On-line coupling of an ion chromatograph to the ICP-MS:

Separations with a cation exchange chromatography column

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Abstract

An ion chromatography system was coupled on-line to the ICP-MS. All separations were made with a cation exchange chromatography column. Fundamental laws about elution parameters affecting individual retention times and elution forms are explained by applying a proper ion exchange mechanism for the isocratic elution (separations with constant eluent concentration) of mono-, di-, tri-, and tetravalent cations and the actinide species MO_2^+ and MO_2^{2+}. A separation method with two eluents has been investigated to separate mono- from divalent ions in order to separate isobaric overlaps of Rb/Sr and Cs/Ba. The ions normally formed by actinides in aqueous solutions in the oxidation states III to VI are M^{3+}, M^{4+}, MO_2^+ and MO_2^{2+}, respectively. Elution parameters were investigated to separate all four actinide species from each other in order to separate isobaric overlaps of the actinides Np, Pu, U and Am. A major question of concern over the possible release of actinides to the environment is the speciation of actinides within their four possible oxidation states. To check the possibility of speciation analysis with ion chromatography, a separation method was investigated to separate U^{4+} and UO_2^{2+} without changing the redox species composition during the separation. First results of Pu speciation analysis showed that Pu could be eluted as three different species. Pu(VI) was always eluting at the same time as Np(V). This was surprising as Pu(VI) is expected to have the same chemical characteristics as U(VI) and thus was expected to elute at the same time as U(VI).

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1   Introduction

Numerous isobaric overlaps due to β-decay and neutron capture restrict the direct determination of fission product and actinide isotopes by mass spectrometry and therefore a chemical separation is required. Very fast and reliable analysis methods have been obtained by coupling an ion chromatography system on-line to the ICP-MS /1-1–1-4/. With cation chromatography often acids can be used as eluents which do not disturb ICP-MS measurements. In earlier experiments all the lanthanides could be separated on a commercially available cation exchange column from Dionex. Furthermore with the same column Pu and U could be analysed isobaric free /1-4/. As the column material proved very stable against strong acids and bases, it was decided to characterise this column further. Dissolved spent fuel contains fission products and actinides in a variety of different cationic species. The ions normally formed by actinides in aqueous solutions in the oxidation states III to VI are M^{3+}, M^{4+}, MO_2^+ and MO_2^{2+}, respectively /1-5/. Furthermore, there are mono- and divalent fission products. The different chemical characteristic of these species can cause extremely different retention times. Often only different eluent concentrations or more than one eluent have to be used for the separation of these cations. Fundamental laws about elution parameters affecting individual retention times and elution forms are explained by applying a proper ion exchange mechanism for the isocratic elution (separations with constant eluent concentration) of mono-, di-, tri-, and tetravalent cations and the actinide species MO_2^+ and MO_2^{2+}. A separation method with two eluents has been investigated to separate mono- from divalent ions in order to separate isobaric overlaps of Rb/Sr and Cs/Ba. Furthermore, elution parameters were investigated to separate all four actinide species from each other in order to separate isobaric overlaps of the actinides Np, Pu, U and Am. A major question of concern over the possible release of actinides to the environment is the speciation of actinides within their four possible oxidation states /1-6–1-7/. To check the possibility of speciation analysis with ion chromatography, a separation method was investigated to separate U^{4+} and UO_2^{2+}. First speciation analysis of Pu showed quite astonishing results, as Pu(VI) was always eluting at the same time as Np(V).

2   System configuration and reagents

The liquid chromatographic system consisted of two Dionex advanced gradient pumps (AGP-1 and AGP-2) and two Dionex BF-4 four way valves (injection valve and post-column valve). The sample loop (0.5 ml) was a 72 cm long Tefzel tube (1.57 mm o.d. x 0.94 mm i.d.). Dionex cation chromatography columns (IonPac CG10, 4 x 50 mm and IonPac CS10, 4 x 250 mm) were used for all separations. The columns are packed with a latex based cation exchange resin carrying negatively charged sulfonate functional groups /2-1/. In order to pump high acid concentrations, acid resistant pistons (DX 52840) had to be used. All the chromatography items except the gradient pumps and the eluent bottles were installed in a glove box connected with a ventilation system for radiological use.

A VG Elemental Plasmaquad PQ2+ inductively coupled plasma mass spectrometer (ICP-MS) had been installed in the same glove box. Platinum sample cones were used in order to analyse high acid concentrations. Data were acquired in the time resolved analysis mode of the software version Plasmaquad 4.3.

The HPLC was run with a flow rate of 1 ml per minute and could directly be coupled to the ICP-MS. Figure 2-1 shows a schematic view of the coupled system. The separation procedure is divided in two different valve positions:
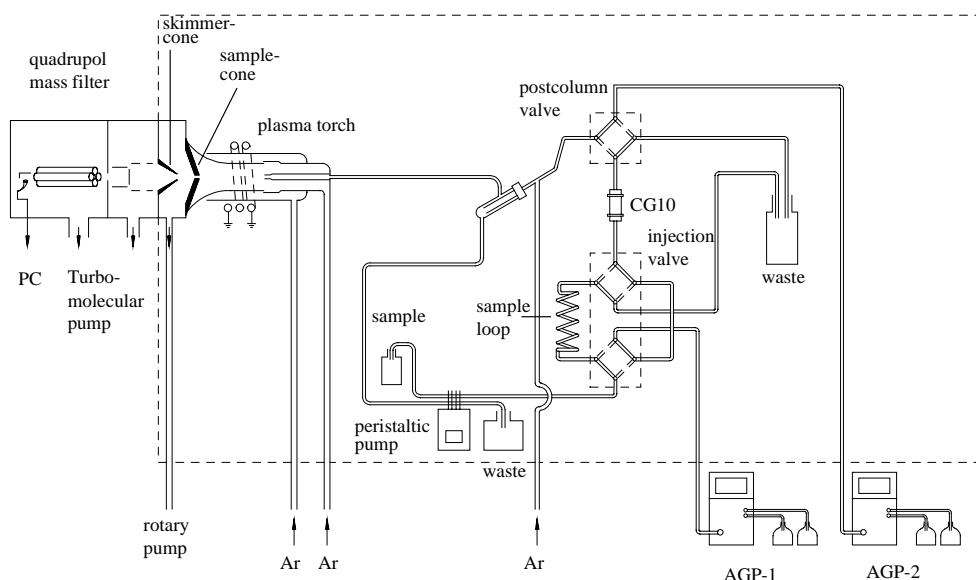

Figure 2-1. *Schematic view of the coupling of the HPLC and ICP-MS systems. In order to analyse highly toxic radioactive samples, all parts of the system which have contact with the samples are installed in a glove box.*

Load: A Gilson Minipuls peristaltic pump was used to suck and push sample through the sample loop of the injector valve into the waste container. The peristaltic pump was also used to suck solution from the spray chamber of the ICP-MS to the waste. The pump operated at 35 revolutions per minute. To fill the loop, the peristaltic pump was equipped with a PVC tube with 0.5 mm inner diameter and a resulting flow rate of 0.84 ml/min. For the outlet of the spray chamber the peristaltic pump was equipped with a PVC tube with 0.9 mm inner diameter and a resulting flow rate of 2.9 ml/min. Eluent was pumped with the AGP1 through the column at a flow rate of 1 ml/min and passed through the post-column valve into the waste container. With the AGP2 1% nitric acid was pumped in the flow mode through the post-column valve into the spray chamber of the ICP-MS.

Inject: After one minute the injection valve was changed to the inject position. At the same time the post-column valve position was changed from position "waste" to "ICP-MS". The sample solution is now sucked and pushed with the peristaltic pump into the waste container. The AGP1 pumps the sample solution in the loop through the chromatographic column and the post column valve in to the spray chamber of the ICP-MS. The AGP2 pumps 1% nitric acid through the post-column valve into the waste container. The elution time of a substance that is not retained was 1.7 minutes with the CG10 column and 2.9 minutes with both the CG10 and the CS10 column.

