fuels
804 (Alonso et al., 1995; Granet et al., 2008; Isnard et al., 2009; Moreno et al., 1999, 1996; Pitois et al.,
805 2008; Plausinaitis et al., 2013), groundwater (Lieziers et al., 2009), and soil and sediment extracts
806 (Taylor et al., 2008)), but two approaches were implemented: few groups introduced a sample
807 pretreatment step prior to the separation technique in order to pre-clean the sample (Granet et al.,
808 2008; Isnard et al., 2009; Taylor et al., 2008), otherwise the sample was directly injected into the
809 separation system (Alonso et al., 1995; Liezers et al., 2009; Moreno et al., 1999, 1996; Pitois et al.,
810 2008; Plausinaitis et al., 2013). In that case, the injection volumes mentioned were high (200 µL
811 (Alonso et al., 1995; Moreno et al., 1999) or 1 mL (Plausinaitis et al., 2013)) compared to
812 conventional values. In the first approach, the recovery of the sample pretreatment step was not
813 specified. LC was all the time performed using ion-exchange columns. A mobile phase gradient was
814 applied once (Granet et al., 2008), otherwise authors realized isocratic separations of Cs isotopes
815 from Ba using either HNO₃ (Alonso et al., 1995; Liezers et al., 2009; Moreno et al., 1999, 1996; Taylor
816 et al., 2008) or a complexing agent (0.1 M oxalic acid at pH 4.8 (Plausinaitis et al., 2013) or 2-hydroxy-
817 2-methylbutyric acid at pH 3.8 (Isnard et al., 2009)) as mobile phase eluent. In many cases, eluent
818 was compatible with ICP-MS introduction, thus the LC separation and the ICP-MS detection were

819 made on-line (Alonso et al., 1995; Liezers et al., 2009; Moreno et al., 1999, 1996; Plausinaitis et al.,
820 2013; Taylor et al., 2008), by connecting the end of the column to the ICP detection system,
821 therefore avoiding risks of contaminations and losses induced by collection of fractions. Generally,
822 the separation time was less than 30 min (see extended form of Table 5 in supplementary
823 information).

824 Plausinaitis *et al.* first optimized the separation working on stable isotopes (^{133}Cs , ^{87}Sr , ^{88}Sr , ^{85}Rb , ^{88}Rb ,
825 ^{134}Ba , ^{135}Ba , ^{137}Ba , and ^{138}Ba) and studied the effect of several parameters, such as the stationary
826 phase nature and the eluent composition, on the quality of the separation (Plausinaitis et al., 2013).
827 Three acids, namely citric, tartaric, and oxalic acids, were tested and chromatograms obtained after
828 separation on an IonPac CS5A stationary phase showed retention times of Rb and Cs were
829 independent from the eluent nature because alkali metals do not form stable complexes with
830 carboxylic acids contrary to Sr and Ba. They also managed to improve their method detection limit by
831 increasing injected volume up to 1 mL without observing peak deformation.

832 In order to purify either UOx or MOx spent nuclear fuels, two groups carried out a first sample
833 preparation step involving purification of the sample from U and Pu by SPE on an AG1X4 resin, then
834 followed by separation of Cs from other fission products by an off-line LC – ICP-MS analysis (Granet
835 et al., 2008; Isnard et al., 2009). Granet *et al.* also compared the interest of performing both SPE
836 extraction and LC separation steps rather than only SPE prior to detection by MC-ICP-MS with N_2O in
837 the CRC to improve Ba removal from the sample matrix (Granet et al., 2008). It can be seen in Figure
838 2 that uncertainties are higher for the fraction analyzed after a single purification by SPE (FP Cs
839 fraction on the graph) than those of fraction purified by the sequential SPE-LC method (HPLC pure Cs
840 fraction on the graph). According to the authors, larger uncertainty in FP Cs fraction arises from the
841 presence of more than 30 ionizable elements which may cause matrix effects. Average $^{137}\text{Cs}/^{135}\text{Cs}$
842 isotope ratios obtained with both methods are in agreement within uncertainties: 3.263 ± 0.017
843 ($n=20$, coverage factor $k=2$ for FP Cs fraction) and 3.255 ± 0.010 ($n=11$, $k=2$ for HPLC pure Cs
844 fraction). These results were also in agreement with TIMS measurements on the same sample (3.245
845 ± 0.007 ($n=4$)), thus demonstrating the reliable performances of the proposed methods.

