Talanta 106 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

C. Gautier [a,*], M. Coppo [a], C. Caussignac [b], I. Laszak [b], P. Fichet [a], F. Goutelard [a]

[a] Commissariat à l'Energie Atomique et aux Energies Alternatives, CEA Saclay, DEN/DANS/DPC/SEARS/LASE, Batiment 459, PC 171, 91191 Gif-sur-Yvette Cedex, France
[b] Commissariat à l'Energie Atomique et aux Energies Alternatives, CEA Saclay, DEN/DANS/DPC/SEARS/LANIE, Batiment 391, PC 33, 91191 Gif-sur-Yvette Cedex, France

ARTICLE INFO

Article history:
Received 11 September 2012
Received in revised form
4 December 2012
Accepted 8 December 2012
Available online 16 December 2012

Keywords:
Extraction chromatography
Uranium
Zirconium
Preconcentration
Speciation
ICP-MS
Method validation
Limit of quantification

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 HNO_3/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 HNO_3 whereas Zr and U were recovered with a HNO_3/$NH_4HC_2O_4$ (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 HNO_3 while Zr and U were simultaneously stripped with a HNO_3/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.

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, ^{235}U and ^{93}Zr, 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 UO_2 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 CO_2 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 ^{235}U and ^{93}Zr 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)

---

[*] Corresponding author. Tel.: +33 1 69 08 18 35; fax: +33 1 69 08 43 23.
E-mail address: celine.gautier@cea.fr (C. Gautier).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.12.019

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 $pH>2$ 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 ($<10^{-6}\,\mathrm{mol\,L^{-1}}$ or $<0.2\,\mathrm{mg\,L^{-1}}$) 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}Ar^{35}Cl^{18}O and ^{40}Ar^{37}Cl^{16}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 $2\,\mathrm{g\,L^{-1}}$ (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 $10\,\mathrm{mg\,L^{-1}}$ 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 $0.011\,\mu\mathrm{g\,L^{-1}}$ 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-amylphosphonate (DAAP) [40], octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO) dissolved in tri-n-butyl phosphate (TBP) [39] and N,N,N′N′ tetra-octyl-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 $18.2\,\mathrm{M\Omega\,cm}$) obtained from a Milli-Q system (Millipore, France). Nitric, hydrochloric and fluorhydric acids were all Ultrex II grade (Baker). Ammonium hydrogen oxalate $NH_4HC_2O_4$ was prepared from oxalic acid dihydrate and diammonium oxalate monohydrate which presented a purity $\geq 99\%$ (Merck). The optimization of the separation methods was performed by using natural U and Zr SPEX standards (SPEX Certiprep Company). The experiments dedicated to the method validation were completed with isotopically enriched standards. ^{96}Zr, ^{233}U and ^{235}U were respectively purchased from Eurisotop, IRMM and NBS with the following enrichments: 86.4%, 98.0% and 93.3%. Given the isotopic compositions of the samples expected from neutron calculation codes, ^{233}U isotope was chosen as a tracer to determine the radiochemical yield of the whole separation. As no ^{93}Zr reference material is commercially available, ^{96}Zr was used to simulate the behavior of ^{93}Zr. All U and Zr standards were diluted in a 1 M $HNO_3 + 0.01$ M HF medium to guarantee the Zr concentration stability over time.

To prevent any contamination of the samples, all Savillex® PFA vials and Teflon (PTFE) vessels were cleaned before use with analytical grade concentrated nitric acid (Merck) and distilled water. Extraction resins were purchased from Triskem International (France). UTEVA and TRU resins were used as 2 mL prepackaged columns with 100–150 μm particle size. Columns with TODGA resin (50–100 μm particle size) were prepared in-house (0.8 cm diameter, 2 cm length).

2.2. Simulated deep clayey Callovo-Oxfordian groundwater

A simplified groundwater composition was used according to previous works [4,50]. The synthetic groundwater was prepared using the following analytical grade products: $NaHCO_3$, Na_2SO_4, NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$. The composition of the synthetic groundwater is detailed in Table 1. This solution was used directly without any degassing and the pH was measured at 7.4. For the optimization of the preconcentration methods, 1 mL of this synthetic groundwater was mixed with a solution containing 20 μg of natural Zr and U standards. For the method validation, the separation experiments were carried out using 0.09 ng of ^{96}Zr and ^{235}U and 1.1 ng of ^{233}U (used as a tracer). The sample was then evaporated to dryness before loading on extraction columns.

2.3. Instrumentation

An Activa M ICP-AES instrument (Horiba Jobin-Yvon) was first used to measure the analyte concentrations during the optimization step of the preconcentration procedures. The Q ICP-MS instrument used for the method validation was an Elan DRCe spectrometer (Perkin–Elmer). The main operating parameters are summarized in Table 2. The alkali and alkali earth metals were analyzed in a 1 M HNO_3 medium. After each preconcentration step, the purified U and Zr samples were analyzed in a HNO_3/$NH_4HC_2O_4$ (0.01 M/0.025 M) medium when using the TRU resin (following a 2 fold dilution); and in a HNO_3/HF (0.5 M/0.005 M) medium when using the TODGA resin (after evaporation to dryness). Special care was taken of the rinsing step of resins and ICP-MS in order to prevent any contamination of the samples [51]. The blank signal of the ICP-MS instrument was an efficient way to control the absence of contamination.

