

POSIVA-96-01

Determination of U oxidation state in anoxic (N₂) aqueous solutions - method development and testing

Kaija Ollila
VTT Chemical Technology

June 1996

POSIVA OY

Annankatu 42 D, FIN-00100 HELSINKI, FINLAND

Phone (90) 228 030 (nat.), (+358-0-) 228 030 (int.)

Fax (90) 2280 3719 (nat.), (+358-0-) 2280 3719 (int.)

ISBN 951-652-000-6
ISSN 1239-3096

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Posiva-raportti – Posiva report

Posiva Oy
Annankatu 42 D, FIN-00100 HELSINKI, FINLAND
Puh. (90) 2280 30 – Int. Tel. +358 0 2280 30

Raportin tunnus – Report code

POSIVA-96-01

Julkaisu-aika – Date

June 1996

Tekijä(t) – Author(s) Kaija Ollila VTT Chemical Technology	Toimeksiantaja(t) – Commissioned by Posiva Oy
Nimeke – Title DETERMINATION OF U OXIDATION STATE IN ANOXIC (N₂) AQUEOUS SOLUTIONS – METHOD DEVELOPMENT AND TESTING	
Tiivistelmä – Abstract <p>This report describes the development and testing of a method for determining uranium oxidation state in aqueous solutions in inert (N₂) atmosphere. The method included the separation of the tetravalent and hexavalent states by anion-exchange chromatography in HCl medium, followed by analysis of the uranium contents of each of the fractions by ICP-MS.</p> <p>First, the fixation and elution of U(VI) was investigated under atmospheric conditions in the absence of U(IV). A suggested detection limit for ²³⁸U(VI), 0.04 ng, could be concluded based on the background measurements of separation. In the next stage, the determination of U(IV) was tested by adding U(IV) alone to the samples. The U(IV) determinations were complicated by the partial instability of the U(IV) solutions in the N₂ atmosphere of the glove box. Finally, a real test of the U(IV)-U(VI) separation was realized by adding the U(VI) as ²³³U(VI) to the samples, in order to see the difference between the oxidized U(IV) and the original U(VI) addition. The results showed that separation occurred almost quantitatively (yield 90 - 100 %) and reproducibly.</p> <p>As the first application, the oxidation state of U was determined for anoxic (N₂) aqueous solutions (including two synthetic groundwaters) after contact with unirradiated UO₂ pellets for 500 days in the glove box. According to the analyses, the uranium was mainly at the U(VI) state.</p> <p>The tests of this study demonstrated the suitability of the method for analysing the oxidation states of uranium at the low concentrations representative for U solubilities in anoxic groundwater. Additionally, the results obtained give some information on the redox state of the aqueous solutions in inert (N₂) atmosphere. Obviously, the trace oxygen content in the atmosphere of the box is enough to cause slightly oxidizing conditions for uranium in the absence of reducing agents (e. g. H₂, iron).</p>	
ISBN ISBN 951-652-000-6	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 33 + 4	Kieli – Language English



Posiva-raportti – Posiva report

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Annankatu 42 D, FIN-00100 HELSINKI, FINLAND
Puh. (90) 2280 30 – Int. Tel. +358 0 2280 30

Raportin tunnus – Report code

POSIVA-96-01

Julkaisuaika – Date

Kesäkuu 1996

Tekijä(t) – Author(s) Kaija Ollila VTT Kemianteekniikka	Toimeksiantaja(t) – Commissioned by Posiva Oy
Nimeke – Title URAAININ HAPETUSTILAN MÄÄRITYS HAPETTOMASSA (N₂) VESILIUOKSESSA – MENETELMÄN KEHITYS JA TESTAUS	
Tiivistelmä – Abstract <p>Tässä raportissa on kehitetty ja testattu menetelmää, jolla voidaan tutkia uraanin hapetustilaa vesiliuoksessa hapettomissa olosuhteissa. Aluksi uraanin hapetustilat (IV, VI) erotetaan anioninvaihtokromatografialla (HCl), minkä jälkeen saatujen fraktioiden pitoisuudet analysoidaan ICP-MS-menetelmällä.</p> <p>Työ aloitettiin tutkimalla U(VI):n kiinnittymistä anioninvaihtohartsiin (4.5 M HCl) hapellisissa (ilma-) olosuhteissa. U(VI) eluoidaan sen jälkeen laimealla hapolla (0.1 M HCl). Tulosten perusteella voitiin esittää määrittäysraja: 0.04 ng ²³⁸U(VI). Seuraavassa vaiheessa testattiin U(IV):n määrittämistä hapettomissa olosuhteissa (typpikaappi). Sitä vaikeutti U(IV):n osittainen hapettuminen typpi-atmosfäärissä. U(IV)-U(VI) hapetustilojen erottuminen osoitettiin lisäämällä U(VI) ²³³U(VI):na, jolloin voitiin nähdä ero hapettuneen U(IV):n ja lisätyn U(VI):n välillä. Erottuminen tapahtui lähes kvantitatiivisesti (saalis 90 - 100 %) ja toistettavasti.</p> <p>Ensimmäisenä sovellutuksena tutkittiin uraanin hapetustila hapettomissa UO₂ pellettien liukenemiskokeissa typpi-atmosfäärissä 500 päivän koeajan jälkeen. Tulosten mukaan uraanin hapetustila oli pääasiassa U(VI) kaikissa vesiliuoksissa (mukana kaksi synteettistä pohjavettä).</p> <p>Suoritettavat testaukset osoittivat menetelmän sopivuuden analysoitaessa uraanin hapetustilaa matalissa pitoisuuksissa, jotka ovat tyypillisiä UO₂-liukoisuuskokeissa hapettomissa olosuhteissa. Saadut tulokset antavat tietoa vesiliuosten redox-tilasta typpi-atmosfäärissä. Ilmeisesti hapettoman kaapin typpi-kaasun sisältämä hiivenhappi on riittävä aiheuttamaan lievästi hapettavat olosuhteet uraanille pelkistimien (esim. H₂, rauta) poissaollessa.</p>	
ISBN ISBN 951-652-000-6	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 33 + 4	Kieli – Language Englanti

CONTENTS

ABSTRACT

TIIVISTELMÄ

1	INTRODUCTION	1	
2	EARLIER INVESTIGATIONS	3	
3	EXPERIMENTAL	10	
	3.1	Chromatographic columns	10
	3.2	Reagents and standards	11
	3.3	Anaerobic conditions	12
	3.4	Separation procedure	13
4	DISCUSSION OF RESULTS	16	
	4.1	Fixation of and elution of U(VI)	16
	4.2	Determination of U(IV)	20
	4.3	U(IV)-U(VI) separations	25
	4.4	U oxidation state in the dissolution experiments of UO ₂	27
5	SUMMARY AND CONCLUSIONS	29	
6	ACKNOWLEDGEMENTS	31	
7	REFERENCES	32	

APPENDICES 1 - 4

1 INTRODUCTION

Speciation of uranium in groundwaters, or in aqueous solutions generally, requires identifying the oxidation states as well as the dominant complexes. The first step is the determination of the oxidation states. It is important to know the oxidation state in which uranium will occur under specified conditions of Eh and pH as this relates to the mobility of uranium. Uranium is known to be mobile in oxidizing groundwater at the soluble U(VI) state, especially when complexed by carbonate. Under reducing conditions, the predominant oxidation state is the U(IV). The uranium concentrations in equilibrium are extremely low. U(IV) is hydrolyzed in solution. However, the complex formation with carbonate affects the relative stabilities of the oxidation states. This makes U(VI) stable in a more reducing redox regime than in the absence of carbonate, increasing solubility. The relative amounts of the U(VI)-carbonate complexes and the U(IV)-hydroxide complexes depend on carbonate concentration, pH and Eh /SKI Project-90 1991/.

At the low uranium concentrations, the most ideal way of analysing the oxidation state would be the direct measurement using laser spectroscopy with high sensitivity, e.g. LIPAS (laser-induced photoacoustic spectroscopy) /Cross et al 1989/. One possibility is to use a separation method for the oxidation states followed by analysing the uranium contents of each of the fractions. A suitable method for separation does not affect the distribution of the oxidation states. The methods reported in the literature have included coprecipitation, adsorption, solvent extractions, ion exchange /Hussonnois et al 1989/. For the analysing the uranium contents of the fractions, ICP-MS (inductively coupled plasma mass spectrometry), provides a method for uranium concentrations down to 0.08 nM l^{-1} .

The aim of this experimental work is to find and test a method suitable for analysing the oxidation states of uranium at the low concentrations typical for anoxic groundwater at great depths in granitic bedrock. As the first application, the solutions after contact with UO_2 pellets in a series of dissolution experiments /Ollila 1995/ under anaerobic conditions are preliminarily analysed for oxidation states. First, a short review of methods found in the literature is given.

2 EARLIER INVESTIGATIONS

Anderson /1984/ made a determination of oxidation state on seawater samples. The method was based on the well-known ability of rare earth fluorides to coprecipitate actinides in the (III) and (IV) oxidation states while leaving the (V) and (VI) oxidation states in solution. In this work, yield monitors [$^{232}\text{U}(\text{IV})$, $^{236}\text{U}(\text{VI})$] in each oxidation state were added to water samples and the oxidation states were separated by a NdF_3 coprecipitation in which only the U(IV) was carried. The precipitate was removed by filtration. Subsequently, TiCl_3 was added to reduce U(VI) and the NdF_3 coprecipitation was repeated. The method permitted > 99 % separation of U(IV) from U(VI). The uranium contents of each fraction were measured by alpha-spectrometry.

$^{232}\text{U}(\text{IV})$ tracer was prepared by reduction with TiCl_3 . Some of the U(IV) tracer (13 - 29 %) was observed to oxidize before it was added to the sample regardless of N_2 -shielding. The U(IV) is much more stable with respect to air oxidation in strong acid than at neutral pH. In spite of the sample acidity, nearly all of the tracer was oxidized in less than half an hour between tracer addition and coprecipitation. The oxidation rate of U(IV) increased with decreasing acidity.

The above-described method was used by Ervanne et al /1994/ when analysing groundwater samples from Palmottu in the Palmottu Analogue Project. Dissolved redox pairs were studied in a uranium-rich groundwater sample by monitoring the Eh change caused by acid/base addition. A good consistency between dissolved U(IV)/U(VI) ratio and the measured redox potential value was observed. The results indicated that dissolved uranium in concentration of $0.8 \mu\text{mol l}^{-1}$ may give nernstian response at the platinum electrode.