846 In only one study, CE was hyphenated with two types of ICP-MS instruments (Single Quadrupole ICP-
847 MS (ICP-Q-MS) and Sector Field Mass Spectrometer (SF-ICP-MS)) to determine fission products in
848 nuclear fuel samples (Pitois et al., 2008). Optimization of the argon flow rate ($0.7\text{-}1.2\text{ L min}^{-1}$) at the
849 interface between CE and ICP-MS in order to obtain the best nebulization efficiency was made
850 monitoring the signal of ^{115}In . Additionally, influence of the phosphate buffer molarity (5-30 mM) and
851 pH (2.5-9.4) on ion migration times were studied. The migration time of barium was longer than that
852 of cesium, which was not expected as barium is doubly charged and smaller than cesium. Ba^{2+} may
853 actually be complexed by the phosphate ion and therefore migrates in the form of $\text{Ba}(\text{H}_2\text{PO}_4)^+$

854 whereas Cs⁺ remains uncomplexed. MDL values of 6×10^6 and 4×10^3 pg L⁻¹ were obtained by CE-ICP-
855 Q-MS and CE-SF-ICP-MS, respectively, and ¹³⁷Cs measurement in a MOx fuel by CE-SF-ICP-MS ($3.56 \pm$
856 $0.19 \mu\text{g mL}^{-1}$) was in good agreement with measurement by gamma-spectrometry ($3.56 \pm 0.07 \mu\text{g mL}^{-1}$).
857 CE procedures have thus the advantage of allowing to separate Cs from isobaric Ba, of
858 necessitating very low samples volumes (dozens of μL versus hundreds of μL for chromatographic
859 separations), of limiting radiation dose to the analyst and of being as well very fast (6 min for the
860 above-mentioned method). However, regarding MDL specified in Table 5, methods based only on
861 separation techniques are generally not very sensitive. Separation techniques should therefore be
862 considered in complement to pretreatment methods for extensive Ba elimination prior to ICP-MS
863 introduction, or else, to study speciation of radium and cesium. In view of attractive binding ability
864 that possess some known cyclic compounds for alkali and alkaline-earth metals, rather than confining
865 to use poorly specific SCX stationary phases, the use of crown ethers-based columns or mobile phase
866 eluents containing a crown ether complexing agent should be a path to improve LC selectivity and
867 explore in combination to ICP-MS detection in the future.

868

869 **4. ICP-MS instrumentation to help overcoming some analytical** 870 **challenges**

871 **4.1. Resolution of interference issues**

872 The decontamination factors offered by the previously described sample handling or separation
873 procedures do not always lead to the sufficient elimination of the interferences, influencing
874 therefore the accurate quantification of the target radionuclide and the detection limit. A
875 complementary approach is based on the advances in ICP-MS instrumentation such as CRC or high
876 mass-resolution instruments to resolve spectral interferences. Resolution of current ICP-MS
877 instruments equipped with high mass resolution capabilities does not exceed 10,000 that is not
878 sufficient to distinguish several of the isobaric and/or polyatomic interferences from ¹³⁷Cs and ²²⁶Ra
879 signals (Table 1). Depending on their concentration in the analyzed fraction, matrix elements may not
880 be responsible for forming spectral interferences in the plasma. Main interfering elements and the
881 concentration threshold from which they induce an overestimate of the target signal are generally
882 identified by preparing monoelemental solutions and mixtures of two elements at various
883 concentrations and weight ratios. Therefore, if they are still present in the final purified fraction
884 above the identified concentration thresholds, mathematical corrections must be implemented.

885 As it can be seen from Table 3 and 4, since their appearance on the market in 2012, Triple
886 Quadrupole ICP-MS (ICP-QQQ-MS) have largely gain in popularity, last generation instruments

