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Neptunium(III) application in extraction chromatography

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ABSTRACT

This paper describes a novel strategy for actinide separation by extraction chromatography with Np(III) valence adjustment. Neptunium(IV) was reduced to Np(III) using Cr(II) and then selectively separated from uranium (IV) on a TEVA resin. After elution, Np(III) was retained on a DGA resin in order to remove any detrimental chromium impurities. Neptunium(III) formation was demonstrated by the complete and selective elution of Np from TEVA resin (99 ± 7%) in less than 12 mL of 9 M HCl from U(IV) (0.7 ± 0.7%). It was determined by UV–visible and kinetic studies that Cr(II) was the only species responsible for the elution of Np(IV) as Np(III) and that the Cr(II) solution could be prepared from 2 to 30 min before its use without the need of complex degassing systems to prevent the oxidation of Np(III) by oxygen. The methodology proposed here with TEVA/DGA resins provides removal of Cr(III) impurities produced at high decontamination factors (2.8×10^3 and 7.3×10^4 respectively).

1. Introduction

Use of nuclear fission for energy generation and weapons testing has led to a global increase of both natural and artificial actinides at ultra trace levels in the environment [1–3]. Monitoring transuranians (TRUs) from a radioprotection perspective is crucial in case of accidental disposals, terrorist acts, or nuclear accidents/emergencies [4,5]. This is not an easy task, since they are generally present at trace levels (fg g^{-1}) [6] in the environment and some isotopes have low specific activities resulting from their long half lives ($t_{1/2} > 10^3$ years) [7]. Thus, the radioelements must be isolated or pre-concentrated [8,9]. In the case of an emergency, the need to use pre-concentration would be made even more difficult by the limited amount of samples available. Neptunium, among the actinides, is an important constituent in high level radioactive waste [10,11]. Because of the long half-life of one of its isotopes (^{237}Np, 2.14×10^6 y) [12] and its numerous oxidation states, it can be mobilized through various terrestrial and aquatic pathways [13,14]. Therefore, it is essential that it be monitored, in complement with other actinides. The proper determination of Np is limited by many instrumental interferences plaguing current analytical methods for this alpha-emitter. In alpha spectrometry, ^{234}U (4.856 MeV) [12], which is relatively abundant in the environment, emits an alpha particle that has a similar energy to the one generated by the decay of ^{237}Np (4.957 MeV) [12,15]; this renders discrimination between them with current instrumentation impossible. In mass spectrometry, the high abundance of ^{238}U in environmental samples leads to abundance sensitivity effects and increases the apparent signal for $m/z = 237$ [7,15]. To mitigate those detrimental interferences, actinide separation is mandatory [6,16], particularly for Np, which is among the least abundant actinides.

While the separation of actinides to high elemental purity is recommended, this can become a laborious endeavour [17]. Extraction chromatography (EXC) has been extensively used to partially or totally extract and separate actinides [18–23]. Its attractiveness for actinide separation resides in its high selectivity towards TRUs, affordable cost, reasonable efficiency, and potential for automation. Yet, the separation of actinides remains challenging by EXC due to the complexity resulting from simultaneously control their valences, particularly for U, Np, and Pu, which possess multiple oxidation states [24–27] in acidic solution. Using nitric acid conditions, Horwitz et al. [28] established a separation strategy to retain Np(IV) and Th(IV) on a TEVA resin, followed by the retention of U(VI) on a UTEVA resin and Pu(III) and Am(III) on a TRU resin. The effective separation of Np(IV) from U(VI) on TEVA resin was obtained because of the low retention of U(VI) ($k' = 3$) compared to Np(IV) ($k' = 5000$) in 3 M nitric acid [28]. However, ferrous sulfamate was used to obtain Np(IV) and Pu(III) and in such reductive conditions, where some U(IV) is formed and will remain in the Np(IV) fraction [15]. Maxwell et al. [29,30] have designed a rapid methodology for the measurement of Np and Pu in 3 M nitric acid. They have first adjusted Np and Pu valences to Np(IV) and Pu(IV) using ferrous

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sulfamate followed by sodium nitrite and then extracting them on a TEVA resin. To eliminate U, which could interfere with both Np and Pu isotopes in alpha and mass spectrometry, Maxwell et al. [29] eluted most of the U(VI) using 3 M nitric acid. At this molarity, Np(IV) and Pu(IV) remained on the resin. Although the 3 M nitric acid was suitable to remove U(VI) adsorbed on TEVA resin, Maxwell et al. [29] used a second purification using a DGA resin, which selectively retains actinides III and IV in those conditions, removing any residual uranium(VI) still remaining after the first extraction. Recently, a completely different scheme of separation was proposed by Guérin et al. [31] in hydrochloric acid conditions to overcome those issues related to the number of resins used as well as valence adjustment difficulties in nitric acid. In this media, Np(IV) and U(IV) were retained on a TEVA resin and Th(IV), Pu(III), and Am(III) were retained on a DGA resin. This strategy prevents the contamination of Th, Pu and Am fractions due to the strong retention of U(IV) in 9 M HCl on TEVA resin, but selective elution of Np(IV) from U(IV) becomes delicate.