Adsorption behaviour of U(VI) on anion-exchange resins was studied by Kraus and Nelson /1956/ in HCl, HNO₃ and H₂SO₄ solutions. Adsorption of uranium occurred from all these media in equilibration experiments, although the characteristic adsorption functions differed widely, see Figure 2-1.

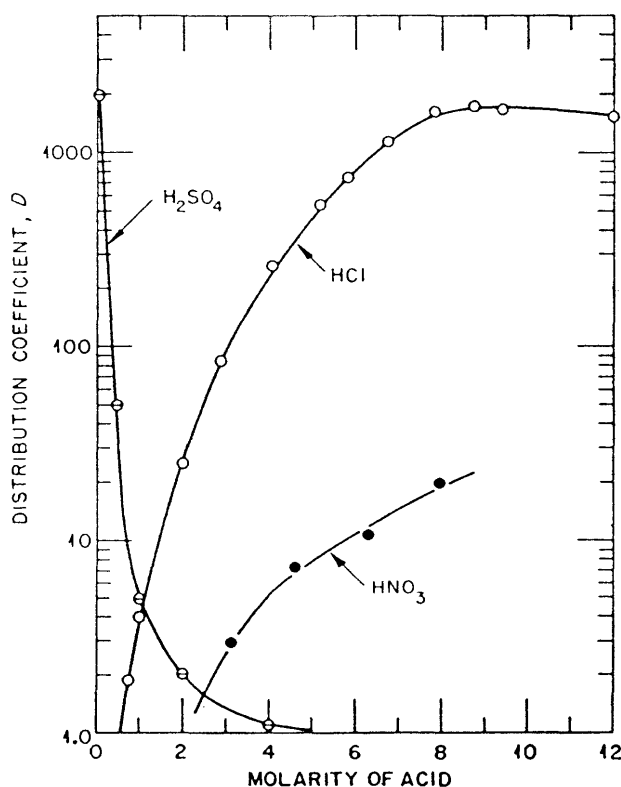


Figure 2-1. Adsorption of U(VI) from various acid solutions /Kraus and Nelson 1956/.

The adsorbability of U(VI) rose steeply with increasing HCl concentration to near 9 M HCl. At higher concentrations it decreased slightly. In nitric acid, the adsorbability of U(VI) became significant near 2 M HNO₃ and then rose to near 8 M HNO₃. Above this concentration the equilibration experiments yielded irreproducible results, probably due to decomposition of the resin by the rather concentrated nitric acid. The adsorption function of U(VI) in sulphuric acid differed markedly from those in HCl or HNO₃. Thus, adsorption was very high at low sulphuric acid concentration, and decreased rapidly with increasing M H₂SO₄ to 4 M H₂SO₄. As a conclusion from these

adsorption studies, HCl would be the most suitable medium for separation of U(VI).

Hussonnois et al /1989/ developed and tested a method based on the separation of U(IV)-U(VI) by ion-exchange chromatography in HCl medium. According to them, the separation by ion exchange is fast enough so as not to alter the initial oxidation states, coprecipitation being relatively slow. The time-resolved laser-induced fluorescence (TRLFS) was used for the determination of the uranium contents after separation. It was possible to measure concentrations as low as 10^{-10} M with this method. In this work, the U(IV) at tracer level was prepared by electrochemical reduction. The reduction cell was connected to the chromatographic column, Figure 2-2. Electrochemical reductions of U(VI) solutions from 10^{-2} M to 10^{-10} M in 6 M HCl gave pure U(IV) solutions.

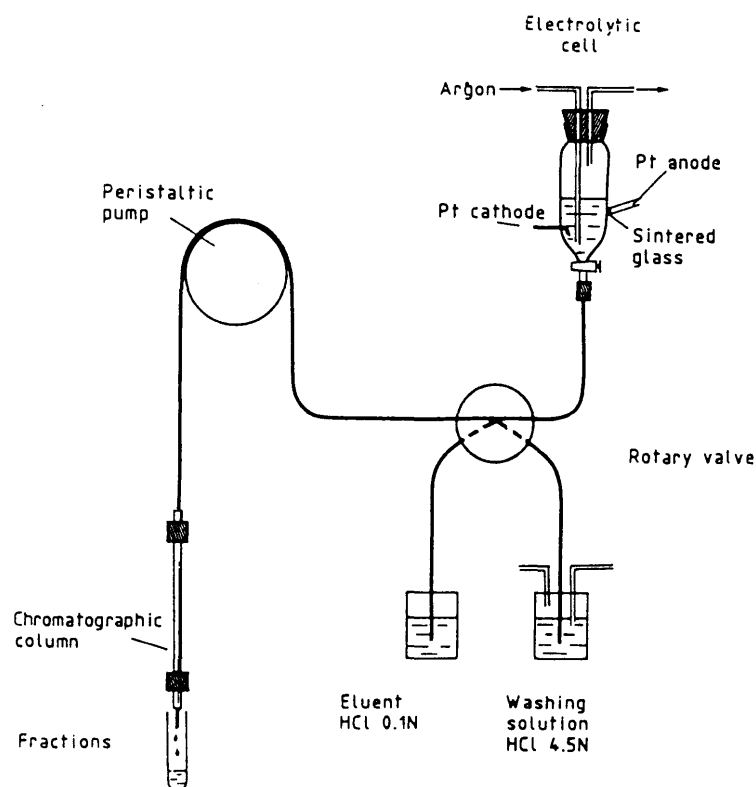


Figure 2-2. Scheme of the reduction cell connected to the chromatographic column /Hussonnois et al 1989/.

Solutions submitted to the U(IV)-U(VI) separation flowed through the column (anionic resin, Dowex 1x8, 400 mesh) with a peristaltic pump at a rate of 0.2 ml/min. The columns could be connected to the reduction cell to perform the whole separation without air contact. When testing the method, it was noticed that U(VI) was fixed at 100 % on the resin with 4.5 M HCl medium and could be recovered by 0.1 M HCl elution. The amount of U(IV) was less than 5 %. U(IV) was recovered at more than 95 % in 4.5 M HCl with less than 1 % of U(VI).

Some results on the oxidation kinetics of the U(IV) state versus the HCl and uranium concentrations were also presented by Hussonnois et al /1989/. It was necessary to perform all the U(IV)-U(VI) separations within 10 minutes after the U(IV) preparation in order to avoid the oxidation of U(IV). Figure 2-3 shows the variation of the U(IV) percentage versus time for different uranium concentrations in 4.5 M HCl. The U(IV) stability showed a rapid decrease with the increase of the pH.

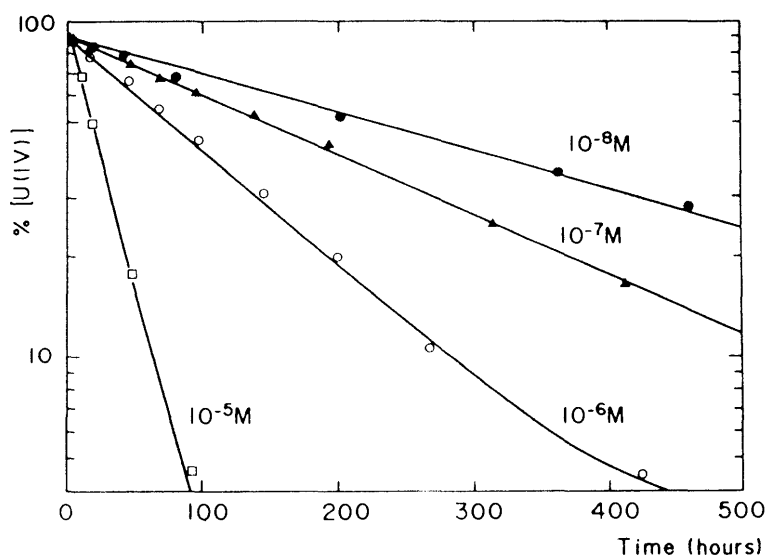


Figure 2-3. Percentage of U(IV) as a function of time for different uranium concentrations in 4.5 M HCl /Hussonnois et al 1989/.

Al Mahamid and Paulus /1989/ determined the oxidation states of ^{239}U in various solid salts by High Performance Liquid Chromatography technique (HPLC), which is generally suitable for fast separations. Optimal conditions of separation were obtained with an equimolar (0.125 M) solution of oxalic and nitric acids. Oxalic acid forms stable anionic complexes with U^{4+} and UO_2^{2+} . In the presence of 0.125 M oxalic acid, these cations should almost exclusively exist in the form of $\text{U}(\text{C}_2\text{O}_4)_4^{4-}$ and $\text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}$, respectively. U(IV) was eluted first at 3.6 min, whereas U(VI) eluted at 9 min. The observed order of elution was probably due to the greater size of the U(IV) anionic complex in comparison with that of U(VI), when both these species have the same negative charge. No detection limits for the method were given in the reference.

Cross et al /1989/ studied the speciation of uranium under well controlled pH and Eh conditions using a combined LIPAS/electrochemical loop. The Eh range was between +280 and -400 mV. Comparison of the observed species was made with those predicted by the thermodynamic geochemical modelling code PHREEQE. An active voltammetry system provided some supporting evidence for changes in uranium speciation at high pH (pH 8).

The Eh of the sample was controlled in the electrochemical cell. It comprised a gold working electrode, an auxiliary electrode and a Ag/AgCl reference electrode. The speciation measurements were carried out at pH 1 and 8 as a function of Eh. The uranium species measured by LIPAS are given in Figure 2-4 for different Eh values, together with those predicted by PHREEQE. Initially, only U(VI) was present. At pH 1, after conditioning the solution at 0 mV, reduction to U(IV) occurred. Conditioning at Eh +160 mV produced a mixture of U(IV), U(V) and U(VI). At Eh +280 mV only U(VI) existed. The distribution of oxidation states at pH 8 was different, see Figure 2-4. After conditioning the solution at Eh -100 and -250 mV, U(VI) was

the only observable species. After that, the Eh was gradually lowered in steps to seek the potentials at which U(VI) reduced and U(V) and U(IV) appeared. At Eh -300 mV a small peak of U(V) appeared, indicating the onset of reduction. At Eh -335 mV U(IV), U(V) and U(VI) were present. At Eh -400 mV, only U(IV) was observed. It was not possible to simulate successfully with PHREEQE the observed experimental data at pH 8 due to inadequacies in the U(IV) and the U(VI) hydrolysis datasets at the date of writing the report /Cross et al 1989/.