887 allowing improved ion transmission and focalization (Agilent 8900 *versus* 8800) (Balcaen et al., 2012;
888 Fernández et al., 2012). Recently, Waersted *et al.* showed that it was possible to carry out direct
889 quantitative analysis of ^{226}Ra with such mass spectrometer analyzer functioning in tandem mass
890 spectrometry and taking advantage of N_2O as reaction gas in the CRC (Wærsted et al., 2018). They
891 effectively noticed that N_2O reacted preferentially with ^{226}Ra (only 0.6% of ^{226}Ra do not react)
892 forming the molecular compound $^{226}\text{Ra}^{16}\text{O}^+$ (atom transfer inducing analyte shift). Thus, by filtering
893 the mass 226 in the first quadrupole and the mass 242 in the second one, they achieved to exclude
894 all possible polyatomic interferences at m/z 226. From the analysis of blanks corresponding to each
895 type of sample, in the extent that they are prepared and measured under the same conditions as real
896 samples, they were able to reach detection limits of 0.42 pg L^{-1} for water samples, 17 pg L^{-1} for water
897 samples containing high amount of salts (conductivity $> 100 \text{ mS cm}^{-1}$), and 750 pg kg^{-1} for rock and
898 soil sample extracts. These values vary by a factor of 40 to 1,800 depending on the nature of the
899 blank analyzed, showing that sensitivity of direct analysis is affected by matrix effects and thus is not
900 yet a reliable option for the majority of applications. The same direct approach was implemented in
901 another study with the objective of quickly identifying ^{226}Ra contamination in urine samples (Xiao et
902 al., 2020). In that case, the IDL met the application requirements as it was circa 6 times lower than
903 the action level set by the National Council on Radiation Protection and Measurements. Other groups
904 who used a CRC to mitigate polyatomic interferences employed He (Ben Yaala et al., 2019; E.M. van
905 Es et al., 2017; Zhang et al., 2015) or a mixture of He and H_2 (Epov et al., 2003; Larivière et al., 2003).
906 When reading Table 3 and Table 4, it is clear that the use of CRC for the determination of ^{226}Ra is not
907 widespread, probably because the main resulting challenges which include finding a gas that react
908 only with Ra (or conversely only with its interferences) and does not negatively affect signal
909 sensitivity, are not solved by any of the typical gases. The capacity of nitrous oxide to react with Ba
910 and not with Cs was also exploited by several authors in order to suppress isobaric Ba interferences
911 (e.g. atom transfer inducing isobar shift such as formation of $^{137}\text{Ba}^{16}\text{O}^+$ or $^{137}\text{Ba}^{16}\text{O}^{16}\text{H}^+$ compounds
912 while ^{137}Cs remains unreacted) (Cao et al., 2016; Granet et al., 2008; Ohno and Muramatsu, 2014;
913 Yang et al., 2016; Zheng et al., 2016, 2016; Zhu et al., 2021a, 2021b, 2020). Indeed, contrary to Ba,
914 reaction between Cs and N_2O cannot happen because it is endothermic (heat of reaction: 106.3 kJ
915 mol^{-1}) and thus thermodynamically unfavorable (Yang et al., 2016). No significant drop in Cs isotopes
916 signals was observed in the different papers. As showed in Figure 3, gas flow rate must be adjusted
917 to maximize signal intensities of the recorded Cs isotopes while removing if possible the totality of
918 the present isobars. The use of other reaction gases, such as CH_3Cl (Taylor et al., 2008) or a mixture
919 of He and N_2O (Amr et al., 2016; Zheng et al., 2014b, 2014a; Zok et al., 2021) was also reported for
920 ^{137}Cs determination but nitrous oxide remains the gas presenting the best performances. This
921 approach is highly recommended, especially for measurements of low level of ^{135}Cs and ^{137}Cs ; it

922 allows to push further the DF of the sample preparation procedures, as demonstrated by Zhu and
923 coworkers (DF for Ba improved from 6×10^9 to 10^{11} , leading to Ba CPS contribution at m/z 135 and
924 137 in the final fraction similar to CPS measured in the chemical procedure blank).

925 To some extent, specific sample introduction systems may also help avoiding certain spectral
926 interferences. Introduction devices including a desolvation membrane module can for instance
927 reduce oxide and hydroxide-based interferences since less water molecules enter the plasma. An
928 APEX-Q-ACM system containing an ACM Nafion fluoropolymer desolvation module has been
929 reported in order to avoid forming Pb and Bi interferences during ^{226}Ra analysis (Yang et al., 2020).
930 But as pointed out by Zheng *et al.*, introduction of a wet aerosol into the plasma may also entail a
931 stronger impact of matrix effects (Zheng et al., 2016). This was experienced in a study in which
932 signals of ^{135}Cs and ^{137}Cs dropped from a factor of 4 when increasing the concentration of stable
933 cesium up to 80 mg L^{-1} using the APEX-Q introduction system whereas they remained practically
934 unchanged without APEX-Q (Figure 4) (Zhu et al., 2021b). On the mentioned figure, one can notice
935 that signal suppression is a bit more pronounced for the lower mass isotope (135) above $20 \mu\text{g L}^{-1}$ of
936 ^{133}Cs with APEX-Q system, which could lead to inaccurate determination of 135/137 isotope ratio.
937 Thus the use of such introduction system should be taken with caution, evaluating all possible side
938 effects, even more when ^{133}Cs is chosen as a yield tracer for ^{135}Cs and ^{137}Cs determination.

939 Quick injection of Cs or Ra, and not of Ba and other elements, can alternatively be achieved using
940 ElectroThermal Vaporization (ETV) (Song et al., 2001; St. C. McIntyre et al., 1997; Sturgeon et al.,
941 1993). The required sample volume is no more than 10 to 100 μL . With such a system, the element
942 discrimination is based on differences in volatilization properties. Chemical modifiers might be used
943 to change analyte properties to enhance the signal and the difference in volatilization and also to
944 improve the transport efficiency to the ICP torch. A typical ETV heating program contains three steps:
945 drying of the solvent, pyrolysis of the sample matrix and/or activation of the chemical modifier, and
946 vaporization of the analytes. The three groups who exploited this kind of introduction system did not
947 perform any purification step upstream of detection, although applying their method to real or
948 simulated samples (snow (Sturgeon et al., 1993), water samples with high salt content (Song et al.,
949 2001), and seawater (St. C. McIntyre et al., 1997)). Fast separation (6 min) of Cs from Ba in solutions
950 containing a 1000-fold excess barium was achieved by Song *et al.* after optimizing the nature and
951 concentration of the modifier (Sturgeon et al., 1993). 0.3 mM KSCN proved to be the most efficient
952 modifier among the 12 modifiers evaluated and the optimized pretreatment and volatilization
953 temperatures were respectively 400 and $1,100^\circ\text{C}$. The resulting MDL for both ^{135}Cs and ^{137}Cs was
954 however high (200 pg L^{-1}) as compared to methods including a sample pretreatment step (MDLs $< \text{pg}$
955 L^{-1} in (Liezers et al., 2009; Yang et al., 2016; Zhu et al., 2021a)). In addition, presence of matrix effects
956 was noted in solutions containing 0.1 M of salt (NaCl, NH_4Cl , NaNO_3 , and NH_4NO_3) thus limiting the