Distilled, deionized water from a Milli-Q system (Millipore), 65% nitric acid, 30% HCl, 96% H_2SO_4, 25% NH_3, all suprapure from Merck, 2-hydroxyisobutyric acid >99% from Aldrich, and ethylenediamine for synthesis from Merck were used. 10 µg/ml multi-element standard solutions from Spex and a 1000 ppm U standard solution from Merck were used. Furthermore, our own actinide standard solutions were used. The Th, Am and Np standard solutions were mono isotopic and contained Th-232, Am-241 and Np-237. The Pu standard solution contained the isotopes: Pu-238 (0.13 mol%), Pu-239 (84.03 mol%), Pu-240 (14.45 mol%), Pu-241 (0.73 mol%) and Pu-242 (0.34 mol%). A mixed actinide standard solution was made containing 5 ppb Am, Np, Th and 7.5 ppb U. Considering the isotopic compositions of the actinide standards the masses 232, 237, 238, 239 and 241 can be assigned to the actinides Th, Np, U, Pu and Am, respectively. An uranium standard was made by dissolving UO_2 in 85% phosphoric acid pro analysis from Merck to get a green 2560 ppm U(IV) solution. The UO_2 had an isotopic composition of 1.1 mol% U-235 and 98.9% U-238.

3 Retention model for a cation exchanger

An ion exchanger in aqueous solution consists of anions, cations and water, where either the cations or the anions are chemically bound to an insoluble matrix. The chemically bound ions are referred to as the fixed ions and the ions of opposite charge are referred to as the counter-ions. The ion exchanger is classified as a cation exchange material when the fixed ion carries a negative charge, and as an anion exchange material when the fixed ion carries a positive charge. Ion exchange reactions are reversible; therefore, ion exchange behaviour can be described in terms of equilibria equations /3-1/.
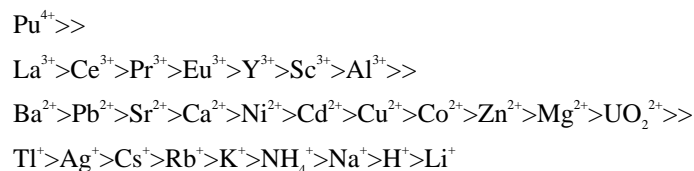
The ion exchange equilibrium for binding of a sample cation, M^m, to a stationary phase (resin) which has been conditioned with an eluent containing a competing cation, E^e, is given by:

$$eM_{sol}^m + mE_{res}^e \leftrightarrow eM_{res}^m + mE_{sol}^e \qquad \text{(Eq.3-1)}$$
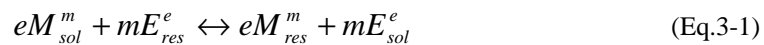
where the subscripts sol and res refer to the mobile and stationary phases, respectively and m and e describe the charge of the sample and eluent cation, respectively. The selectivity coefficient for the system is given by:

$$K_{M,E} = \frac{\left[M_{res}^m\right]^e \left[E_{sol}^e\right]^m}{\left[M_{sol}^m\right]^e \left[E_{res}^e\right]^m} \qquad \text{(Eq. 3-2)}$$

where the brackets indicate the ion concentration in mmoles/ml for the solution phase and in mmoles/g for the resin phase. For accurate calculations of equilibrium constants, we should really use the activities of the ions instead of their concentrations. However, activity coefficients are sometimes difficult to measure, especially within the ion exchange resin matrix. In ion chromatography, ionic concentrations are often low and ion activities approach unity. For the sake of simplicity only ion concentrations are used in this discussion /3-2/. The equilibrium constant is called the selectivity coefficient, because it provides information on the likelihood of exchange between two particular ions. Selectivity coefficients for the uptake of cations by a strong acid cation exchange resin are generally in the following order /3-1/:

$Pu^{4+}>>$

$La^{3+}>Ce^{3+}>Pr^{3+}>Eu^{3+}>Y^{3+}>Sc^{3+}>Al^{3+}>>$

$Ba^{2+}>Pb^{2+}>Sr^{2+}>Ca^{2+}>Ni^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Zn^{2+}>Mg^{2+}>UO_2^{2+}>>$

$Tl^+>Ag^+>Cs^+>Rb^+>K^+>NH_4^+>Na^+>H^+>Li^+$

The ions normally formed of actinides in aqueous solutions in the oxidation states III to VI are M^{3+}, M^{4+}, MO_2^+ and MO_2^{2+}, respectively. The equilibria, which govern ion-exchange separations, are mainly influenced by the charge of the analyte ion. Thus, the following affinity order for a cation exchanger is expected:

$$M^{4+} > M^{3+} \geq MO_2^{2+} > MO_2^{+}$$
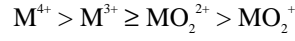
The ions MO_2^{+} and MO_2^{2+} are linear groups where the oxygens carry a net negative charge. Consequently, the charge on M where the functional groups are to be coordinated becomes higher than the ionic charge and the stability order can change to /3-3/:

$$M^{4+} > MO_2^{2+} \geq M^{3+} > MO_2^{+}$$
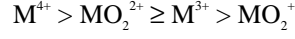
Under conditions where the sample cation M^m exists in trace amounts compared to the much higher concentration of competing ion E^e in the eluent and since the sample cation M^m occupies usually less than 1% of the total resin capacity C (where C is the concentration of functional groups in the resin in mmole/g) it follows:

$$\Rightarrow \left[M_{sol}^{m} \right] << \left[E_{sol}^{e} \right] \tag{Eq. 3-3}$$

$$\Rightarrow \left[M_{res}^{m} \right] << \frac{C}{e} \approx \left[E_{res}^{e} \right] \tag{Eq. 3-4}$$

Substituting in (Eq. 3-2) gives:

$$K_{M,E} = \left(\frac{\left[M_{res}^{m} \right]}{\left[M_{sol}^{m} \right]} \right)^{e} \left[E_{sol}^{e} \right]^{m} \left(\frac{C}{e} \right)^{-m} \tag{Eq. 3-5}$$

The capacity factor k´ of the sample cation is defined as the amount m_{res} in the resin phase of a column, divided by the amount V_{sol} in the solution phase, with m_{res} in g and V_{sol} in ml:

$$k´ = \frac{\left[M_{res}^{m} \right]}{\left[M_{sol}^{m} \right]} \cdot \frac{m_{res}}{V_{sol}} \tag{Eq. 3-6}$$

From eq. (3-5) and (3-6) follows:

$$k´ = \left(K_{M,E} \right)^{\frac{1}{e}} \frac{m_{res}}{V_{sol}} \left(\frac{C}{e} \right)^{\frac{m}{e}} \left[E_{sol}^{e} \right]^{-\frac{m}{e}} \tag{Eq. 3-7}$$

The retention times t and t_0 are defined as the retention times of the ion M^{m+} and of a non-retained substance, respectively. t_0 is also equal to the average time an ion spends in the mobile phase, and can be calculated as follows:

$$\frac{\left[M_{sol}^{m} \right] \cdot V_{sol}}{\left[M_{sol}^{m} \right] \cdot V_{sol} + \left[M_{res}^{m} \right] \cdot m_{res}} \cdot t = t_0 \tag{Eq. 3-8a}$$

Through rearrangement it is possible to get another expression for the capacity factor k´.

$$\frac{t - t_0}{t_0} = \frac{\left[M_{res}^{m} \right] \cdot m_{res}}{\left[M_{sol}^{m} \right] \cdot V_{sol}} = k´ \tag{Eq. 3-8b}$$