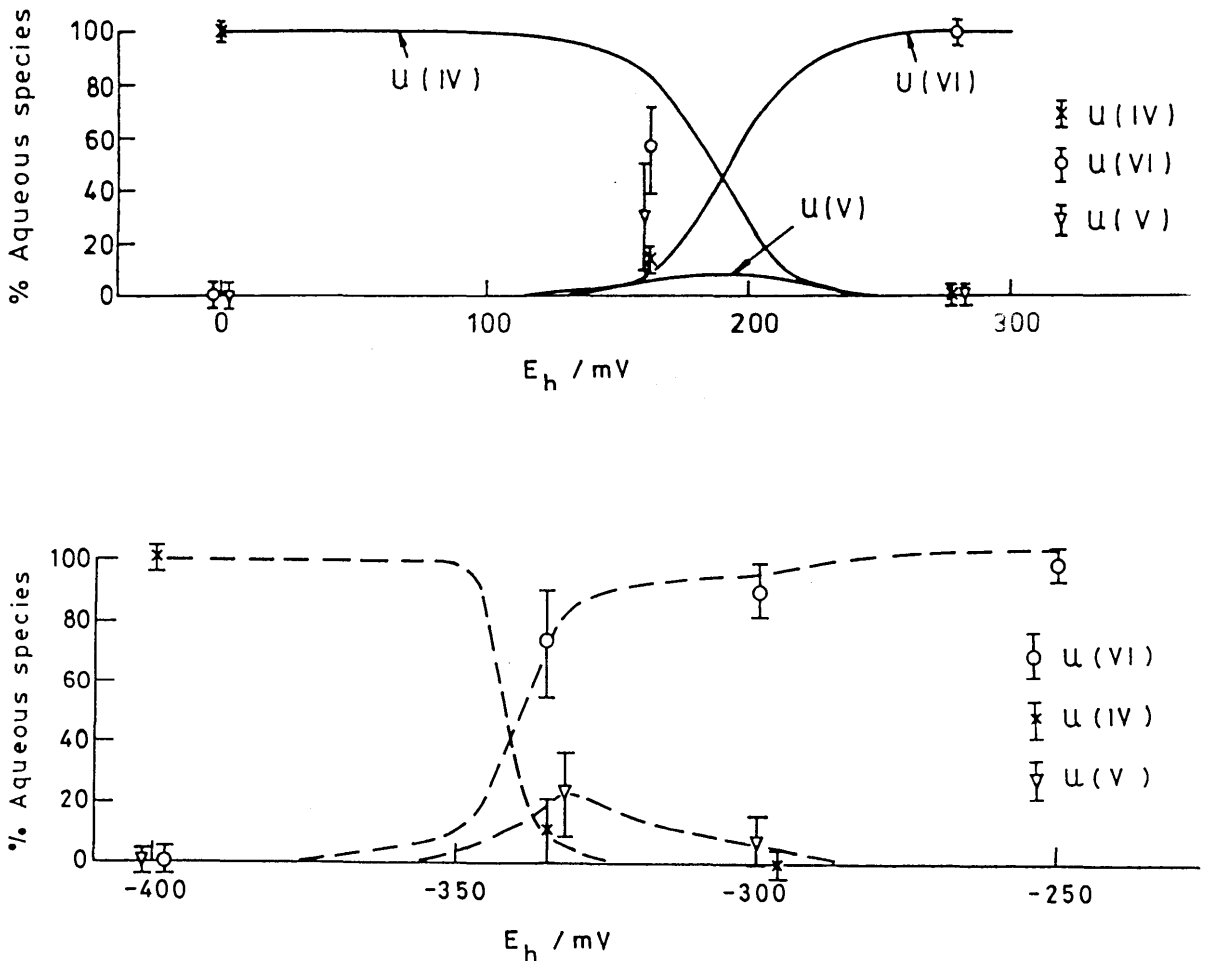


Figure 2-4. Uranium oxidation state versus Eh measured by LIPAS at pH 1 (upper figure) and pH 8 (lower figure). Comparison of the species measured at pH 1 with those predicted by PHREEQE /Cross et al 1989/.

As a conclusion from the review of the methods used in the literature, the separation of U(IV)-U(VI) by ion-exchange chromatography in HCl medium was selected the most suitable for our experimental conditions in the anaerobic glove box. The separation by ion exchange is classified according to Hussonnois et al /1989/ as a fast method, while, e.g., coprecipitation and adsorption are relatively slow. This would be advantageous in terms of the possible repartition of the oxidation states during separation. The stability of both U(IV) and U(V) states is known to be very sensitive to the oxygen content of the solutions. Thus the separations (including U-IV) will be performed under nitrogen atmosphere in the glove box. The uranium contents of each fraction will be analysed with ICP-MS, which provides a method for uranium concentrations down to 0.08 nM l^{-1} .

3 EXPERIMENTAL

3.1 Chromatographic columns

U(IV) - U(VI) separations were made in Econo low-pressure chromatography columns (50 mm in length, 5 mm in diameter, 1 ml in maximum volume), which were filled with the anionic resin, Dowex 1x8 (Cl⁻ form, 200 - 400 mesh, Fluka Chemie AG). The columns had a borosilicate glass barrel and a reservoir made of polypropylene, see Figure 3-1. A porous polymer bed support at the bottom of the column retains fine particles. The column of anionic resin was packed tight with glass-wool. It was possible to adjust the flow rate through the column with the help of a peristaltic pump. However, this proved to be unnecessary, as the flow rate through the column with the loose plug was suitable, 0.2 ml/min, for the separations without the pump.

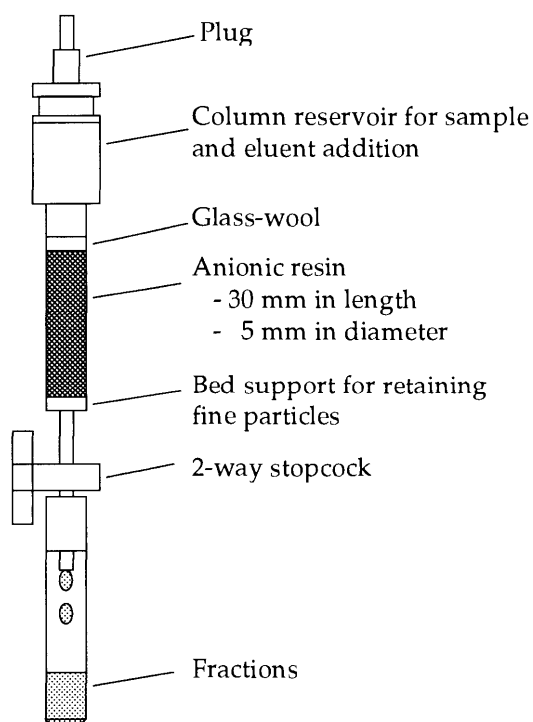


Figure 3-1. Chromatographic column for U(IV)-U(VI) separations.

The anionic resin was washed with deionized water and 0.1 M HCl before use to eliminate impurities. For separations in the glove box (N_2), the resin in 0.1 M HCl was deaerated with N_2 , transferred into the box and allowed to equilibrate with the atmosphere (N_2) of the box for at least one week, in an attempt to remove the trace oxygen from the resin. Also in the box, the resin was washed with deaerated deionized water and 0.1 M HCl before use. One column filled with anionic resin was used for two parallel separations. Purification (0.1 M HCl) and regeneration of the resin (4.5 M HCl) were performed between those separations. Then the resin was discarded and a new column (acid-washed) filled with fresh resin was used for the following separations.

3.2 Reagents and standards

In testing the fixation and elution of U(VI) under atmospheric conditions, the U(VI) solutions were prepared by diluting with 1% nitric acid (suprapur) from the stock solution of $0.42 \text{ mM } ^{238}\text{U(VI) l}^{-1}$. The stock solution was prepared by dissolving uranium(VI) dichloride oxide trihydrate, $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (Strem Chemicals, Inc.), in 1% nitric acid. $^{233}\text{U(VI)}$ tracer was used under atmospheric conditions. Dilutions (from $4 \text{ }\mu\text{M } ^{233}\text{U l}^{-1}$ - solution) were made with 1% nitric acid as above.

In testing the U(IV)-U(VI) separations under anaerobic conditions, the U(IV) solutions were prepared by diluting with deaerated 0.1 M HCl (suprapur) from the stock solution of $4 \text{ }\mu\text{M } ^{238}\text{U(IV) l}^{-1}$. The stock solution was prepared by dissolving uranium(IV) chloride (anhydrous, Strem Chemicals, Inc.), UCl_4 , in deaerated 1 M HCl. The uranium(IV) chloride ampoule was opened and stored in the glove box in order to minimize oxidation. The U(VI) solutions were prepared from the $^{233}\text{U(VI)}$ - stock solution ($0.4 \text{ }\mu\text{M l}^{-1}$) in the following way: The stock solution was deaerated with N_2 under atmospheric

conditions and transferred into the box. The dilutions were made with deaerated 0.1 M HCl under anaerobic conditions.

The ^{238}U standard solutions for ICP-MS were diluted from the stock solution of $42\ \mu\text{M}\ ^{238}\text{U}\ \text{l}^{-1}$ (Plasma Standard, Baker Instra-analyzed Reagent). The ^{233}U standard solutions were diluted from the stock solution of $43\ \mu\text{M}\ ^{233}\text{U}\ \text{l}^{-1}$. The dilutions were made using similar acid solutions with the samples (1 M HNO_3 , 0.1 M HCl-1% HNO_3 , see p. 15).

The acid solutions (4.5 M HCl, 0.1 M HCl) were diluted from suprapur concentrated hydrochloric acid. For separations under anaerobic conditions, the solutions were deaerated with N_2 and were allowed to equilibrate in the glove box for at least one week.

All solutions and standards were prepared in polypropylene bottles (acid-washed, 2 M HNO_3).

3.3 Anaerobic conditions

The testing of U(IV)-U(VI) separations was performed mainly under anaerobic conditions in the glove box filled with nitrogen. The glove box (Mecaplex) has a gas-purification system for producing and maintaining a pure atmosphere free of moisture and oxygen within the glove box. The nitrogen gas is continuously recirculated in a closed circuit and purified by the filters (adsorbers: molecular sieve, CuO catalyst). After a pure atmosphere has been attained in the glove box, the inert system adsorbs the impurities in the glove box that have either diffused through the gloves or have entered with materials. The saturated filters can automatically be regenerated.

The trace oxygen content in the atmosphere within the glove box normally stays below 1 ppm (~ 0.1 ppm), but may occasionally fluc-

tuate when working with gloves. During the regeneration process of the gas-purification system, which is done at intervals of 2-3 months, the oxygen content is temporarily increased (a few ppm). The solutions for testing U(IV)-U(VI) separations were transferred into the vacuum chamber (N_2) of the glove box in the process of regeneration.

