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U and Pu separation with U/TEVA resin: Influence of some parameters on chromatographic cycle performances

Christophe Maillard¹ · Didier Maloubier² · Olivier Boulay¹ · Victor Savigny¹ · Alexandre Quemet¹

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Abstract

Due to unexpected Pu behavior using the U/TEVA resin and the most-recognized reagents, some key separation stages need to be studied for the U–Pu separation: Pu valency adjustment, Pu elution solution composition, resin loading rate and Pu elution solution stability over time. The new Pu elution solution developed in the study, composed of 3×10^{-3} mol L⁻¹ ascorbic acid / 3×10^{-3} mol L⁻¹ sulfamic acid / 2 mol L⁻¹ HNO₃, helps obtaining a more robust method: recovery yields over 80% and decontamination factor up to 2×10^4 . The best separation performances were obtained when the new Pu elution solution was freshly prepared, the resin loading rate did not exceed 30% and with a waiting time for the valency adjustment between the addition of H₂O₂ and the start of the chromatographic cycle set at 42 h regardless the Pu quantity involved.

Keywords Chromatography · Separation · Uranium · Plutonium · Pu valency adjustment · U/TEVA

Introduction

Uranium and plutonium are the two most essential elements of the nuclear fuel cycle. Uranium is present in all the steps of the nuclear fuel cycle, from the uranium mine to the reprocessing process [1]. The accurate measurement of uranium isotope and mass fraction is necessary for safeguards and forensics purposes or to verify material conformity. Plutonium is present only in the reprocessing process or in reprocessed fuel in large quantity: at 5–10% in weight for fuel used in pressurized water reactor and at 20–30% in weight for fuel used in fast-neutron reactor [2]. Pu isotope composition and mass fraction is important to verify material conformity, for nuclear accountancy or to manage criticality issues.

U and Pu isotopic composition measurement is mostly performed by Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) or Thermal Ionization Mass Spectrometry

(TIMS) [3]. A bias is observed when two elements possessing an isotope of equal mass are present in the sample (for instance ²³⁸U/²³⁸Pu and called isobaric interference). To prevent isobaric interferences it is usually required to purify each element prior analysis. Using a purified fraction of an element is also useful to avoid poor ionization yield due to the presence of a major element in the mass spectrometer ion source [4].

Several methods relative to the U–Pu separation prior mass spectrometry analysis have been described in literature. U–Pu separation has been performed for many years by microporous (AG-1X4, Dowex 1X4) [5–7] and macroporous (AG MP-1) anionic resins [8, 9]. Later on the resins composed of inert supports on which specific extractants are impregnated, appeared. The TEVA (for TEtraValent Actinides) resin [10] is recommended by the ISO 8299:2019 standard [11] dedicated to determine isotopic and elemental U and Pu concentrations of nuclear materials in nitric acid solutions by TIMS.

Morgenstern et al. [12] used another resin also composed of an inert support impregnated by an extractant: the U/TEVA resin (for Uranium and TEtraValent Actinides). This resin is made of polymer Amberlite XAD-7 microspheres soaked into dipentyl-pentylphosphonate and is used to obtain purified fractions of trivalent elements, Pu, Np and U. Plutonium at oxidation state IV and uranium at oxidation state VI are very well retained on the UTEVA resin, much

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unlike trivalent element [10]. The weight distribution ratios (D_w) are 1500 mL g⁻¹ for Pu(IV) and 500 mL g⁻¹ for U(VI) in [HNO₃] = 6 mol L⁻¹ [13]. Pu needs to be in tetravalent form to be fixed on the resin. The valency adjustment was performed using H₂O₂, that reduces the Pu to Pu(III) [14]. However, unlike the TEVA resin, the U/TEVA resin does not require H₂O₂ destruction by heating to obtain Pu(IV). It is empirically supposed that, when in contact with the extractant, Pu is reoxidized in Pu(IV). As the III valency elements are not retained on the resin, the reduction of Pu(IV) to Pu(III) with reductive reagents allow to eluate specifically the Pu from the resin. For uranium, decreasing the eluent acidity leads to a sharp drop in the affinity of U for the UTEVA resin (D_w U(VI) < 4 mL g⁻¹ in [HNO₃] = 0.02 mol L⁻¹) and allows its recovery. This method implemented by Morgenstern used a single column of U/TEVA resin with only non-corrosive reagents suitable with glove box environment.