(Eq. 3-7) can now be written as follows:

$$\frac{t - t_0}{t_0} = \left(K_{M,E}\right)^{\frac{1}{e}} \frac{m_{res}}{V_{sol}} \left(\frac{C}{e}\right)^{\frac{m}{e}} \left[E_{sol}^e\right]^{-\frac{m}{e}} \quad \text{or in the logarithmic form as}$$

$$\log\left(\frac{t - t_0}{t_0}\right) = \frac{1}{e}\log\left(K_{M,E}\right) + \log\left(\frac{m_{res}}{V_{sol}}\right) + \frac{m}{e}\log\left(\frac{C}{e}\right) - \frac{m}{e}\log\left[E_{sol}^e\right] \quad \text{(Eq. 3-9)}$$

(Eq. 3-9) is of fundamental importance in ion chromatography, since it provides a quantitative relationship between the retention times and the elution parameters. For an experiment with the same column several items can be considered to be constant. The relation between the retention time of a sample cation and the eluent concentration can be reduced to:

$$\log\left(\frac{t - t_0}{t_0}\right) = C_1 - \frac{m}{e}\log\left[E_{sol}^e\right] \quad \text{(Eq. 3-10)}$$

Up till now the model describes a proper ion exchange process, where a sample cation M^m competes with an eluent cation E^e. An eluent ligand can also cause a sample cation to move down the column by complexation. Complexation serves the dual purpose of reducing the effective charge on the solute cation (and hence its affinity for the cation exchange sites) and also introduces a further dimension of selectivity between solutes which does not exist when ion exchange is the only retention mechanism in operation.

4 Isocratic separations

Dissolved spent fuel contains fission products and actinides in a variety of different cationic species. The different chemical characteristic of these species can cause extremely different retention times. Often only different eluent concentration or more than one eluent has to be used for the separation of these cations. Isocratic separations (separations with constant eluent concentration) of monovalent, polyvalent and actinide species with different HCl, ethylenediammonium dichloride and H_2SO_4 concentrations were made to estimate the retention times for these eluents.

4.1 Separations with HCl

The effect of different hydrochloric acid concentrations on the retention times of mono-, di-, tri-, tetravalent and the complex cations MO_2^+ and MO_2^{2+} was investigated by separating Spex multielement standard solutions and actinide solutions. Hydrochloric acid can be used up to 2 M without causing drift problems with the ICP-MS. The signals of a 2 ppb standard solution in 2 M HCl were suppressed to about 80% of the signals obtained in 1% HNO_3. A 0.1 M HCl eluent was found to elute the monovalent cations in appropriate time and peak shapes. The smaller an analyte cation is the more it is hydrated and the faster it is eluted. The reason for the wide peak width of Ag^+ could be different complexes with Cl$^-$ ions (Figure 4-1). By increasing the eluent concentration up to 1 M, some of the di- and trivalent cations could be eluted in appropriate time. Figure 4-2 shows the separation of a solution containing lanthanides and uranium. The uranyl cation UO_2^{2+} forms strong complexes with chloride ions and elutes before the trivalent lanthanides. La^{3+} as the least hydrated lanthanide is retained most and could only be eluted as a wide peak.
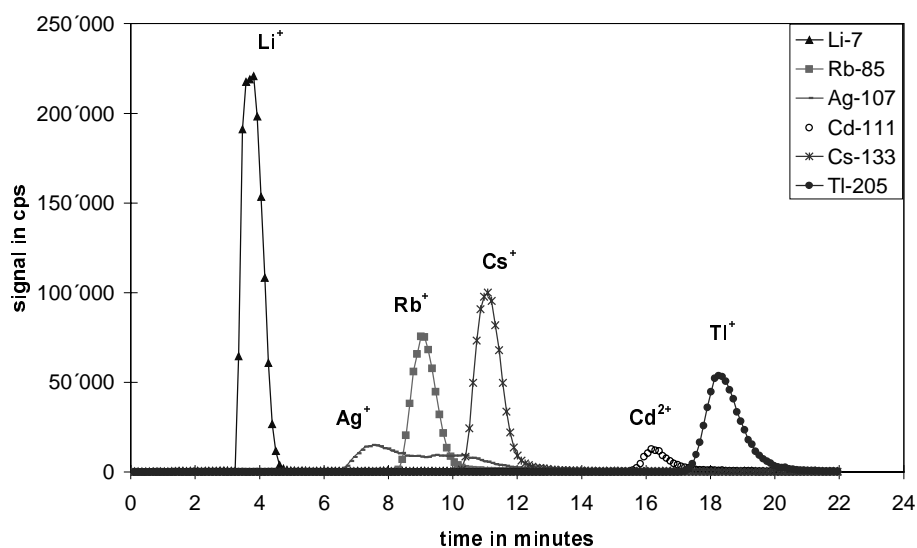

Figure 4-1. *Isocratic separation of 0.5 ml 10 ppb Li, Rb, Ag, Cd, Cs and Tl with a 0.1 M HCl eluent.*
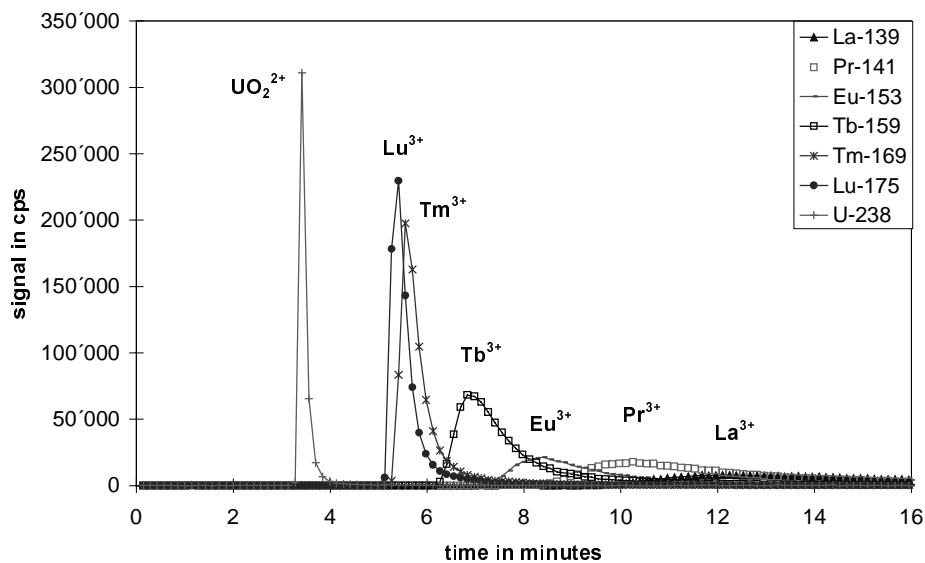
Figure 4-2. *Isocratic separation of 0.5 ml 10 ppb Spex1+U with a 1 M HCl eluent.*