3.4 Separation procedure

In order to make possible the fast separation of U(IV)-U(VI) by anion-exchange chromatography, it was necessary to acidify the sample to form chloride complexes of uranium. This breaks up colloids and/or unknown hydrolyzed and complexed species present in the sample /Hussonnois et al 1989/. The adsorbability of U(VI) rises steeply with increasing HCl concentration /Kraus and Nelson 1956, see p. 4/. Simultaneously, the adsorbability of U(IV) at higher Cl concentrations also becomes significant /Hakanen 1996/. Hussonnois et al /1989/ have concluded that U(VI) is fixed at 100% on the resin with 4.5 M HCl medium. Under these conditions, U(IV) flows through the column. Subsequently, U(VI) may be recovered by elution with 0.1 M HCl. For ICP-MS, the U(IV) fractions in strong (4.5 M HCl) acid must be evaporated to dryness and redissolved in less strong acid. The quantitative recovery of U was ensured by dissolving the evaporation residue in 1 M HNO_3 , which is not too strongly acidic for ICP-MS analyses.

In our experiments, the acidification of the sample was done by the addition of an equal volume of concentrated HCl (suprapur) to an equal volume of sample. After numerous tests, the following procedure for separation of U(IV)-U(VI) under anaerobic conditions was chosen (total U conc.: 0.5 ... 10 ng, 0.002 ... 0.04 nM /sample):

1. Pretreatment of the anionic resin in the column:

The column was washed with 0.1 M HCl (6ml = ten times the volume of the resin). At the end, a 2 ml sample was collected.

→ FRACTION 1 (2 ml)

The column was treated with 4.5 M HCl (6 ml). At the end, a 2 ml sample was collected.

→ FRACTION 2 (2 ml)

(Fractions 1 and 2 were taken for analysis in order to ensure the purity of the system.)

2. Addition of the sample solution (see previous page):

The sample solution (1 ml) was pipetted into the column reservoir and was allowed to flow through the column (0.2 ml/min) into a test tube.

→ FRACTION 3 (1 ml)

3. Flushing of U(IV) from the column:

4 ml of 4.5 M HCl was pipetted into the column reservoir and was allowed to flow through the column into two test tubes.

→ FRACTION 4 (2 ml)

→ FRACTION 5 (2 ml)

600 µl of 0.1 M HCl (one column volume) was pipetted into the column and was allowed to flow through the column into a test tube.

→ FRACTION 6 (600 µl)

(The purpose of the latter stage was to rinse 4.5 M HCl out of the column.)

4. Elution of U(VI) from the column:

8 ml of 0.1 M HCl was pipetted into the column and was allowed to flow through the column into four test tubes.

→ FRACTION 7 (2 ml)

→ FRACTION 8 (2 ml)

→ FRACTION 9 (2 ml)

→ FRACTION 10 (2 ml)

After separation in the glove box, the fractions in the test tubes were transferred to atmospheric conditions. The fractions in 4.5 M HCl (2 - 6) were evaporated to dryness in Teflon beakers and redissolved in 1 M HNO₃. In an attempt to minimize sorption onto the walls of the test tubes, HNO₃ (1%) was added to the fractions in 0.1 M HCl (1, 7 - 10). Sorption of U was observed to occur from 0.1 M HCl.

Finally, the fractions were analysed in U with ICP-MS. The standard dilutions were made in both 1 M HNO₃ and 0.1 M HCl (1% HNO₃).

4 DISCUSSION OF RESULTS

4.1 Fixation and elution of U(VI)

Fixation and elution of U(VI) was investigated under atmospheric conditions in the absence of U(IV) in order to preliminarily develop the separation procedure presented earlier. The method was tested at the following concentration levels of U(VI) in sample (1 ml): 0.0004, 0.004 and 0.04 nM (0.1, 1, 10 ng). These levels were chosen as representative for U solubilities measured under anaerobic conditions (N₂) in synthetic granitic groundwaters /Ollila 1995/. In real reducing groundwater the concentration of U(VI) should be even lower, U(IV) being the dominant oxidation state. A ²³³U(VI) tracer was added to selected sample solutions under atmospheric conditions.

Figure 4-1 shows a typical progress for two parallel separations of U(VI) in the column in the absence of U(IV). ²³³U tracer was added to the samples. The fractions were collected and analysed in the same way as in the presence of U(IV), see p. 14, with the exception that fraction 5 was not taken under atmospheric conditions. Flushing was done with 2 ml of 4.5 M HCl. Fraction 5 has been drawn equal to fraction 4 in the chromatogram, in order to be able to follow the list of the fractions on p. 14. The first two fractions show the background level for 0.1 M and 4.5 M HCl, respectively. The U(VI) (9.8 ng) in 4.5 M HCl was added after this. Fractions 3 - 6 in 4.5 M HCl show the same background level as fraction 2 in 4.5 M HCl in the absence of U(IV). This is followed by the elution of U(VI) with 0.1 M HCl. Practically all the U(VI) is eluted in fraction 6. A small amount (1- 2 %) is left in fractions 8 and 9, which can be minimized by adding the amount of anionic resin. In the testing of the method, the same amount of resin was used for every separation. Finally, the background level is reached in fraction 10. Both ²³⁸U and the tracer ²³³U elute in the similar way. The agreement between parallel samples is very good.

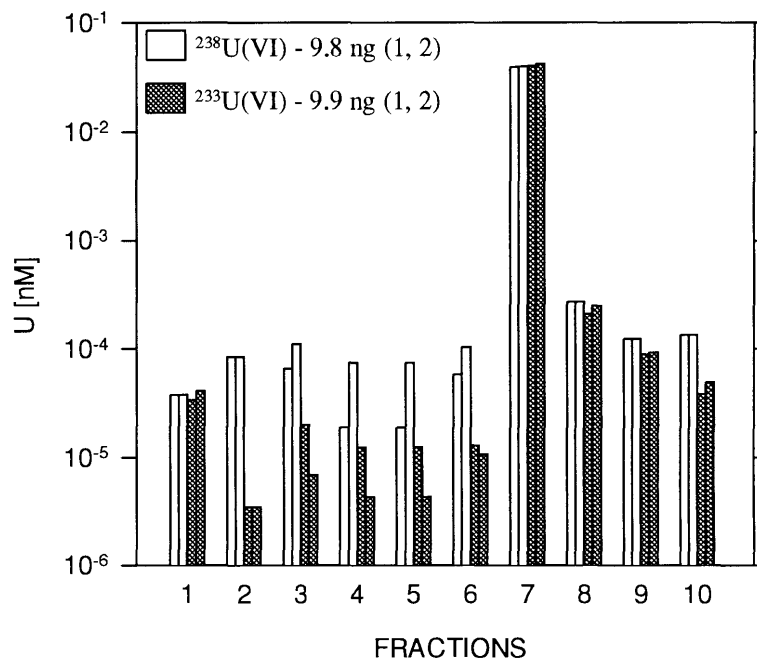


Figure 4-1. Fixation and elution of U(VI) by anion exchange. The chromatogram shows the results for two parallel samples.

The yield determination for U(VI) separation was made by analysing the uranium content in the final sample solution (for two parallel samples) and by comparing the result of separation with it. One millilitre of sample solution (4.5 M HCl) was evaporated to dryness and redissolved in 1 M HNO₃ in Teflon beakers. The yield of redissolving was tested to be 100 %. Parallel samples gave practically the same U content. Based on the yield determinations in the U(VI) elutions of Figure 4-1, the $^{238}\text{U(VI)}$ and $^{233}\text{U(VI)}$ were fixed and eluted at 97 % (96.2, 97.2 %) and 98 % (95.9, 99.6 %), respectively. The ICP-MS measurements are more sensitive and precise for ^{233}U due to lower background. Figure 4-2 gives the results for four parallel $^{238}\text{U(VI)}$ and $^{233}\text{U(VI)}$ elutions. The U contents in the elutions were 0.04 nM (10 ng) and 0.004 nM (1 ng), respectively.

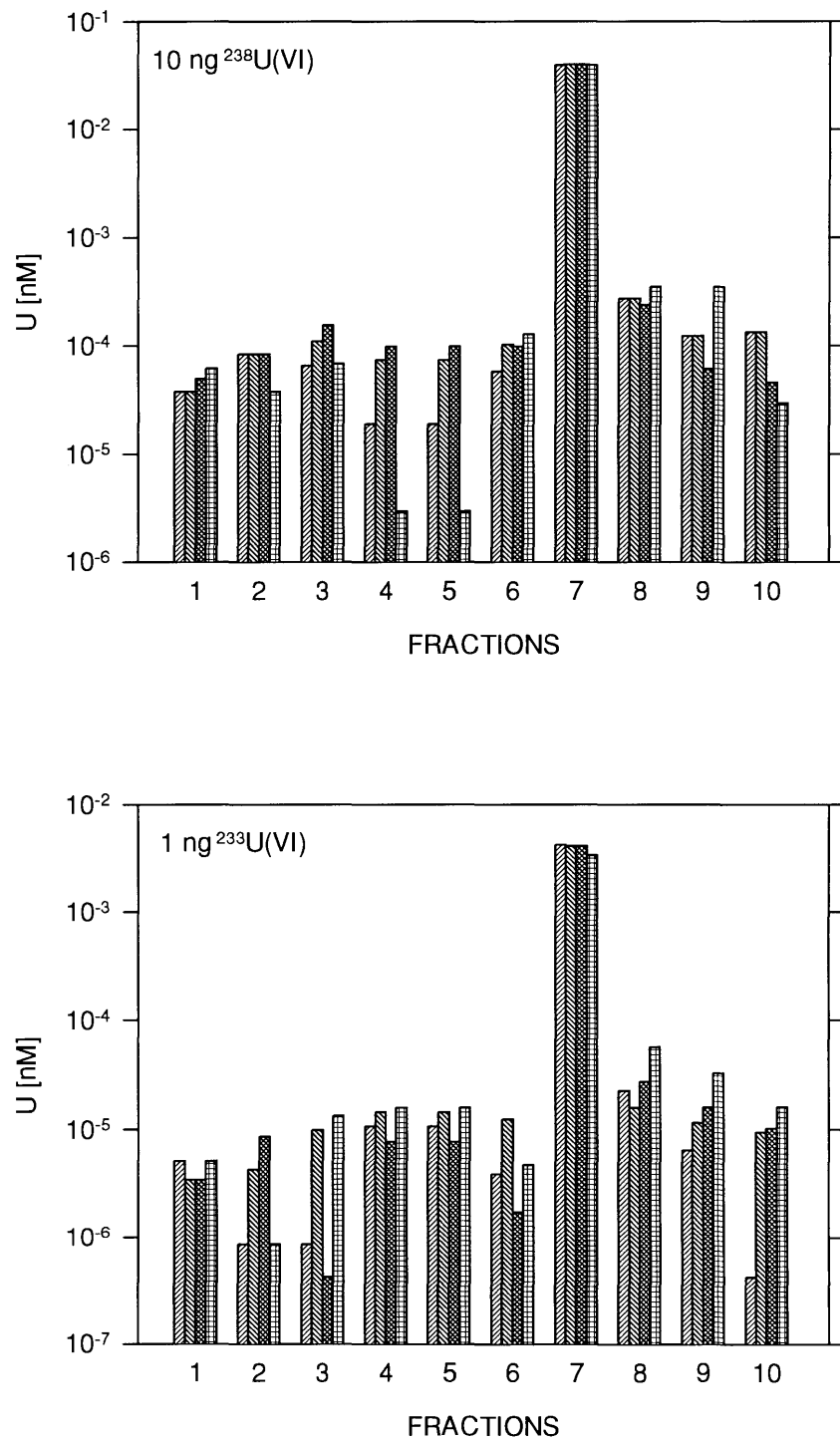


Figure 4-2. Fixation and elution of U(VI). The chromatograms show the results for four parallel ^{238}U (upper figure) and ^{233}U (lower figure) samples.