Guérin et al. [31] proposed to selectively oxidize U(IV) to U(VI) with hydrogen peroxide in 13 M HNO_3 to perform an efficient separation. Although U(IV) was selectively separated from Np(IV), the fraction containing uranium was contaminated with a large amount of iron impurities and it required an evaporation step and a redissolution in 6 M HCl to enable the co-precipitation of U(IV) with HF as U(VI) does not precipitate as a fluoride. In addition, Np was partially eluted (5%) into the uranium fraction. Finally, the use of 13 M HNO_3 + 5% H_2O_2 was pinpointed to reduce the reusability of the resin, thus highlighting the need for a new strategy to separate Np from U in the separation scheme.

Many researchers have demonstrated that trivalent actinides such as Am(III) or Pu(III) are poorly retained in nitric or hydrochloric acid conditions on TEVA resin, even independently of the acid molarity [28,29]. Therefore, reducing Np in a Np(III) valence could provide an efficient approach to separate Np and U. While Np(III) possesses a stability zone in acid conditions [32], it is rapidly oxidized to Np(IV) by the oxygen present in the air [27]. It therefore requires an oxygen-free environment, a condition not generally met during conventional actinide separation.

Previous investigations have demonstrated that neptunium(III) could be prepared in an inert atmosphere using zinc amalgam [27,33]. Also, neptunium(III) valence was adjusted and characterized using V(II) [34] and Cr(II) [35], two very strong reducing reagents. These studies focus essentially on kinetic parameters and not on analytical applications. Thompson et al. [35] had formed chromium(II) by oxidizing metal chromium in perchloric acid, after degassing the solution with argon and CO_2. On the other hand, V(II) was prepared by reduction of an amalgam of metallic vanadium after degassing the solution with argon [34]. The reduction of Np(IV) to Np(III) may be advantageous to enable its separation over U(VI) or U(IV) in HCl media since actinides(III) do not exhibit any retention on TEVA resin [28]. This would also provide less harsh conditions which could prevent the degradation of the resin and improving its reusability.

This manuscript proposes a new strategy to separate U(IV) from Np(IV) on TEVA resin by reducing Np(IV) to Np(III) in hydrochloric acid with Cr(II), which to our knowledge is the first direct application of Np(III) oxidation state on extraction chromatographic resins. Chromium(II) has been selected over vanadium(II) because Cr(II) is a better reducer, is easy to obtain from metallic chromium, is not passivated, and is less expensive than V(II) salts [36]. Initially, the reduction of Np(IV) to Np(III) by Cr(II) will be demonstrated as a potential alternative in extraction chromatography. Then, the applicability of Np(III) with respect to Np and U selective elution on the TEVA resin will be explored. Spectroscopic evidence regarding the Cr(II) formation in solution and its effectiveness on Np(IV) reduction will be discussed. Finally, the retention of Np(III) on DGA resin will be shown as a decontamination strategy to remove the high amount of Cr(III) from Np and U fractions.

2. Materials and methods

2.1. Instrumentation

All measurements of actinides (U and Np) were made using a Canberra alpha spectrometer (Canberra, Concord, ON, Canada). The operational conditions for alpha spectrometry have been published elsewhere [37]. Chromium solutions were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Perkin Elmer Optima 3000, Waltham, MA). A UV–visible spectrometer HP-8452A (Agilent, Mississauga, ON, Canada) was used for the time-dependant determination of chromium species in 9 M HCl.

Actinide studies were performed using a flow injection system, as shown in Fig. 1. All solvents were contained in high-density polyethylene (HDPE) (VWR, Mississauga, ON, Canada) bottles closed with acrylate caps sealed with rubber rings. Actinide samples and chromium solutions were put in 50 mL polypropylene conical tubes (Sarstedt, Newton, NC), sealed with rubber rings and closed with the same caps as for solvents. Both the bottles and the conical tubes were put under nitrogen pressure (+10 PSI) using a manifold and linked to 10-port selectors (Vici Valco Instrument Co., Inc., Houston, TX). The tubing used was made from high purity Teflon® and purchased from the Mandel Scientific Company inc. (Guelph, ON, Canada) as well as screws, ferrules and adaptors. The 10-port selector was linked with two 2-position, 6-valve port selectors (Fig. 1) to allow the distribution of the solvents and reagents selectively in a TEVA resin, a DGA resin or a TEVA resin followed by a DGA. Reagents and sample fractions were manually collected in conical tubes using remote controlling of each selector.

