



Zr and U determination at trace level in simulated deep groundwater by Q ICP-MS using extraction chromatography

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ABSTRACT

In the framework of trace element analysis by Q ICP-MS in a simulated deep Callovo-Oxfordian groundwater, separation procedures based on extraction chromatography were developed to eliminate the high salt contents and to concentrate Zr and U simultaneously. Theoretical and experimental speciation studies showed the importance of adjusting the medium to HNO₃/HF (0.5 M/0.005 M) to guarantee the stability over time of the analytes before removal of the matrix. Two preconcentration methods based on TRU[®] and TODGA[®] resins were optimized for the simultaneous isolation of Zr and U prior to Q ICP-MS measurements. Using TRU resin, alkali and alkali earth metals contained in the deep groundwater were removed with 2 M HNO₃ whereas Zr and U were recovered with a HNO₃/NH₄HC₂O₄ (0.02 M/0.05 M) medium. For the separation protocol based on TODGA resin, alkali and alkali earth metals were eliminated with 3 M and 11 M HNO₃ while Zr and U were simultaneously stripped with a HNO₃/HF (0.5 M/0.2 M) medium. The procedure optimized on TODGA resin was validated with the French AFNOR NF T90-210 standard by studying linearity, limits of quantification (LOQ) and separation yields. The LOQ was determined at 0.008 µg L⁻¹ for Zr and U after the separation. Both analytes were recovered quantitatively. Compared to a sample dilution implemented to reduce the matrix effects, the developed preconcentration method allowed improving the sensitivity up to a 20 fold factor for Zr and U measurements at trace level by Q ICP-MS.

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1. Introduction

In the past decades, metallic fuels, such as UZr metallic alloys, were used as nuclear fuels. Direct disposal in deep geological repository can be an option for the long-term management of spent nuclear fuels [1]. Such alternative is based on a multibarrier concept consisting of natural and engineered barriers that would isolate or delay the contact of spent fuels with water as well as the transport of the dissolved radionuclides in the biosphere. Transport by groundwater is the only credible mechanism for the migration of radionuclides contained in the spent fuels from the repository to the biosphere [2]. As a consequence, it is necessary to evaluate the spent nuclear fuel source term which corresponds to the combination of the rate of spent fuel dissolution and the rate of release of the various radionuclides [2–4].

Leaching experiments on spent nuclear fuels have usually been carried out to determine the source term. Most works have been focused on UO_{2(s)} matrices with various experimental conditions in terms of groundwater compositions or redox conditions [2,4,5].

For the studied spent UZr metallic fuels, the leaching and the release of two major radionuclides, ²³⁵U and ⁹³Zr, have to be investigated in the prospect of direct disposal in a deep geological repository. In France, the reference groundwater to be considered is a deep clayey Callovo-Oxfordian groundwater containing high concentrations of salts (alkali and alkaline earth metals) [4,6]. Tribet et al. [4] proposed a methodology to investigate the behavior of UO₂ fuels in contact with this reference groundwater and to measure uranium releases. Fuel pellets have to be immersed in a reactor containing 150 mL of the simulated deep clayey Callovo-Oxfordian groundwater. The reactor is pressurized to 3.5 bars with 3000 ppm CO₂ in Argon. Then, an aliquot has to be sampled at different intervals during the leaching period of one year. The samples have to be collected the first day, then each week during the first two weeks and afterwards each month during the first six months and finally every three months. Because of the overall duration of experiments, only a small volume (around 1 mL) of the solution can be withdrawn for subsequent analyses. Therefore, this issue implies the determination of ²³⁵U and ⁹³Zr isotopes in a high salt content matrix of simulated deep clayey Callovo-Oxfordian groundwater. It could be possible to perform the leaching experiments in hot cells of the LECI laboratory (Laboratory for Studies on Irradiated Fuel)

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whereas the subsequent analyses could be carried out at the LASE laboratory (Laboratory for Operator Support Analyses). Thus, a sample transfer is required between these two laboratories which are located at the CEA (French Alternative Energies and Atomic Energy Commission) Saclay, but in separated buildings.

Due to its composition [4], the Callovo-Oxfordian groundwater must be considered as a complexing medium towards U and Zr. Based on thermodynamic data, Robit-Pointeau demonstrated that carbonated species of uranyl ion are predominant in such a medium and that uranium is stabilized in solution [7]. The chemistry of Zr in aqueous medium is extremely complex because of its propensity to extensive hydrolysis and polymer formation [8–11]. Several studies have been conducted to determine Zr stability constants with various ligands (inorganic [8,9,12–15] or organic ligands [16,17]). Davydov et al. underlined that Zr concentration decreased in solutions for $\text{pH} > 2$ because of the formation of colloid particles [16]. Zr speciation has not been characterized in an environmental context, such as seawater or groundwater. Hence, Zr analysis in groundwater requires a preliminary speciation investigation to ensure the stability over time of the analyte concentration in solution and to guarantee the accuracy of subsequent measurements. Indeed, a delay of a few weeks can be foreseen between the sampling of leaching solutions and their analyses because of the regulatory and radiological requirements related to sample transfer between the two involved laboratories (LECI and LASE).