3. Results and discussion

3.1. Speciation

The development of U and Zr preconcentration methods requires the speciation characterization of these elements. Their chemical properties are strongly different in solution [7,9,52]. Previous works showed that U(VI) is complexed and stabilized in a medium such as the deep Callovo-Oxfordian groundwater [7]. But, Zr behavior has not been specified in such a matrix. A theoretical study was performed to simulate a deep Callovo-Oxfordian groundwater containing Zr at trace level at different pH values at 25 °C. The underground temperature might be different from 25 °C in the very vicinity of the UZr metallic fuel at first. But the difference of temperature is not significant enough to induce a drastic change in Zr speciation [53]. As for the redox potential, Zr exists in aqueous solution in the +IV oxidation state only. Therefore, the pH of the aqueous phase is the main factor controlling the speciation of zirconium. A concentration of 15 μg L^{-1} Zr (1.6×10^{-7} M) was chosen so that it could be measured with Q ICP-MS after a 100 fold dilution. Based on thermodynamic data [53], in-house computer calculations were carried out by using the same method as in Ref. [17] but with no ionic strength correction. All calculations were made at zero ionic strength, instead of 0.1 M for the Callovo-Oxfordian groundwater and 0.3 M for the HNO_3/HF adjusted groundwater. Because major species are utterly predominant at the pH of interest (respectively pH = 7.4 in Fig. 1 and pH = 0.3 in Fig. 3), the influence of the ionic strength was considered negligible on the identification of these species. Fig. 1 illustrates the theoretical distribution diagram of Zr(IV) as a function of pH in the conditions of a deep Callovo-Oxfordian groundwater. The theoretical speciation diagram is consistent with the works of Davydov et al. [16]. In such a medium (pH = 7.4), the Zr(IV) predominant species is the $Zr(OH)_{4(aq)}$ complex which can evolve into colloid particles and lead to the decrease of the Zr concentration in solution [16]. Due to the uncertainties associated with the stability constants [53], this approach was complemented with experimental studies to investigate the stability of Zr and U in solution at trace level. Fig. 2 depicts the Zr and U concentrations evolution over 8 days in the conditions of a simulated deep Callovo-Oxfordian groundwater. The theoretical concentration of 15 μg L^{-1} is considered as a reference to calculate the trueness in %. From the "A test" of the AFNOR NF T90-210 standard [54], the maximum accepted confident limits were fixed at 10% for the concentrations stability over time. Without any adjustment of the deep Callovo-Oxfordian groundwater with complexing agents, the U concentration did not evolve within one week. On the other hand, the Zr concentration experienced a 50% decrease during the same period, showing a good agreement with the theory but unsuited to our requirements.

Consequently, a complexing agent has to be introduced to stabilize the Zr concentration in the deep Callovo-Oxfordian groundwater. Connick and McVey studied the complexing ability of various ligands and underlined that oxalate and fluoride form the most stable complexes with Zr [9]. Furthermore, Chartier et al. noticed that a mixture of HNO_3/HF (0.5 M/0.005 M) enabled to measure stable Zr isotopic ratio values within a few months [32]. As the Ca concentration is rather high in the deep Callovo-Oxfordian groundwater, oxalic acid cannot be used because it induces its

Table 1
Chemical composition of synthetic deep Callovo-Oxfordian groundwater.

Concentration	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^-
mol L^{-1}	0.044	0.009	0.006	0.001	0.041	0.017	0.001
mg L^{-1}	1012	360	144	39	1456	1594	89

Table 2
ICP-AES and ICP-MS operating parameters.

Parameters	Activa ICP-AES	Elan DRCe Q ICP-MS
Plasma power	1000 W	1100 W
Cool gas flow rate	11 L min^{-1}	15 L min^{-1}
Auxiliary gas flow rate	0 L min^{-1}	1.2 L min^{-1}
Nebulizer gas flow rate	0.87 L min^{-1}	0.91 L min^{-1}
Sample uptake rate	1 mL min^{-1}	1 mL min^{-1}
Nebulizer type	Concentric	GemTip Cross Flow Ryton
Spray chamber type	Cyclonic	Scott (double pass) type
Medium used for rinsing and analysis after TRU separation		0.01 M HNO_3+0.025 M $NH_4HC_2O_4$
Medium used for rinsing and analysis after TODGA separation		0.5 M HNO_3+0.005 M HF

