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Isotopic signature of selected lanthanides for nuclear activities profiling using cloud point extraction and ICP-MS/MS

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ABSTRACT

The presence of fission products, which include numerous isotopes of lanthanides, can impact the isotopic ratios of these elements in the environment. A cloud point extraction (CPE) method was used as a preconcentration/separation strategy prior to measurement of isotopic ratios of three lanthanides (Nd, Sm, and Eu) by inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). To minimise polyatomic interference, the combination of interferents removal by CPE, reaction/collision cell conditions in He and NH_3 mode and tandem quadrupole configuration was investigated and provided optimal results for the determination of isotopic ratio in environmental samples. Isotopic ratios were initially measured in San Joaquin soil (NIST-2709a), an area with little contamination of nuclear origin. Finally, samples collected from three sites with known nuclear activities (Fangataufa Lagoon in French Polynesia, Chernobyl and the Ottawa River near Chalk River Laboratory) were analysed and all exhibited altered isotopic ratios for $^{143/145}$Nd, $^{147/149}$Sm, and $^{151/153}$Eu. These results demonstrate the potential of CPE and ICP-MS/MS for the detection of altered isotopic ratio in environmental samples collected in area subjected to nuclear anthropogenic contamination. The detection of variations in these isotopic ratios of fission products represents the first application of CPE in nuclear forensic investigations of environmental samples.

1. Introduction

Isotopic fractionation has been reported for a number of elements in the environment (Hou et al., 2003). This fractionation typically originates as the result of partitioning between isotopes based on differences in their masses. For example, Goldstein and Hemming (Goldstein et al., 2010) have reported variations in the $^{143/144}$Nd isotopic ratio from continental and seawater samples worldwide. However, several elements (including uranium) that are used in nuclear applications can also exhibit anthropogenic fractionation (commonly referred to as enrichment and depletion), which will affect their isotopic signature. The process of producing energy from uranium fission also generates numerous radioisotopes. These fission products are generated through variable yields that peaked around isotopes of masses 85–95 and 130–140. The second fission peak includes light members of the lanthanide elements and others elements such as Cs and I that can be used to track nuclear-related events (Zheng et al., 2014) (Ohno et al., 2013), For example, Hidaka et al. (Hidaka et al., 1988). reported using the isotopic signature of Nd to determine that nuclear fission was involved in the case of the Oklo natural reactor providing clues to explain the noted discrepancy in the ^{235}U/^{238}U ratio.

Controlled and uncontrolled releases of pollutants from nuclear power plants and nuclear weapons testing have disseminated fission products, including isotopically modified lanthanides. Some fission products such as iodine and caesium are volatile and can remain airborne for a significant distance. By comparison, lanthanides, as present in spent nuclear fuels, are mainly refractory and have a more limited distribution in the environment (Seliman et al., 2012). Therefore, environmental samples collected near nuclear sites could exhibit different isotopic signatures, which could be correlated to previous contamination.

To assess variations in the isotopic signature of numerous elements, techniques such as thermal ionisation mass spectrometry (TIMS), accelerator mass spectrometry (AMS), and inductively

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coupled plasma mass spectrometry (ICP-MS) are frequently used. However, to properly assess variations in isotopic ratios, proper and complete digestion of the sample and adequate removal of interferents are needed. While sample digestion is typically performed on solid samples by either acid digestion or alkaline fusion, many strategies exist for lanthanide pre-concentration/separation.

Among them, chromatographic and extraction processes have been proposed in a number of applications related to elemental composition or isotopic ratio measurements of lanthanides. Among them, solid phase extraction (SPE) has gained in popularity for environmental preconcentration/separation of a number of elements. Amongst the various commercially available products, diglycolamide (DGA)-based resins have shown promise for applications that involve lanthanides (Horwitz et al., 2005a).

However, SPE is not without drawbacks for isotopic analysis when used for batch preconcentration. In general, appreciable enrichment factors ($EF = [Analyte]_{eluant}/[Analyte]_{digestate} > 50$) are difficult to achieve in a timely manner as non-negligible volumes of eluants (several mL) are needed to perform back-extraction of the analyte due in part to column void volume (Zhang et al., 2007). In addition for SPE designed with ligands exhibiting low extraction yields (%EXC<10), breakthrough volume are frequently reached before appreciable enrichment factors can be obtained. Therefore, ligands exhibiting high extraction yields values (%EXC > 99%) are needed to achieve a high degree of enrichment, which unfortunately often translate in limited elution, as evidenced by Croudace et al. (Croudace et al., 2006). Strategies such as stacking multiple cartridges can be used to compensate for the lack of complete retention, but would inevitably result in an increase in the system void volume. In the case of lanthanides preconcentration, DGA resins exhibit lower extraction capacities for lighter lanthanides (Ansari et al., 2012), which are elements of interest in nuclear isotope forensics.

