Comparison of Solvent Extraction and Extraction Chromatography Resin Techniques for Uranium Isotopic Characterization in High-Level Radioactive Waste and Barrier Materials

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Abstract

The development of Deep Geological Repositories (DGP) to the storage of high-level radioactive waste (HLRW) is mainly focused in systems of multiple barriers based on the use of clays, and particularly bentonites, as natural and engineered barriers in nuclear waste isolation due to their remarkable properties.

Due to the fact that uranium is the major component of HLRW, it is required to go in depth in the analysis of the chemistry of the reaction of this element within bentonites.

The determination of uranium under the conditions of HLRW, including the analysis of silicate matrices before and after the uranium-bentonite reaction, was investigated. The performances of a state-of-the-art and widespread radiochemical method based on chromatographic UTEVA resins, and a well-known and traditional method based on solvent extraction with tri-n-butyl phosphate (TBP), for the analysis of uranium and thorium isotopes in solid matrices with high concentrations of uranium were analysed in detail.

In the development of this comparison, both radiochemical approaches have an overall excellent performance in order to analyse uranium concentration in HLRW samples. However, due to the high uranium concentration in the samples, the chromatographic resin is not able to avoid completely the uranium contamination in the thorium fraction.

Keywords

high-level radioactive waste; UTEVA; TBP; uranium; thorium

1. Introduction

Many researchers are devoted to the development of Deep Geological Repositories (DGP) to the storage of high-level radioactive waste (HLRW). Mainly the selected solution is based on a system of multiple barriers. Most of security of the disposal relies on an engineered barrier. Clays are ideal materials for natural and engineered barriers for nuclear waste isolation due to their high sorption capacity, low permeability, and swelling capability. In experimental conditions, it is found that the radioactive wastes are immobilised and their diffusion prevented trough physical-chemical mechanism with a clay barrier, such as precipitation, adsorption or a chemical reaction including the formation of secondary stable mineral phases. At present, bentonite is established as the most appropriate clay to form the engineered barrier in the DGP (Kaufhold et al., 2015).

Previous papers have analysed the capacity of retention and the kinetics reaction properties of bentonites in relation to several radionuclides such us ^{152}Eu (Alba et al., 2011; Mrabet et al., 2014; Villa-Alfageme et al., 2014), additionally trivalent simulators of actinides have been used to study their potential retention capacity of HLRW by bentonites (Alba et al., 2009; Alba and Chaín, 2007). Determination of radionuclides in HLRW is important for nuclear waste management. Because uranium is the major component of HLRW, it is required to go in depth in the analysis of the chemistry of this element within bentonites and other clays and for this, specific radiochemical methods must be developed. Additionally, uranium undergoes a decay chain containing several radioactive isotopes, such as thorium and polonium, that have also to be analysed within HLRW.

A complete control of the geochemical behaviour of uranium under the specific conditions created by HLRW includes the analysis of silicate matrices before and after the uranium-bentonite reaction. Because this step is crucial when performing a complete study of the reaction properties of the system uranium-bentonite. It is then key to develop suitable methods for this kind of determinations.

Among the methods proposed in the literature to determine uranium in several matrices, the most recent ones are focused on behaviour of selected fission products and actinides on UTEVA resin (Skinner and Knight, 2016), purification of uranium using *n*-tri butyl phosphate (TBP) as extractant and *n*-decanol as phase modifier (Pradeep and Biswas, 2017), extraction of uranium from simulated highly active feed in a micromixer-settler with 30% TBP and 36% TiAP solvents (Kumar et al., 2017), diluted salts by TBP and dialkyl amides (Ansari et al., 2016), or uranyl selective polymeric membrane electrodes (Badr et al., 2014). However, it is not analysed the suitability and the sensitivity of currently available radiochemical methods when uranium must be quantified in complex matrices related to HLRW.

For this reason, in this study the performances of one state-of-the-art and widespread radiochemical method for the analysis of uranium (and additionally thorium and polonium) isotopes in solid matrices (Mas et al., 2012) was analysed in detail when it is

applied to the measurement of matrices with high concentrations of uranium. This method combines a sequential separation of polonium-thorium-uranium using chromatographic UTEVA (Triskem Int.) resins and alpha spectrometry as radiometric measurement method. Additionally, a well-known and traditional method was used to compare the performance of the UTEVA resins. In that case, uranium and thorium were extracted using tri-n-butyl phosphate (TBP) as solvent extraction method, combined with AG1-X8 ion-exchange resin (Villa et al., 2011). This method has the main drawback that is time consuming, but is a routine and robust method to extract uranium, thorium and plutonium as part of the nuclear reprocessing process (Dey and Bansal, 2006).

The analysed matrices were uranyl nitrates, and bentonites after a hydrothermal treatment with uranyl nitrate. The main objective of this paper is to analyse the performance of the UTEVA method to be used as a routine method to evaluate uranium, and additionally thorium and polonium, in HLRW samples, where high uranium concentrations are expected.