2.2. Reagents and materials

Solutions of environmental-grade HCl (Anachemia, Montréal, QC, Canada) and reagent grade ammonium oxalate ($(NH_4)_2C_2O_4$) (Fisher Scientific, Fair Lawn, NJ) were prepared using high-purity water (18 MΩ cm) from a Mili-Q purification system (Milipore, Bedford, MA). Neptunium-237 (97 Bq mL^{-1}) and natural uranium (1000 mg L^{-1}) solutions were obtained from National Institute of Standards and Technology (Gaithersburg, MD) and SCP Science (Baie D'Urfé, QC, Canada) respectively. Titanium trichloride ($TiCl_3$) 20% (w/v) in 3% HCl (v/v) (Alfa Aesar, Ward Hill, MA) was used to reduce Np and U to Np(IV) and U(IV). The chromium(II) solution was freshly prepared before Np(IV) reduction by dissolving 3.85×10^{-3} mol of metallic chromium powder (The British drug houses LTD, Poole, England) in 30 mL of 9 M HCl in a conical tube. Actinides were separated using TEVA and DGA resins (2 g cartridge, 50–100 μm particle size) from Eichrom Technologies Inc. (Lisle, IL).

2.3. Method development

Elution profiles were determined after loading U and Np as U(IV) and Np(IV) by the reduction of their higher valences with $TiCl_3$ (1% v/v) in 9 M HCl on properly rinsed and conditioned TEVA or DGA (Table 1, Steps 1 and 2) resin. Then, impurities and actinides were eluted with the corresponding reagents in fractions of 1 mL collected in conical tubes of 15 mL. These solutions were completed with 5 mL of nanopure water, co-precipitated and analyzed by alpha spectrometry. For an elution profile using a solution of dissolved H_2, the solution was prepared by dissolving 3.85×10^{-3} mol of metallic zinc (Zn) (Mallinckrodt, Inc., Paris, KY) and Cr(III) solution with 3.85×10^{-3} mol of $CrCl_3 \cdot 6H_2O$ (J.T. Baker, Inc., Philipsburg, NJ) in 30 mL of 9 M HCl.

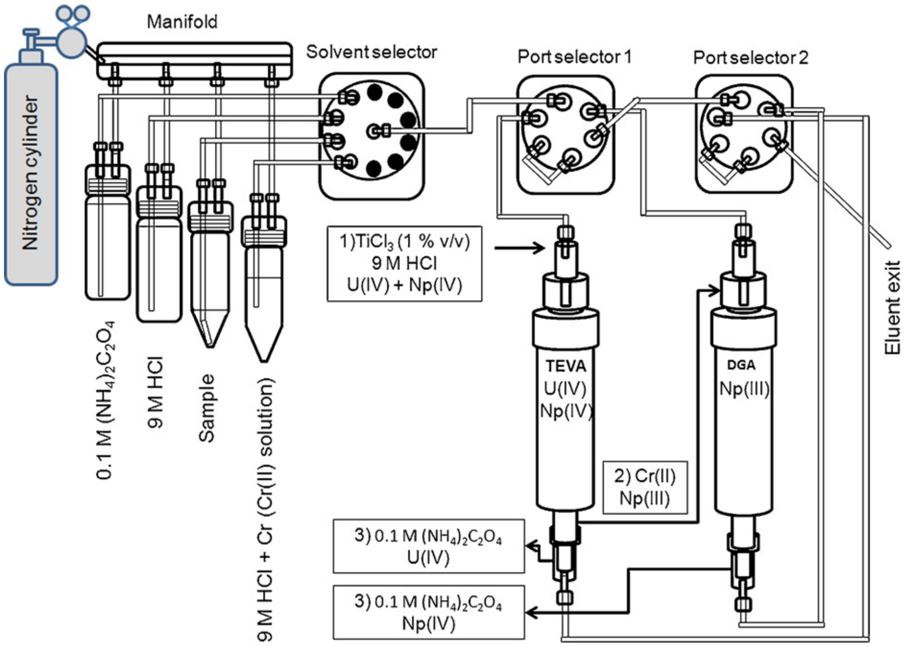

Fig. 1. Schematic representation of the assembly for the separation of U(IV) from Np(IV) via its reduction to Np(III) and the chemical separation used.