Recently, Labrecque et al. developed a new separation strategy for lanthanides based on cloud point extraction (CPE) (Labrecque and Lariviere, 2014). This approach is based on micellar extraction driven by a selective ligand in an aqueous media followed by a modification in the media temperature to initiate phase separation. This strategy was effective for the quantitative enrichment factors (>140-fold) and separation of all lanthanides from the matrix, including the lighter ones. Moreover, it was determined that CPE approach was compatible with most solid digestion techniques, including alkaline fusion, enabling the quantification of lanthanides in solid environmental samples such as soils and sediments.

In addition to the challenge associated with preconcentration, removal of interfering ions need to be addressed when dealing with isotopic ratio determination. For lanthanides, the presence of elements such as barium can be problematic (Labrecque and Lariviere, 2014). As some of those polyatomic interferences require instrumental resolving power (R) exceeding 10,000 for separation (e.g. $^{136}Ba^{16}O^{1}H$ (m = 152.90731 amu (Haynes, 2014)) and ^{153}Eu (m = 152.92124 amu (Haynes, 2014)) at m/z 153; $R=|m/\Delta m| = 10{,}977$), their presence can limit the ability to precisely measure the Eu isotopic ratio even with high-resolution mass spectrometers. Recently, Sugiyama and Woods (Sugiyama and Woods, 2012) have shown that inductively coupled plasma tandem quadrupole reaction cell mass spectrometry (ICP-MS/MS) could be used to reduce interferences caused by polyatomic ions, even those requiring high resolving power, for many lanthanides. The instrumental design of the ICP-MS/MS, in which an octopole reaction system (ORS) is in-between two quadrupoles (Q) that filter the ions entering (Q_1) and exiting (Q_2) the ORS, could provide an alternative to high resolution requirements. This design limits the number of species in the ORS as well as enables analysis in mass-shift mode, a useful strategy for interference removal, as recently demonstrated by Whitty-Leveillé et al (Whitty-Leveillé et al., 2016). for Sc. The use of ICP-MS/MS has been shown to be instrumental in the measurements of other fission products present in minute quantities near contaminated sites (Zheng et al., 2014) (Ohno et al., 2013), Therefore, combining this type of instrumentation with the proper removal of barium and preconcentration of lanthanides during the sample preparation could facilitate isotopic ratios measurements.

This research describes the application of alkaline fusion/CPE/ICP-MS/MS as a tool to evaluate variations in isotopic ratios of selected lanthanides as tracers for nuclear anthropogenic contamination in the environment. The applicability of the CPE/ICP-MS/MS conditions presented to reduce polyatomic interferences relevant to Nd, Sm and Eu, was assessed and compared to SPE. Finally, the proposed methodology was tested and validated for isotopic ratio analysis as indicators of anthropogenic contamination. To our knowledge, this is the first reported attempt to use CPE as a preconcentration/separation strategy for determination of isotopic ratios.

2. Experimental

2.1. Samples and sample preparation

Four samples have been analysed during this investigation: 1) sediments from the Fangataufa lagoon in French Polynesia (IAEA-384), purchased from the International Atomic Energy Agency (IAEA, Monaco); 2) an agricultural soil sample from San Joaquin in central California (NIST-2709a), purchased from the National Institute of Standards and Technologies (NIST, Gaithersburg, MD); 3) freshwater sediment samples collected from the Ottawa River near Chalk River Laboratory in August 2005 (Taylor et al., 2008) (this sample was sieved and homogenised prior to digestion); and 4) samples collected near the Chernobyl (Ukraine) nuclear power plant, which have also been part of an IAEA intercomparison study (Guerin et al., 2010).

The solid samples have been prepared using alkaline fusion using an automated fusion unit (M-4 fluxer, Corporation Scientifique Claisse, Québec, Canada). For this, 0.5 g of dry sample is mixed with 3.4 g of flux and subjected to the protocol presented in Table S4. The melt is then poured into a 100 mL solution of 3 mol L^{-1} HNO_3. This fusion procedure led to dissolved samples that are stable over the course of several weeks. To facilitate cloud point extraction, the solutions are treated with polyethylene glycol (PEG-6000) to reduce the amount of silica in solution following the procedure described by Gagné et al. (Gagne et al., 2013). A centrifuge (Thermo Fisher Scientific Sorvall Legend XTR, Bremen, Germany) is used to facilitate the silica removal through PEG co-condensation. This silica removal step avoids nebuliser clogging and facilitates surfactant-rich phase redispersion. The sample dissolution/preconcentration efficiency of the method for the lanthanides has already been demonstrated elsewhere through comparison between measured and certified values of NIST-2709a (Labrecque and Lariviere, 2014).

2.2. CPE system

A schematic representation of the CPE strategy is presented in Fig. 1. The optimisation process of the CPE conditions for the quantitative extraction of lanthanides are reported elsewhere (Labrecque and Lariviere, 2014) and only the conditions used in this investigation are reported here. An aliquot sample of 6.5 mL of the solution prepared by fusion containing 3 mol L^{-1} HNO_3 is mixed with the following reagents necessary for the CPE: 100 µL of a solution of 0.01 mol L^{-1} of CTAB, followed by 400 µL of an aqueous