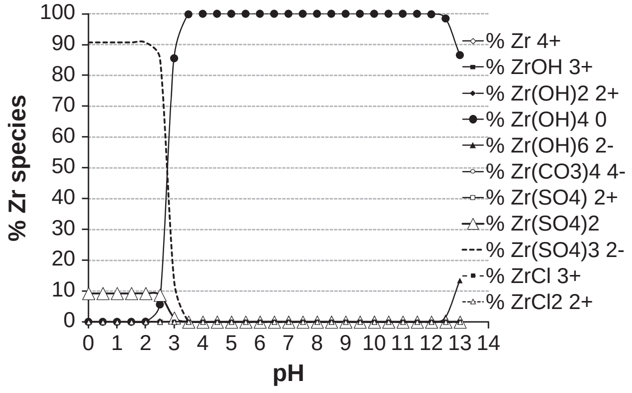

Fig. 1. Theoretical distribution diagram of Zr(IV) species as a function of pH in the conditions of a simulated deep Callovo-Oxfordian groundwater (with a Zr total concentration of 15 μg L^{-1}).

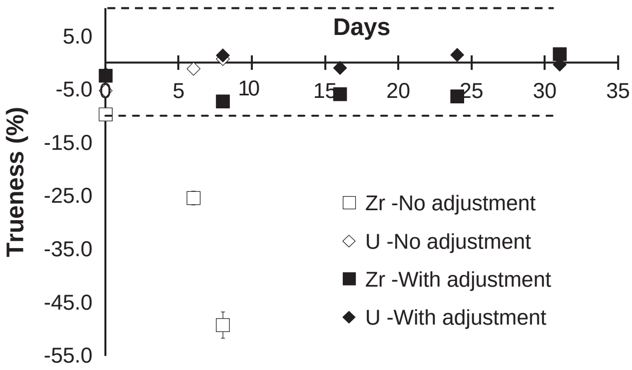

Fig. 2. Evolution of Zr and U concentrations in the conditions of a simulated deep Callovo-Oxfordian groundwater without chemical adjustment and with an adjustment to 0.5 M HNO_3+0.005 M HF (the reference total concentration of Zr and U was 15 μg L^{-1}).

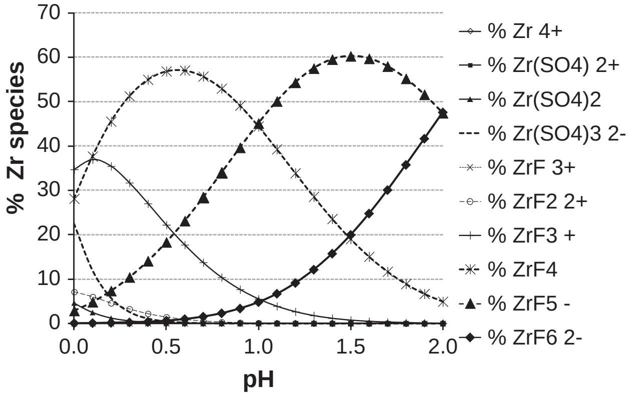

Fig. 3. Theoretical distribution diagram of Zr(IV) species as a function of pH in the conditions of a simulated deep Callovo-Oxfordian groundwater adjusted to 0.5 M HNO_3+0.005 M HF (with a Zr total concentration of 15 μg L^{-1}).

precipitation (CaC_2O_4 solubility product constant equals to 2×10^{-9} at 25 °C). HF appears as the most promising complexing agent when associated with HNO_3 (CaF_2 solubility product constant equals to 4×10^{-11} at 25 °C). When the deep Callovo-Oxfordian groundwater is adjusted to 0.5 M HNO_3+0.005 M HF (pH=0.3), $CaF_{2(s)}$ is not to be considered because of the high HNO_3 acidity: the main calcium species are Ca^{2+} and $CaNO_3^+$. From the speciation diagram presented in Fig. 3, it can be seen that the ZrF_3^+ and ZrF_4 complexes are the predominant Zr(IV) species when the Callovo-Oxfordian groundwater is adjusted to 0.5 M HNO_3+0.005 M HF (pH=0.3). Furthermore, the experimental studies showed that the Zr(IV) and U(VI) concentrations are perfectly stable over a month when using this conditioning medium (Fig. 2). Consequently, from now on, all our U/Zr trace level samples in simulated Callovo-Oxfordian groundwater will be adjusted to 0.5 M HNO_3+0.005 M HF before applying any preconcentration procedure so as to guarantee Zr chemical stability in solution.

