

Short communication

Method for the separation of uranium(IV) and (VI) oxidation states in natural waters

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Abstract

A low-pressure cation-exchange method has been developed for separating U(IV) and U(VI) in natural, high carbonate waters. Uranium(IV)/(VI) solutions were prepared in 0.125 M H₂C₂O₄–0.25 M HNO₃, equilibrated with a N₂ atmosphere, applied to a Dowex AG 50W-X8 cation-exchange resin, and eluted with 0.125 M H₂C₂O₄–0.25 M HNO₃. Uranium(IV) eluted in four 10-ml fractions whereas U(VI) eluted within 9 to 19 10-ml fractions. Additional U(IV)/U(VI) separations were done on solutions containing known concentrations of PO₄³⁻, Ca²⁺, Na⁺, Cl⁻, SO₄²⁻, CO₃²⁻, and F⁻. Interferences with U(VI) elution were observed at 0.05 M Ca²⁺.

Keywords: Water analysis; Uranium; Inorganic ions; Metal cations

1. Introduction

Elevated levels of U are found in shallow ground waters of agricultural drainage water evaporation ponds in the San Joaquin Valley (SJV), CA, USA. Drainage waters are periodically pumped into evaporation ponds where they are evapoconcentrated. Consequently, the ponds undergo wetting and drying cycles which affect the solubilities of redox sensitive elements in the pond waters and sediments. These basins support migrating and native waterfowl, which are threatened by elevated levels of potentially toxic U [1].

In the aqueous environment, U(VI) (uranyl, UO₂²⁺) is the most soluble U oxidation state. Under strongly reducing conditions, U(VI) can be reduced

to U(IV) (uranous), which is thought to precipitate as an insoluble oxide (UO_{2(s)}) [2]. Recent research suggests that U(IV) may be more soluble than previously thought — particularly in high carbonate alkalinity and saline waters [3–6]. Studies with Th [an actinide with a chemistry similar to U(IV)] in high carbonate alkalinity waters show that Th(IV) is quite soluble due to the formation of Th(IV)-carbonate species [7]. Humic and fulvic acids form soluble complexes with U(IV) in addition to U(VI) [8]. Uranium(V) is generally considered electrochemically unstable and is unlikely to exist in appreciable concentrations in natural waters.

In natural waters, dissolved ions such as Ca²⁺, CO₃²⁻, and PO₄³⁻ commonly interfere with the determination of U oxidation states. One method applied to seawater is based on the coprecipitation of U(IV) with NdF₃ [9,10]. This method is subject to interferences from dissolved Ca²⁺ (~0.01 M). High pressure liquid column chromatography has been

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used to separate $^{239}\text{U(IV)}$ and $^{239}\text{U(VI)}$ species with anion-exchange resins in relatively pure laboratory solutions free of potential interfering ions [11]. The separation of U oxidation states has also been performed with cation-exchange resins in solutions free of interfering ions [12]. Other U(IV)/U(VI) separation methods include the use of various complexing ions such as arsenazo (I, II, and III) which form distinct complexes with U(IV) and U(VI) which can be colorimetrically identified [13–15]. Arsenazo compounds are also used as extractants for U(IV) and U(VI). These methods are subject to interferences from Th(IV), F^- , Fe^{3+} , phosphates, vanadates, and arsenates. Another separation method for U oxidation states involves the pH dependent chelation of different oxidation states of U by a diketone (dibenzoylmethane, DBM) in an organic solvent [16,17]. This method has not been tested for use with natural waters. When we attempted to use the DBM extraction method with solutions containing soluble PO_4^{3-} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} and F^- and known concentrations of U(VI), we found the DBM method unsatisfactory in the presence of carbonates, PO_4^{3-} , F^- and SO_4^{2-} (Table 1). These anions, which form stable, dissolved U(VI)-species, interfered with the chelation method. The DBM extraction was severely limited in the presence of dissolved CO_3^{2-} and to a lesser extent, SO_4^{2-} . This made the extraction procedure unsuitable for the pond waters high in CO_3^{2-} and SO_4^{2-} concentrations. Therefore, we developed a new method using low-pressure chromatographic separation.