The Analytical Methods Committee (CETAMA) is a unit of the French Alternative Energy and Atomic Energy Commission (CEA) set up to improve the measurement quality of nuclear facilities [15]. The CETAMA provides certified reference material (CRM), organizes inter-laboratory comparison (ILC) and takes part in the standardization of analytical methods. CETAMA proposes suitable scientific and technical developments. One CETAMA working group is dedicated to the U/Pu separation and writes a method designated as “method N°397”. This method proposes two separation protocols using either an anionic resin or the U/TEVA resin. The protocol using the U/TEVA resin offers some modifications compared to the method developed by Morgenstern et al. [12]. The hydroxylammonium chloride reagent used to elute Pu, potentially carcinogenic [16], is replaced by sulfamic acid. Hydroxylammonium chloride was chosen as a Pu(IV) reductive reagent, sulfamic acid was chosen as an anti-nitrous reagent which avoids an early destruction of the ascorbic acid. The possibility to use a valency adjustment using the Fe(II)-NaNO₂ system [17–20] was also tested and proposed.

This paper aims at studying the influence of several parameters on U/Pu separation performances (Pu and U recovery yields, Pu decontamination in regard of U and U decontamination in regard of Pu): the Pu initial oxidation state, using hydroxylammonium chloride reagent and using of sulfamic acid reagent for Pu elution, the Pu valency adjustment with H₂O₂ or Fe(II)-NaNO₂ systems, the resin loading rate and the elution solutions stability over time. This paper summarizes the different optimizations and testing performed during the method N°397 reduction.

Experimental

Reagents

All solutions were prepared using ultra-pure water (resistivity 18.2 MΩ cm) obtained from a Milli-Q system (Millipore, France). Nitric acid ($w_t = 68\%$) and hydrogen peroxide ($w_t = 30\%$) were chemically pure (Normapur grade) and purchased from VWR. AgO powder was obtained from Sigma-Aldrich ($w_t(\text{Ag}) = 84.8\text{--}89.3\%$). The ascorbic acid, hydroxylammonium chloride and sulfamic acid powder were prepared from powder with > 99% purity (RP Normapur, VWR).

Fe(II) solution (0.5 mol L⁻¹) was prepared by dissolution of FeSO₄·7H₂O powder (> 99% purity, Merck) in water containing H₂SO₄ 48% (500 μL per L of water).

NaNO₂ solution (3 mol L⁻¹) was prepared by dissolution of the powder (> 99% purity, Merck) in water containing NaOH 48% (500 μL per L of water).

Three Pu elution solutions were prepared. The first solution containing hydroxylammonium chloride (NH₃OH-Cl) reagent (hereafter referred to as Pu/H solution) consisted of 3.10⁻³ mol L⁻¹ ascorbic acid / 3.10⁻³ mol L⁻¹ hydroxylammonium chloride / 2 mol L⁻¹ HNO₃. The second solution had the same composition as the Pu/H solution except for the medium (2 mol L⁻¹ HCl instead of 2 mol L⁻¹ HNO₃) (hereafter referred to as Pu/H* solution). The third solution, containing sulfamic acid (hereafter referred to as Pu/S solution) consisted of 3.10⁻³ mol L⁻¹ ascorbic acid / 3.10⁻³ mol L⁻¹ sulfamic acid / 2 mol L⁻¹ HNO₃.

U/TEVA extraction resin was purchased from Triskem International as 2 mL prepacked columns with 100–150 μm particle size (corresponding to 0.78 g of resin). The columns were used in gravity mode. The flow-rate was approximately 25 mL h⁻¹ ($v = 50$ cm h⁻¹).

“In house” radioactive solutions were used to study the Pu and U behavior during the chromatographic cycle by alpha spectrometry. A uranium solution enriched in ²³³U isotope and a plutonium enriched in ²³⁸Pu isotope were selected for the high alpha specific activity (A_{sp}) of their main isotope (²³³U: $A_{sp} = 3.57 \times 10^8$ Bq g⁻¹ and ²³⁸Pu: $A_{sp} = 6.33 \times 10^{11}$ Bq g⁻¹) and were mixed depending the experiments. A solution, enriched in ²³⁹Pu ($A_{sp} = 2.30 \times 10^9$ Bq g⁻¹) and a solution of natural uranium were also used, mainly for the resin loading rate study. The isotope composition of these “in-house” solutions was determined by Thermal Ionization Mass Spectroscopy (Table 1).