3.2. Investigation and optimization of preconcentration methods

3.2.1. Preconcentration method based on UTEVA resin

The separation procedure using UTEVA resin was based on previous literature works from the literature [40,43,55]. Osvath et al. developed a sequential protocol to recover purified Zr and U fractions from nuclear waste samples [43]. After conditioning a UTEVA column and loading the sample in 8 M HNO_3+0.1 M $(NH_4)_2S_2O_8$, Zr is first stripped with 4 M HCl and then U with 0.1 M HCl. A similar approach was applied to separate U and Zr from the synthetic deep Callovo-Oxfordian groundwater. First, alkali and alkali earth metals were quantitatively eluted using 8 M HNO_3, but 15% of Zr were also co-eluted. Following the work of Horwitz et al. on U(VI) [40], 0.01 M HCl was used to elute uranium from UTEVA. A 70% recovery yield was obtained but without any Zr stripping. To allow for Zr to be eluted, the addition of HF to HNO_3 8 M would be possible but would increase the co-elution of Zr with alkali and alkali earth metals [38]. Although oxalic acid would be a solution for Zr, no U recovery would be observed [50,55]. As no convenient eluent was found in the literature regarding the simultaneous recovery of U and Zr, no further experiments were implemented using UTEVA resin.

3.2.2. Preconcentration method based on TRU resin

The development of TRU-based preconcentration method was also supported by previous works [39,47,56]. Quidelleur et al. performed a one-step U-Pu-Cs-lanthanides-steel separation [47], loading their sample in 2 M HNO_3 on the TRU resin. The elements of the steel matrix (Fe, Ni, Cr, Mo and Mn) were first eliminated with a 2 M HNO_3 step, whereas Pu was eluted next with a 1 M $HCl+0.075$ M $H_2C_2O_4$ mixture. Finally, U was stripped with a 0.02 M $HNO_3+0.1$ M $NH_4HC_2O_4$ mixture (in these conditions, the predominant form of oxalic acid is hydrogen oxalate $HC_2O_4^-$ at pH=1.7). Regarding our study, alkali and alkali earth metals were quantitatively eluted first using 10 mL of 2 M HNO_3 (same step as in [39]). Then, U and Zr were stripped simultaneously with 5 mL of 0.02 M $HNO_3+0.1$ M $NH_4HC_2O_4$ with a good recovery yield ($\geq 80\%$). Nonetheless, the presence of hydrogen oxalate in the purified fractions may hamper the subsequent ICP-MS measurements [57]. A supplementary step is usually applied to eliminate this organic compound with multiple cycles of dissolution/evaporation to dryness using a concentrated HNO_3/H_2O_2 mixture [47,55]. This operation is time consuming and can also induce trace-level contamination of samples. To avoid the use of oxalates, diluted HCl and a HNO_3/HF (0.5 M/0.2 M) mixture were tested to recover U and Zr from TRU column. Unfortunately, these two options were completely unsuccessful. Hence, it was decided to lower the hydrogen oxalate concentration in our $HNO_3/NH_4HC_2O_4$ eluting mixture. As a matter of fact, the same U and Zr recoveries were obtained with a $HNO_3/NH_4HC_2O_4$ (0.02 M/0.05 M) mixture. Moreover, Chartier et al. emphasized that a 0.025 M oxalate concentration was suitable for Zr, both for its stabilization in solution and its ICP-MS measurement [32]. Consequently, the $HNO_3/NH_4HC_2O_4$ (0.02 M/0.05 M) mixture was chosen for the simultaneous stripping of U and Zr, followed by a 2 fold dilution prior to the Q ICP-MS analysis. The TRU-based optimized preconcentration procedure is summarized in Table 3. The percentage recoveries are higher than 95% for alkali and alkali earth metals in 2 M HNO_3 and higher than 80% for both U and Zr in $HNO_3/NH_4HC_2O_4$ mixture.

3.2.3. *Preconcentration method based on TODGA resin*

A similar approach was applied for the investigation of the preconcentration procedure based on TODGA resin [41,49]. The separation protocol of U and Zr from geostandards developed by Pourmand and Dauphas [49] was adapted to our study. After conditioning a TODGA column and loading the sample in 3 M HNO_3, Na, K and Mg were quantitatively eluted with 3 M HNO_3. Then, Ca was stripped from TODGA column with 11 M HNO_3 and then U and Zr with 3 M $HNO_3+0.2$ M HF. Our results were consistent with the data obtained by Pourmand and Dauphas [49]. The preconcentration procedure was then optimized to reduce the elution time by decreasing the resin quantity and the elution volumes. The influence of the stripping solution was also investigated. Decreasing the HNO_3 concentration from 3 M to 0.5 M did not change significantly the elution profiles related to U and Zr. On the other hand, reducing the HF concentration from 0.2 M to 0.05 M lowered the Zr recovery to 60%. The same result was obtained while using a $HNO_3/H_2C_2O_4$ mixture [41]. Consequently, the 0.5 M $HNO_3+0.2$ M HF mixture was chosen to recover quantitatively U and Zr from the TODGA resin. However, preliminary Zr measurements with the Q ICP-MS instrument showed some memory effect signs, even though PFA-made nebulizer and spray chamber were used. As a result, the purified fractions were further evaporated to dryness and redissolved and analyzed in a 0.5 M $HNO_3+0.005$ M HF medium. The TODGA-based optimized preconcentration procedure is described in Table 4. The percentage recoveries are higher than 90% for both U and Zr.