We separated U(IV) from U(VI) on a cation-exchange resin using 0.125 M $\text{H}_2\text{C}_2\text{O}_4$ –0.25 M HNO_3 to elute the U species. Eluent fractions were collected and analyzed for U with inductively coupled plasma mass spectrometry (ICP-MS). The separation method was tested for its applicability to agricultural subsurface drainage waters in the SJV. Synthetic waters containing soluble PO_4^{3-} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , CO_3^{2-} , F^- and known concentrations of U(IV) and U(VI) were tested with the method to determine potential interferences with dissolved ions.

2. Experimental

2.1. Materials

Reagent-grade oxalic acid and Fisher trace-metal-grade concentrated HNO_3 were used to make an eluent of 0.125 M $\text{H}_2\text{C}_2\text{O}_4$ –0.25 M HNO_3 from deionized, organic-free water. Uranium(IV) in the form of a UCl_4 solid (in a sealed glass ampoule under $\text{N}_{2(g)}$) was purchased from ROC/RIC (Orange, CA, USA). An atomic absorption standard of U(VI) (1000 mg l^{-1}) in 5% nitric acid was purchased from Aldrich (USA).

2.2. Chromatographic apparatus

The columns consisted of Beckman and Dickson 60-ml plastic, luer-lock syringes and polycarbonate, luer-lock stopcocks. A small plug of silanized glass

Table 1
Recovery of 3.0 μg U(VI) from various solutions using 0.5 M dibenzoylmethane^a

Treatment	Recovery (%)		
	Treatment		
	No Added PO_4^{3-} or F^-	2 mg l^{-1} P– PO_4^{3-}	1 mg l^{-1} F^-
Deionized water	98.4±0.1	59.8±0.2	96.1±0.1
0.1 M NaCl	92.7±0.1	64.0±0.2	74.1±0.2
0.1 M NaOH	94.8±0.1	81.1±0.1	88.7±0.1
0.1 M Na_2SO_4	87.3±0.2	59.9±0.0	70.1±0.2
0.1 M NaHCO_3	68.4±0.5	80.0±0.3	87.2±0.3
0.1 M Na_2CO_3	28.0±0.7	72.0±0.4	72.8±0.3

^a Mean of triplicate samples.

wool was placed at the syringe tip of each column. A Bio-Rad Dowex AG 50W-X8 H-saturated cation-exchange resin with a 200 to 400 mesh size, a medium pore size, and a cation-exchange capacity of 1.7 mequiv. ml⁻¹ (resin bed) was hydrated with eluent prior to packing in the columns. The hydrated resin was poured to a volume of 40 ml (which gave a column height of 6.5 cm and a width of 2.6 cm) and had a 20-ml pore volume. The columns were washed with 200 ml of eluent to stabilize the resin or until the outgoing eluent was colorless.

2.3. Glove box

A shop-built glove box was used to maintain a low O_{2(g)} atmosphere. It consisted of a clear, 115 cm×61 cm×55 cm polycarbonate housing with portholes for attachable gloves. Small holes in the box permitted purge gas (N₂) in and out of the box and vacuum lines in. A portable balance was positioned in a box housing within the glove box. This allowed the UCl₄ solid to be weighed in the absence of the purge gas stream.

2.4. Procedures for the cation-exchange method

All solutions were placed in the glove box. They were loosely covered, and purged with N₂ gas for at least 20 min prior to use. The glove box was then purged for 20 min to ensure removal of O_{2(g)}. The ampoule containing the UCl₄ was opened and approx. 0.1 g of UCl₄ was weighed out within the glove box and dissolved in 100 ml of deionized water. This solution was diluted with eluent by transferring approx. 1 ml of the concentrated UCl₄ solution into 50 ml of eluent. A U(VI) stock solution was made in eluent by diluting the 1000 mg U(VI) l⁻¹ standard (Aldrich).