The evolution of the chromium species was studied by UV–visible and elemental analysis. First, the effectiveness of the Cr(II) solution to reduce Np(IV) in Np(III) was determined by dissolving the chromium powder in 9 M HCl at predetermined intervals before its loading (0–30 min). The chromium contained in the supernatant was determined by ICP-AES. Next, the evolution of the chromium species was determined by UV–visible studies. To do so, chromium powder (3.85×10^{-4} mol) was dissolved in 3 mL of 9 M HCl in a quartz cell (1 × 1 × 4 cm), partially covered with plastic cap to enable to vent the hydrogen formed during the following reactions:

$$Cr_{(s)} \overset{H^+}{\rightleftharpoons} Cr(II)_{(aq)} + H_{2(g)} \overset{H^+}{\rightleftharpoons} Cr(III)_{(aq)} + H_{2(g)}$$

No solvent degassing or special precautions to eliminate the presence of oxygen were used.

2.4. Separation procedure

The complete procedure for the separation of Np(IV) from U(IV) using a TEVA and a DGA resin by the reduction of Np(IV) to Np(III) is described in Table 1. Resins were first rinsed with 20 mL of 0.1 M $(NH_4)_2C_2O_4$ to remove impurities that might be present from previous loadings and conditioned with 10 mL of 9 M HCl (Table 1, Steps 1 and 2). Then, U and Np previously reduced using 100 μL of $TiCl_3$ in 10 mL of 9 M HCl that always contained 25.5 Bq L^{-1} of ^{237}Np and/or 10.0 Bq L^{-1} of $^{(238+234)}$U were loaded on TEVA resin (Table 1, Step 3). TEVA resin was rinsed with 10 mL of 9 M HCl to removed Ti(III) partially retained on the resin (Table 1, Step 4). Chromium(II) solution (12 mL loaded on the resins) (3.85×10^{-3} mol of Cr was dissolved in 30 mL of 9 M HCl) prepared 5 min before its use was then sequentially loaded on TEVA and DGA resin (Table 1, Step 5). This step enables the production of Np(III), which will be eluted from the TEVA resin and then extracted on a DGA resin, while U(IV) will remain on the TEVA resin. Chromium(III) formed by the oxidation of Cr(II) with HCl was partially retained by both resins and was eluted using 20 mL of 9 M HCl (Table 1, Steps 6 and 8). Uranium and neptunium were eluted in individual fractions using 10 mL of 0.1 M ammonium oxalate (Table 1, Steps 7 and 9).

3. Results and discussion

3.1. Formation of Np(III) using Cr(II)

Because this methodology was designed for low level radioactivity samples, so it would be impossible to confirm neptunium's valence states by spectroscopic methods here, as has been done in other cases [38,39]. Therefore, conclusions regarding Np's valence states were inferred from its EXC elution behaviour. Neptunium(IV) was fixed on a TEVA resin and eluted with the solution generated by the dissolution of metallic Cr in 9 M HCl. The elution profile of Np in presence of chromium is shown in Fig. 2. Less than 12 mL are required to elute Np from the TEVA resin. The elution is believed

Table 1
Protocol of U(IV) and Np(IV) separation on TEVA and DGA resins.

Step	Volume (mL)	Medium	Resin	Description
1	20	0.1 M $(NH_4)_2C_2O_4$	TEVA/DGA	Resins rinsing
2	10	9 M HCl	TEVA/DGA	Resins conditioning
3	10	U(IV), Np(IV) in 9 M HCl	TEVA/DGA	Sample loading
4	10	9 M HCl	TEVA	Titanium removal
5	12	Cr(II) in 9 M HCl	TEVA/DGA	Np(III) elution
6	20	9 M HCl	DGA	Cr(III) removal
7	10	0.1 M $(NH_4)_2C_2O_4$	DGA	Np elution
8	20	9 M HCl	TEVA	Cr(III) removal
9	10	0.1 M $(NH_4)_2C_2O_4$	TEVA	U elution