3.3. *Method validation*

The preconcentration procedures using TRU and TODGA resins were optimized to isolate U and Zr from a synthetic deep Callovo-Oxfordian groundwater. Following the ISO 17025 standard guidelines, these methods needed to be validated [58], however no unique technique is specified to evaluate linearity, separation yields and limits of quantification (LOQ). Several approaches can be used to determine LOQ, such as the concepts based on instrumental repeatability, RSD of net signal, accuracy and precision, calibration graph, uncertainty, accuracy profile [59,60]. The classical LOQ concept is based on 10 times the standard deviation of the blank although this limit is only related to precision [59]. Recently, an approach based on the AFNOR NF T90-210 standard was investigated [54,61–63]. This standard is dedicated to the validation of analytical protocols in the field of water analysis. It proposes a guide to evaluate the initial performance of a quantitative method based on linear calibration curves. Relevant statistical tests are outlined to characterize linearity, separation yields and limits of quantification [54]. Consequently, the AFNOR NF T90-210 standard can be applied to validate both optimized preconcentration procedures.

The "B test" of the AFNOR NF T90-210 standard describes a method to check whether a presupposed LOQ can be acceptable [54]. It presents the advantage to assess experimentally a LOQ value, which is a more realistic manner than to calculate one. The accuracy of the presupposed LOQ is validated if the following inequalities are fulfilled:

$$z_{LOQ}-2\times s_{LOQ}>LOQ-60\%\times LOQ \quad (1)$$

$$z_{LOQ}+2\times s_{LOQ}<LOQ+60\%\times LOQ \quad (2)$$

where z_{LOQ} is the calculated mean concentration (based on a standard least square calibration) and s_{LOQ} is the calculated standard deviation of intermediate precision (dealing with a precision of a single laboratory).

Preliminary tests were performed to evaluate the LOQ from the prediction bands of calibration graphs [59] because only calculations from the calibration curves are required. A 0.008 μg L^{-1} LOQ was presupposed both for U and Zr after the preconcentration step.

Table 3
Analytical procedure for U and Zr determination from a simulated deep Callovo-Oxfordian groundwater using TRU resin, 100–150 μm, preconditioned 2 mL column.

Steps	Reagents	Volumes (mL)	Actions
1	H_2O mQ	5	Column rinsing
2	0.02 M $HNO_3+0.05$ M $NH_4HC_2O_4$	5	Column rinsing
3	H_2O mQ	5	Column rinsing
4	2 M HNO_3	5	Column rinsing
5	2 M HNO_3	5	Column conditioning
6	2 M HNO_3	0.5	Column loading
7	2 M HNO_3	0.5	Savillex rinsing
8	2 M HNO_3	9	Alkali and alkali earth metals elution
9	0.02 M $HNO_3+0.05$ M $NH_4HC_2O_4$	5	U and Zr elution
10	0.01 M $HNO_3+0.025$ M $NH_4HC_2O_4$	10	U and Zr measurements

Table 4
Analytical procedure for U and Zr determination from a simulated deep Callovo-Oxfordian groundwater using TODGA resin, 50–100 µm, column.

Steps	Reagents	Volumes (mL)	Actions
1	H_2O mQ	5	Column rinsing
2	0.5 M HNO_3+0.2 M HF	5	Column rinsing
3	3 M HNO_3	5	Column rinsing
4	3 M HNO_3	5	Column conditioning
5	3 M HNO_3	0.5	Column loading
6	3 M HNO_3	0.5	Savillex rinsing
7	3 M HNO_3	4	Na, K, Mg elution
8	11 M HNO_3	5	Ca elution
9	0.5 M HNO_3+0.2 M HF	5	U and Zr elution
10	0.5 M HNO_3+0.005 M HF	10	U and Zr measurements

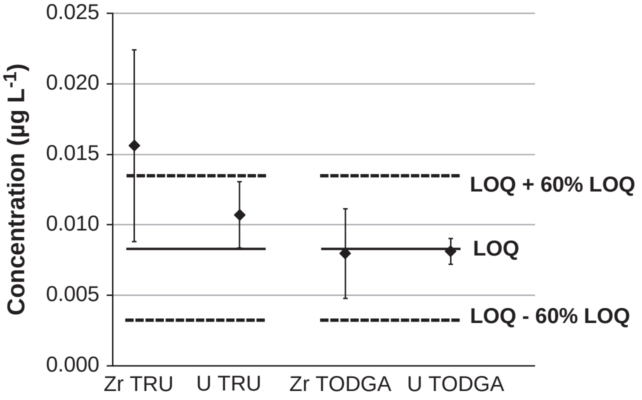

Fig. 4. Verification of the presupposed LOQ (µg L^{-1}) for U and Zr using TRU and TODGA extraction chromatography according to the "B test" of the AFNOR NF T90-210 standard.