For all hydrochloric acid concentrations, NpO_2^+ was found not to be retained at all. UO_2^{2+} could be eluted as a sharp peak for HCl concentration > 0.3 M. A hydrochloric acid concentration up to 2 M had to be used to elute Am^{3+} and Pu^{3+} as sharp peaks (Figure 4-3). Th^{4+} could be eluted as a wide peak after 13 minutes, whereas no Pu^{4+} could be found.
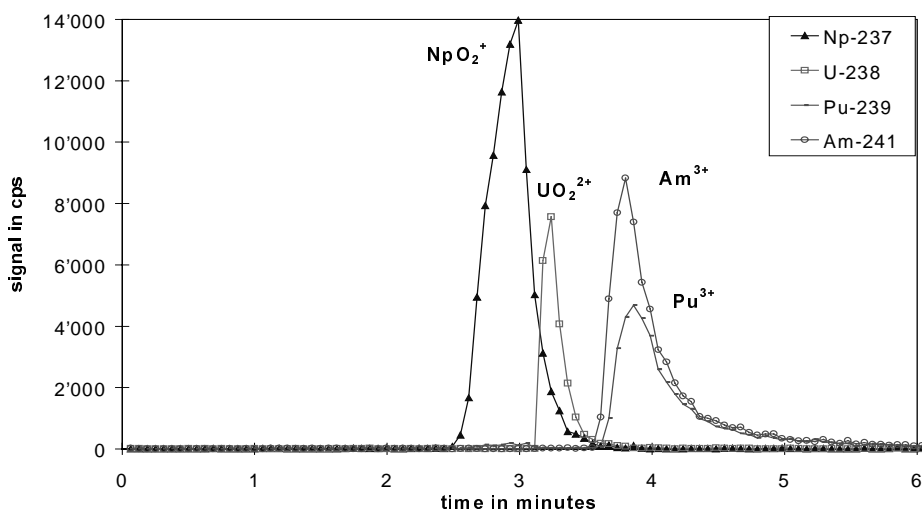

Figure 4-3. *Isocratic separation of 0.5 ml 1 ppb Pu, Am, Np and 0.5 ppb U with a 2 M HCl eluent.*
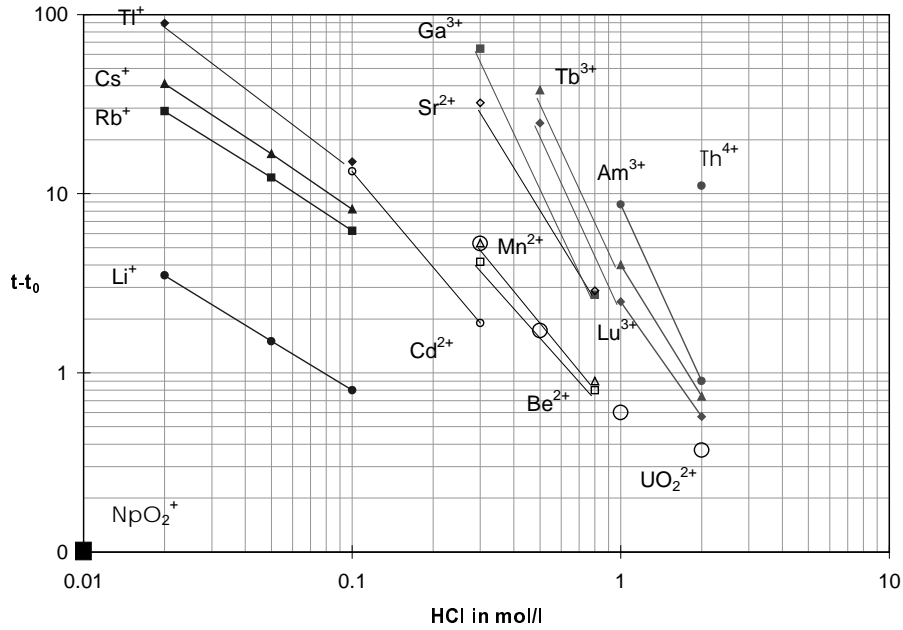
Figure 4-4. *Adjusted elution times for different cations vs. eluent concentration.*

To get an overview, the dead time corrected retention times can be plotted against the eluent concentration. From (Eq.3-10) it follows that with a single positive counter-ion the slope for mono-, di-, tri- and tetravalent species should be -1, -2, -3 and -4, respectively. For the monovalent cations, slopes in the range -0.9 to -1.1, for the divalent cations slopes in the range -1.7 to -2.5 and for the trivalent cations slopes in the range -3.2 to -3.4 were found. For the retention times of UO_2^{2+} no linear relation was found, presumably because of complex building with Cl^- ions (Fig. 4-4).

4.2   Separations with ethylenediammonium chloride

Sevenich and Fritz used ethylenediammonium as the counter-cation and tartrate as a complexing anion to separate polyvalent metal ions /4-1/. The complexing anion was found to improve the sharpness of the separations and the ethylenediammonium cation was found to shorten the retention times. The effect on separations by using ethylene-diammonium as the counter-cation instead of H^+ (for separations with HCl) was investigated by performing separations with ethylenediammonium dichloride. The retention times of mono-, di-, tri-, tetravalent and the complex cations MO_2^+ and MO_2^{2+} for different ethylenediammonium dichloride concentrations were investigated by separating Spex multielement standard solutions and actinide solutions. Ethylene-diammonium dichloride solutions up to 0.3 M did not suppress the signals in the ICP-MS. For a separation the eluent is introduced in the ICP-MS only for a short time. No drift problems arised after some analysis. Introducing the eluent for a longer time periods might cause drift problems. For ethylenediammonium dichloride eluents shorter retention times and better peak shapes for di- and trivalent cations were obtained compared to HCl eluents. With 0.1 M ethylenediammonium dichloride all the lantha-nides could be eluted within two minutes as sharp peaks whereas Th^{4+} could not be eluted within 20 minutes. The selectivity of the ion exchanger is not enough to separate
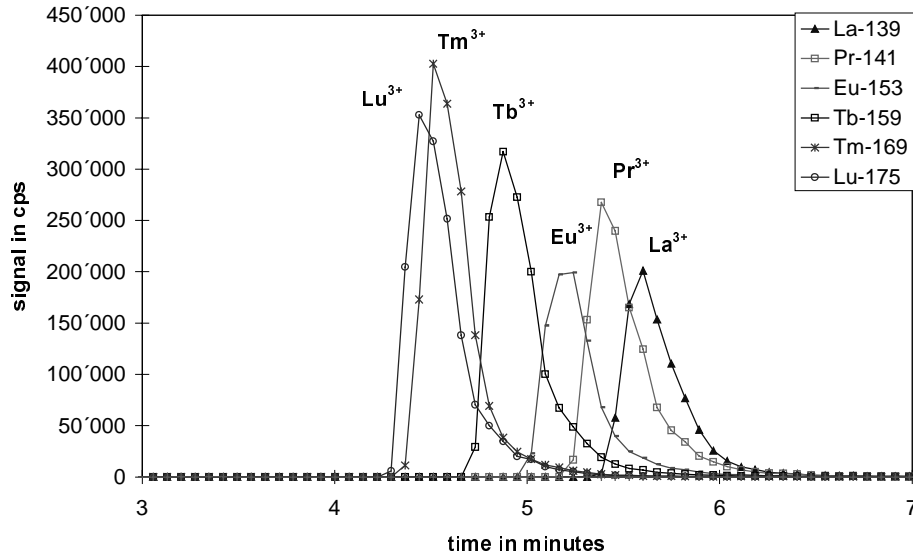
Figure 4-5. *Isocratic separation of 0.5 ml 10 ppb Spex1 +U with a 0.1 M ethylenediammonium dichloride eluent.*

the lanthanides (Figure 4-5). To increase the selectivity, a chelating agent such as hydroxyisobutyric acid has to be used as described in /1-4/. Figure 4-6 shows the separation of an actinide standard solution. Am^{3+} and Pu^{3+} eluted at the same time as sharp peaks. UO_2^{2+} eluted as a wide peak. For all ethylenediammonium dichloride concentrations NpO_2^+ was found not to be retained at all.
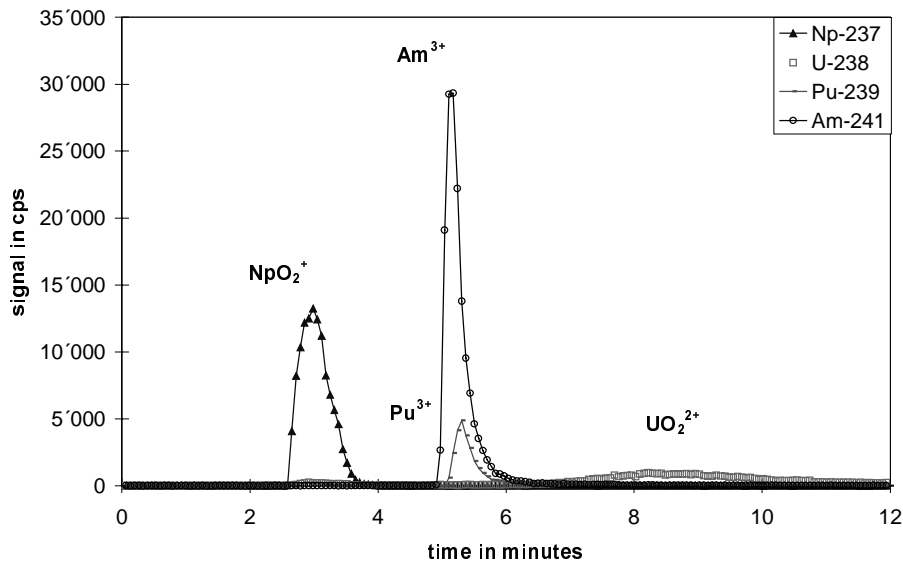