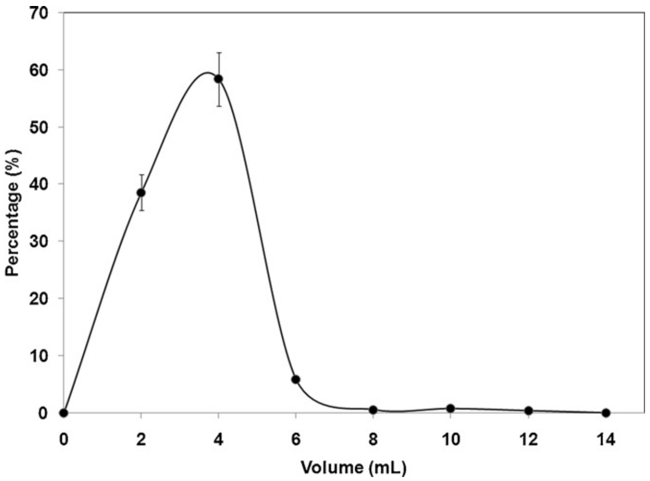

Fig. 2. Elution profile of Np(IV) on TEVA resin with Cr(II) in 9 M HCl.

to originate from the following redox reaction between Np(IV) and Cr(II) [35]:

$$\mathrm{Np(IV)} + \mathrm{Cr(II)} \overset{\mathrm{HCl}}{\rightleftharpoons} \mathrm{Np(III)} + \mathrm{Cr(III)} \quad (\Delta E^\circ/V = 0.57)$$

However, the reaction of metallic chromium with HCl is known to produce Cr(II), but also Cr(III) and H_2 [32,36], which could somehow be responsible for the elution of Np(IV) from TEVA resin. Therefore, a solution containing Cr(III) and one saturated in hydrogen were also investigated as eluents. In those conditions, Np(IV) was not eluted from the TEVA resin even after 15 mL of loading solution (result not shown). Retention of Np as Np(IV) on the TEVA resin was validated by the absence of Np in an additional loading of 10 mL of 9 M HCl. This observation is consistent with the relatively high k' (1000) [28] value of Np(IV) in 9 M HCl. Since Np(IV) was not eluted on the TEVA resin by either 9 M HCl, H_2, or Cr(III), it is possible to presume that Np remains as Np(IV) in the presence of those reagents. Chromium(III) ($E^\circ/V = 1.36$) [40] cannot reduce Np(IV) to Np(III) ($E^\circ/V = 0.15$) [40] and does not create competition effects on the resin sites since the Np(IV) already extracted is not displaced from the resin. Hydrogen produced during the reduction of H^+ with chromium did not affect the valence of Np(IV) even if the reduction potential of H_2 ($E^\circ/V = 0$) [40] is slightly lower than for Np(IV)/Np(III). As It has been demonstrated that trivalent actinides such as Am(III) and Pu(III) are poorly retained on TEVA resin [28,29], it is therefore logical that Cr(II) reduces Np(IV) to Np(III), as observed by Np elution from the TEVA resin (Fig. 2). As a result, it can be concluded that Cr(II) ($E^\circ/V = -0.424$) [40] is sufficiently stable under the conditions used to reduce Np(IV) in Np(III) which can then be easily eluted from TEVA resin in 9 M HCl.

3.2. Selective elution of Np(III) from U(IV)

After the conditions were determined for the formation of Np(III), it was critical to assess if this change in Np valence would enable its selective elution from U(IV). Initially, U(IV) and Np(IV) were loaded separately on a TEVA resin. The percentage of actinides present in the 9 M HCl rinse solutions (Table 1, Steps 3 and 4) were determined (Table 2). The absence of measured activity in those fractions confirms that U(IV) and Np(IV) are efficiently extracted on the TEVA resin.

Table 2
Percentage of U and Np using a TEVA resin in sample and rinsing with 9 M HCl, in Cr(II) and in 0.1 M $(NH_4)_2C_2O_4$ solution ($n = 10$).

Fraction	U	Np
9 M HCl	0.7 ± 0.7	0.2 ± 0.2
Cr(II) in 9 M HCl	0.7 ± 0.7	99 ± 7
0.1 M $(NH_4)_2C_2O_4$	99 ± 7	0.2 ± 0.2

A solution of 12 mL of Cr(II) in 9 M HCl was loaded on that TEVA resin (Table 1, Step 5) followed by 10 mL of 0.1 M $(NH_4)_2C_2O_4$. Both fractions were counted by alpha spectrometry for U and Np. Neptunium was completely found in the chromium(II) fraction (99 ± 7%) while absent from the oxalate one (0.2 ± 0.2%) (Table 2). On the contrary, uranium was absent from the chromium(II) solution (0.7 ± 0.7%) and exclusively present in the oxalate one (99 ± 7%). Note that elution of U(IV) with 0.1 M HCl and 0.1 M $(NH_4)_2C_2O_4$ was tested and found to be effective in a limited volume (10 mL) (result not shown). Currently, 0.1 M $(NH_4)_2C_2O_4$ was used to elute U(IV), but 0.1 M HCl may also be a justifiable choice. Based on the standard potentials of U(III) ($E^\circ/V = -0.52$) [40], Cr(II) ($E^\circ/V = -0.424$) [40] cannot reduce U(IV) to U(III); this explains why uranium(IV) was not eluted by the Cr(II) solution. Therefore, a complete analytical separation between U(IV) and Np(IV) by the selective reduction of Np(IV) to Np(III) with Cr(II) is possible.