A solution (called ²³⁸U-²³⁹Pu) with U/Pu mass ratio of 4.2 ([U] = 316 mg L⁻¹ and [Pu] = 75 mg L⁻¹) was prepared using an ‘in house’ solution enriched in ²³⁸U isotope and a solution enriched ²³⁹Pu isotope. A CRM-138 solution (U/

Table 1 Isotope abundance of U and Pu for the selected solutions

Solutions	Date	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
^{233}U	2006/07/06*	98.64	0.548	<0.01	<0.01	0.797
^{238}U - ^{239}Pu	2018/10/31**	–	0.0170	0.737	0.0270	99.2
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
^{238}Pu	2015/02/26*	84.7	13.6	1.52	0.045	0.226
^{239}Pu	2011/02/14*	0.263	89.3	9.82	0.340	0.223
^{238}U - ^{239}Pu	2018/10/31**	0.1445	68.3	28.7	0.776	2.07
CRM-138	1987/10/01**	0.010	91.8	7.92	0.227	0.033

(*) date of TIMS analysis, (**) date of the certificate

Pu mass ratio = 2.10^{-3}) corresponding to a concentration of 96.5 mg L^{-1} Pu and containing U impurity ($193 \mu\text{g L}^{-1}$ U) was also used. It was purchased from the National Institute of Standards & Technology (NIST). The isotope composition of these solutions was given by the certificate (Table 1).

Instruments

The alpha spectrometer used for Pu and U analysis is a Canberra Alpha Analyst with 12 chambers equipped with PIPS (Passivated Implanted Planar Silicon) detectors and APEX software for spectrum treatment.

The spectrophotometer used for Pu analysis is a UV/Vis Varian Cary-4000. Pu is quantitatively oxidized to Pu(VI) by AgO and measured at 830 nm [21].

The mass spectrometer used for uranium analysis was an ICP/MS Thermo X7 serie II. It is equipped with a spray chamber and a discrete dynodes detector.

An overall uncertainty of 10% taking into account the dilutions, the volumes of the solutions and analysis results by alpha spectrometry and UV/Vis spectrophotometry was applied to each recovery yield value (4% for the U analysis by ICP-MS).

Uranium–plutonium separation procedures

The operating procedure, developed in this work, is made of 7 steps (Fig. 1):

- (1) Before entering the glove box where all the experiments were performed, the U/TEVA column was conditioned with 5 mL of 6 mol L^{-1} HNO_3 .
- (2) A plutonium acidification step and a valency adjustment step were needed before loading the sample onto the column. The nitric concentration was first adjusted to 6 mol L^{-1} by the addition of concentrated nitric acid. Then, the valency adjustment step was performed. Two Pu valency adjustment methods were used: using H_2O_2

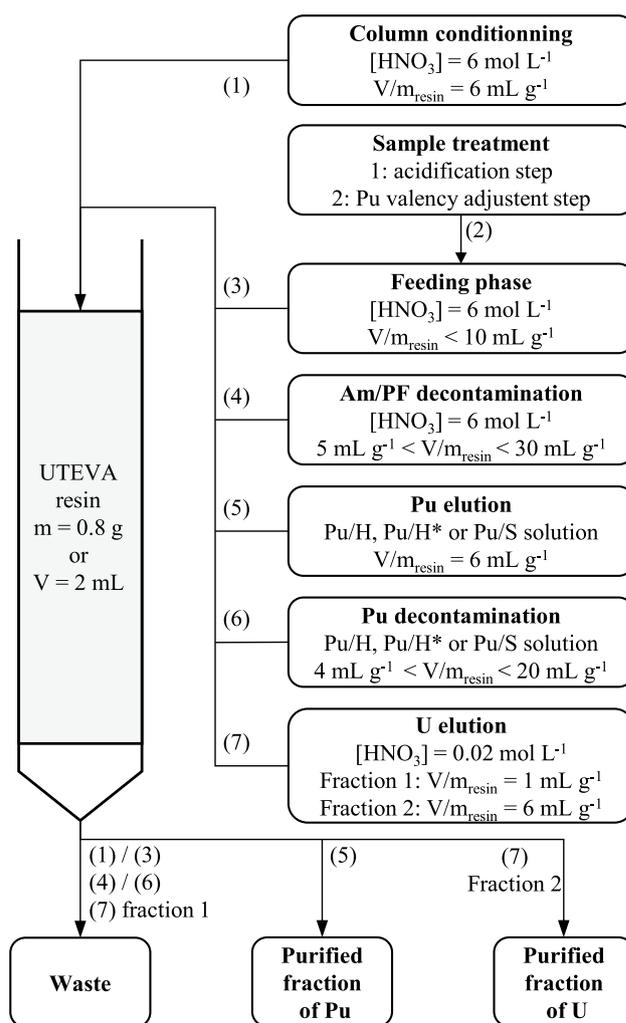


Fig. 1 Separation scheme used for the U and Pu separation study

or Fe(II)/ NaNO_2 system. With the H_2O_2 system, the H_2O_2 was added to achieve a concentration of 0.1 mol L^{-1} in the solution. The solution was then kept a certain time to ensure the valency adjustment was completed.