2. Experimental

2.1. Sample preparation

In the comparative study between both radiochemical methods, a simulated HLW material was prepared by using two different matrices: uranyl nitrate 6-hydrate $UO_2(NO_3)_2 \cdot 6H_2O$ (supplied by Panreac) and FEBEX bentonite (from the Cortijo de Archidona deposit, Almería, Spain) (Enresa, 2000). Eight aliquots of this simulated HLW material were prepared and arranged in two groups.

In a first group, four aliquots of 0.0048 g of pure uranyl (0.0022 g of uranium) were analysed. ^{232}U, ^{229}Th and ^{209}Po were initially added to the aliquots as internal tracers. The first two aliquots (U-UTEVA-1 and U-UTEVA-2) were analysed following the UTEVA procedure later described, and only the second two aliquots (U-TBP-1 and U-TBP-2) were analysed following the TBP extraction procedure because it is a well-established method that we use as standard method of analysis.

105 In a second group, a total of four aliquots were prepared to check the performance of
106 UTEVA chromatographic resin. ^{232}U was added as internal tracer to those four aliquots in
107 order to quantify uranium separation through UTEVA columns and subsequent alpha
108 spectrometry measurement. First, two aliquots of uranyl nitrate were prepared containing
109 0.55 g of pure uranyl (corresponding to 0.260 g of uranium), and labelled as URANYL-1
110 and URANYL-2. These results were checked against the previous results from the first
111 group of aliquots.

112 Second, two aliquots were prepared by the hydrothermal reaction of 0.032 g of uranyl
113 (0.015 g of uranium) with 300 g FEBEX bentonite and 1.1 g of $ZrO(NO_3)_2 \cdot 7H_2O$ (as
114 tetravalent simulator of uranium) (Villa-Alfageme et al., 2014). After the hydrothermal
115 reaction, the solid and liquid remnant were examined. The solid product aliquot contained
116 reacted bentonite, zircon silicate and reacted uranium in both phases (labelled as ZrU-
117 Solid**)** (Villa-Alfageme et al., 2015). The liquid product aliquot contained dissolved
118 zircon and uranium (labelled as ZrU-Liquid). Additionally, in order to validate the
119 analysis of the two aliquots (ZrU-Solid and ZrU-Liquid), a comparison with gamma-ray
120 spectrometry technique was carried on.

121 *2.2. UTEVA chromatographic extraction method*

122 This procedure was adapted from (Mas et al., 2012) for the matrices described and it is
123 schematized in Fig. 1a.

124

125 1. *Digestion of the solid matrix*. Uranyl samples were digested with concentrated
126 nitric acid. Whereas bentonites were total digested by a combination of
127 HNO_3-HCl-HF (5 mL - 2 mL - 1 mL). Samples were gently heated and stirred
128 until complete dissolution and taken to dryness. Residue is again dissolved in
129 15 mL of 8 mol L^{-1} nitric acid.

2. Fe^{3+} carrier was added and pH raised to 8.5 with ammonium hydroxide to get the precipitation of iron hydroxides and actinides, the supernatant was removed by siphoning and discarded after settling for at least 8 h.

3. UTEVA column was preconditioned loading 3.5 mL of 3 mol L^{-1} HNO_3 three times.

4. Precipitate was dissolved in 15 mL of 3 mol L^{-1} HNO_3 - 1 mol L^{-1} $Al(NO_3)_3$ and 200 mg ascorbic acid. Dissolved sample was loaded into the resin.

5. *Elution of Am/Pu/Sr/Po/Ra*. The column was rinsed with 5 mL of 3 mol L^{-1} HNO_3 - 1 mol L^{-1} $Al(NO_3)_3$, afterwards with 10 mL of 3 mol L^{-1} HNO_3 three times and finally rinsed with 5 mL of 9 mol L^{-1} HCl (Oliveira and Carvalho, 2006).

6. *Elution of thorium*. Column was rinsed with 4 mL of 5 mol L^{-1} HCl - 0.05 mol L^{-1} oxalic acid five times eluting the thorium fraction.

7. *Elution of uranium.* The column was finally rinsed with 5 mL of 1 mol L^{-1} HCl three times eluting the uranium fraction.

2.3. TBP liquid-liquid solvent extraction method

The procedure followed for the uranium, thorium and polonium separation was adapted from the TBP procedure described in (Martínez-Aguirre, A., García-León, M., Ivanovich, 1994). It is outlined in Fig. 1b and is in detail below:

1. Pretreatment of the sample was carried out following step 1 described in *2.2*.

2. Uranium was precipitated with iron hydroxide and then taken to dryness.

3. The precipitate was dissolved in 10 mL of 8 mol L^{-1} HNO_3 and introduced into a 50 mL funnel for the solvent extraction.

4. 5 mL TBP were added to the funnel.

5. *Extraction of polonium*. The funnel was shaken for 15 min and the aqueous phase removed. Additionally, 10 mL of 8 mol L^{-1} HNO_3 were added and the process repeated. This was repeated three times to get an aqueous final solution of 30 mL containing the polonium.