3.3. Performance of chromium(II) as an eluent

While Np(III) formation and separation from U(IV) on the TEVA resin had been demonstrated, questions remained regarding the stability and the conditions necessary to generate a solution containing Cr(II). The next few paragraphs focus on these issues with respect to radiochemical automation.

The kinetics of the redox reaction between Cr(II) and Np(IV) on TEVA resin was studied by using a solution of Cr and 9 M HCl prepared at specific times (Fig. 3). It was measured that 98 ± 2% of the Np was eluted when the time elapsed between the preparation of the Cr(II) and the elution of Np(III) range from 2 to 30 min (Fig. 3). Note that 1 min after preparation, the reaction was nearly complete. The reduction of Np(IV) with Cr(II) is known to be a second order reaction independent of the Cr(III) concentration. Thompson et al. [35] obtained the following rate law:

$$-\frac{d[\mathrm{Np(IV)}]}{dt} = 4.29 \quad \mathrm{M^{-1}s^{-1}}[\mathrm{Np(IV)}][\mathrm{Cr(II)}][\mathrm{H^+}]^{-1.27\pm0.02}$$

Using this equation, it is possible to calculate that the Np(III) formation at equilibrium should be complete in approximately 20 s, considering that roughly 20% of the metallic chromium was dissolved. This time is an approximation since the reaction was done in a continuous flow. A total reaction time of 180 s seemed sufficient to form and elute Np(III). The kinetic oxidation parameters of

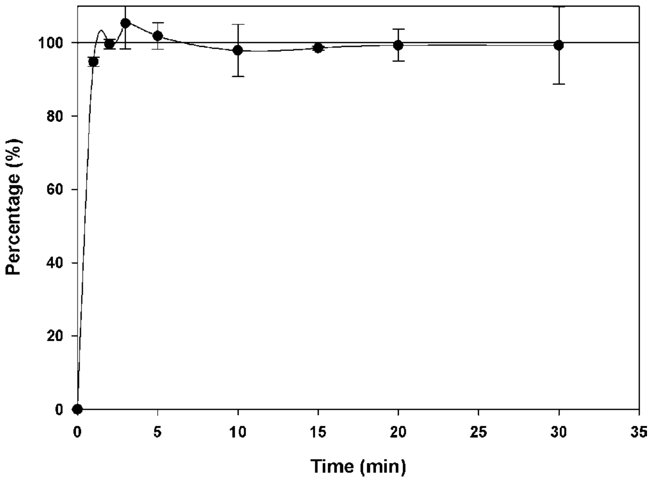

Fig. 3. Yield of Np(III) as a function of the time preparation of the chromium solution in 9 M HCl.

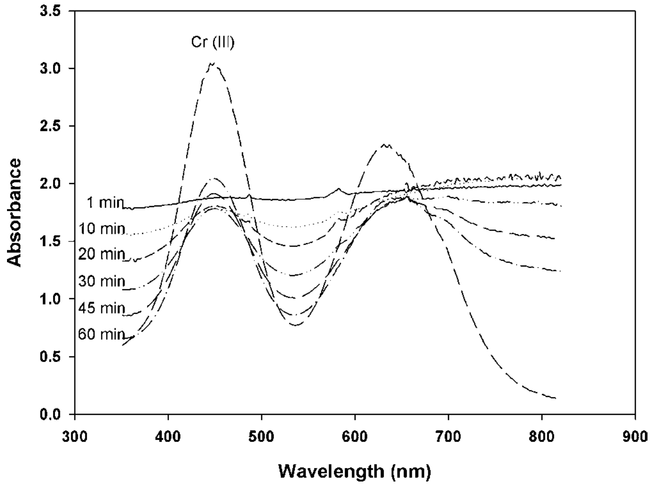

Fig. 4. UV-visible evolution of the Cr solution in 9 M HCl.