The optimum time will be discussed in the results and discussion section. The valence adjustment with Fe(II)/NaNO₂ method was done by adding 100 µL of 0.5 mol L⁻¹ ferrous sulfate heptahydrate solution to the sample, mixing, waiting for 20 min, then adding 100 µL of a 3 mol L⁻¹ sodium nitrite solution and letting the mixture sit for an entire night. Uranium, mainly in (VI) oxidation state in nitric acid solution, is not affected by these two valency adjustment methods (H₂O₂ or Fe(II)/NaNO₂).

- (3) After introducing the resin in the glove box, the sample is deposited on top of the column.
- (4) The resin is then washed with 4 mL to 23 mL, corresponding to 5 to 30 mL g⁻¹ of resin, of 6 mol L⁻¹ HNO₃ to decontaminate the column from trivalent elements (americium or fission products).
- (5) Pu is eluted by 4.5 mL, corresponding to 6 mL g⁻¹ of resin, of Pu/S or Pu/H or PuH* solutions.
- (6) The remaining Pu is washed by 3 mL to 16 mL, corresponding to 4 to 20 mL g⁻¹ of resin, of Pu/S or Pu/H or Pu/H* solutions.
- (7) Finally, U is eluted by 0.02 mol L⁻¹ HNO₃. 0.8 mL corresponding to 1 mL g⁻¹ of resin is first poured and disposed of as dead volume. Then 4.5 mL, corresponding to 6 mL g⁻¹ of resin are poured and recovered.

Experiments

Several experiments were implemented to study the influence of the different parameters on the U/Pu separation performances: the Pu initial oxidation state, the Pu/H solution use, the Pu/S solution use, the Pu adjustment valency conditions, the resin loading rate (*i.e.* n(Pu + U)/resin capacity ratio) and the Pu elution stability over time. An experiment was also implemented to study the recovery yield of uranium impurity in a Pu matrix. All experiments (1 to 17) and their operational conditions are summarized in the Table 2. Experiments 6, 7, 8 and 12 were performed with the ²³⁸U-²³⁹Pu solution and experiment 17 from the CRM-138 solution. The other experiments were performed from a mix of ²³³U, ²³⁹Pu, ²³⁸Pu, and natural uranium solutions (Table 1).

Influence of the Pu initial oxidation state

Two experiments were carried out to evaluate the influence of the Pu initial oxidation state on the separation performances: from a Pu(IV/VI) solution (experiment 1) and from a Pu(VI) solution (experiment 2). For both experiments, the U and Pu masses involved were the same: m(U) = 310 µg, m(Pu) = 3.3 µg. In experiment 1, the Pu oxidation state was Pu(IV/VI). In experiment 2, the 100% Pu(VI) solution was ensured by adding AgO

Table 2 Summary and results of the experiments

Exp	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
m(U) (µg)	310	310	1000	1000	400	632	632	632	28	1000	10,000	632	28	28	20,000	56,000	0.94
m(Pu) (µg)	3.3	3.3	10	10	55	150	150	150	0.020	10	100	150	6000	6000	2000	5000	480
Resin capacity	<1%	<1%	1.4%	1.4%	<1%	1.1%	1.1%	1.1%	<1%	1.4%	14%	1.1%	8%	8%	30%	82%	<1%
Pu oxidation by Ag(II)	No	Yes	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Pu valency	H ₂ O ₂	Fe(II)NaNO ₂	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂	Fe(II)NaNO ₂	H ₂ O ₂	Fe(II)NaNO ₂									
Time (*)	2 h	2 h	2 h	2 h	20 h	2 h	20 h	20 h	2 h	2 h	2 h	20 h	2 h	42 h	42 h	42 h	20 h
Pu elution solution	Pu/H	Pu/H*	Pu/S	Pu/S	Pu/S	Pu/S	Pu/S	Pu/S	Pu/S	Pu/S	Pu/S						
RY(Pu)	88%	90%	5%	100%	24%	14%	10%	90%	80%	93%	89%	83%	19%	80%	98%	99%	90%
DF(Pu/U)	>924	>625	>10	>430	7900	—	—	—	>3100	>270	>200	—	>400	>2.10 ⁴	>200	14	—
RY(U)	65%	86%	98%	91%	100%	99%	100%	93%	64%	98%	98%	100%	54%	48%	91%	64%	90%
DF(U/Pu)	1180	178	3.3	>2450	1000	2.8	—	—	>135	>2700	441	—	2.10 ⁴	2200	3326	1500	3000

(%) Time between the Pu valency adjustment step and the chromatographic cycle

powder: molar ratio $\text{AgO}/\text{Pu} = 4$ (contact: overnight). The U/Pu separation procedure was then applied. Pu valency adjustment was performed with the H_2O_2 method and a waiting time of 2 h. The Pu elution was performed using the Pu/H solution.