957 use of this direct analysis method in environmental samples with high salt content. Instead of KSCN,
958 a seawater reference material (NASS-3) was proposed as a modifier by two other groups (St. C.
959 McIntyre et al., 1997; Sturgeon et al., 1993). In paper dealing with ^{226}Ra determination, the ETV-ICP-
960 MS approach implemented was also less sensitive (MDL of 34 pg L^{-1}) (St. C. McIntyre et al., 1997)
961 than methods based on SPE procedures prior to ICP-MS (experimental MDLs $< \text{pg L}^{-1}$ have been
962 reached (Benkhedda et al., 2005; Bonin et al., 2020; Cozzella et al., 2011; Hsieh and Henderson,
963 2011; Lagacé et al., 2017; Larivière et al., 2003; Varga, 2008)). Nevertheless, papers that used ETV are
964 not recent; since, much progress has been done on ICP-MS and related instrumentation devices, thus
965 it could be interesting to “dust” this technique and see if it can be competitive to other approaches
966 when combined to a sample preparation step. Note that the small sample volume required for an
967 ETV-ICP-MS analysis could also allow to push further the EF of the previously reported methods.
968 To resolve unspectral interferences, authors employed most of the time the isotopic dilution method
969 (Bourquin et al., 2011; Foster et al., 2004; Hsieh and Henderson, 2011; Kayzar and Williams, 2016;
970 Larivière et al., 2007; Moreno et al., 1999, 1996; Pietruszka et al., 2002; Scott et al., 2019; Varga,
971 2008; Vieira et al., 2021; Zhu et al., 2020) or performed external calibration combined to the use of
972 an internal standard during analysis, the choice of the IS being really different from one study to
973 another in case of Ra (e.g. ^{103}Rh (Ben Yaala et al., 2019; Varga, 2008; Verlinde et al., 2019; Yang et al.,
974 2020), ^{115}In (Ben Yaala et al., 2019), ^{195}Pt (Ben Yaala et al., 2019; Bonin et al., 2020), ^{232}Th (E.M. van Es
975 et al., 2017; E. M. van Es et al., 2017), Tl (Dalencourt et al., 2018), ^{169}Tm (Wærsted et al., 2018), (Tb,
976 Ho, Bi) (Lagacé et al., 2017), Ir 193 (Xiao et al., 2020) or ^{209}Bi (Joannon and Pin, 2001)). ^{209}Bi was used by
977 Joannon and Pin (Joannon and Pin, 2001) whereas it can induce polyatomic interferences at mass
978 226 as experienced for instance by Gourgiotis *et coll.* (Verlinde et al., 2019) and Clarisse *et coll.* (Ben
979 Yaala et al., 2019) who recommended not to use it. They however do not mention control of the
980 presence of this possible interference. ^{169}Tm was chosen because it reacted as ^{226}Ra with the reaction
981 gas N_2O in the article in question. Only a few groups performed external calibration with matrix-
982 matched standards (Larivière et al., 2005; Xiao et al., 2020) or used the standard addition method
983 (Benkhedda et al., 2005; Epov et al., 2003; Larivière et al., 2003; Park et al., 1999; W. Wang et al.,
984 2021) since they are both more burdensome to implement than the abovementioned methods.
985 Matrix-matched standards are also never truly representative of the real samples and, as an
986 example, Larivière *et coll.* (Larivière et al., 2005) only mimicked the alkaline-earth composition of a
987 real well water sample.

988

989 **4.2. Factors influencing sensitivity, detection limits, accuracy, and precision**