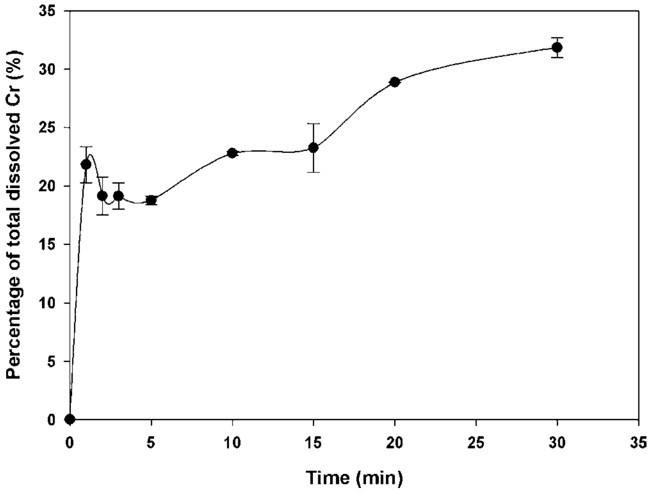

Fig. 5. Percentage of chromium dissolved in 9 M HCl as a function of time.

Np(III) to Np(IV) with O_2 are not well defined, but it has been proposed that O_2 will oxidize Np(III) to Np(V) in few seconds [41]. Yet Np(III) remained as a stable species under experimental conditions. Perhaps Cr(II) is a strong reducing reagent that is rapidly oxidized in the presence of dissolved oxygen to form Cr(III) [42] and thus prevents Np(III) oxidation. This hypothesis supports the fact that the initial solution did not need to be purged with argon in order to remove dissolved oxygen. Finally, the oxidation kinetics of Cr(II) with H^+ has to be far slower than the reduction of Np(IV) to explain the preferential redox reaction between Cr(II) and Np(IV).

The time-related evolution of the chromium species in 9 M HCl was determined by UV–visible in conditions analogous to those used during the formation of Np(III). At $t = 1$ min a large broad band from 550 to 800 nm, corresponding to the Cr(II) complex $CrCl^+$ [43], can be observed (Fig. 4). As the redox reaction progress, two bands centred around 450 and 650 nm become apparent, which correspond to the chloro complex of Cr(III) $CrCl_2{}^+$ [43]. Even after 30 min, a Cr(II) spectral contribution is still detectable, supporting the observed reduction of Np(IV) in Np(III) on TEVA resin as shown in Fig. 3. While Cr(II) is present even 30 min after the preparation of the reagent, preparing fresh Cr(II) solution is advisable (5 minutes). Since Cr(III) is constantly formed, more Cr(III) can be retained on TEVA and DGA resins, which may increase the risk of contamination of U or Np fractions and ultimately prevent proper analysis by alternative spectrometric methods.

The evolution of the concentration of Cr dissolved as a function of time was also determined by ICP-AES (Fig. 5). It can be observed that during the first few minutes of the reaction, a large amount of chromium is rapidly dissolved (20% in 1 min) (Fig. 5). The chromium present at that time was mostly Cr(II), based on UV–visible data. Then, the dissolution rate of Cr^0 tends to decrease drastically. The rapid dissolution of Cr^0 may explain why reduction of Np(IV) to Np(III) (Fig. 3) is observed in less than one minute. One hypothesis that may explain the unique Cr^0 dissolution curve is that at the beginning of the reaction, the smallest metal particles are rapidly dissolved, while the largest one are dissolved slowly.

3.3.1. *Neptunium(III) retention and elution on DGA resin*

As stated previously, some of the chromium in the system is Cr(III) which could interfere with the Np(III) chemistry on the resin. Therefore, in order to eliminate Cr(III) from the Np fraction, it was proposed that DGA resins could be efficient to selectively retain Np(III) over Cr(III). Yet very little information is available about Np(III) extractions on DGA resin but it is known that Am(III) is extracted in 9 M HCl [44].

Neptunium(III) solution was loaded 10 times on a DGA resin and then the Np in the residual solution was measured. It was determined that all Np(III) was retained on the DGA resin (0.2 ± 0.4% in the residual fraction), which could then be easily eluted using 0.1 M $(NH_4)_2C_2O_4$ (100 ± 7%). With 0.1 M HCl, however, the elution volume required varied significantly (from 8 to 18 mL) while with 0.1 M $(NH_4)_2C_2O_4$ the elution volume required remained constant at 10 mL (result not shown). Therefore, $(NH_4)_2C_2O_4$ was preferred to elute Np ions from DGA resin (Table 1, Step 7). Note that neptunium was eluted from TEVA resin as Np(III), but since the dissolved oxygen was not removed from the Cr(II) solutions, some Np(III)