6. 20 mL Xilene were added to the funnel.

7. *Extraction* of *thorium*. 15 mL of 1.5 mol L^{-1} HCl were added to the funnel and the solution shaken for 10 minutes. The aqueous phase was removed and the process was repeated three times to finally obtain 45 mL of HCl solution, containing thorium (including eventually some traces of uranium).

8. Extraction *of uranium*. 15 mL of MiliQ water were added and the solution was shaken for 10 minutes. The aqueous phase was removed and the process was repeated again three times to get 45 mL of H_2O solution, containing the uranium fraction.

9. Purification *of thorium*. Thorium solution obtained from the solvent extraction might present traces of uranium, for this reason it was essential to make a final purification of thorium. This was done by chromatographic separation. 6.5 mL of AG1-X8 resin was preconditioned adding 10 mL 9 mol L^{-1} of HCl twice. Thorium solution was taken to dryness, redissolved in 4 x 10 mL of 9 mol L^{-1} HCl and loaded into the resin. Resin was rinsed three times with 10 mL of 9 mol L^{-1} HCl. Uranium was retained by the resin and a purified Th fraction was obtained after the rinsing.

2.4. Alpha-particle spectrometry

Purified uranium and thorium phases were electroplated onto stainless steel discs (Martínez-Aguirre, A., García-León, M., Ivanovich, 1994) and measured and polonium was self-deposited onto a silver disk (Le Moigne et al., 2013). Counting of thorium,

uranium (electro-deposited) and polonium (self-deposited) isotopes was done using alpha detector PIPS type (Canberra) in an array comprised of 10 chambers. Measurements were undertaken at CITIUS (Centro de Investigación, Tecnología e Innovación, Universidad de Sevilla) laboratory at Universidad de Sevilla. The resolution of the peaks was found to be between 60 and 40 keV in all cases.

2.5. Gamma-ray spectrometry

The gamma-ray measurements were carried on by a Canberra n-type hyper-pure germanium gamma-ray detector (HPGe), located at Centro de Investigación, Tecnología e Innovación Universidad de Sevilla, CITIUS, with a nominal relative photo-peak efficiency of 60% at 1332 keV. The detector chamber was set up by a lead shield (10 cm thick standard lead) and an inner copper layer (5 mm) protecting the detector against environmental background radiation. The electronic chain consisted of a Canberra preamplifier 2002, and a Canberra Inspector 2000 DSP digital electronic chain. Gamma-ray spectra were analysed with Genie2K software.

Hydrothermal reaction products were collected by filtration using 0.45 μm Milipore filters and air-dried at 60 ºC. In order to measure natural ^{235}U activity in the sample, the gamma-ray emission of 143.8 keV (10.9% total yield) was selected.

Counting efficiency were calculated through Monte Carlo simulations using LABSOCS program (Hurtado and Villa, 2010) for the two counting geometries used: a 0.45 μm Millipore filter (ZrU-Solid) and a 100 mL cylindrical beaker (ZrU-Liquid). The composition of the solid sample was essential to compute correctly the simulated efficiency of this counting geometry.

Finally, Monte Carlo efficiencies were successful compared to the experimental ones obtained through the preparation of solid and aqueous standards spiked with a known amount of diluted uranyl solution.

2.6. Scanning electron microscopy

The morphology and chemical composition of the hydrothermal products were investigated using a SEM-FEG HITACHI S-4800 a scanning electron microscope equipped with an Xflash 4010 (BRUKER) for energy dispersive X-ray (EDX) analysis, located at Microscopy Service in ICMS (CSIC-Universidad de Sevilla).

3. Results and discussion

In this section, the obtained activities and isotopic ratios using both radiochemical methods are shown for each isotope fraction, and a discussion about the chemical recovery, cross-contamination, and maximum load capacity is carried out.

3.1. Uranium fractions

The results obtained for uranium activity for each aliquot and radiochemical method (TBP or UTEVA) are presented in Table 1 and Fig. 2. The components contributing to the combined measurement uncertainty such as count rates of sample and tracer, chemical recovery, tracer activity and mass of the sample and the tracer are calculated as one standard deviation.

Table 1 shows that both UTEVA column method and TBP method are capable of extracting the uranium from the analysed aliquot with an acceptable chemical yield. The chemical yield using the added ^{232}U internal tracer is around 45% for the solvent extraction method and 65% for the chromatographic extraction method.

With respect to the isotopic ratios, the values obtained for ^{234}U and ^{238}U ($^{234}U/^{238}U$), and ^{235}U and ^{238}U ($^{235}U/^{238}U$) are 0.45 and 0.095 respectively. These values do not correspond to those of natural uranium, ~1 and 0.046 respectively (Brennecka et al., 2010). However, this is in agreement with the values measure in commercial uranium reagents (Iturbe, 1992). Specifically, the $^{234}U/^{238}U$ isotopic ratio for U-UTEVA-2 sample is 20% lower than the ratios obtained for U-TBP-1, U-TBP-2 and U-UTEVA-1 samples, and it is also 40% higher for the $^{235}U/^{238}U$ ratio (see Table 1). It can be asserted that this behaviour is not due to the pre-treatment because this step is common for samples U-TBP-1, U-TBP-2, U-UTEVA-1 and UTEVA-2. This effect has not been observed in the analysis of

environmental samples following UTEVA method. Further studies should be conducted in that respect.