990 Since the tendency is to be able to determine Cs and Ra radionuclides at ultra-trace levels, authors
991 are constantly looking for ways to improve the analytical sensitivity in order to lower the detection
992 limit of their method. It depends in first place on the choice of the mass spectrometer analyzer and
993 its configuration. As example, values of instrumental detection limits mentioned in literature for the
994 analysis of ^{226}Ra range from 0.045 to 433 pg L^{-1} for ICP-MS with a Single Quadrupole analyzer (ICP-Q-
995 MS or ICP-(CC)-Q-MS) (Johanna Sabine Becker et al., 1999; J. Sabine Becker et al., 1999; Cozzella et
996 al., 2011; Epov et al., 2003; Evans et al., 2015; Joannon and Pin, 2001; Lagacé et al., 2017; Tsai et al.,
997 2010), from 0.053 to 100 pg L^{-1} for Triple Quadrupole ICP-MS operating in MS mode (Bonin et al.,
998 2020; Dalencourt et al., 2018; E. M. van Es et al., 2017; Verlinde et al., 2019; W. Wang et al., 2021),
999 from 0.09 to 33 pg L^{-1} for single collector ICP-MS (SF-ICP-MS or High Resolution ICP-MS (HR-ICP-MS))
1000 (Becker and Dietze, 1999; Copia et al., 2015; Larivière et al., 2005; Park et al., 1999; Vieira et al.,
1001 2021; Yang et al., 2020; Zoriy et al., 2005) and from 0.05 to 1 pg L^{-1} for multicollector ICP-MS (MC-
1002 ICP-MS) (Bourquin et al., 2011; Foster et al., 2004; Sharabi et al., 2010). It may seem surprising that
1003 similar and low IDL as these obtained with HR-ICP-MS and MC-ICP-MS can be obtained with ICP-Q-
1004 MS or ICP-QQQ-MS since those instruments are known to be less sensitive. However, as mentioned
1005 before, IDL interpretation and comparison must be done considering the matrix used for its
1006 assessment. The impact of the analysis mode on ^{226}Ra analysis was evaluated in a study by comparing
1007 instrumental sensitivity and IDL obtained in three different configurations: MS, MS/MS and MS/MS
1008 with CRC filled with He (Dalencourt et al., 2018). Slopes of the calibration curves obtained in MS/MS
1009 and MS/MS with CRC analysis modes were respectively 10 and 20 times lower compared to the MS
1010 configuration, with an increase in calculated IDL by a factor of 16 (8 pg L^{-1}) and 28 (14 pg L^{-1}),
1011 respectively. A lower sensitivity is often effectively observed in MS/MS because some ions are
1012 deflected in their flight path before arriving to the second quadrupole and are thus not counted by
1013 the detector. When using a CRC, collisions between the target analyte and the collision gas may also
1014 be responsible for additional ion losses. Amr *et al.* (Amr et al., 2016) however measured comparable
1015 IDL for ^{137}Cs in MS (60 pg L^{-1}) and MS/MS mode (54 pg L^{-1}). Due to significant loss of sensitivity,
1016 MS/MS was not much employed for ^{226}Ra measurement (Wærsted et al., 2018; Xiao et al., 2020),
1017 however when measuring low level of ^{135}Cs in presence of high concentration of stable ^{133}Cs , using
1018 such analysis mode is almost inevitable in order to reduce peak tailing of mass 133 at mass 135,
1019 therefore minimizing abundance sensitivity (Zhu et al., 2020). Based on this approach, Zhu *et al.*
1020 achieved to improve the abundance sensitivity from 10^{-7} to 10^{-11} (3 orders of magnitude greater than
1021 the theoretical value of 10^{-14}) on ICP-QQQ-MS Agilent 8800 passing from the use of one quadrupole
1022 to two successive quadrupoles (Zhu et al., 2021a). Note however that it is not always sufficient to
1023 correct the tailing contribution of ^{133}Cs depending on the $^{135}\text{Cs}/^{133}\text{Cs}$ ratio in the sample and of the
1024 intrinsic abundance sensitivity of the instrument. Indeed, as highlighted in the review of Bu *et al.*,

1025 $^{135}\text{Cs}/^{133}\text{Cs}$ in environmental samples contaminated by global fallout from nuclear tests can be as low
1026 as 10^{-9} (Bu et al., 2016). Though SF-ICP-MS has the advantage to be more sensitive than ICP-QQQ-MS,
1027 its abundance sensitivity is not enough for such samples (up to 10^{-6} in medium resolution) whereas
1028 abundance sensitivity of ICP-QQQ-MS compete well with these of TIMS (10^{-10} - 10^{-11}) and AMS (10^{-10})
1029 (Bu et al., 2016).