Given the expected concentrations of ^{235}U and ^{93}Zr isotopes ($< 10^{-6} \text{ mol L}^{-1}$ or $< 0.2 \text{ mg L}^{-1}$) in leaching solutions, Inductively coupled plasma mass spectrometry (ICP-MS) can be considered as the most promising technique for their simultaneous measurements. ICP-MS is a versatile tool to determine radionuclides and enables to achieve very low detection limits for many elements in short time analysis [18–20]. Neutron code calculations indicate that no isobaric interferences are to be expected between the radionuclides of interest and the isotopes in the spent UZr fuels. Nonetheless, the presence of high salt concentrations may reduce the analytical performance of ICP-MS by generating spectral and non-spectral interferences [20,21]. The deep Callovo-Oxfordian groundwater can induce the formation of polyatomic ions such as $^{40}\text{Ar}^{35}\text{Cl}^{18}\text{O}$ and $^{40}\text{Ar}^{37}\text{Cl}^{16}\text{O}$ which interfere with ^{93}Zr . Non-spectral interferences, also known as matrix effects, can be divided into two categories, namely reversible and irreversible [22,23]. Reversible effects involve analyte signal suppression or enhancement compared to the one expected from the same analyte concentration in a matrix-free solution [21,24,25]. For a solution containing Na at a concentration of 2 g L^{-1} (close to the one measured in the deep Callovo-Oxfordian groundwater), a 50% suppression up to a 50% enhancement of signal intensity was reported depending on the elements [23]. Irreversible effects are related to deposition of matrix salts or oxides in the sample introduction system (nebulizer tips) and at the MS interface (sampling cones) which results in gradual signal losses until irreversible clogging [21]. As a result, the high concentrations of salts contained in the deep Callovo-Oxfordian groundwater have to be reduced. Sample dilution is the common approach used [21,26,27]. In our study, a 100 fold dilution should be recommended to achieve a Na concentration of 10 mg L^{-1} suitable for ICP-MS analysis [28]. However, this option is not compatible with our requirements in terms of detection limits for U and Zr determination at trace level.

For the last few years, interfaces based on liquid or aerosol dilution have been developed to improve matrix tolerance of Q ICP-MS instruments [29]. Wilbur et al. reported a limit of detection of $0.011 \mu\text{g L}^{-1}$ for uranium contained in high matrix certified reference materials by using a high matrix interface [29]. Nonetheless, those results are not sufficient to achieve the

required detection limits. Consequently, chemical separation of the analytes from the sample matrix is the only appropriate solution to minimize the interferences generated by the high salt contents [21,30]. Various techniques can be applied to eliminate the matrix, such as precipitation [26,31], co-precipitation [32], liquid-liquid extraction [15,32–34] or ion chromatography [35]. Additionally, extraction chromatography has become a leading technique for separation and preconcentration of radionuclides in the environmental, biological and nuclear fields [36]. The combination of an organic extractant coated on an inert support delivers the selectivity of solvent extraction with the ease of use of resin based methods [37,38]. Numerous works emphasized the efficiency of extraction chromatography to isolate uranium or zirconium prior to their measurements by radiometric or ICP-MS techniques [19,30]. Three extraction resins present a high potential for our issue: UTEVA[®], TRU[®] and TODGA[®] [39–41]. The organic extractants impregnated on the inert polymeric resin are respectively: diamyl-amyolphosphonate (DAAP) [40], octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO) dissolved in tri-n-butyl phosphate (TBP) [39] and N,N,N' tetraoctyl-1,5-DiGlycolAmide [41]. Tsai et al. developed a separation protocol based on UTEVA resin to analyze U in environmental samples (such as soil, groundwater and seawater) [42]. Osvath et al. determined ^{93}Zr in radioactive waste samples by applying co-precipitation and extraction chromatography using UTEVA [43]. Maxwell et al. combined UTEVA and TRU resins to isolate U from water and bioassay samples [44]. Tagami and Uchida [45] and Rozmaric et al. [46] also described a procedure dedicated to U preconcentration from complex matrices (soils, drinking and seawater) using TRU resin. Concerning isotopic measurements of spent nuclear fuels, Quidelleur et al. optimized an analytical method based on TRU resin to isolate U from a steel matrix [47]. Hoshi et al. separated Zr from fission products contained in a simulated high level effluent by using TODGA resin [48]. Pourmand and Dauphas recently determined distribution coefficients of 60 elements (including metals, high-field strength elements and actinides) on TODGA resin [49]. This extraction resin was proven to be efficient for achieving U and Zr preconcentration from a geostandard. However, no study has been devoted so far to the simultaneous preconcentration of U and Zr from a high salt content matrix, such as the deep Callovo-Oxfordian groundwater.

The aim of this work is to develop a procedure based on extraction chromatography to concentrate simultaneously U and Zr from a simulated deep Callovo-Oxfordian groundwater and to collect purified fractions to be subsequently analyzed by Q ICP-MS. Since U and Zr display different chemical behaviors in solution, the speciation of these analytes is first discussed in the paper so as to guarantee their concentration stability with time. Then, the investigation and the optimization of preconcentration procedures are described for the selected extraction resins (UTEVA, TRU and TODGA[®]). The French AFNOR NF T90-210 standard was applied to validate the optimized separation protocols. The limits of quantification and the separation yields were experimentally determined. The method validation enabled to choose the most appropriate preconcentration method for the determination of U and Zr at trace level by Q ICP-MS.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared using ultra-pure water (resistivity $18.2 \text{ M } \Omega \text{ cm}$) obtained from a Milli-Q system (Millipore, France). Nitric, hydrochloric and fluorhydric acids were all Ultrex II grade (Baker). Ammonium hydrogen oxalate $\text{NH}_4\text{HC}_2\text{O}_4$ was prepared

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