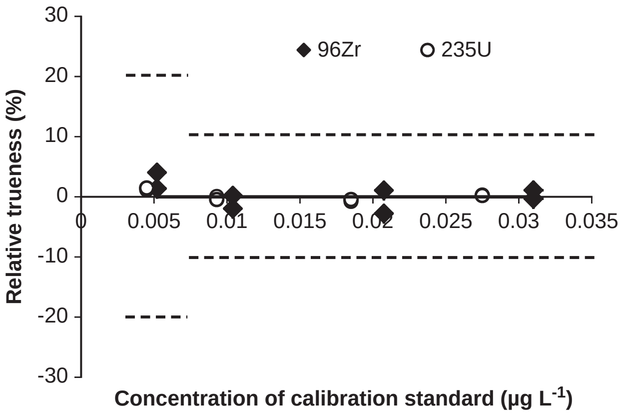

Fig. 5. Relative trueness (in %) as a function of the concentration of the ^{96}Zr and ^{235}U calibration standards in a 0.5 M HNO_3+0.005 M HF medium according to the "A test" of the AFNOR NF T90-210 standard (the dotted lines represent the maximum accepted confident limits which are respectively fixed at 20% for the lowest concentration of the calibration standard and 10% for the other ones).

Table 5
Statistical data related to the verification of separation yields for U and Zr using TODGA extraction chromatography according to the "C test" of the AFNOR NF T90-210 standard.

Isotope	^{96}Zr	^{235}U	^{233}U
Addition (ng)	0.09	0.09	1.1
Number of series	3	3	3
Number of repetitions per series	2	2	2
Mean separation yield (%)	9.1×10^{1}	9.3×10^{1}	9.5×10^{1}
Relative standard deviation of intermediate precision (%)	1.9×10^{1}	5.7	6.7
Difference from targeted 100% yield	8.7	6.9	5.4
Acceptable separation yield	Yes	Yes	Yes

The two protocols were repeated twice during three consecutive days, using ^{96}Zr and ^{235}U standards. The corresponding results are presented in Fig. 4. It is clear that inequalities (1) and (2) are both valid for the Zr and U fractions obtained with the TODGA resin, confirming the accuracy of the presupposed LOQ at 0.008 µg L^{-1}. Conversely, as illustrated in Fig. 4, the presupposed LOQ was not validated whatever the analyte for the TRU resin separation. Higher values of mean concentrations z_{LOQ} were measured in comparison to the targeted LOQ. Despite thorough care was taken of the reagents purity and of the rinsing steps of both extraction columns and ICP-MS, sample contaminations occurred when the TRU-based protocol was applied at trace level. It was particularly observed for Zr which is known for its sticky nature as a high field strength element [51,64,65]. Additionally, the memory effects are emphasized with the $HNO_3/NH_4HC_2O_4$ mixture of the TRU-based protocol, rather than with the HNO_3/HF mixture of the TODGA-based protocol. As a result, the protocol based on the TODGA resin was the only one for which the LOQ targeted at 0.008 µg L^{-1} was validated with the "B test". Thus, the separation method using the TODGA resin was selected as the most appropriate for our U and Zr trace level measurements by Q ICP-MS.

At that point, the "A test" of the AFNOR NF T90-210 standard was performed on the TODGA-based preconcentration protocol [54]. This test allows validating a calibration curve for a concentration range by comparing the measured trueness to the maximum accepted confident limits for the different calibration standards. In our case, the relative trueness (in %) represents the deviation from a 100% recovery and the maximum accepted confident limits are respectively fixed at 20% for the lowest concentration and 10% for the other ones. The U and Zr standards were all prepared in 0.5 M HNO_3+0.005 M HF, that is the medium obtained after a separation on the TODGA resin. The relative truenesses obtained for the ^{96}Zr and ^{235}U calibration standards are depicted in Fig. 5. It can be observed that all values are within the maximum accepted confident limits. Therefore, it can be concluded from the "A test" that the ^{96}Zr and ^{235}U calibration curves are acceptable for the studied concentration range (0.005–0.03 µg L^{-1}) and medium (0.5 M HNO_3+0.005 M HF).

Finally, the "C test" of the AFNOR NF T90-210 standard was used to characterize the influence of the TODGA-based preconcentration step and to evaluate whether the separation yield is acceptable within 10% trueness from a 100% value [54]. The associated statistical data are presented in Table 5. The mean separation yield is acceptable for all the studied isotopes (^{96}Zr, ^{235}U and ^{233}U). Hence, there is no need to use ^{233}U as a tracer and no separation yield correction has to be applied to the U and Zr determination.

Since the TODGA-based preconcentration protocol was validated with the AFNOR NF T90-210 standard, it was decided to assess its contribution to the improvement of sensitivity for Zr and U determination. Accordingly, the limits of detection (LOD, assuming LOD=LOQ/3) obtained with and without the elimination of the deep Callovo-Oxfordian groundwater matrix were compared. The former LOD was determined at 0.03 µg L^{-1} when using the "B test" validated TODGA protocol. The latter LOD was obtained with a simple 100 fold dilution prior to the ICP-MS measurement and was determined at 0.6 µg L^{-1} for Zr and 0.2 µg L^{-1} for U. Therefore, it can be concluded that the TODGA-based protocol improves the U and Zr sensitivities by a 10 and a 20 fold factor, respectively.