1030 Similarly, magnetic sector field ICP-MS can be operated in three different modes, namely low (300),
1031 medium (4,000) and high resolution (10,000), but increasing the resolution has also for consequence
1032 to decrease the ion signal. Except Yang *et al.*, Varga *et al.* (medium resolution) (Varga, 2008; Yang et
1033 al., 2020), and Vieira *et al.* (“intermediate” resolution $R=2000$ obtained by equipping the instrument
1034 with a “flattop peak medium resolution kit”), all groups that used a magnetic sector field mass
1035 spectrometer conducted analyses of Cs and Ra in low resolution to have the greatest sensitivity.
1036 Additionally, customization of the ICP-MS instrument by changing the sample introduction system
1037 (e.g. APEX desolvating nebulizers which exist in 4 different forms: APEX-Q, APEX-IR, APEX-HF, the
1038 latest one being APEX-omega, as it can be seen in the corresponding column in Tables 3, 4, and 5 for
1039 other examples) or by adding extra tools (e.g. guard electrode (Becker and Dietze, 1999), retardation
1040 energy filters (Scott et al., 2019)) can be implemented to push the instrument to its extreme
1041 detection capability. As an example, the coupling of an ICP-QQQ-MS with an APEX-HF desolvating
1042 nebulizer rather than with a conventional Scott spray chamber induced an improvement of the ^{226}Ra
1043 signal sensitivity by a factor of 10 which allowed to reach an IDL of 0.2 pg L^{-1} (Verlinde et al., 2019). A
1044 similar sensitivity gain was also experienced in case of cesium isotopes determination and can be
1045 explained by an enhanced transportation of analytes combined to the fact that less water molecules
1046 enter the plasma (Zheng et al., 2016). In several articles, Dietze *et coll.* compared the efficiency in
1047 terms of sensitivity, IDL, and precision of various sample introduction systems coupled either to SF-
1048 ICP-MS (Meinhard nebulizer (1 mL min^{-1}) with Scott spray chamber, microconcentric nebulizer (0.085
1049 mL min^{-1}) with minicyclonic spray chamber, and ultrasonic nebulizer with an aerosol desolvation unit
1050 (2 mL min^{-1})) (Becker and Dietze, 1999) or ICP-Q-MS (cross-flow nebulizer (1 mL min^{-1}) with Scott
1051 spray chamber, microconcentric nebulizer ($0.085 \text{ mL min}^{-1}$ or 0.2 mL min^{-1}) with minicyclonic or Scott
1052 spray chamber, direct injection high efficiency nebulizer (DIHEN, 0.1 mL min^{-1}), and ultrasonic
1053 nebulizer (2.2 mL min^{-1})) (Johanna Sabine Becker et al., 1999; J. Sabine Becker et al., 1999) for the
1054 analysis of long-lived radionuclides including ^{226}Ra . These experiments were conducted on pure
1055 standard solutions, and since the different nebulizers were not operated at the same flow rate, one
1056 should compare the absolute sensitivity achieved rather than the sensitivity. Experiments with the
1057 ICP-Q-MS demonstrated the DIHEN offers the best performances (IDL: 110 pg L^{-1} , RSD: 0.8%).
1058 However, with such an introduction system, the totality of the sample enters in the plasma as
1059 compared to conventional concentric nebulizers (only 1-2% of the sample), and spectral and non-

1060 spectral interferences have therefore a stronger impact. To reduce risks of forming interferences one
1061 should be tempted to reduce the solution uptake rate, but a decrease of the uptake rate from 100 to
1062 $1 \mu\text{L min}^{-1}$ was accompanied by a loss in sensitivity and precision, respectively by a factor of 14 and 6
1063 (Johanna Sabine Becker et al., 1999). The use of guard electrode to attenuate the plasma discharge
1064 to the cone (Becker and Dietze, 1999) and retardation lenses (Scott et al., 2019) were also reported
1065 in order to reduce wide spread of ion energies of the ion beam and thus enhance ion transmission
1066 and sensitivity and reduce background.

1067 Measurement parameters, such as integration time and number of sweeps, have also a great impact
1068 on the quality and relevance of the produced data and should therefore be adjusted to meet the
1069 application requirements (e.g. multielement analysis, volume of sample at disposal, detection limit
1070 required, precision). The effect of integration time on the measurement of ^{226}Ra in standard solutions
1071 spiked at various concentration levels was studied (Dalencourt et al., 2018). The longest integration
1072 time (30 s) was chosen since it led to the lowest uncertainty (RSD < 10%) even in poorly concentrated
1073 solutions (some pg L^{-1}). It can be seen in extended forms of Tables 3, 4, and 5 in supplementary
1074 information that integration times for ^{226}Ra measurement varied from 4 to 30 s whereas a typical
1075 value of 5 s was employed by most of authors when specified in case of ^{134}Cs , ^{135}Cs , and ^{137}Cs .

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1077 **5. Applications overview**

1078 The first application field involving the quantification of Ra and Cs isotopes by ICP-MS is related to
1079 radiological environmental monitoring. Legislations exist concerning Ra concentrations in drinking
1080 water but guidelines are slightly different from one agency to another. The World Health
1081 Organization (WHO) fixed a maximum permissible activity of 1 and 0.1 Bq L^{-1} (27.4 and 0.01 pg L^{-1}) for
1082 ^{226}Ra and ^{228}Ra , respectively ("Guidelines for drinking-water quality, fourth edition," 2011). The
1083 council directive 2013/51/Euratom recommended 0.5 and 0.2 Bq L^{-1} (13.7 and 0.02 pg L^{-1}) for ^{226}Ra
1084 and ^{228}Ra , respectively (Sands and Galizzi, 2006), and the United States Environmental Protection
1085 Agency (US EPA) established a maximum activity of 0.185 Bq L^{-1} for combined ^{228}Ra and ^{226}Ra
1086 (Environmental Protection Agency (EPA), 2002), which corresponds to 5.06 and 0.02 pg L^{-1} for pure
1087 ^{226}Ra and ^{228}Ra , respectively. Based on precautionary principle, these guidelines are often expanded
1088 to other matrices, both liquid and solid. There is no legislation regarding ^{137}Cs , but the US EPA fixed a
1089 maximum contamination threshold for beta and photon emitters in drinking water corresponding to
1090 4 millirem per year ($0.04 \text{ mSv per year}$) (US EPA, 2002). ^{226}Ra concentration was for instance
1091 determined by ICP-MS in different kinds of environmental waters (e.g. surface or ground waters
1092 more or less charged in salts) in various parts of the world including Italy (Copia et al., 2017), United
1093 Kingdom (Hsieh and Henderson, 2011), Germany (Zoriy et al., 2005), Canada (Benkhedda et al., 2005;