The background level for the separation and analysis of $^{233}\text{U(VI)}$ is roughly 0.02 ng (10^{-5} nM) according to Figure 4-2. It is one order of magnitude higher for $^{238}\text{U(VI)}$. Based on the background measurements of separation (Figure 4-2, fractions 1 - 6, see p. 14) suggested detection limits for both uranium isotopes can be calculated:

$$0.04 \text{ ng } ^{238}\text{U(VI)}$$

$$0.005 \text{ ng } ^{233}\text{U(VI)}$$

The reproducibility of U(VI) fixation and elution was excellent. The results of the parallel elutions of $^{238}\text{U(VI)}$ and $^{233}\text{U(VI)}$ varied 9.5 ± 0.04 ng and 1.0 ± 0.01 ng, respectively. The yields varied 96 ± 1 % (^{238}U) and 97 ± 3 % (^{233}U).

Finally, a test with a low U(VI) content of 0.01 ng (0.0004 nM) was performed, see Figure 4-3. Both ^{238}U and ^{233}U were added to the sample. Also in this case the yields were good, 96 and 97 % for $^{238}\text{U(VI)}$, 88 and 88 % for $^{233}\text{U(VI)}$.

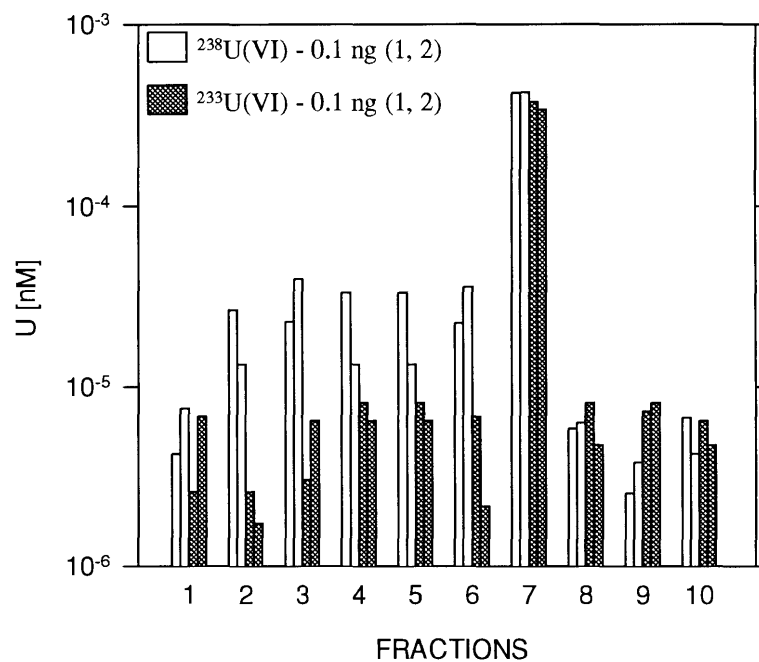


Figure 4-3. Fixation and elution of U(VI). The chromatogram shows the results for two parallel samples.

4.2 Determination of U(IV)

After the testing of fixation and elution of U(VI) under atmospheric conditions, the experimental work was carried out in inert atmosphere (N_2) in the glove box. The trace oxygen content in the atmosphere of the box is normally low (~ 0.1 ppm), but may fluctuate when working with gloves. In preliminary experiments, it was noticed that some oxidation of U(IV) happens in lower acidity solutions (e. g. 0.1 M HCl). The oxidation may be minimized by using higher acidity solutions (e. g. 5 M HCl) and/or by the addition of some reducing agent. On the other hand, the use of these higher acidity solutions in the glove box may cause some damage to the purifying system of the gas. In consequence of this, the U(IV) stock solutions were prepared in 1 M HCl and dilutions were made by 0.1 M HCl when testing separation procedure. At this stage of the method development, no reducing agents were added to solutions.

The tests in the box were started by adding U(IV) alone to the sample. The dilutions were systematically made the same day as separations, in the same way as was done under atmospheric conditions. The sample solution (equal volume of conc. HCl added to equal volume of sample) was allowed to stand for one hour before addition to the column for the first separation, and 3 - 4 hours for the parallel separation. Normally the parallel separations gave similar results. The oxidation state in 4.5 M HCl would seem to be stable, at least for this time period.

A typical chromatogram of U(IV) sample solution (dilution with 0.1 M HCl) is given in Figure 4-4, for two parallel samples. Again, the first two fractions show the background level for 0.1 M HCl and 4.5 M HCl, respectively (see p. 14). The sample solution (1.3 ng U) was added after this (fraction 3). The uranium at the oxidation state of IV does not fix on the anionic resin in 4.5 M HCl medium and

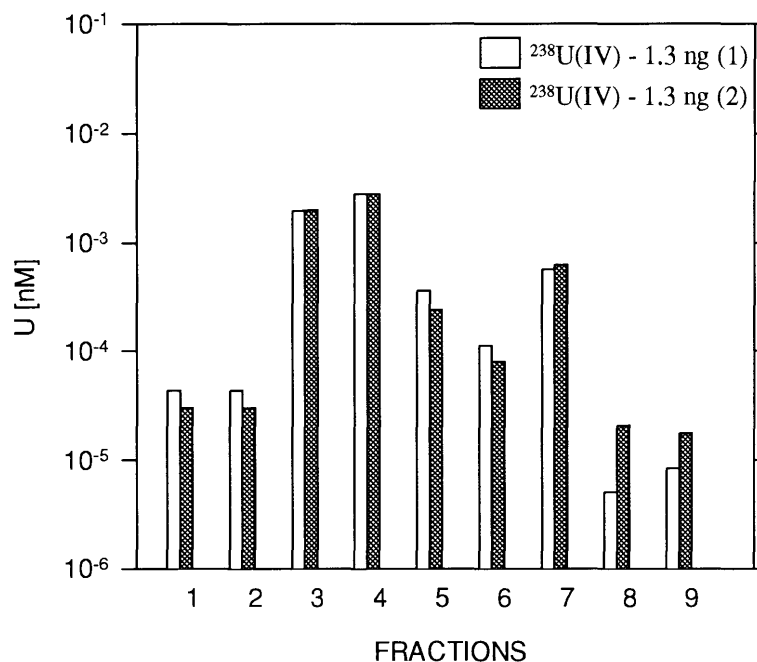


Figure 4-4. Separation of U(IV) in the column of anionic resin. The samples were prepared by dilution with 0.1 M HCl.

flows through the column. Testing showed, somewhat surprisingly, that 4 ml of 4.5 M HCl was needed to flush all the U(IV) from the column. The sum of the fractions 3 (1 ml), 4 (2 ml) and 5 (2 ml) gives the content of U(IV). The migration of U(IV) seemed to retard in the column for some reason. The chromatogram also shows the presence of U in fraction 7, where the U(VI) elution occurs. This probably means that the U(IV) partially oxidizes before or after the addition to the column. The sorption onto the resin is also possible. The first alternative would seem the most probable. The distribution of the oxidation states calculated from the chromatogram (Figure 4-4) is the following:

- (1) 90 % U(IV), 10 % U(VI)
- (2) 89 % U(IV), 11 % U(VI)

The yield in both cases was 100 %. The agreement between parallel samples is excellent. In order to see the reproducibility of this distri-

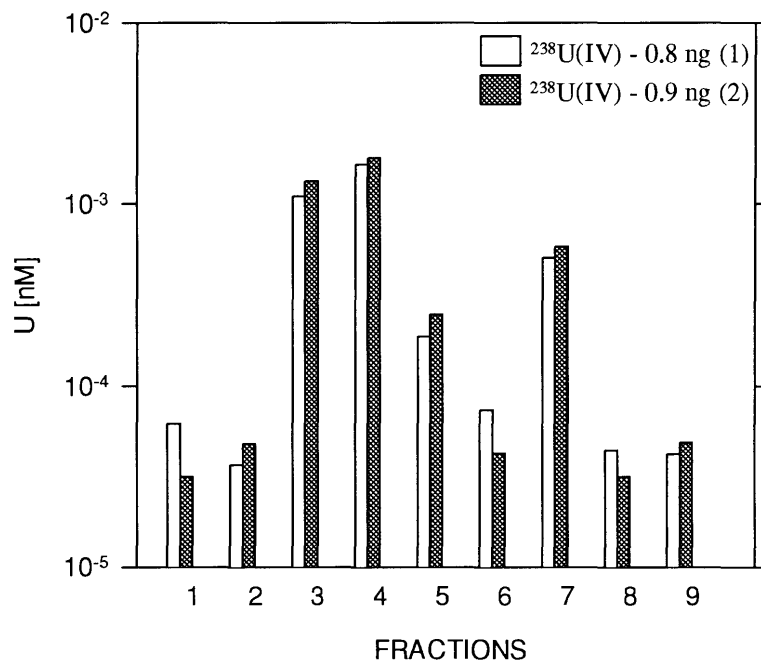


Figure 4-5. Separation of U(IV) in the column of anionic resin. The samples were prepared by dilution with 0.1 M HCl.

bution, a parallel test was made, Figure 4-5. The U contents in the samples were a little lower, 0.8 and 0.9 ng. Again, the parallel samples give similar results. The oxidation state distribution (the yield of 100 %) shows a five per cent increase in the oxidized uranium:

- (1) 84 % U(IV), 16 % U(VI)
- (2) 84 % U(IV), 16 % U(VI)