Influence of using the Pu/H solution

Five experiments (experiments 3 to 7 in Table 2) were performed to evaluate the U/Pu separation performances when the Pu/H solution was used for Pu elution and Pu column decontamination. The resin loading rate was below 2%. The Pu valency adjustment conditions were different. Experiments 3, 4 and 6 were performed using the H_2O_2 method and the time was set at 2 h between the Pu adjustment valency step and the chromatographic cycle. Experiment 5 was also performed using the H_2O_2 method but with a time set at 20 h between the Pu adjustment valency step and the chromatographic cycle. Experiment 7 was performed using the $\text{Fe(II)}/\text{NaNO}_2$ method. The time was set at 20 h between the Pu adjustment valency step and the chromatographic cycle.

Influence of substituting hydroxylammonium chloride by sulfamic acid

Substituting hydroxylammonium chloride by sulfamic acid was studied. Experiments 3, 4 and 6 used the Pu/H solution and experiments 9 and 10 used the Pu/S solution for the Pu elution. These experiments were performed using a resin loading rate below 2% and using the H_2O_2 method for the Pu valency adjustment. The time was set at 2 h between the Pu adjustment valency step and the chromatographic cycle.

Influence of the Pu valency adjustment conditions

Experiments 9 to 14 used the Pu/S solution for Pu recovery. Experiments 9, 10 and 12 were performed with a resin loading rate below 2%. Experiments 9 and 10 used the H_2O_2 method for the Pu adjustment valency. The time between the Pu adjustment valency step and the chromatographic cycle was set at 2 h. Experiment 12 was performed using the $\text{Fe(II)}/\text{NaNO}_2$ method. The time between the Pu adjustment valency step and the chromatographic cycle was set at 20 h. Additional experiments (noted experiment 11, 13 and 14) were performed using a resin loading rate of 8% for experiments 13 and 14 and 14% for experiment 11. They were performed using the H_2O_2 method. The time between the Pu adjustment valency step and the chromatographic cycle was set at 2 h for experiments 11 and 13 and at 42 h for experiment 14.

Influence of the resin loading rate

The resin loading rate was increased to study the influence of the Pu and U initial mass: 8% for experiment 14, 30% for experiment 15 and 82% for experiment 16. Other parameters were the same in these 3 experiments: H_2O_2 method for the Pu adjustment valency, time between the Pu adjustment valency step and the chromatographic cycle set at 42 h and Pu/S solution for the Pu elution.

Pu elution solution stability

The U/Pu separation performance as function of time between the solution preparation and its use was studied for the Pu/H and Pu/S solution. At $t = 0$, the Pu/H and Pu/S solutions were prepared. Two separations using the Pu/H and Pu/S solutions for Pu elution solution were performed to obtain the Pu recovery yield. These separations, performed at $t = 0$, were used as reference. Then, each Pu/H and Pu/S solution were split into two solutions: one solution was stored on a laboratory bench and one solution was stored in a refrigerator to be protected from light. Different separations using the same experimental conditions (loading rate $< 2\%$, H_2O method, time = 2 h, Pu/S solution) were performed after different storage day: $t = 7, 21$ and 30 days for the Pu/H solution and $t = 1, 2, 3, 7, 15, 21$ and 30 days for the Pu/S solution.

U/Pu separation in Pu matrix solution

Experiment 17 was performed according to a U–Pu separation procedure optimized for a Pu matrix sample. The goal was to isolate the uranium, present as impurity. It was carried out with a CRM-138 solution. The Pu valency treatment and the Pu elution were performed using respectively the $\text{Fe(II)}/\text{NaNO}_2$ method and the Pu/S solution. Compared to the separation scheme described in Fig. 1 there were some modifications. The volume used for Pu elution is greater ($V/m_{\text{resin}} = 19 \text{ mL g}^{-1}$). It is the same order of magnitude as the total volume used in the previous experiments for the Pu elution and the Pu decontamination phases (experiments 1 to 16, $V_{(\text{elution} + \text{decontamination})}/m_{\text{resin}} = 26 \text{ mL g}^{-1}$). A Pu decontamination phase using $2 \text{ mol L}^{-1} \text{ HNO}_3$ ($V/m = 6 \text{ mL g}^{-1}$) was added to decontaminate the column of any organic compounds of the Pu elution solution Pu/S before the U elution phase ($0.02 \text{ mol L}^{-1} \text{ HNO}_3$, $V/m_{\text{resin}} = 19 \text{ mL g}^{-1}$). Uranium was eluted with a bigger volume because eluting the uranium with a lower volume ($V/m = 6 \text{ mL g}^{-1}$, Fig. 1) led sometimes to a lower U recovery yield which is not acceptable when the U initial amount is less than $1 \mu\text{g}$.