1094 Lagacé et al., 2017; W. Wang et al., 2021), Central Asia (Schettler et al., 2015), Japan (Yang et al.,
1095 2020), Korea (Kim et al., 1999; Park et al., 1999), United Arab Emirates (Larivière et al., 2005), Israel
1096 (Sharabi et al., 2010), Azerbaijan (Varga, 2008), North Sea (Vieira et al., 2021), Pacific (Bourquin et al.,
1097 2011), and Antarctic (Foster et al., 2004). The obtained values ranged from 0.0007 to 2.3 pg L⁻¹ for
1098 lake and river waters (Benkhedda et al., 2005; Lagacé et al., 2017; Schettler et al., 2015; Sharabi et
1099 al., 2010; W. Wang et al., 2021; Yang et al., 2020), from 0.08 to 446 pg L⁻¹ for well and ground waters
1100 (Copia et al., 2017; Kim et al., 1999; Lagacé et al., 2017; Larivière et al., 2005; Park et al., 1999;
1101 Schettler et al., 2015; Zoriy et al., 2005), and from 0.037 to 0.18 pg L⁻¹ for ocean and sea waters
1102 (Bourquin et al., 2011; Foster et al., 2004; Hsieh and Henderson, 2011; Varga, 2008; Vieira et al.,
1103 2021), with significant variations worldwide as already reported by the International Atomic Energy
1104 Agency (IAEA) (International Atomic Energy Agency, 2014). Strangely, determination of Cs isotopes
1105 by ICP-MS has been rarely carried out in liquid samples (Amr et al., 2016; Asai et al., 2020; Epov et al.,
1106 2004; Ohno and Muramatsu, 2014; Song et al., 2001; Sturgeon et al., 1993; Zhu et al., 2021b). For
1107 solid samples, additional sample preparation steps must be conducted before any purification and
1108 preconcentration procedure. Among them, the most crucial step consists in digesting the organic
1109 and/or mineral matrix to release analytes to the solution. In case of uncomplete release,
1110 concentrations and isotopic ratios will be underestimated, thus efficiency of the method employed
1111 for this step must also be evaluated. Different digestion techniques have been employed in papers,
1112 including acid leaching digestion using concentrated acids/oxidizing agents (e.g. HNO₃, HCl, HClO₄,
1113 H₂O₂ or HF) (Amr et al., 2016; Ben Yaala et al., 2019; Bonin et al., 2020; Cao et al., 2016; Dalencourt
1114 et al., 2018; Epov et al., 2003; Granet et al., 2008; Kayzar and Williams, 2016; Larivière et al., 2003;
1115 Meeks et al., 1998; Moreno et al., 1999, 1996; Pietruszka et al., 2002; Russell et al., 2014b; Scott et
1116 al., 2019; Yang et al., 2016; Zheng et al., 2014b, 2014a; Zhu et al., 2020), microwave-assisted acid
1117 digestion (Kayzar and Williams, 2016; Kim et al., 1999; Larivière et al., 2007; Meeks et al., 1998; Tsai
1118 et al., 2010; Wærsted et al., 2018) or borate fusion (Russell et al., 2014a; Taylor et al., 2008; Zhu et
1119 al., 2020). As illustrated by Table 6 and Table 7, in order to validate their method, many groups have
1120 analyzed various types of CRMs, sometimes not necessarily certified in activity for the target analyte.
1121 Only one group conducted an interlaboratory comparison as another approach for method
1122 validation. This was made with two other laboratories who measured ²²⁶Ra in 5 sediments using
1123 alpha or gamma spectrometry while themselves realized direct ²²⁶Ra analysis in digested sediments
1124 with an ICP-(CC)-Q-MS (Ben Yaala et al., 2019). Two quantification approaches were assessed,
1125 namely analysis in the standard (STD) or in the Kinetic Energy Discrimination (KED) configuration,
1126 followed by subtraction of the apparent ²²⁶Ra concentration measured in matrix-matched solutions
1127 of each digested sediment sample to remove the contribution of polyatomic interferences. As shown
1128 in Figure 5, results obtained by all methods were in good agreement. However, it can be noticed that

1129 uncertainty provided by radiometric methods was higher for the two samples containing a high level
1130 of ^{226}Ra whereas when considering samples with the lowest ^{226}Ra concentrations, uncertainties were
1131 smaller for radiometric methods than for the ICP-MS approaches, highlighting the complementarity
1132 of methods.