4. Conclusions

This study shows the development of a procedure to determine Zr and U at trace level in a simulated deep Callovo-Oxfordian groundwater. Theoretical and experimental studies of speciation characterization demonstrated the importance of adjusting the medium to HNO_3/HF (0.5 M/0.005 M) to guarantee the stability of the analytes in solution before their analysis. Extraction chromatography was applied to eliminate large amounts of salts (alkali and alkali earth metals) and to concentrate simultaneously Zr and U prior to Q ICP-MS measurements. The preconcentration procedures were optimized using TRU® and TODGA® resins. Both protocols were then evaluated with relevant statistical tests as outlined in the AFNOR NF T90-210 standard. The TODGA-based preconcentration procedure was the only one validated in terms of linearity, limits of quantification and separation yields. It allowed improving the sensitivity up to a 20 fold factor for Zr and U measurements at trace level by Q ICP-MS. In the prospect of a direct disposal of UZr metallic fuels in a deep geological repository, this work can be implemented for the analysis of the leaching solutions and the investigation of ^{93}Zr and ^{235}U release.

Acknowledgments

The authors thank Jeanne Enaux (CEA Saclay—DEN/DANS/DPC/SECR/L3MR) for preparing the synthetic deep Callovo-Oxfordian groundwater and Aude Bombard (Triskem International) for providing TODGA resin and thoughtful advice about Zr chemistry.