Figure 4-6. *Isocratic separation of 0.5 m1 1 ppb Pu, Am, Np and 0.5 ppb U with a 0.1 M ethylenediammonium dichloride eluent.*
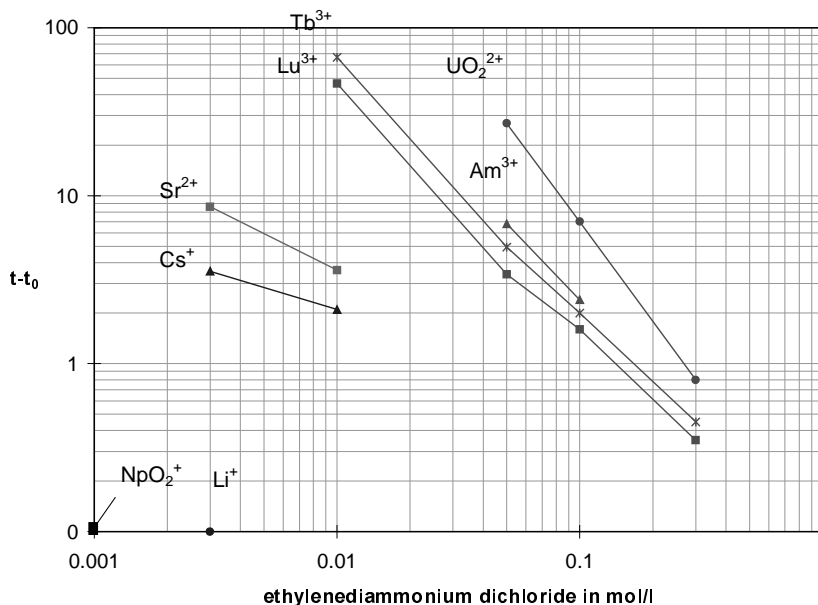
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Figure 4-7. *Adjusted elution time for different ethylenediammonium dichloride concentrations.*

In Figure 4-7 the dead time corrected retention times were plotted versus the eluent concentration. From (Eq. 3-10) follows that with a double positive counter-ion (ethylenediammonium) the slope for single, double, tri and tetravalent species should be -0.5, -1, -1.5 and -2 respectively. For the monovalent cation Cs^+ a slope of -0.4, for the divalent cation Sr^{2+} a slope of -0.7 and for the trivalent cations slopes of about -1.5 were found. For UO_2^{2+} a linear relation was found with a slope of –2.

4.3   Separations with H_2SO_4

Tri- and especially tetravalent cations are often difficult to elute from the column. Memory effects from previous separations often cause problems. The effect of different H_2SO_4 concentrations on the retention times of tri-, tetravalent and the complex cations MO_2^+ and MO_2^{2+} was investigated by separating actinide solutions. Figure 4-8 shows the separation of an actinide standard solution with 1 M H_2SO_4. All the actinide species are eluted as sharp peaks.

A 2 ppb multielement standard solution in 1 M H_2SO_4 was introduced directly in the ICP-MS. No signal drift was found for an aquisition time of ten minutes. However, the signals in 1 M H_2SO_4 were suppressed to about 60% of the signals obtained in 1% HNO_3. By applying only the Dionex CG 10 guard-column all the actinide species could be eluted as rather sharp peaks with only 0.4 M H_2SO_4 (Figure 4-9).

Figure 4-10 shows the elution time for different ionic species. Np(V) was not retained on the column and eluted after 1.7 minutes. U(VI) eluted with 0.1 M H_2SO_4 just after Np(V), whereas Th(IV) and Am(III) would hardly move down the column. With 0.5 M H_2SO_4 all the actinide species can be eluted in less than 3 minutes.
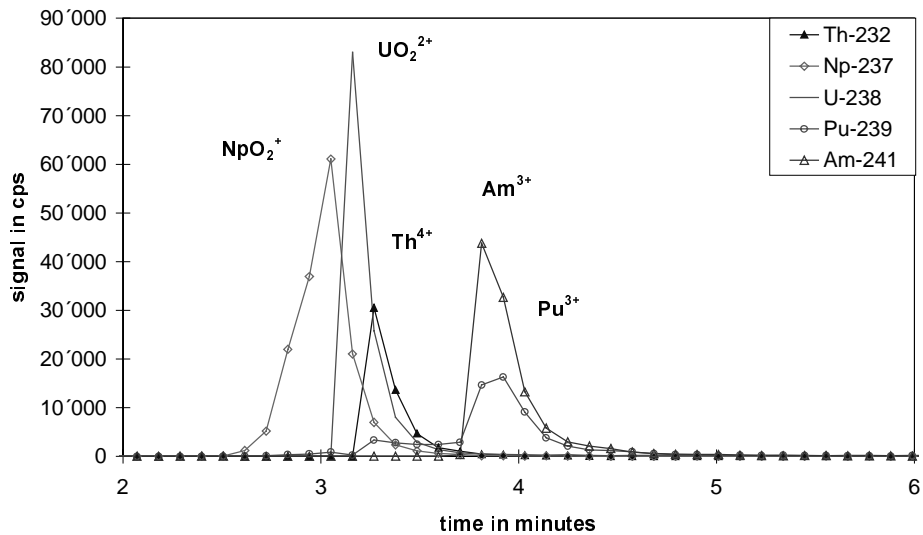
Figure 4-8. *Isocratic separation with 1 M H₂SO₄ of 0.5 m1 1% HNO₃ containing 5 ppb Pu, Am, Np, Th and 7.5 ppb U solution.*
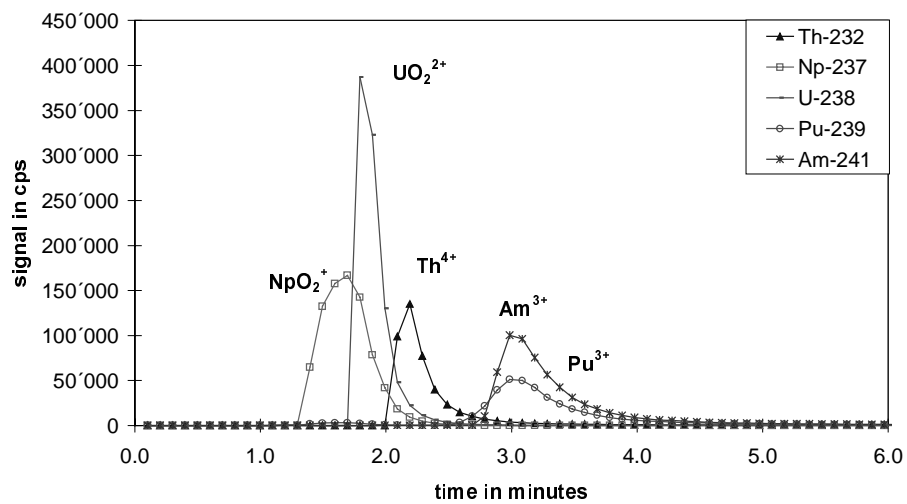