1133 As part of the measurement of uranium series nuclides, Scott *et al.* have brought a new database on
1134 ^{226}Ra concentration and $^{226}\text{Ra}/^{230}\text{Th}$ isotopic ratio in several rock standards not certified in ^{226}Ra ,
1135 which could serve other studies (Scott et al., 2019). It is also worth noting that CRMs are certified in
1136 concentration (e.g. ^{226}Ra , ^{134}Cs , or ^{137}Cs), but no standard certified in isotopic ratio ($^{226}\text{Ra}/^{228}\text{Ra}$,
1137 $^{135}\text{Cs}/^{137}\text{Cs}$) are available at this time. Therefore, validation of methods developed for measurement of
1138 ^{135}Cs or $^{135}\text{Cs}/^{137}\text{Cs}$ were often made comparing values by another group who analyzed the same CRM
1139 with another method, and sometimes even with another detection technique.

1140 Other application fields include the reconstitution of the history of a particular site, the identification
1141 of the origin of a contamination, or the study of ocean circulation. Copia *et al.* studied for instance
1142 the uranium and radium hydrogeochemical background in groundwater samples collected from the
1143 Gran Sasso aquifer (Italy) between 2008 and 2014, with the aim of investigating correlations between
1144 the measured concentrations and the seismic activity of the region (Copia et al., 2017). An
1145 earthquake has effectively occurred in 2009 which is comprised across the time period of their study.
1146 Isotopic ratios were measured by SF-ICP-MS after applying an optimized sample preparation
1147 procedure (Copia et al., 2015). The obtained results highlighted a rise of the $^{226}\text{Ra}/^{238}\text{U}$ ratios
1148 measured in samples collected after the ground shaking, which was interpreted as a change in
1149 water–rock interaction processes. Taylor *et al.* measured ratios of the fission products ^{135}Cs and ^{137}Cs
1150 in various samples contaminated by three different sources (soils and sediments from the Chernobyl
1151 exclusion zone, sludge from a nuclear waste storage facility in Canada, and sediments collected in
1152 Ottawa river), and thus demonstrated that $^{135}\text{Cs}/^{137}\text{Cs}$ is an adequate indicator of radioactive
1153 contamination source (Taylor et al., 2008). In another example, the direct measurement of $^{135}\text{Cs}/^{137}\text{Cs}$
1154 and $^{134}\text{Cs}/^{137}\text{Cs}$ was achieved in rainwaters collected after the Fukushima accident using ICP-QQQ-MS
1155 and nitrous oxide as reaction gas (Ohno and Muramatsu, 2014). The average measured value of the
1156 $^{135}\text{Cs}/^{137}\text{Cs}$ ratio over 6 rainwater samples was 0.37 ± 0.03 , which do not match either with the
1157 isotopic signature of 1962 global fallout (2.7) nor with that of Chernobyl (0.46), thus indicating
1158 another contamination source.

1159

1160 **6. Conclusion**

1161 Methods merging the latest progresses in SPE and in ICP-MS remain the best approaches to achieve
1162 measurement of Ra and Cs isotopes at ultra-trace levels. Development of sample preparation

1163 methods are however currently still conducted in the old-fashioned way, by optimizing one
1164 parameter at a time, which can be very time-consuming in view of the complexity of some
1165 procedures aforementioned, and most importantly, does not take into account that parameters are
1166 not necessarily independent. To gain in efficiency, new optimizations should be thought using design
1167 of experiments (e.g. factorial design), as this statistic tool proved to be very helpful in other
1168 application fields (Baig et al., 2009; Leardi, 2009). In the future, improvement of sorbent specificity as
1169 well as instrumental sensitivity (e.g. newer ion paths and sample introduction systems that for
1170 instance do not entail loss of 98% of the sample in the nebulization chamber) will also for sure open-
1171 up new application opportunities. The use of specific sorbents combined to the development of
1172 simpler extraction procedures should for instance favor miniaturization of the methods enabling to
1173 further improve the sensitivity while requiring both less sample amounts and phases (Mariet et al.,
1174 2019; Ou et al., 2019). This could boost the understanding of radium and cesium transfer pathways in
1175 the environment (e.g. soil to plants transfer through pore water, or accumulation in micro-
1176 organisms), research fields which are currently hampered by the lack of suitable methods for
1177 samples of both low volume and concentration. Increasing current set of data in these areas will
1178 serve to model dissemination of these radionuclides around contaminated sites which would also be
1179 valuable information and tool when making a diagnosis in view of former uranium mining sites
1180 rehabilitation. To manage to do this, emerging sorbents identified as the most promising in academic
1181 laboratories, and the technical know-how to prepare them, need to be exported to industry. In
1182 addition, a lack of CRM certified in isotopic ratios ($^{226}/^{228}$ and $^{135}/^{137}$) has been highlighted by the
1183 community. In this regard, investment of laboratories making such kind of sources would bring
1184 significant benefits, especially to better evaluate and correct mass discrimination effect in ICP-MS, to
1185 avoid in-house tracers preparation, and to facilitate comparison between methods with or without
1186 the same detection technique.

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