On the other hand, thorium was not detected in any of the two methods in the electrodeposited U fraction. Since thorium concentration is very small in uranyl matrices, thorium contamination in U fraction was evaluated from the analysis of ^{229}Th tracer.

One of the drawbacks of the use of UTEVA resins for uranium analysis is its limitation on the maximum accepted uranium concentration and its dependence on the type of matrix. The manufacturer recommends a maximum load capacity of the UTEVA resin (Triskem Int.) for U is approximately 0.015 g per 2 mL of the pre-packaged UTEVA columns. In order to check the UTEVA performance several experiments were carried out using only UTEVA columns for the analysis of two aliquots of pure uranyl (URANYL-1, URANYL-2). In the experiments with pure uranyl the maximum capacity of the column for the measurement of U was exceeded, since 0.260 g of uranyl was analysed. The results in Table 2 show that the chemical yields drop below 1% when exceeding the capacity of the column. These results indicate that for UTEVA method it is very important not exceed the load capacity, because the chemical yield decreases drastically, and therefore, an increase of the resin weight required to analyse samples with high concentration of uranium is cost-prohibitive.

Additionally, as in most analytical situations, the presence of significant concentrations of matrix elements can affect the proper operation of methods based on UTEVA resin (Horwitz et al., 1992). Therefore, the performance of these resins was evaluated also in matrices with high silicate content (high refractory fraction). In order to check the UTEVA performance several experiments were carried out using only UTEVA columns for the analysis of two aliquots of zirconium-uranium disilicate, formed after a hydrothermal treatment with FEBEX and $ZrO(NO_3)_2$-$UO_2(NH_3)_2$ (Villa-Alfageme et al., 2015), containing the solid fraction (ZrU-Solid) and the liquid one (ZrU-Liquid) (see Section 2.1. for description).

The characterization of the solid fraction was carried out through SEM micrographs of the reacted FEBEX with ZrO^{2+} (Fig. 3). The solid sample shows lamellar particles with a

chemical composition consisting mainly of ZrO^{2+} as interlayer cations (Figs. 3a–3d), and agglomerations of small particles with brilliant appearance (Fig. 3b, point 1) with a chemical composition compatible with phase containing zirconium (Fig. 3e). Moreover, the SEM/EDX analysis of a different zone (Fig. 3c, point 2) indicated that the treated clay mineral contain iron, probably released upon degradation of the container (Fig. 3f).

Finally, the ZrU-Solid and ZrU-Liquid samples were analysed using both UTEVA radiochemical method and alpha-particle spectrometry, and gamma-ray spectrometry technique. This all translates in the results shown in Table 2. The activity of 235U for ZrU-Solid and ZrU-Liquid samples through gamma-ray spectrometry was 7.6±1.5 Bq and 3.5±1.4 Bq respectively. Both methods give results in total agreement validating the use of UTEVA resin for the analysis of complex matrices.

3.2. Thorium fractions

The results obtained for the concentrations of thorium activity for each aliquot and radiochemical method are presented in Table 3.

Natural thorium is not measured in the Th fraction above the limit of detection through any of the radiochemical methods. The chemical yields obtained through ^{229}Th are similar to those obtained for the U fraction. According to the obtained thorium yields, both methods are apparently suitable for Th measurements.

However, the percentage of U in the Th fraction of the analysed samples has been obtained and shown in Fig. 4. Note that a significant difference between the two methods (UTEVA and TBP) is shown in relation to the Th detected. In the samples separated by UTEVA chromatography columns (U-UTEVA-1 and U-UTEVA-2), U isotopes peaks clearly appear in the Th fraction contaminating the results. The contamination of U has been possibly detected because the analysed samples were high activity samples (about 10 Bq). This contamination of U in the Th fraction is not usually observed in the analysis of low-level environmental samples by UTEVA method because the percentage of the initial U activity presented in the spectra of Th was calculated to be a 1.5%

290 approximately. On the other hand, this contamination does not exist in the samples
291 separated by the TBP solvent extraction method.

292 Therefore, the U-Th separation procedure using UTEVA columns efficiently separates
293 the Th fraction from uranium, but about 1.5% of the initial uranium contaminates the Th
294 fraction (Mas et al., 2012). This is especially relevant in those matrices where the activity
295 of U is at least one order of magnitude higher than the activity of Th.

296 *3.3. Polonium fraction*

297 The results obtained for the concentrations of polonium activity for each aliquot and
298 radiochemical method are presented in Table 4. Radiochemical yields around 55-60% are
299 obtained for both methods using ^{209}Po as tracer.

