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

Keywords

Radium; Cesium; Sample handling; Inductively Coupled Plasma – Mass Spectrometry; Solid Phase Extraction; Separation.

Abbreviations

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

1. Introduction

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

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

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

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

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

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

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

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

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

2.1. Solid phase extraction: the most spread technique

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

2.1.1. Ra and Cs extraction using variety of SPE supports

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

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

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

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

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

2.1.2. Key parameters for an optimal SPE

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

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

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

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

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

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

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

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

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

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

In many cases, the instrumental detection limit (IDL) was determined by measuring the signal of the target analyte in clean blanks (diluted HNO_3 solutions) (Table 3), which does not take into account the matrix composition (eluent solution and presence of remaining interfering elements) of the fraction injected in ICP-MS after sample purification. This results in an overestimated IDL. Though not perfect, the following approach was used by Wang and coworkers to take into account matrix effects: they quantified ^{226}Ra in several matrices with the standard addition methods and used the different slopes of the curves to estimate impact of the amount of total dissolved solids (TDS) on the 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

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

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

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

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

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

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

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

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

2.2. Other purification techniques

2.2.1. Dispersive solid phase extraction alone or associated with SPE

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

proved by Russell *et al.* who specified that under 30 min, Cs ions were still detected in solution while Cs uptake was maximum after 60 min and remained unchanged after 24 h (Russell *et al.*, 2014a).

dSPE was mainly applied for Cs extraction and only inorganic resins were employed, namely AMP (Cao *et al.*, 2016; Yang *et al.*, 2016; Zheng *et al.*, 2016, 2014b, 2014a; Zhu *et al.*, 2021b; Zok *et al.*, 2021), AMP loaded on silica gel (Russell *et al.*, 2014a), or KNiFC embedded in a PAN matrix (Cs resin) (Asai *et al.*, 2020) in case of Cs, and MnO₂ resin (Varga, 2008) for Ra. Adsorption is generally performed under stirring to favor ion diffusion towards sorbent. Mass transfer is also facilitated with small sorbent's particles (nanoparticles being the best) that have a high surface-to-volume ratio (Poole, 2019) and depends on temperature. Asai *et al.* used Cs resin with particle size distribution of 100-600 µm and realized extraction at room temperature but in other articles, temperature is not given, meaning the effects of temperature was not explored in any paper though it could result in a further decrease of the procedure time (Asai *et al.*, 2020).

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

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

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

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

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

2.2.2. Precipitation/co-precipitation associated with SPE

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

was mostly used by authors (Bourquin et al., 2011; Cozzella et al., 2011; Sharabi et al., 2010; Zoriy et al., 2005). This technique consists in mixing the sample with potassium permanganate and manganese dichloride. The formation of the MnO_2 precipitate is then driven by adjustment of the pH to 8-9 (Sharabi et al., 2010; Vieira et al., 2021). Above 9 precipitation of Mg may occur (Vieira et al., 2021).

Since MnO_2 can enclosed a variety of elements other than Ra (e.g. Th, U, Po, Ac, and Pb), procedures include further purification by SPE using 1 (Cozzella et al., 2011; Zoriy et al., 2005) and up to 3 (Bourquin et al., 2011) or 4 (Sharabi et al., 2010) resins. According to Cozzella *et al.*, supernatant contained most of Ca and part of Sr and subsequent SPE using AG50W-X8 resin was thus essentially made to separate Mn, and Ba from Ra (Cozzella et al., 2011). Dissolution of the MnO_2 precipitate prior to SPE was performed using HCl from 6 M (Bourquin et al., 2011; Sharabi et al., 2010; Vieira et al., 2021) to 9 M (Cozzella et al., 2011). A representative and low experimental MDL of 0.17 pg L^{-1} was obtained by applying this procedure on six urine samples from unexposed workers of a research site (Cozzella et al., 2011). The proposed method was also able to reach mean recoveries of up to 76% with only 5% RSD ($n=6$), requiring a global time of 2 days for sample preparation and analysis of a batch of 4 samples. The limiting step is co-precipitation since it requires one night to fully form the precipitate and let it decant.

For the purification of digested soil samples, some groups opted for lead-sulphate co-precipitation followed by additional extraction on AG50W-X12 resin (Kim et al., 1999; Tsai et al., 2010). The Pb(Ra)SO_4 co-precipitate obtained was then dissolved in a mixture of 0.1 M EDTA and 5 M ammonium acetate adjusted to pH 4.5-5 before loading on the AG50W-X12 cation exchange resin to eliminate other cations also entrapped in the precipitate and including Pb whose presence may lead to the formation of hydride ($^{208}\text{Pb}^{16}\text{O}^1\text{H}_2^+$) and oxide ($^{208}\text{Pb}^{18}\text{O}^+$) at m/z 226 in the ICP plasma. The carbonate co-precipitation method was employed twice, by addition of a NaCO_3 carrier resulting in the formation of Ca(Ra)CO_3 (Foster et al., 2004; Hsieh and Henderson, 2011). This method is however not recommended for very large sample volumes since carbonates are known to be more soluble than sulphate-compounds (International Atomic Energy Agency, 2010).

In case of Cs, Ba removal by precipitation of Ba(OH)_2 was employed only once without performing other purification technique (Meeks et al., 1998). No conclusion on the efficiency of this one-stage approach can however be drawn since no recoveries are mentioned.