References

[1] AIEA, Vienna, IAEA-TECDOC-1243, 2001.
[2] S. Rollin, K. Spahiu, U.B. Eklund, J. Nucl. Mater. 297 (2001) 231.
[3] L. Johnson, C. Ferry, C. Poinssot, P. Lovera, J. Nucl. Mater. 346 (2005) 56.
[4] M. Tribet, C. Jegou, V. Broudic, C. Marques, P. Rigaux, A. Gavazzi, Mater. Sci. Eng. 9 (2010) 012009.
[5] V.V. Rondinella, M. Betti, F. Bocci, T. Hiernaut, J. Cobos, Microchem. J. 67 (2000) 301.
[6] C. Latrille, J. Ly, M. Herbette, Radiochim. Acta 94 (2006) 421.
[7] V. Robit-Pointeau, PhD Thesis, Paris XI University, France, 2005.
[8] S.U. Aja, S.A. Wood, A.E. Williams-Jones, Appl. Geochem. 10 (1995) 603.
[9] R.E. Connick, W.H. McVey, J. Am. Chem. Soc. 71 (1949) 3182.
[10] A.S. Solovkin, S.V. Tsvetkova, Russ. Chem. Rev. 31 (1962) 655.
[11] A.J. Zielen, R.E. Connick, J. Am. Chem. Soc. 78 (1956) 5785.
[12] R.E. Connick, W.H. Reas, J. Am. Chem. Soc. 73 (1951) 1171.
[13] B. Noren, Acta Chem. Scand. 23 (1969) 379.
[14] T. Sasaki, T. Kobayashi, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 45 (2008) 735.
[15] A. Bombard, PhD Thesis, Nantes University, France, 2005.
[16] Y.P. Davydov, D.Y. Davydov, L.M. Zemskova, Radiochemistry 48 (2006) 358.
[17] T. Kobayashi, T. Sasaki, I. Takagi, H. Moriyama, J. Nucl. Sci. Technol. 46 (2009) 142.
[18] C. Gautier, M. Bourgeois, H. Isnard, A. Nonell, G. Stadelmann, F. Goutelard, J. Chromatogr. A 1218 (2011) 5241.
[19] X.L. Hou, P. Roos, Anal. Chim. Acta 608 (2008) 105.
[20] D. Lariviere, V.F. Taylor, R.D. Evans, R.J. Cornett, Spectroc. Acta Part B Atom. Spectr. 61 (2006) 877.
[21] C. Agatemor, D. Beauchemin, Anal. Chim. Acta 706 (2011) 66.
[22] R.F.J. Dams, J. Goossens, L. Moens, Mikrochim. Acta 119 (1995) 277.
[23] I. Rodushkin, T. Ruth, D. Klockare, J. Anal. At. Spectrom. 13 (1998) 159.
[24] J.A. Olivares, R.S. Houk, Anal. Chem. 58 (1986) 20.
[25] S.H. Tan, G. Horlick, J. Anal. At. Spectrom. 2 (1987) 745.
[26] W. Klemm, G. Bombach, K.P. Becker, Fresenius J. Anal. Chem. 364 (1999) 429.
[27] P. Leonhard, R. Pepelnik, A. Prange, N. Yamada, T. Yamada, J. Anal. At. Spectrom. 17 (2002) 189.
[28] J. Nakagawa, Y. Tsuchiya, Y. Yashima, M. Tezuka, Y. Fujimoto, J. Health Sci. 50 (2004) 164.
[29] S.M. Wilbur, L.C. Jones, Open Chem. Biomed. Meth. J. 3 (2010) 135.
[30] N. Vajda, C.K. Kim, Anal. Chem. 83 (2011) 4688.
[31] T.J. Shaw, T. Duncan, B. Schnetger, Anal. Chem. 75 (2003) 3396.
[32] F. Chartier, H. Isnard, J.P. Degros, A.L. Faure, C. Frechou, Int. J. Mass Spectrom. 270 (2008) 127.
[33] Y.K. Agrawal, S. Sudhakar, Sep. Purif. Technol. 27 (2002) 111.
[34] A.G. Espartero, J.A. Suarez, M. Rodriguez, G. Pina, Appl. Radiat. Isot. 56 (2002) 41.
[35] C.H. Lee, M.Y. Suh, K.S. Choi, J.S. Kim, Y.J. Park, W.H. Kim, Anal. Chim. Acta 475 (2003) 171.
[36] L.E. Jassin, J. Radioanal. Nucl. Chem. 263 (2005) 93.
[37] E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, S.L. Maxwell, M.R. Nelson, Anal. Chim. Acta 310 (1995) 63.
[38] A. Quemet, R. Brennetot, E. Chevalier, E. Prian, A.L. Laridon, C. Mariet, P. Fichet, I. Laszak, F. Goutelard, Talanta 99 (2012) 207.
[39] E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, Anal. Chim. Acta 281 (1993) 361.
[40] E.P. Horwitz, M.L. Dietz, R. Chiarizia, H. Diamond, A.M. Essling, D. Graczyk, Anal. Chim. Acta 266 (1992) 25.
[41] E.P. Horwitz, D.R. McAlister, A.H. Bond, R.E. Barrans, Solvent Extr. Ion Exch. 23 (2005) 319.
[42] T.L. Tsai, C.C. Lin, T.C. Chu, Appl. Radiat. Isot. 66 (2008) 1097.
[43] S. Osvath, N. Vajda, Z. Molnar, E. Szeles, Z. Stefanka, J. Radioanal. Nucl. Chem. 286 (2010) 675.
[44] S.L. Maxwell, J. Radioanal. Nucl. Chem. 275 (2008) 497.
[45] K. Tagami, S. Uchida, Anal. Chim. Acta 592 (2007) 101.
[46] M. Rozmaric, A.G. Ivsic, Z. Grahek, Talanta 80 (2009) 352.
[47] S. Quidelleur, M. Granet, I. Laszak, H. Isnard, E. Pons-Branchu, R. Brennetot, C. Caussignac, J. Radioanal. Nucl. Chem. 280 (2009) 507.
[48] H. Hoshi, Y.Z. Wei, M. Kumagai, T. Asakura, Y. Morita, J. Alloys Compd. 374 (2004) 451.
[49] A. Pourmand, N. Dauphas, Talanta 81 (2010) 741.
[50] A. Vinsot, S. Mettler, S. Wechner, Phys. Chem. Earth 33 (2008) S75.
[51] C.E. McGinnis, J.C. Jain, C.R. Neal, Geostand. Newslett. 21 (1997) 289.
[52] C. Gotz, G. Geipel, G. Bernhard, J. Radioanal. Nucl. Chem. 287 (2011) 961.
[53] P. Brown, E. Curti, B. Grambow, Chemical Thermodynamics of Zirconium, OECD, Elsevier Science, 2005.
[54] AFNOR, NF T90-210 standard, 2009.
[55] P. Grinberg, S. Willie, R.E. Sturgeon, Anal. Chem. 77 (2005) 2432.
[56] J.B. Truscott, L. Bromley, P. Jones, E.H. Evans, J. Turner, B. Fairman, J. Anal. At. Spectrom. 14 (1999) 627.
[57] H.L. Xie, Y.J. Li, X.D. Nie, L.B. Li, Chin. Chem. Lett. 17 (2006) 945.
[58] ISO, EN ISO/IEC 17025 standard, 2005.
[59] J.M. Mermet, Spectroc. Acta Part B Atom. Spectr. 63 (2008) 166.
[60] J.M. Mermet, G. Granier, Spectroc. Acta Part B Atom. Spectr. 76 (2012) 214.
[61] K. El Mrabet, PhD Thesis, Paris University, France, 2008.
[62] J. Martins, C. Esteves, T. Simoes, M. Correia, C. Delerue-Matos, J. Agric. Food Chem. 59 (2011) 6847.
[63] A. Rachidi, D.B. Mazini, S. Barrijal, G. Duflos, P. Caillaud, Les Technol. Lab. 5 (2010) 4.
[64] X.J. Yang, C. Pin, Anal. Chim. Acta 458 (2002) 375.
[65] I. Rodushkin, E. Engstrom, D.C. Baxter, Anal. Bioanal. Chem. 396 (2010) 365.