300 It must be highlighted the need to place the silver disk vertically during the
301 autodeposition process, and finally washing it with acetone and distilled water to avoid
302 the deposition of U traces on the disk. This is important in this case due to the very high
303 concentration of uranium in the sample.

304 Finally, traces of natural ^{210}Po in uranyl samples were detected. The origin is the decay
305 chain of ^{238}U. However, high uncertainties for the activities are obtained because these
306 activities are very close to the minimum detectable activity.

307 **4. Conclusions**

308 The standard TBP method has proven to be an efficient and robust technique to analyse
309 uranium and thorium concentration for all kinds of samples (either HLRW or low-level
310 environmental samples). On the other hand, the uranium-thorium separation method
311 using UTEVA columns works efficiently even applied in complex matrices. However,
312 UTEVA radiochemical method reaches a total separation of the uranium fraction from
313 thorium fraction, but a maximum of 1.5% of the initial uranium contaminates the Th
314 fraction. This is especially relevant in those matrices where the concentration of U is

orders of magnitude higher than that of Th. Therefore, further studies should be carried out to elucidate the use of UTEVA resins in the analysis of HLRW materials.

Acknowledgements

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333 Tables

334

335 **Table 1.** Activity (Bq) and isotopic ratios of the uranium isotopes using the
336 radiochemical method with TBP (U-TBP-1 and U-TBP-2) and the radiochemical method
337 with UTEVA (U-UTEVA-1 and U-UTEVA-2). MDA is the Minimum Detectable
338 Activity.

Sample	**^{234}U (Bq)**	**± σ**	**^{235}U (Bq)**	**± σ**	**^{238}U (Bq)**	**± σ**
U-TBP-1	10.8	0.3	2.19	0.07	23.6	0.7
U-TBP-2	10.7	0.3	2.18	0.07	23.4	0.7
U-UTEVA-1	9.9	0.3	2.18	0.07	22.1	0.7
U-UTEVA-2	9.0	0.3	3.25	0.10	23.9	0.7
Sample	**^{234}U/^{238}U**	**^{235}U/^{238}U**	**^{232}U recovery**	**MDA ^{234}U (Bq)**	**MDA ^{235}U (Bq)**	**MDA ^{238}U/ (Bq)**
U-TBP-1	0.46	0.093	44%	0.05	0.08	0.06
U-TBP-2	0.46	0.093	47%	0.05	0.07	0.06
U-UTEVA-1	0.45	0.099	63%	0.04	0.08	0.05
U-UTEVA-2	0.38	0.136	65%	0.05	0.09	0.05

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Table 2. Activity (Bq) and isotopic ratios (in activity) of the uranium isotopes using the UTEVA radiochemical method for pure uranyl matrices (URANYL-1 and URANYL-2) and the product of a hydrothermal treatment with FEBEX and $ZrO(NO_3)_2$-$UO_2(NH_3)_2$ in the solid fraction (ZrU-Solid) and liquid (ZrU-Liquid). Chemical yields are not included for samples under hydrothermal treatment, since most of the uranium is lost in that process, not during the radiochemical procedure. MDA is the Minimum Detectable Activity.

Sample	**^{234}U (Bq)**	**± σ**	**^{235}U (Bq)**	**± σ**	**^{238}U (Bq)**	**± σ**
URANYL-1	666	79	144	17	1541	183
URANYL-2	548	92	78	13	1120	189
ZrU-Solid	52.9	2.4	7.9	0.4	109.3	5.0
ZrU-Liquid	16.1	4.6	3.0	0.7	36.2	7.1
Sample	**^{234}U/^{238}U**	**^{235}U/^{238}U**	**^{232}U recovery**	**MDA ^{234}U (Bq)**	**MDA ^{235}U (Bq)**	**MDA ^{238}U/ (Bq)**
URANYL-1	0.432	0.0938	0.54%	0.05	0.08	0.06
URANYL-2	0.489	0.0695	0.30%	0.05	0.07	0.06
ZrU-Solid	0.485	0.0723	--	0.04	0.08	0.05
ZrU-Liquid	0.446	0.0830	--	0.05	0.09	0.05

Table 3. Activity (Bq) of thorium isotopes using the radiochemical procedure with TBP (U-TBP-1 and U-TBP-2) and the radiochemical process with UTEVA (U-UTEVA-1 and U-UTEVA-2). The chemical recovery is shown through ^{229}Th. MDA is the Minimum Detectable Activity.

Sample	**^{230}Th(Bq)**	**± σ**	**^{232}Th (Bq)**	**± σ**	**^{229}Th recovery**	**MDA ^{230}Th (Bq)**	**MDA ^{232}Th (Bq)**
U-TBP-1	< MDA		< MDA		60	0.12	0.06
U-TBP-2	< MDA		< MDA		52	0.04	0.05
U-UTEVA-1	< MDA		< MDA		71	0.07	0.03
U-UTEVA-2	< MDA		< MDA		51	0.05	0.05

Table 4. Activity (Bq) of ^{210}Po using the radiochemical procedure with TBP (U-TBP-1 and U-TBP-2) and the chemical procedure with UTEVA (U-UTEVA-1 and U-UTEVA-2). MDA is the Minimum Detectable Activity.