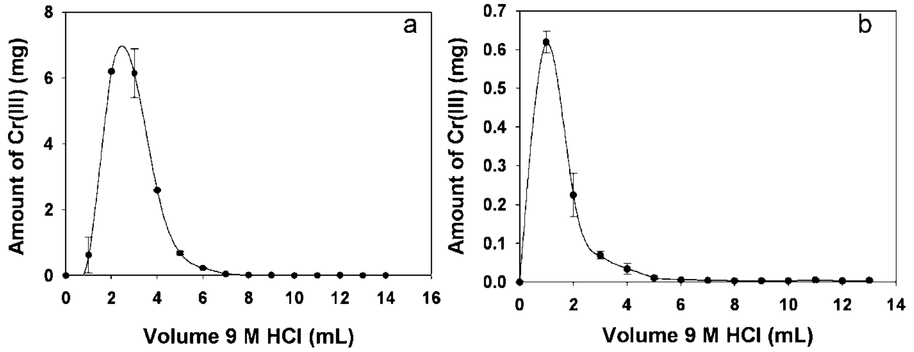

Fig. 6. Elution profile of Cr(III) using 9 M HCl on (a) DGA resin and (b) TEVA resin.

Table 3
Percentage of U and Np measured in their respective fraction after their complete separation using the method from Table 1.

Sample	U	Np
1	97	104
2	78	101
3	92	100
4	97	100
5	88	106
6	102	108
7	101	109
8	92	98
9	100	102
10	99	101
Average	95	103
SD	7	4

should be reoxidised rapidly to Np(IV). On TEVA resin, the elution profiles of U(IV) were done with the same eluents as for the DGA resin (result not shown). Uranium (IV) was eluted in 14 mL with 0.1 M HCl and with 10 mL using 0.1 M $(NH_4)_2C_2O_4$. Ammonium oxalate was chosen to elute U(IV) since it is the most efficient eluent (Table 1, Step 9).

3.3.2. Selective removal of Cr(III) from TEVA and DGA resins

Colorimetrically, it is easy to observe that Cr(III) is partially retained on TEVA and DGA resins by the intense green chloro complex $CrCl_2^+$. The strategy proposed for this study was to remove Cr(III) from Np(III) and U(IV), by placing it in conditions where Cr(III) will be selectively eluted while both U(IV) and Np(III) will be retained on TEVA and DGA resins respectively. Then U and Np can be selectively eluted using appropriate solvents determined previously.

The elution profiles of Cr(III) in 9 M HCl on TEVA and DGA resins were determined in order to reduce the chromium concentration that could be detrimental for some actinide detection techniques such as mass spectrometry. In alpha spectrometry, using the lanthanum co-precipitation technique, it was determined that Cr(III) in a concentration similar to the total amount of chromium dissolved did not affect the signal measured (102 ± 4%). Chromium (III) can be almost entirely removed using approximately 8 mL of 9 M HCl for both the TEVA and DGA resins (Fig. 6). As expected from the behaviour of Am(III), the total amount of chromium retained on the DGA resin was approximately 16 times higher than on TEVA resin (16 ± 1 mg compare to 0.99 ± 0.05 mg, respectively).

The amount of chromium was measured by ICP-AES for the U and Np fractions with the method proposed in Table 1. In the U and the Np fractions, $3.5 \pm 0.1 \times 10^{-4}$ mg and $2.1 \pm 0.6 \times 10^{-4}$ mg of Cr were measured, respectively. For the U and Np fractions, a decontamination factor of 2.8×10^3 and 7.3×10^4 respectively were obtained for Cr(III).

3.4. Figures of merits of the methodology

The overall method (Table 1), including chromium removal, was tested using solutions of mixed U and Np in 10 mL of 9 M HCl. The U and Np amounts were measured in their respective solutions for 10 consecutive separations (Table 3). It was determined that the quantity of U and Np were in great agreement with those measured individually (respectively 95 ± 7% and 105 ± 5%) considering the incertitude on the values. Also, the resin reusability seems unchanged for 10 consecutive analyses, an interesting fact to consider for including Np(III) in a complete actinide separation scheme. Using this method, it is possible to determine the amount of U and Np by reducing Np(IV) to Np(III) on TEVA resin selectively from U(IV), and removing most of the Cr used.

4. Conclusions

Neptunium(IV) may be rapidly and easily reduced to Np(III) on TEVA resin using a solution of Cr(II) in 9 M HCl. This reduction leads to rapid and selective elution of Np(III) from TEVA resin which is retained on DGA resin, allowing its separation from U(IV), which interferes in alpha and mass spectrometry analysis. Impurities of Cr(III) formed during the reaction can be removed from Np and U fraction using an excess of 9 M HCl. This approach, combined with other separation strategies, could lead to a procedure for rapid and automated separation of actinides for emergency preparedness and routine analysis.

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