Results

The U–Pu separation performances were estimated using the recovery yield (RY) and decontamination factor (DF). The uranium and plutonium recovery yields (RY(U) and RY(Pu), respectively) in the U and Pu elution phases are calculated using Eq. (1).

$$RY(X)(\%) = \frac{A_{elution} \cdot V_{elution}}{A_{sample} \cdot V_{sample}} \quad (1)$$

with $X=U$ or Pu . $A_{elution}$ and A_{sample} are the volumic activity ($Bq L^{-1}$) of element X in the X elution phase and in the sample, respectively and $V_{elution}$ and V_{sample} are the volumes (L) of the X elution phase and of the sample, respectively.

The decontamination factors of U and Pu in regard of Pu and U (DF(U/Pu) and DF(Pu/U)) were calculated using Eq. 2.

$$DF(X/Z) = \frac{RY(X)}{RY(Z)} \quad (2)$$

where $RY(X)$ is the recovery yield of element X in the X elution phase and $RY(Z)$ is the recovery yield of element Z in the X elution phase.

Results and discussion

All of the results are summarized in the Table 2.

Influence of the Pu initial oxidation state

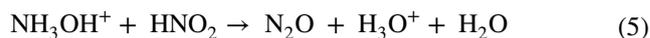
The RY(Pu) and DF(Pu/U) obtained from a Pu(IV/VI) solution (experiment 1) and from a Pu(VI) solution (experiment 2) are high: $RY \geq 88\%$ and $DF(Pu/U) \geq 625$. The RY(U) and the DF(U/Pu) are also high for both experiment: $RY \geq 65\%$ and $DF(U/Pu) \geq 178$. Experiment 1 leads to a U recovery yield of about 65%, lower than in Experiment 2 ($RY = 86\%$). A larger volume of elution solution would have probably led to a better recovery yield. Despite the lower U recovery yield, DF(U/Pu) for Experiment 1 is excellent: $DF(U/Pu) = 1180$. These experiments showed the Pu valency adjustment with the H_2O_2 system is efficient for sample containing mainly Pu(IV/VI) or Pu(VI): the separation performances are satisfactory.

Influence of using the Pu/H solution

Experiment 3, 4 and 6 performed with the same Pu adjustment valency conditions (H_2O_2 method with a duration set at 2 h), showed the Pu recovery yield is random: $RY(Pu) = 5\%$ for experiment 3, 100% for experiment 4 and 24% for experiment 6. Except for experiment 3, the Pu decontamination

factors in regard of U are high: $DF(Pu/U) = 430$ for experiment 4. Increasing the time between the Pu adjustment valency step and the chromatographic cycle at 20 h (experiment 5) do not improve the Pu recovery yield ($RY(Pu) = 24\%$). Likewise, using the Fe(II)/ $NaNO_2$ method for the Pu adjustment valency condition (experiment 7) led also to a low Pu recovery yield ($RY(Pu) = 10\%$). Using H_2O_2 is therefore not the cause of the Pu unexpected behavior. The U behavior in these experiments is less problematic: the U recovery yield is high ($RY(U) \geq 91\%$ for experiments 3 to 7). However, the U purified fraction is polluted with Pu in experiment 3 and 6 (experiments where a low Pu recovery yield was observed). It is probable that a fraction of the plutonium not recovered by the passage of the Pu/H solution leaked during the uranium elution phase, due to the low acidity of the U eluting solution leading to the decrease of the Pu affinity for the resin [13].

The degradation of the NH_3OH-Cl reagent during the Pu/H solution preparation and aging time could explain the behavior of Pu [22–24]. According to Bennet et al. [25], in nitric medium, hydroxylammonium chloride is degraded by a nitrosation reaction (Eq. (3) to (5)). These reactions are self-catalyzed and favored by acidity.



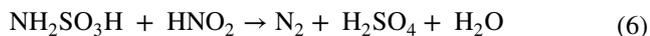
Moreover, ascorbic acid is reactive with nitrous species, and this reaction leads to its oxidized form, dehydroascorbic acid which has no effect on the Pu oxidation state [26, 27]. This reagent degradation hypothesis with nitric acid seems to be confirmed by the results of experiment 8 where the Pu elution solution Pu/H* was prepared in 2 mol L^{-1} HCl medium, instead of 2 mol L^{-1} HNO_3 . This experiment led to a high Pu recovery yield $RY(Pu) = 90\%$.