Sample	^{210}Po (Bq)	± σ	MDA (Bq)
U-TBP-1	0.00025	0.00013	0.00024
U-TBP-2	0.00064	0.00017	0.00021
U-UTEVA-1	0.00069	0.00017	0.00016
U-UTEVA-2	0.00045	0.00011	0.00016

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398 Table captions

399 **Table 1.** Activity (Bq) and isotopic ratios of the uranium isotopes using the
400 radiochemical method with TBP (U-TBP-1 and U-TBP-2) and the radiochemical method
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402 Activity.

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406 the solid fraction (ZrU-Solid) and liquid (ZrU-Liquid). Chemical yields are not included
407 for samples under hydrothermal treatment, since most of the uranium is lost in that
408 process, not during the radiochemical procedure. MDA is the Minimum Detectable
409 Activity.

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411 (U-TBP-1 and U-TBP-2) and the radiochemical process with UTEVA (U-UTEVA-1 and
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413 Detectable Activity.

414 **Table 4.** Activity (Bq) of ^{210}Po using the radiochemical procedure with TBP (U-TBP-1
415 and U-TBP-2) and the chemical procedure with UTEVA (U-UTEVA-1 and U-UTEVA-
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Figures

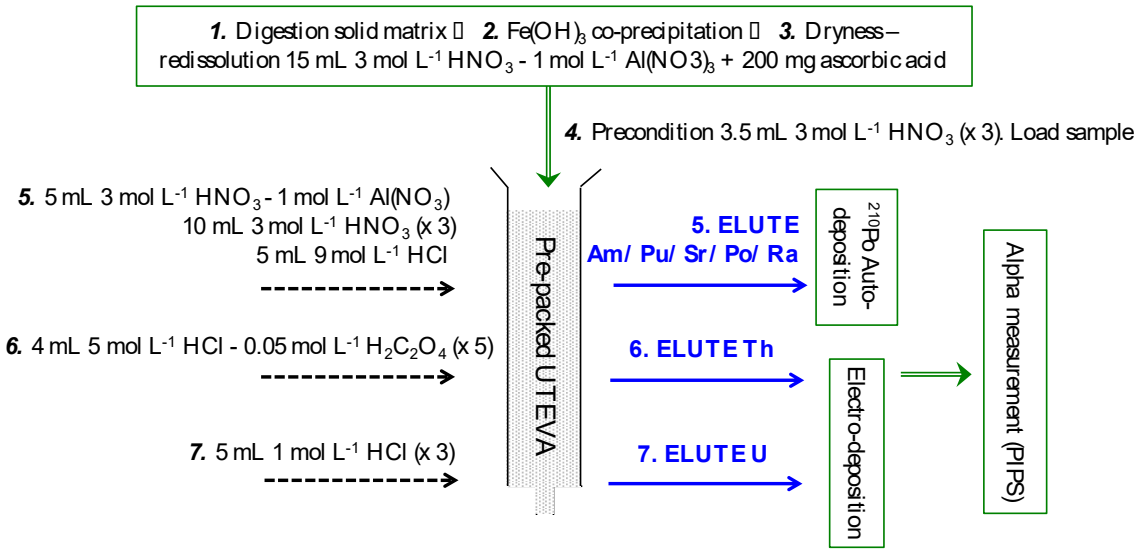
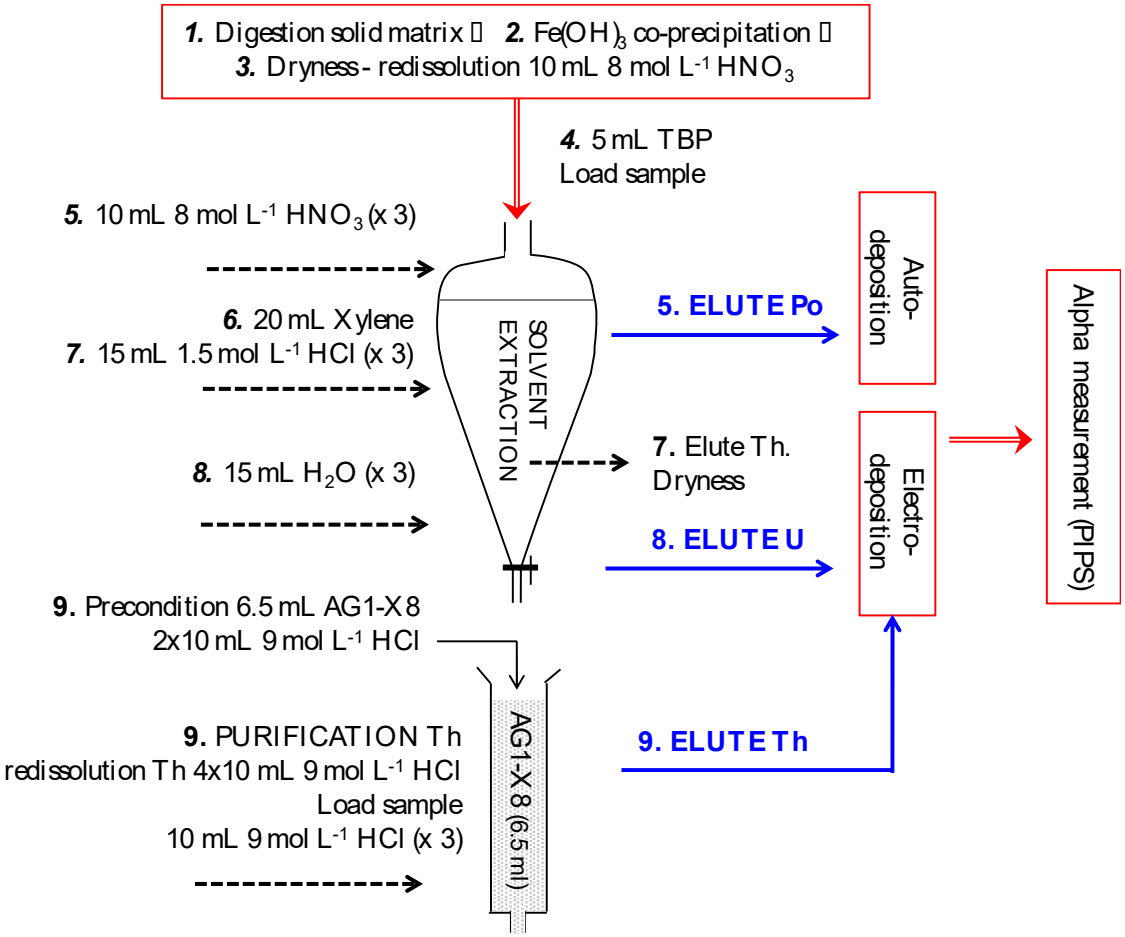