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

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

2.3. Research on emerging sorbents to improve extraction techniques

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

Nanometer-sized materials are particularly interesting as they exhibit large surface area. Depending on the preparation method, they can be prepared in different forms including nanoparticles, nanofibers, nanoribbons or nanowires. Recently, Alby *et al.* (Alby et al., 2018) published a comprehensive review in which they compare different inorganic nanostructured materials, namely titanate, vanadate, tungsten, manganese oxides, hexacyanoferrates, metal sulfides, and ammonium molybdophosphates in order to fix Cs. Though the coefficient distribution values did not seem to vary significantly from one family to another, due to their structures, the sorption capacities were really different, vanadate oxides and metal sulfides-based materials presenting the best ones (i.e. 4.00 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 (Mertz et al., 2013) and 3.29 mmol g⁻¹ for vanadate nanofibers (Sarina et al., 2014)). Nevertheless, some of them can only be used over a limited pH range otherwise their sorption capacities are altered (e.g. pH 1 for vanadosilicates, pH 6 for vanadate nanotubes and pH 7-9 for titanate nanotubes and silicotitanates). This may constitute a limit for some applications. In a more general review about radionuclides trapping, a state of the art of progress in synthesis and application for other types of nanomaterials was done: Metal-Organic Frameworks (MOFs, formed by a network of coordination bonds between metal ions and organic ligands) and covalent organic frameworks,

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

Development of composite or hybrid sorbents was also investigated for Ra and Cs extraction, the objective being to create a more performant solid support by taking advantage of the specific properties of two different materials or more (synergic effect). Two Ra composite sorbents made of a PAN polymer coated with MnO_2 (Dulanská et al., 2015) or of a silica gel and MnO_2 (Dulanská et al., 2018) were studied for the determination of ^{226}Ra in natural waters. Contrary to procedures developed with previous commercial or self-prepared MnO_2 resins which often employ a mixture of $\text{HCl}/\text{H}_2\text{O}_2$ to elute Ra that entails destruction of the resin and leaching of high amount of Mn in the extract, they were able to elute Ra with HCl or HNO_3 solutions. In the study on MnO_2 -PAN sorbent, they only evaluated the effect of calcium concentration (from 70 to 2,070 mg L^{-1}) on Ba recovery (analogue of Ra used during the optimization step) whereas experiments were done on a larger panel 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 MnO_2 - SiO_2 sorbent. In both cases, salt content did not entail a significant decrease, Ba recovery being higher than 95% for the whole concentration range tested, and above 77% in case of Ra extraction from spiked mineral waters. No additional information on the sorption capacity was available.

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

Due to their large specific surface area, adjustable pore size, and ease-of-functionalization, MOFs have also been investigated for Cs removal (Asgari et al., 2019; Naeimi and Faghihian, 2017). A MOF based on Nd-benzene tricarboxylic acid was designed to have high sorption capacities for Cs^+ and Sr^{2+} and achieved maximum capacities around 0,7 mmol g^{-1} for both ions (Asgari et al., 2019). Its performances were not tested in presence of interfering elements nor on a real medium. Group of

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

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

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

coefficients of several metal cations were measured in dSPE, therefore by batch experiments with 50 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 interfering ions tested (Li⁺, Na⁺, K⁺, Rb⁺, NH₄⁺, Ag⁺, Mg²⁺, Ca²⁺, and Sr²⁺), highlighting the presence of specific cavities. Presence of specific recognition sites was also confirmed by the fact that the corresponding non-imprinted polymer exhibited a K_d value for Cs⁺ around two times less than the IIP. Batch measurements were conducted to estimate the IIP capacity (0.4 mmol g⁻¹). It was then applied to the determination of Cs in spiked groundwater and tap water and the dSPE procedure developed (200 mL of sample, adsorption at pH 9 for 20 min, and desorption with 2 mL HNO₃ 0.1 M for 7 min) allowed to reach recoveries above 95% (n=3). Therefore, at first sight this approach seems promising and it would be interesting in future years to inquire if it can be a viable alternative to current sorbents.

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

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

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

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

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

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

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

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

4.1. Resolution of interference issues

The decontamination factors offered by the previously described sample handling or separation procedures do not always lead to the sufficient elimination of the interferences, influencing therefore the accurate quantification of the target radionuclide and the detection limit. A complementary approach is based on the advances in ICP-MS instrumentation such as CRC or high mass-resolution instruments to resolve spectral interferences. Resolution of current ICP-MS instruments equipped with high mass resolution capabilities does not exceed 10,000 that is not sufficient to distinguish several of the isobaric and/or polyatomic interferences from ¹³⁷Cs and ²²⁶Ra signals (Table 1). Depending on their concentration in the analyzed fraction, matrix elements may not be responsible for forming spectral interferences in the plasma. Main interfering elements and the concentration threshold from which they induce an overestimate of the target signal are generally identified by preparing monoelemental solutions and mixtures of two elements at various concentrations and weight ratios. Therefore, if they are still present in the final purified fraction above the identified concentration thresholds, mathematical corrections must be implemented. As it can be seen from Table 3 and 4, since their appearance on the market in 2012, Triple Quadrupole ICP-MS (ICP-QQQ-MS) have largely gain in popularity, last generation instruments

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

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

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

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

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

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

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

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

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

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

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

5. Applications overview

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

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

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

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

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

6. Conclusion

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

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

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