Influence of substituting hydroxylammonium chloride by sulfamic acid

The U/Pu separation using the Pu/S solution (experiments 9 and 10) showed good performances: $RY(Pu) \geq 80\%$ and $DF(Pu/U) \geq 270$. No U leak was observed before its elution step. The U recovery yield is close to 100% for experiment 10. It is lower for experiment 9 ($RY(U) = 64\%$). But another wash ($V/m_{resin} = 6 mL g^{-1}$) helps to recover the remaining U ($RY(U) = 36\%$). The $DF(U/Pu)$ values (> 135) showed the Pu/S solution efficiency for Pu decontamination.

Using sulfamic acid instead of hydroxylammonium chloride helps conserving the U/Pu separation performances. It reacts rapidly, smoothly and completely with nitrous acid to

give nitrogen and with nitric acid to produce N_2O (Eq. (6) and Eq. (7)).



Due to its anti-nitrous properties, sulfamic acid prevents the oxidation of species like ascorbic acid in nitric solutions [28, 29].

Influence of the Pu valency adjustment conditions

Experiments 9 to 11 (H_2O_2 method) led to a good Pu purification: $RY(Pu) \geq 80\%$ and $DF(Pu/U) \geq 200$. The experiment 12 (Fe(II)/ $NaNO_2$ system) led also to a high Pu recovery yield ($RY(Pu) = 100\%$).

However, a different Pu behavior is observed for experiment 13. Pu was mainly recovered during the phase of decontamination of the column from Am ($Pu/Pu_{init} = 80\%$) which means that Pu is not retained on the resin. Only 19% are recovered in the Pu fraction. This unexpected Pu behavior can only be explained by bad Pu adjustment valency conditions.

Experiment 14 was performed with the same conditions as experiment 13, except that the time between the Pu adjustment valency step and the chromatographic cycle was increased to 42 h. A Pu recovery yield of 80% was obtained for experiment 14, similar to the recovery previously obtained for experiments 9 to 12 ($RY(Pu) > 80\%$). The rest of Pu (20%) is found in the following phase, namely the decontamination phase of the column from Pu.

These differences in the results are probably due to the initial Pu mass: for experiments 9 to 11 the Pu masses were less or equal to 100 μg , while for experiments 13 and 14 the Pu masses were 6 mg. According to Morgenstern et al. [12], the H_2O_2 addition to the Pu solution leads to a solution of 80% Pu(III) and 20% Pu(IV). In contact with the U/TEVA resin which affinity for tetravalent element is high [13], the Pu(III)/Pu(IV) balance is shifted in favor of Pu(IV) which is fixed on the column. The efficiency of this method ($H_2O_2 + U/TEVA$) depends on the ratio between the number of resin exchange sites (2.10^{20} sites per mL of U/TEVA) and the number of Pu atoms injected in the column. Below a threshold value between 23, corresponding to 6 mg of Pu, and 1400, corresponding to 100 μg of Pu, the Pu extraction is not quantitative. For the experiment 14, the waiting time following the addition of H_2O_2 ($t = 42$ h) is long enough to obtain a Pu(IV) solution before its passage on the resin. The excess of H_2O_2 is degraded over the hours and Pu(III) is oxidized to Pu(IV) by the nitrate ions [30], reaction catalyzed by nitrous acid [31]. Therefore, the waiting time recommended between the addition of H_2O_2 and the start of

the chromatographic cycle depends on the initial Pu mass: $mPu \leq 100 \mu\text{g}$, $t = 2$ h; $mPu > 100 \mu\text{g}$, $t = 42$ h.

Influence of the resin loading rate

Experiments 14 to 16 were performed with similar initial plutonium quantity (2000 to 6000 μg). The U initial masses were increased to increase the resin loading rate: 8% for experiment 14, 30% for experiment 15 and 82% for experiment 16. For a resin loading rate of 8 and 30%, the Pu and U recovery yields (RY) are higher than 80%. $DF(Pu/U)$ is higher than 200 and $DF(U/Pu)$ is higher than 2.10^3 . For a resin loading rate equal to 82%, the Pu recovery yield is very good ($RY(Pu) = 99\%$) but an uranium leak ($mU/mU_{init} = 7\%$) was observed during the Pu recovery step, that led to a low Pu decontamination factor ($DF(Pu/U) = 14$). Therefore, a limitation of the resin loading rate to a maximal value of 30% is recommended to obtain good U–Pu separation performances.