Fig. 1a. UTEVA chromatographic extraction method.



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431 **Fig. 1b.** TBP liquid-liquid solvent extraction method.

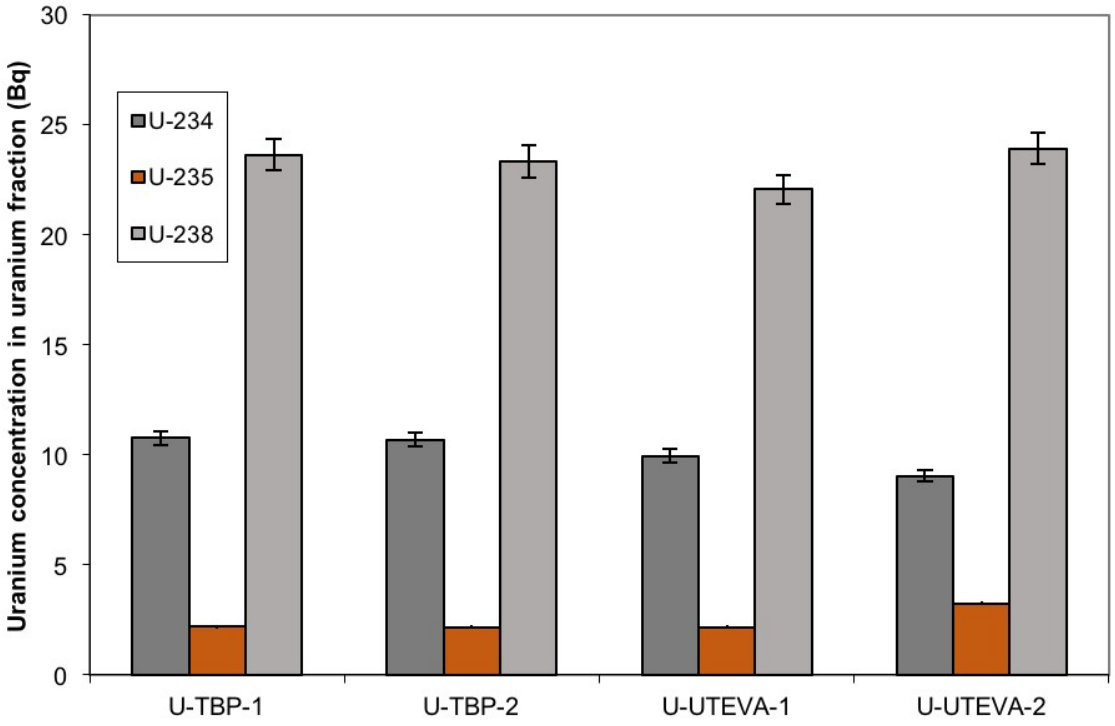
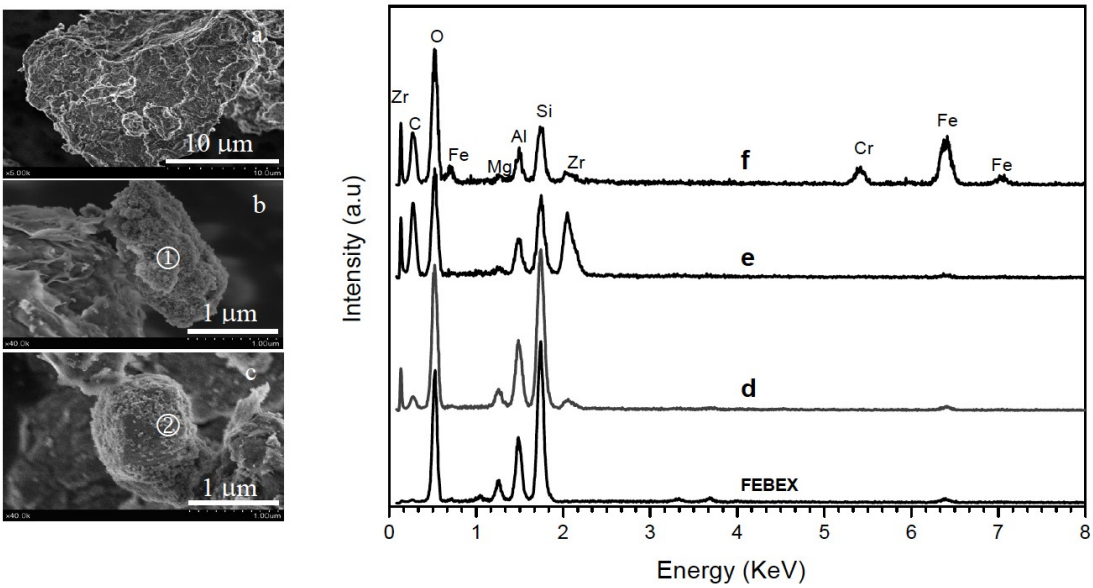