Figure 4-9. *Isocratic separation with 0.4 M H₂SO₄ of 0.5 m1 1% HNO₃ containing 5 ppb Pu, Am, Np, Th and 7.5 ppb U. Only the precolumn CG10 was applied.*
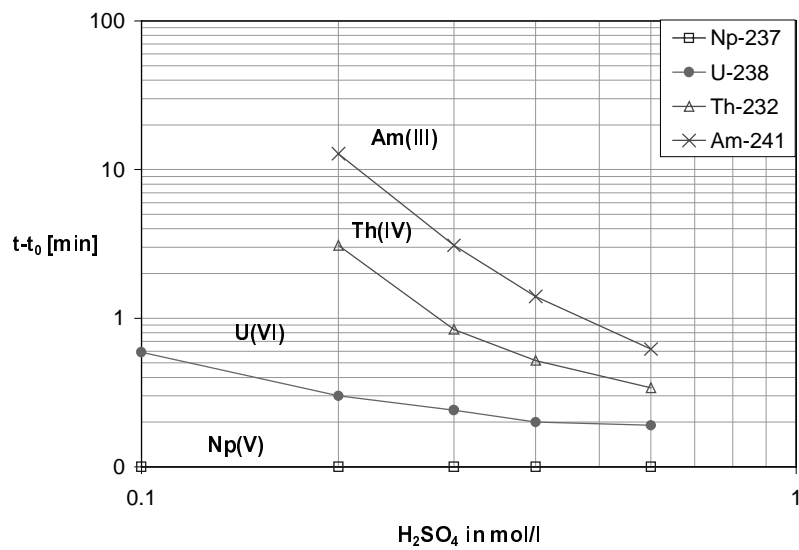
Figure 4-10. *Adjusted elution times for actinides in different oxidation states. 0.5 ml 5 ppb Am, Np, Th and 7.5 ppb U were eluted isocratically with H_2SO_4 on the CG10 column.*

5　Separation with more than one eluent

Separation methods for actinides and fission products were investigated by using the information obtained from isocratic elutions.

5.1　Separation of Rb/Sr and Cs/Ba

Direct mass spectrometric determinations of Rb isotopes in spent fuel solutions often are disturbed by isobaric overlaps with natural Sr. Furthermore, Cs isotopes show isobaric overlaps with Ba. With a group separation of the alkali and earthalkali elements before the mass spectrometric determination it is possible to avoid interferences. Figure 5-1 shows the separation of a standard solution containing 10 ppb Rb, Sr, Cs and Ba. The monovalent alkali elements are eluted with 0.1 M HCl. Ba only could be eluted as a wide peak for HCl concentrations up to 0.8 M. Therefore, the earthalkali have been eluted with ethylenediammonium dichloride. Figure 5-1 shows that the elements Rb and Cs are completely separated from the elements Sr and Ba. Figure 5-2 shows the separation of a leach solution with the same eluents. The Cs isotopes are completely separated from the Ba isotopes.
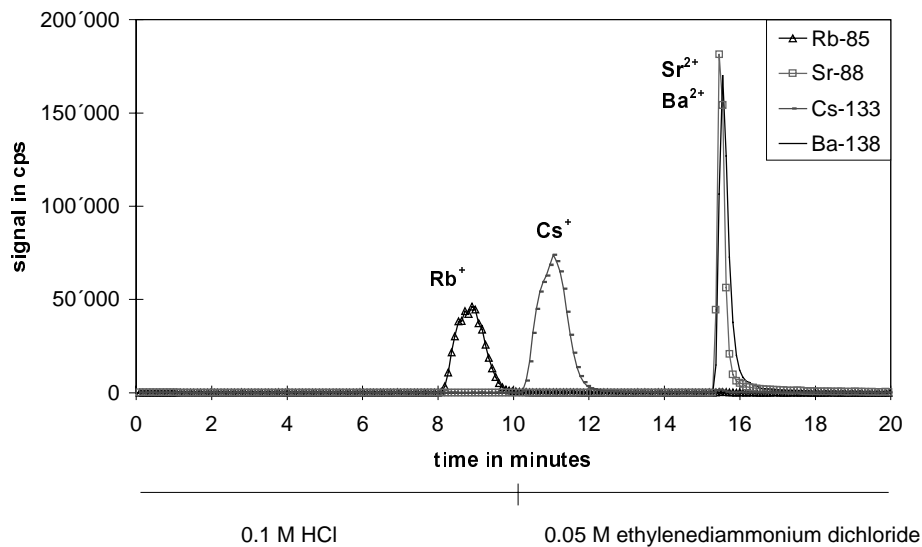

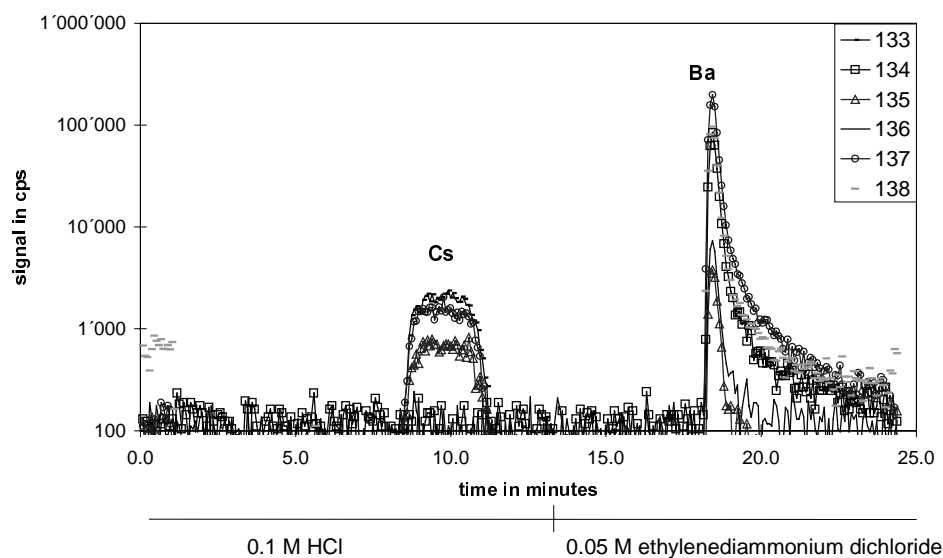***Figure 5-1.***　*Separation of 0.5 ml 10 ppb Rb, Sr, Cs and Ba standard solution.*

Figure 5-2. *Separation of 0.5 ml spent fuel solution.*

5.2 Redox state separations of actinides

Isobaric interferences especially between Pu and Am and Pu and U disturb direct mass spectrometric measurements. The complex formation constants for different actinides in the same oxidation state show only slight differences. Thus, as long as no specific complex building agent is added, the retention time of different actinides in the same oxidation state do not differ significantly. Due to their stability in aqueous solutions, Th^{4+}, UO_2^{2+}, Am^{3+} and NpO_2^+ were taken as representatives for the four different oxidation species /5-1–5-2/. Elution parameters were investigated to separate all four actinide species from each other.

Figure 5-3 shows the separation of all four actinide species. NpO_2^+ and UO_2^{2+} are separated with a 0.3 M HCl. With this eluent all the tri- and tetravalent species hardly move down the column (Figure 4-4). With an ethylenediammonium dichloride eluent the trivalent Am^{3+} could be eluted as a sharp peak. To elute tetravalent cations, a complex building agent such as hydroxyisobutyric acid had to be used. Pu was eluted as 3 different species.