Pu elution solution stability

The results are showed in Fig. 2. For the Pu/H solution, the Pu recovery yield decreased of about 60% for the solution stored in the refrigerator and of about 90% for the solution stored on the bench during the first seven days compared to the recovery yield obtained at $t = 0$. After 21 days, the Pu was not eluted by the Pu/H solution: the Pu recovery yield was about 0%. The Pu/H solution cannot be stored before use to obtain the optimal performance separation.

For the Pu/S solution, the Pu recovery yield decreased from about 10% for the solution stored in the refrigerator or

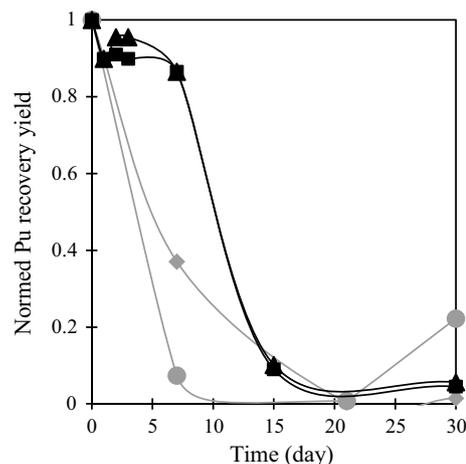


Fig. 2 Influence of time between preparation and use for the Pu/H solution stored on a bench (●) or in a refrigerator (◆) and for the Pu/S solution stored on a bench (■) or in a refrigerator (▲) on the recovery yields of the Pu. The recovery yield were normed compared to the recovery yield obtained at t_0

on the bench during the first day of storage compared to the recovery yield obtained at $t=0$ (the Pu recovery yields were about 90%). This decrease is not significant as the Pu recovery yield uncertainty is about 10%. The Pu recovery yield stays constant during the first seven days of storage, either on the bench or in the refrigerator. Between 7 and 15 days of storage, the Pu recovery yield decreased for both storage conditions: about 90% at 7 days and 10% at 15 days. The Pu/S solution cannot be stored for more than 7 days to have good performance separation. The storage location directly on the bench or in the refrigerator do not have any impact on the separation performance. However, to make sure to have the optimal performance separation, using the Pu/S solution freshly prepared is recommended.

U/Pu separation in Pu matrix solution

Experiment 17 led to very good performances. Indeed, U and Pu recovery yields are high (R.Y (U) > 90%, RY (Pu) > 90%) as well as the decontamination factor of U toward Pu ($DF(U/Pu) \approx 3000$).

It is notable that an experiment realized in the same conditions as experiment 17 showed that adding oxalic acid to the U elution solution did not reduce the volume required to recover U quantitatively as expected. In addition, it may lead to the co-elution of Pu remaining traces and consequently to the decrease of the U decontamination factor toward Pu.

Conclusions

This work aimed at studying the robustness of U/Pu separation described in the CETAMA method N°397 before its release. A Pu random behavior was firstly observed when a hydroxylammonium chloride/ascorbic acid/ HNO_3 solution was used to elute Pu. The degradation of hydroxylammonium chloride in nitric media by a nitrosation reaction probably explained the poor Pu behavior. The addition of an anti-nitrous reagent like sulfamic acid instead of hydroxylammonium chloride to the ascorbic acid / nitric acid mixture helped to stabilize it, and gave good result for Pu elution. The substitution of hydroxylammonium chloride eliminates a potentially carcinogenic reagent. Its replacement is beneficial in regard of the REACH process. Another advantage of this substitution is avoiding using hydroxylammonium in chloride form, absolutely not allowed in glove-box working environment.

Another key stage of this U–Pu separation was also consolidated: the Pu valency adjustment by H_2O_2 . The conditions vary with the mass of Pu involved. For a UTEVA 2 mL column, if the plutonium mass involved is less or equal to 100 μg , the waiting time recommended between the addition of H_2O_2 and the start of the chromatographic cycle is 2 h. If

the plutonium mass is greater than 100 μg , the waiting time recommended is 42 h. A maximum resin loading rate of 30% and a freshly prepared Pu/S solution are recommended.

This consolidated separation, was tested for a U matrix (Pu in minority) and a Pu matrix (U in minority) solutions. The performances are very good with U and Pu recovery yields greater than 80% and decontamination factors $DF(U/Pu)$ and $DF(Pu/U)$ up to 2.10^4 , making the H_2O_2 /UTEVA resin method suitable for mass spectrometry analyses. Moreover this U/Pu separation uses no corrosive reagent and can be easily implemented in glove box.

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