The stock solution (U-IV in 1 M HCl) for the previous two test cases (Figures 4-4 and 4-5) was prepared only a few days before the analyses. Figure 4-6 shows the results for the test case, for which the stock solution had stood in the inert atmosphere for half a year. This did not seem to have an effect on the distribution of the oxidation states:

- (1) 91 % U(IV), 9 % U(VI)
- (2) 92 % U(IV), 8 % U(VI)

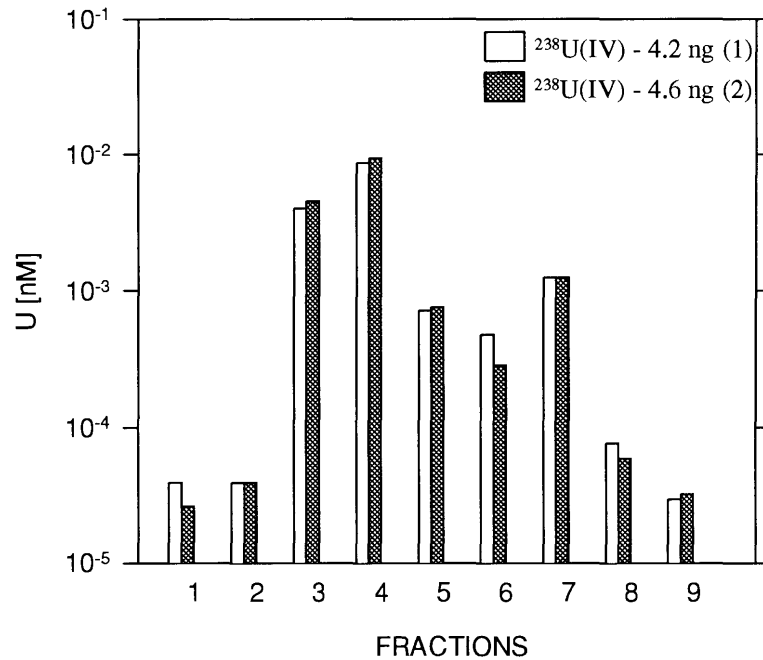


Figure 4-6. Separation of U(IV) in the column of anionic resin. The samples were diluted with 0.1 M HCl.

U(IV) in 1 M HCl is obviously relatively stable. The oxidation of U(IV) during the dilution of the stock solution with 0.1 M HCl seems probable, because the stability of U(IV) solutions is known to decrease with decreasing acidity /Anderson 1984, Hussonnois et al 1989/. It seems necessary to add reducing agents (e.g. H_2 , iron) in solutions in order to keep U(IV) stable. The trace oxygen content in the atmosphere of the box is obviously enough to create oxidizing conditions in lower acidity solutions.

A result along the same lines was given by the test in which the dilution of the U(IV) stock solution was made with synthetic Allard groundwater. The groundwater was probably in equilibrium with the inert N_2 atmosphere, because it had been standing in the box for one year. The pH value was 8.7 /Ollila 1995/.

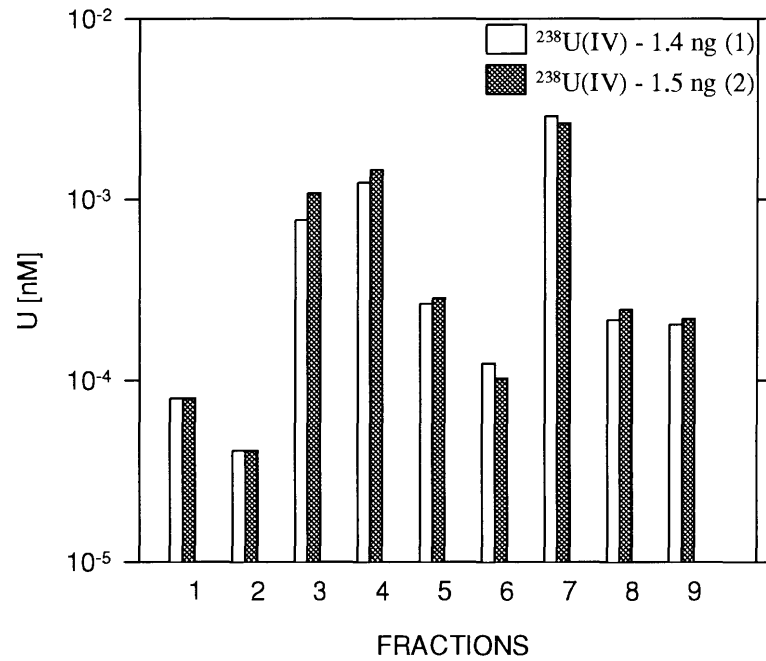


Figure 4-7. Separation of U(IV) in the column. The samples were prepared by dilution with Allard groundwater (pH= 8.7).

The chromatogram of Figure 4-7 gives the distribution of the oxidation states (the yield of 95 %) in this sample:

- (1) 42 % U(IV), 58 % U(VI)
- (2) 49 % U(IV), 51 % U(VI)

The amount of oxidized uranium increased considerably, when the dilution of the U(IV) solution was made with the solution of higher pH. This is in agreement with the studies of Cross et al /1989/, in which the oxidation state was measured as a function of pH (pH 1 and 8). The U(IV) was stable even at positive Eh values in the acidic solution, while low negative Eh values were needed to stabilize U(IV) in the solution of pH 8, see Figure 2-4, p. 8.

4.3 U(IV) - U(VI) separations

In spite of the fact that U(IV) is partially oxidized in lower acidity solutions, an attempt was made to add both U(IV) and U(VI) to the sample in order to make a real test of U(IV)-U(VI) separation. The U(VI) was added as $^{233}\text{U(VI)}$ to the samples, in order to see the difference between the oxidized $^{238}\text{U(IV)}$ and the original U(VI) addition. The $^{233}\text{U(VI)}$ stock solution was diluted with 0.1 M HCl under atmospheric conditions, deaerated with N_2 and transferred into the glove box the day before the analyses. A test was made to make sure that U(VI) in 0.1 M HCl in the glove box does not reduce within few days. It was not observed to occur. Two series of parallel separations were made, using different contents of $^{238}\text{U(IV)}$ and $^{238}\text{U(VI)}$.

Figures 4-8 and 4-9 give the chromatograms for both separations. The contents of $^{238}\text{U(IV)}$ and $^{233}\text{U(VI)}$ in the samples were 2.7 - 6.8 ng and 1.1 - 2.7 ng, respectively. The chromatograms (fraction 7, p. 14)

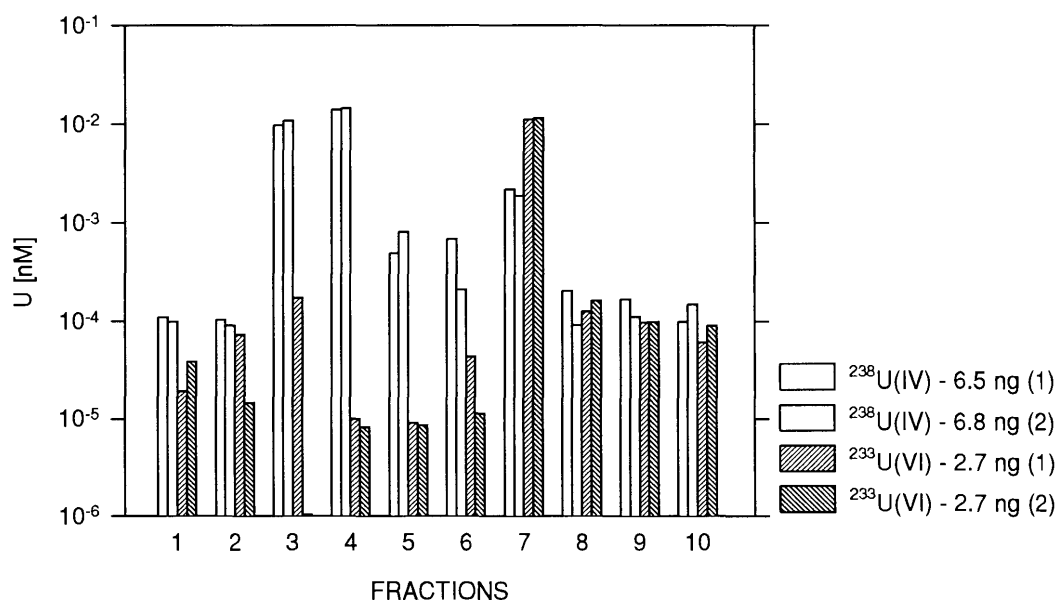


Figure 4-8. $^{238}\text{U(IV)}$ and $^{233}\text{U(VI)}$ separations by anion exchange. Dilutions with 0.1 M HCl.

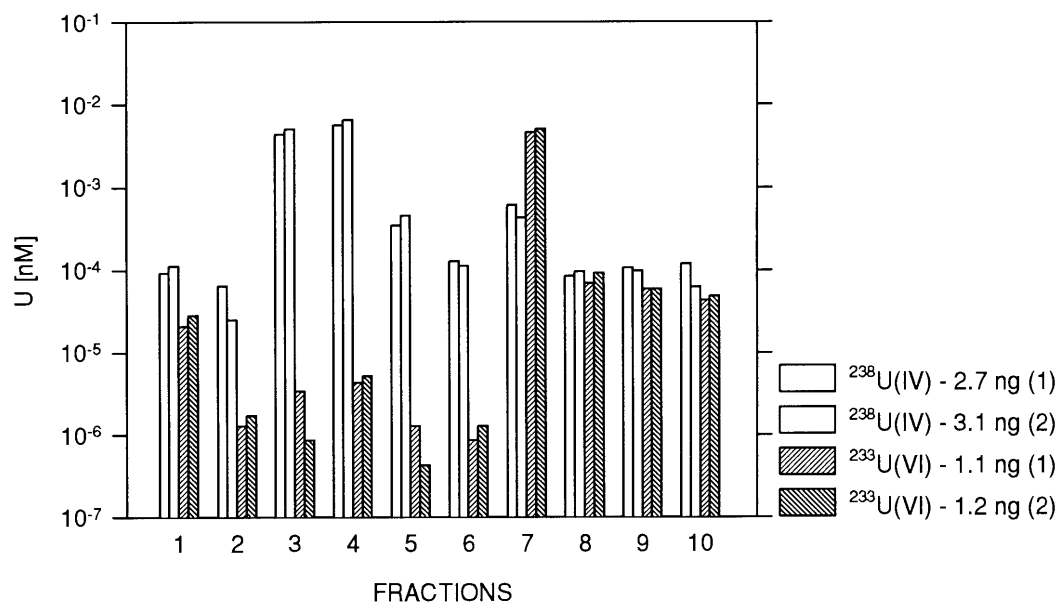


Figure 4-9. $^{238}\text{U(IV)}$ and $^{233}\text{U(VI)}$ separations by anion exchange. Dilutions with 0.1 M HCl.

show the partial oxidation of $^{238}\text{U(IV)}$ in good agreement with the earlier test cases (section 4.2). The results presented as distribution of the oxidation states (Figure 4-8) are as follows for the ^{238}U . The values in paranthesis give the percentages for the second series of separations (Figure 4-9):

(1) $^{238}\text{U(IV)}$: 90 (92) %

$^{238}\text{U(VI)}$: 10 (8) %

(2) $^{238}\text{U(IV)}$ 92 (95) %

$^{238}\text{U(VI)}$ 8 (5) %

$^{233}\text{U(VI)}$ is seen in fraction 7, where the elution of U(VI) starts. No $^{233}\text{U(VI)}$ was observed in the U(IV) fractions (3 - 5, see p. 14). There is a good agreement between the parallel separations in both test cases. The yields varied 89 - 100 % for ^{238}U and 92 % for ^{233}U .