To make sure all actinide species are eluted at the end of a separation, a 1 M H_2SO_4 eluent was used instead of hydroxyisobutyric acid. Figure 5-4 shows the separation of an actinide standard solution in 1% HNO_3. All four representatives for the different actinide species (NpO_2^+, UO_2^{2+}, Th^{4+} and Am^{3+}) are separated as sharp peaks. The tetravalent actinides are now eluted before the trivalent actinides due to strong complexation with sulfate anions. Pu elutes as three different species. A very small part at the same time as NpO_2^+. One part elutes as Pu^{3+} and another as Pu^{4+}. The two peaks are bridged. The reason for this could be a background problem.
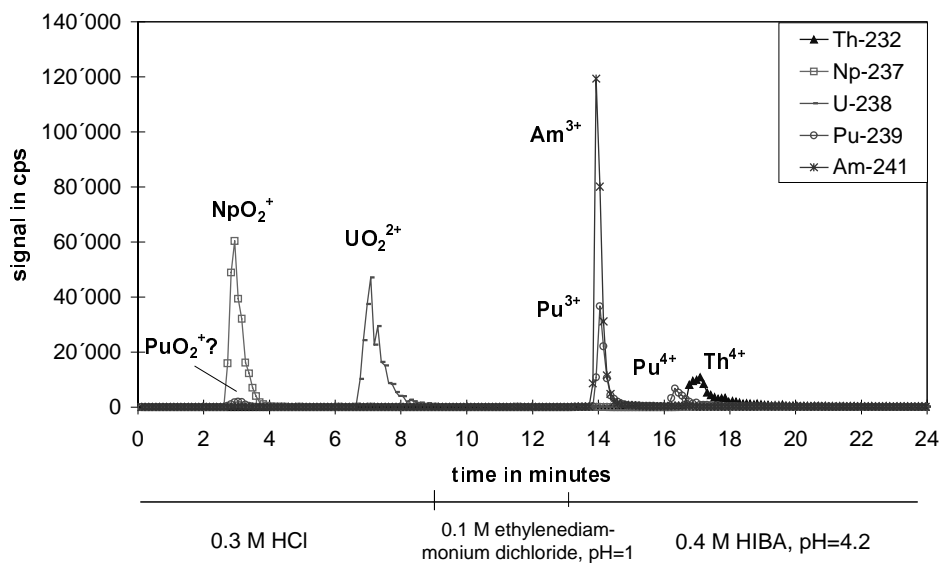
Figure 5-3. *Separation of 0.5 ml 1% HNO₃ containing 5 ppb Pu, Am, Np, Th and 7.5 ppb U.*
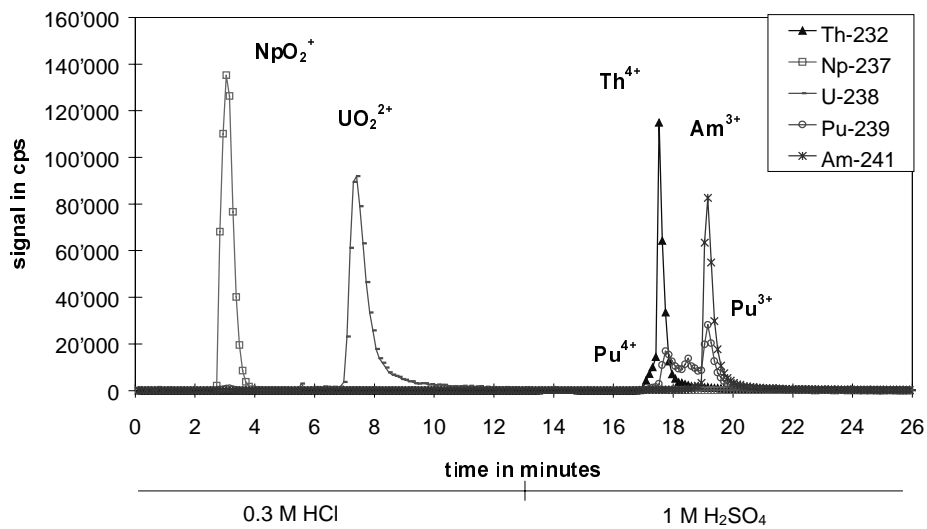

Figure 5-4. *Separation of 0.5 ml 1% HNO₃ containing 5 ppb Pu, Am, Np, Th and 7.5 ppb U.*
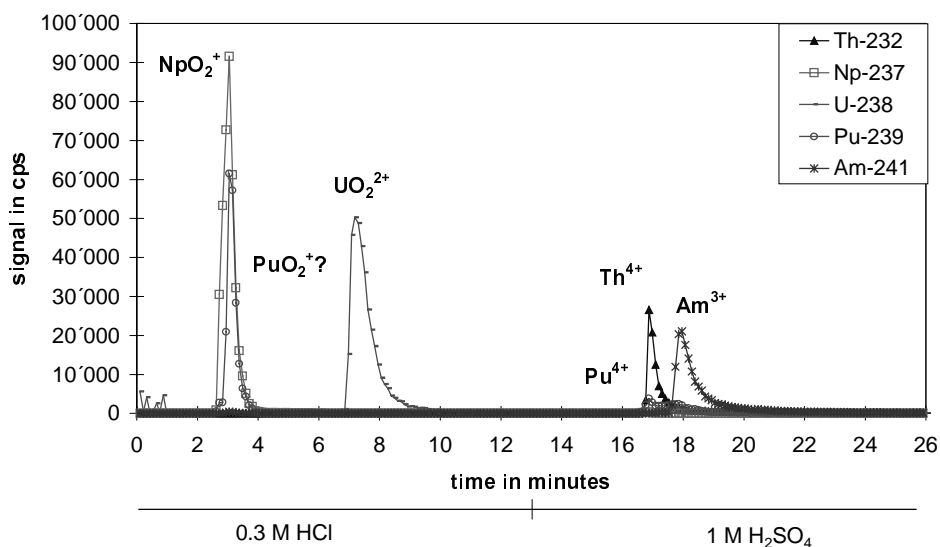
Figure 5-5. *Separation of 0.5 ml 0.0001 M KMnO$_4$ in 1% HNO$_3$ containing 5 ppb Pu, Am, Np, Th and 7.5 ppb U solution.*

In order to separate Am and Pu, the reduced Pu species (Pu^{3+}, Pu^{4+}) have been oxidised with KMnO$_4$ /5-3/. Figure 5-5 shows the separation of an actinide standard solution containing 0.0001 KMnO$_4$ in 1% HNO$_3$. Most of the Pu is now eluting at the same time as NpO$_2^+$. If the Pu really was oxidised to PuO$_2^{2+}$ this is quite astonishing, as PuO$_2^{2+}$ is expected to have the same chemical characteristics as UO$_2^{2+}$ and hereby is expected to elute at the same time as UO$_2^{2+}$. Pu was oxidised with other agents as well, but it elutes always at the same time as NpO$_2^+$. However, it is hard to believe that PuO$_2^{2+}$ has the same chromatographic characteristics as NpO$_2^+$ and this remains to be explained. The small part of Pu which is eluting as Pu^{3+} and Pu^{4+} could be background peaks.