Fig. 2. Activity concentration (Bq) and isotopic ratios of the uranium isotopes using the radiochemical method with TBP (U-TBP-1 and U-TBP-2) and the radiochemical method with UTEVA (U-UTEVA-1 and U-UTEVA-2).



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444 **Fig. 3**. SEM micrographs of the reacted FEBEX with a solution of ZrO2+: (a) a general
445 view; (b) bright particles agglomerates mainly made up of zirconium; and (c) iron
446 particles coming from container degradation. EDX spectra of: (d) lamellar particles; (e)
447 zirconium agglomerates; (f) iron particles; and a FEBEX spectrum as reference.

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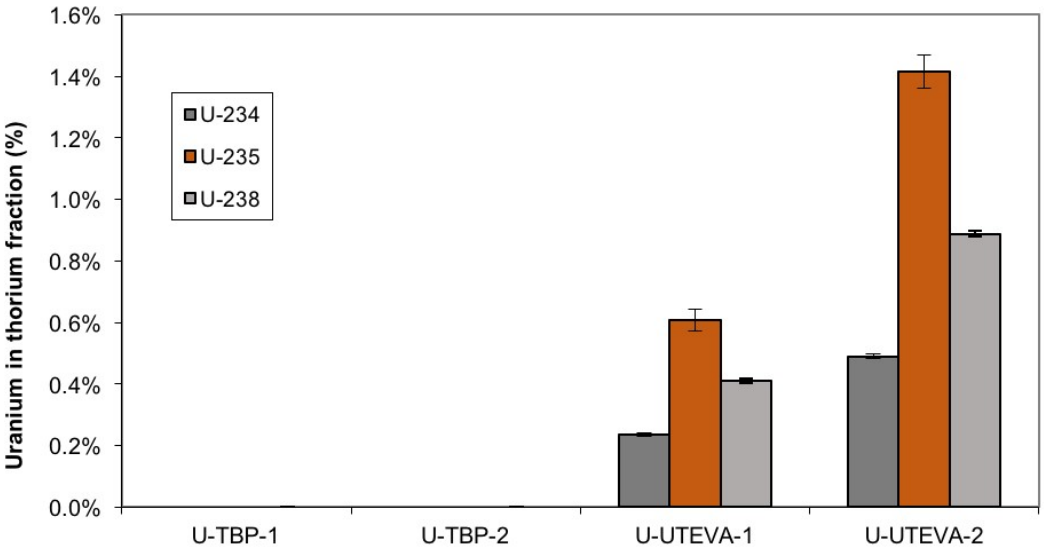

Fig. 4. Percentage of uranium measured in thorium fraction in uranyl aliquots measured by TBP (U-TBP-1 and U-TBP-2) and UTEVA (U-UTEVA-1 and U-UTEVA-2).

Figure captions

Fig. 1a. UTEVA chromatographic extraction method.

Fig. 1b. TBP liquid-liquid solvent extraction method.

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