4.4 U oxidation state in the dissolution experiments of UO_2

As the first application of the method, the oxidation state of U was determined for anaerobic (N_2) aqueous solutions which had been in contact with unirradiated UO_2 pellets for 500 days in the glove box. The aqueous solutions included deionized water, NaHCO_3 solutions with varying carbonate content (0.98 - 9.83 mmol/l, 60 - 600 mg/l) and synthetic groundwaters (Allard groundwater, bentonite water). These dissolution experiments have been reported in detail elsewhere /Ollila 1995/. The U contents in solutions were 2 - 10 $\mu\text{g/l}$ (8 - 40 nM/l). The solutions (5 ml sample) were microfiltered (membranes of 0.45 μm pore size) before the analyses. Then an equal volume of concentrated HCl was added to an equal volume of sample.

Based on the results of the earlier testing phase of the method, it is predictable that the main part of U is in oxidized form in the solutions. The pH of the solutions varied 7.0 ... 9.1. No reducing agent (e.g. iron) had been added to the solutions. The redox measurements (glassy carbon electrode) also gave positive Eh values (+150 ... +180 mV). The following, Table 1, gives the results of the analyses, as an average of two parallel samples. The detailed chromatograms are given in Apps. 1 - 4. As expected, uranium was mainly at the U(VI) state, only a small fraction being at the U(IV) state. The excellent reproducibility of the method is again observed in the chromatograms.

Table 1. Oxidation state of uranium in solutions after contact with UO_2 pellets in inert atmosphere (N_2). The results are the averages of two parallel samplings.

	<i>pH</i>	<i>Fraction U(VI) (%)</i>	<i>Fraction U(IV) (%)</i>	<i>Yield (%)</i>
<i>Deionized water</i>	7.0	99.0 ± 0.4	1.0 ± 0.4	80
<i>NaHCO₃ (60 ppm HCO₃⁻)</i>	9.1	96.9 ± 0.8	3.1 ± 0.8	86
<i>NaHCO₃ (120 ppm HCO₃⁻)</i>	9.1	96.8 ± 0.3	3.2 ± 0.3	72
<i>NaHCO₃ (275 ppm HCO₃⁻)</i>	9.1	96.8 ± 0.5	3.2 ± 0.5	97
<i>NaHCO₃ (600 ppm HCO₃⁻)</i>	9.1	98.2 ± 0.1	1.8 ± 0.1	88
<i>Allard groundwater</i>	9.0	91.5 ± 0.2	8.5 ± 0.2	94
<i>Bentonite water</i>	8.9	96.9 ± 0.7	3.1 ± 0.7	91

5. SUMMARY AND CONCLUSIONS

The aim of this experimental study was to develop and test in detail a chemical procedure for analysing the oxidation states of uranium at the low concentrations representative for anoxic groundwater at great depths in granitic bedrock. These conditions were simulated in the glove box with inert atmosphere (e. g. N_2). A short review of methods found in the literature was made. Based on this review, the separation of U(IV)-U(VI) by anion-exchange chromatography in HCl medium followed by the analysis of the uranium contents of each of the fractions by ICP-MS, was selected as most suitable for our experimental conditions in the anaerobic glove box. The separation of the tetravalent and hexavalent states included fixation of the U(VI) on anionic resin in 4.5 M HCl and elution afterwards with 0.1 M HCl. The U(IV) flows in 4.5 M HCl through the column.

First, the fixation and elution of U(VI) was investigated under atmospheric conditions in the absence of U(IV), in order to preliminarily test the separation procedure. A suggested detection limit for $^{238}U(VI)$, 0.04 ng, could be concluded based on the background measurements of separation. In the case of $^{233}U(VI)$, the sensitivity is even higher. The yields of U(VI) fixation and elution were typically 95 - 100 per cent.

In the next stage, the determination of U(IV) was tested by adding U(IV) alone to the sample. The tests in the glove box showed that in lower acidity solutions (0.1 M HCl) 10 - 15 % of U(IV) oxidizes probably due to the trace oxygen content in the inert atmosphere (N_2). The amount of oxidized uranium increased considerably, when the U(IV) was added to synthetic groundwater (Allard), pH 8.7. Fifty per cent of the U had the U(VI) state. It seems necessary to add reducing agents (e. g. H_2 , iron) in solutions in order to keep U(IV) stable. Due to the partial instability of U(IV), a real test of the

U(IV)-U(VI) separation was realized by adding the U(VI) as $^{233}\text{U(VI)}$, in order to see the difference between the oxidized U(IV) and the original U(VI) addition. The results obtained showed that separation occurred almost quantitatively (yield 90 - 100 %) and reproducibly.

Finally, as the first application, the oxidation state of U was determined for anaerobic (N_2) aqueous solutions (including two synthetic groundwaters) after contact with unirradiated UO_2 pellets for 500 days in the glove box. According to the analyses, uranium was mainly at the U(VI) state, only a small fraction (1 - 9 %) being at the U(IV) state.

The results give some information on the redox state of the aqueous solutions in inert atmosphere (N_2). Obviously, the trace oxygen in the atmosphere of the box is enough to cause slightly oxidizing conditions for uranium in the absence of reducing agents (e. g. H_2 , iron). This is in agreement with the solubilities measured in the above-mentioned UO_2 dissolution studies /Ollila 1995/. The measured concentrations of U at steady state were at the level of the thermodynamically calculated solubilities of U_4O_9 ($\text{UO}_{2.25}$), which is a surface oxidation product of UO_2 .

6 ACKNOWLEDGEMENTS

Teollisuuden Voima Oy is gratefully acknowledged for financial support. The author takes pleasure in thanking Ms. R. Zilliacus and Dr. R. Rosenberg (VTT Chemical Technology, Molecular Structure and Chemical Analytics) for performing the ICP-MS analyses. The author wishes to thank Mr. M. Hakanen (University of Helsinki, Laboratory of Radiochemistry) for valuable discussions. The contributions of Ms. K. Helosuo and Ms. M. Lipponen also deserve acknowledgements.