5.3   Separation of U(IV) and U(VI)

The green U(IV) solution in 85% phosphoric acid was diluted with 2 M HCl to a 2.4 ppm U solution. In 2 M HCl U(IV) is slowly oxidised by atmospheric oxygen so that U(VI) and U(IV) species are expected to exist in the solution /5-4/. The suitability of the elution parameters to separate U(IV) and U(VI) species was tested by separating 0.5 ml of this solution with the same chromatographic conditions used for Figure 5-4. Figure 5-6 shows that U(VI) is eluted as a large peak. The reason for this large peak can be explained as follows: U(VI) is eluting with a 0.3 M HCl eluent after about 8 minutes. The sample itself contained 2 M HCl which made a part of the U(VI) to elute already after 3 minutes. The HCl concentration is diluted with the eluent and the remaining U(VI) is eluted as a large peak. The small peak before the U(IV) peak is probably a background peak.
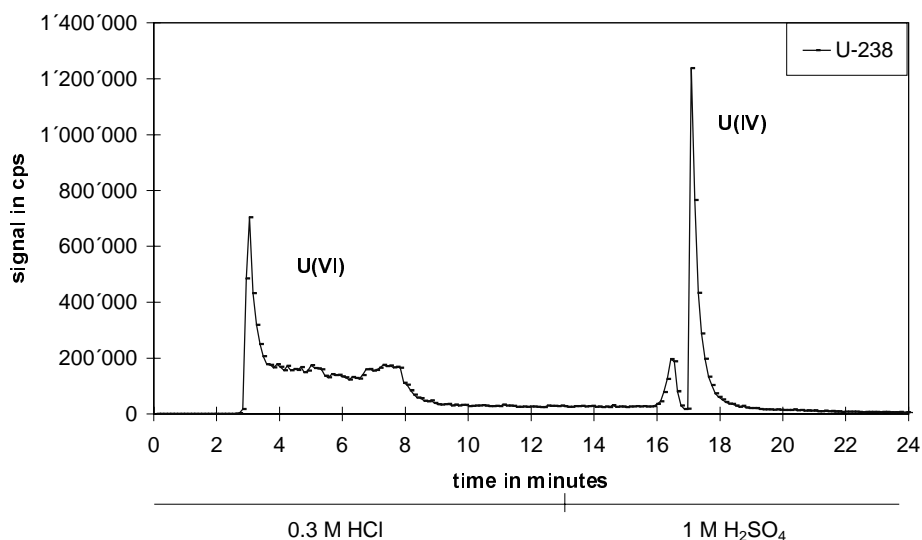
Figure 5-6. *Speciation of 0.5 ml 2.4 ppm U solution in 2 M HCl containing U(VI) and U(IV) species.*

The separation method was optimised in order to elute the whole U(VI) as one peak. Figure 5-7 shows the separation of an actinide standard solution in 1% HNO_3. The actinides MO_2^+ and MO_2^{2+} are eluted with 1 M HCl after about 3 minutes and the actinides M^{3+} and M^{4+} are eluted with 1 M H_2SO_4 after about 9 minutes. With the same chromatographic conditions a 256 ppb U solution in 2 M HCl containing U(VI) and U(IV) species was separated (Figure 5-8). The U(VI) species are completely separated from the U(IV) species. Any shifting in the redox state composition during the separation would lead to bridged peak shapes. No bridged peak between the two oxidation forms were found and thus no U^{4+} was oxidised to UO_2^{2+} on the column.
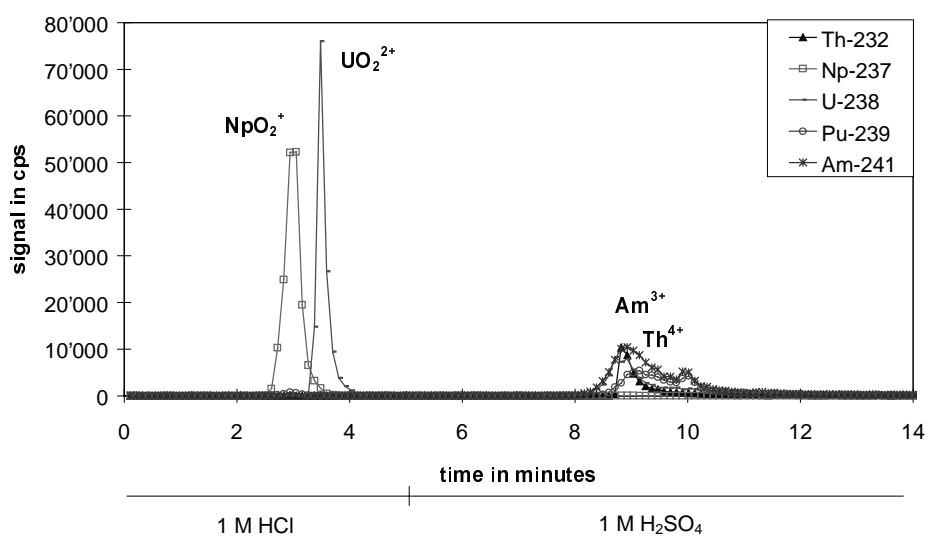

Figure 5-7. *Separation of 0.5 ml 1% HNO$_3$ containing 5 ppb Pu, Am, Np and 7.5 ppb U.*
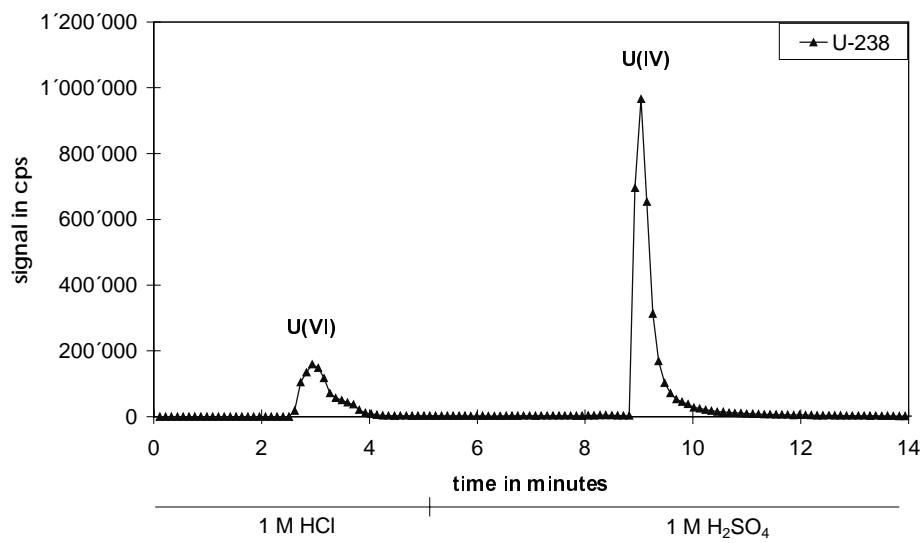
Figure 5-8. *Speciation of 0.5 ml 256 ppb U(IV) in 2 M HCl after a few days.*

6   Conclusions

Isocratic elution of mono-, di, tri- and tetravalent and actinide cations with hydrochloric acid, ethylenediammonium dichloride, hydroxyisobutyric acid and sulfuric acid gave a good overview of elution parameters affecting retention times of individual cationic species. The knowledge could be applied to investigate elution parameters to separate fission products and actinides in different oxidation states. Since redox reactions are often relatively rapid, any separation method must be evaluated carefully to ensure that no shift in the redox equilibria occurs during the separation process. Elution parameters to separate U(VI) from the U(IV) could be optimised to get good peak shapes, and not bridged peak shapes, which would be expected for species changing their oxidation state during separation. Following this work the separation method was further optimised by only applying the CG10 column. With this method the U(VI)/U(IV) composition for U solutions down to 10^{-9} M could be analysed in less than 8 minutes. Furthermore, some kinetic studies for the oxidation of U(IV) with O_2 were made /6-1/. First results of Pu speciation analysis showed that Pu could be eluted as three different species. Pu was oxidised with $KMnO_4$ to Pu(VI) which eluted always at the same time as Np(V). This is surprising, as Pu(VI) is expected to have the same chemical characteristics as U(VI) and thus is expected to elute at the same time as U(VI). In further experiments it will be checked if Pu really was oxidised to Pu(VI).

7   Acknowledgements

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