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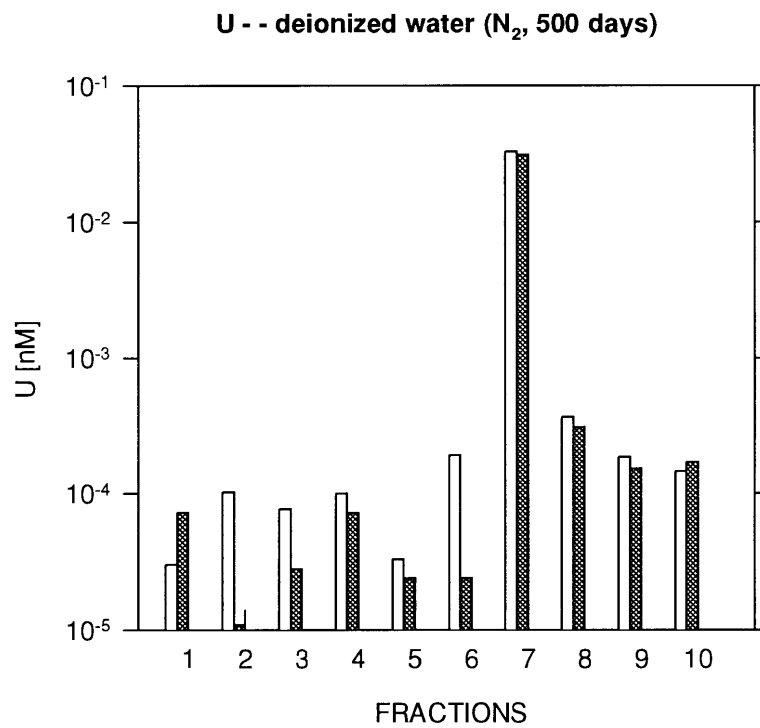
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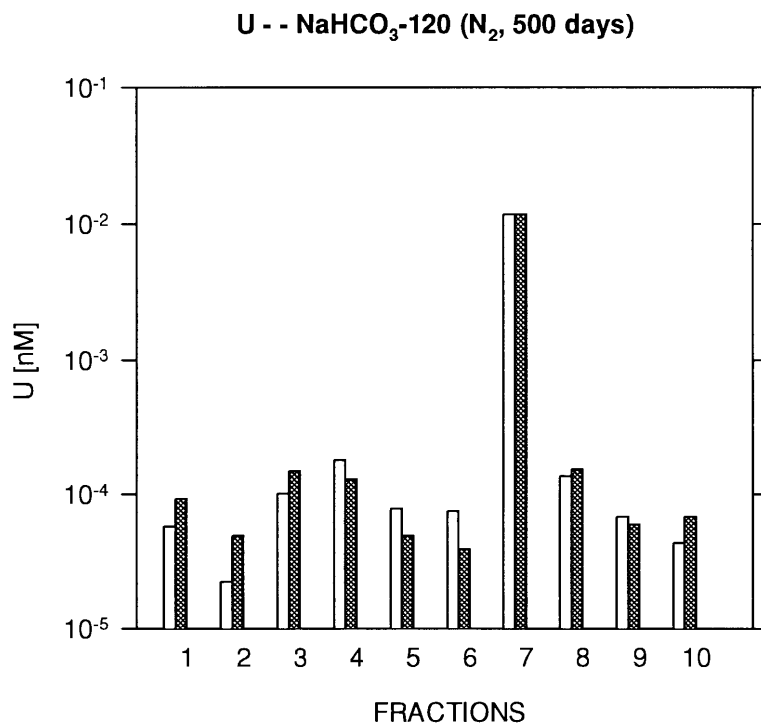
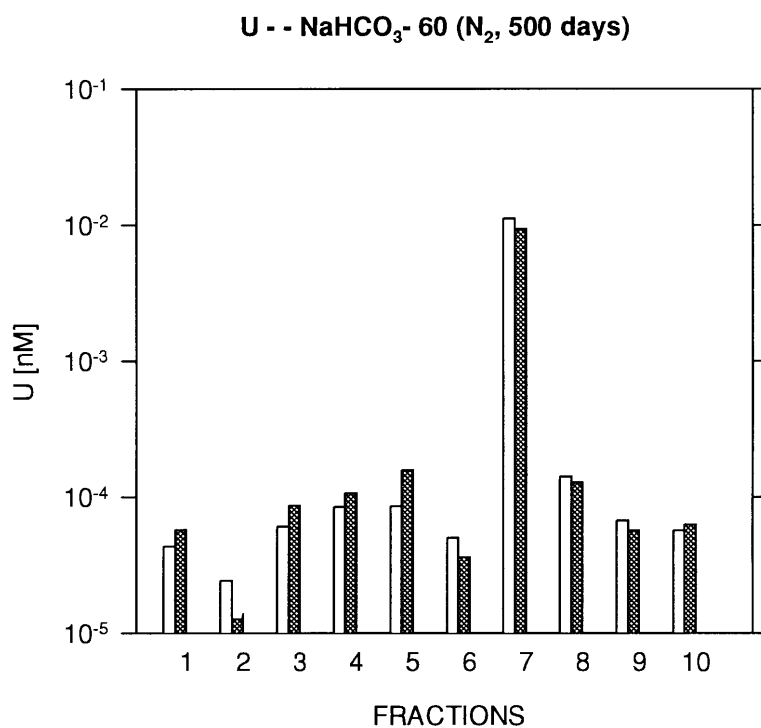
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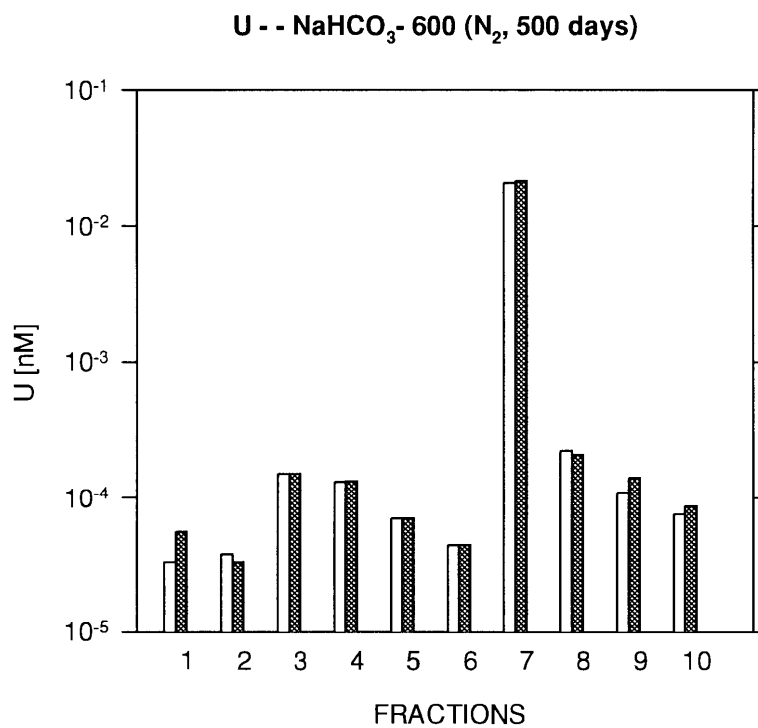
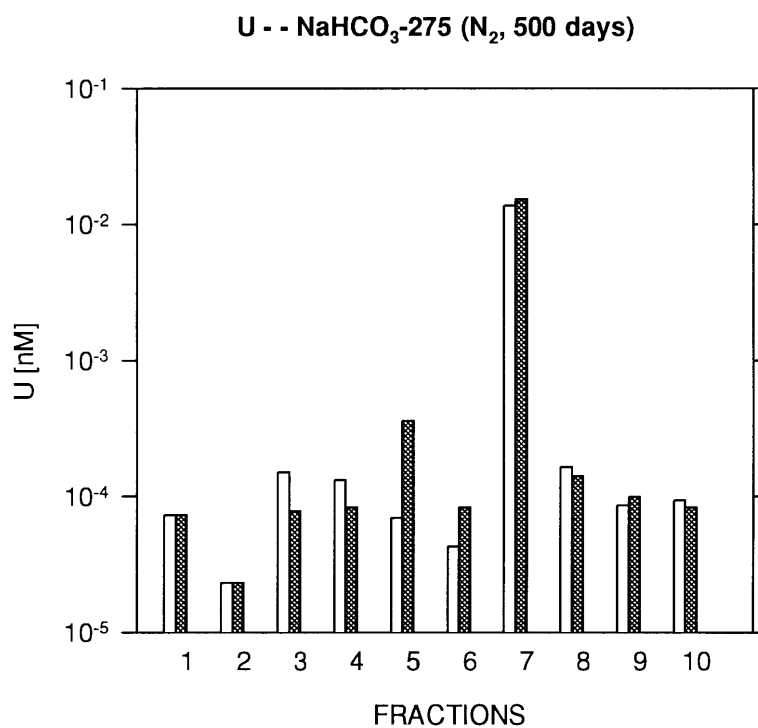
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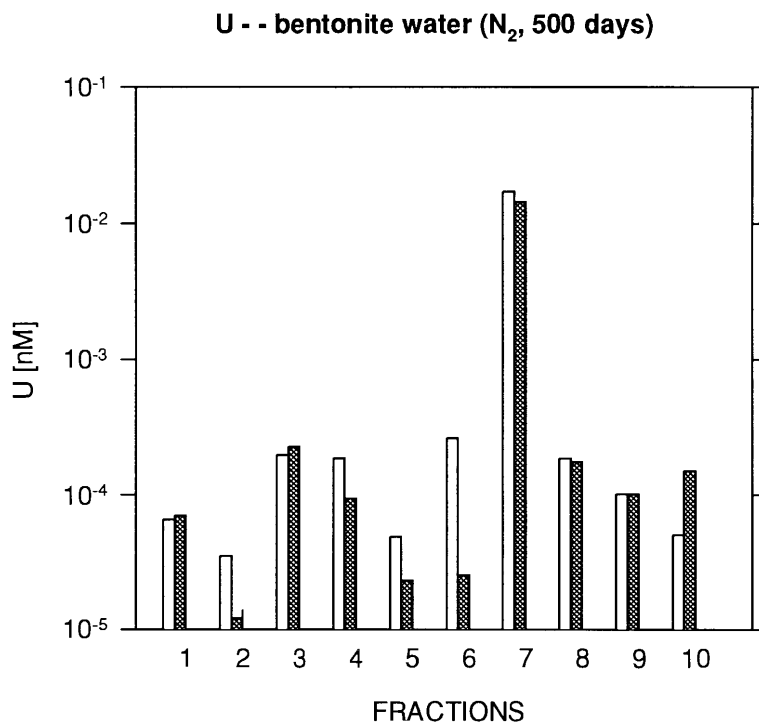
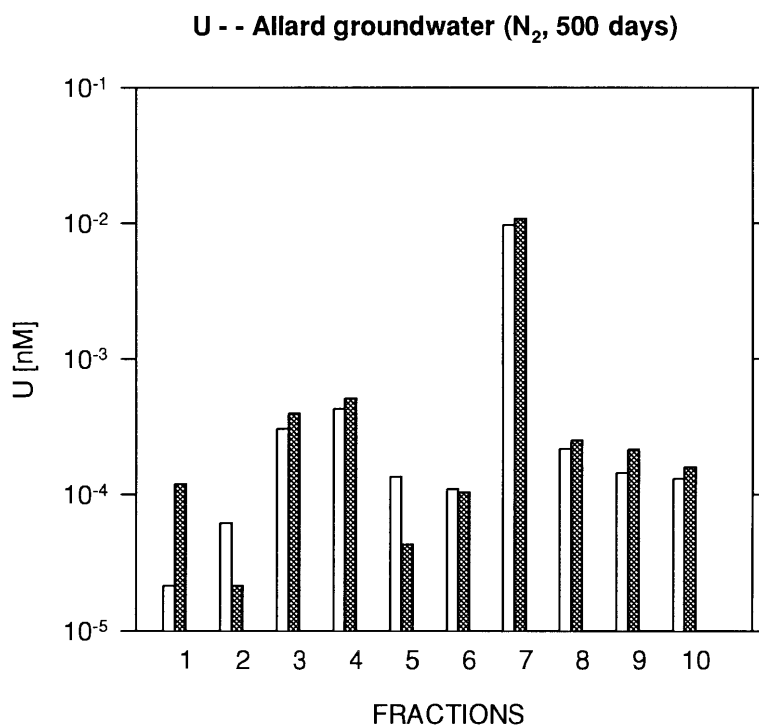
U(IV)-U(VI) separation in deionized water, pH 7.0, after contact with UO_2 pellets in inert atmosphere (N_2). The chromatograms for two parallel samples (fractions, p. 14).



U(IV)-U(VI) separation in NaHCO₃ solutions (HCO₃⁻ contents of 60 mg/l, pH 9.1, upper figure, and 120 mg/l, pH 9.1, lower figure) after contact with UO₂ pellets in inert atmosphere (N₂). The chromatograms for two parallel samples (fractions, p. 14).



U(IV)-U(VI) separation in NaHCO₃ solutions (HCO₃⁻ contents of 275 mg/l, pH 9.1, upper figure, and 600 mg/l, pH 9.1, lower figure) after contact with UO₂ pellets in inert atmosphere (N₂). The chromatograms for two parallel samples (fractions, p. 14).



U(IV)-U(VI) separation in synthetic groundwaters (Allard groundwater, pH 9.0, upper figure, and bentonite water, pH 8.9, lower figure) after contact with UO₂ pellets in inert atmosphere (N₂). The chromatograms for two parallel samples (fractions, p. 14).

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POSIVA-96-01 Determination of U oxidation state in anoxic (N₂) aqueous solutions –
method development and testing
Kaija Ollila
VTT Chemical Technology
April 1996



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9641/96/SSA

19.6.1996

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Pyydämme Teitä vahvistamaan tilauksemme sekä mainitsemaan kaikessa tilausta koskevassa kirjeenvaihdossa ja laskutuksessa tilausnumeromme.

Kunnioitavasti

POSIVA OY

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A handwritten signature in black ink, appearing to be "P. B." followed by a horizontal line.

LIITTEET

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