The columns were washed with at least 50 ml of eluent to remove dissolved O₂. Fifty μl of U [containing approx. 6.4 mg U(IV) l⁻¹ and 5.8 mg U(VI) l⁻¹ in eluent] were carefully applied to the column, to insure minimal disturbance to the resin bed, and twenty 10-ml elution fractions were collected.

To determine if there were interferences with ions commonly found in the SJV subsurface drainage waters and ground waters, several solutions con-

Table 2

Recovery of approx. 2.3 μg U(IV)/0.2 μg U(VI) from various solutions using cation exchange and an eluent of 0.125 M H₂C₂O₄-0.25 M HNO₃

Treatment	Recovery (%) ^a	
	U(IV)	U(VI)
Deionized water	99.9	99.9
0.05 M NaCl	99.9	94.9
0.03 mM PO ₄ ³⁻	100	97.4
0.05 mM F ⁻	100	100
0.05 M Na ₂ SO ₄	99.0	99.3
0.05 M CaCl ₂	99.5	79.5
0.01 M CaCl ₂	—	98.3
0.003 M CaCl ₂	—	99.5
0.05 M Na ₂ CO ₃ ^b	100	93.5

^a Mean of duplicate samples.

^b Sample carbonate alkalinity was neutralized with nitric acid prior to separation.

taining PO₄³⁻, Ca²⁺, Na⁺, Cl⁻, SO₄²⁻, CO₃²⁻ and F⁻ (Table 2) were made. Known quantities of U(IV) and U(VI) were added to the synthetic solutions in the glovebox and 150 μl of these solutions were applied to the column. Twenty-five 10-ml fractions were collected.

2.5. Analysis of uranium

Uranium was determined by ICP-MS (VG Plasmaquad 2T, Fisons Instruments, USA). Bismuth was used as the internal standard. The ICP-MS sensitivity was greatly improved with an enhanced interface (detection limit of ~9 μg l⁻¹ U).

3. Results and discussion

3.1. Cation-exchange procedure

The separation of approx. 0.32 μg U(IV) and 0.29 μg U(VI) by cation exchange is shown in Fig. 1. This figure represents the results of two columns and two replicates per column. The U(IV) elutes within the first four 10-ml fractions and the U(VI) elutes within nine to nineteen 10-ml fractions. The U(IV)

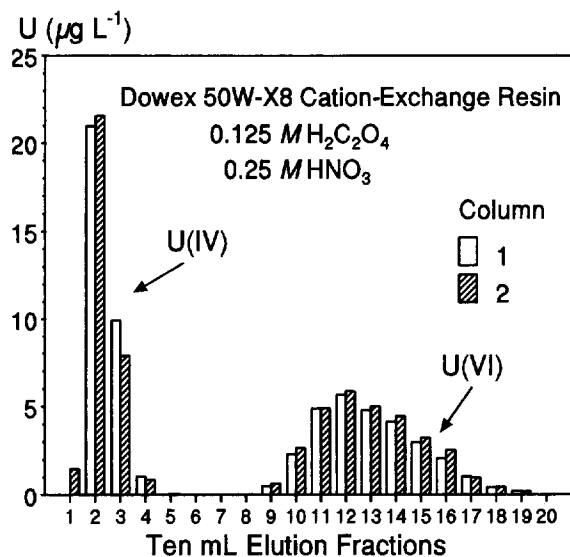


Fig. 1. The elution of 0.32 µg U(IV) and 0.29 µg U(VI).

peak is sharp whereas the U(VI) peak is somewhat broad.

3.2. Cation exchange procedure with solutions containing potential interfering ions

In the presence of known concentrations of U(IV), U(VI), PO₄³⁻, Ca²⁺, Na⁺, Cl⁻, SO₄²⁻, CO₃²⁻ and F⁻, the elution of U(IV) occurs within the five 10-ml fractions whereas U(VI) elutes within eight to twenty-two 10-ml fractions with the exception of the solution containing Ca²⁺ (Table 2). The greater peak broadness is probably due to the presence of the interfering dissolved ions. This factor decreases the separation efficiency of the columns causing the U(IV) and U(VI) peaks to elute closer together.

There is some interference with the separation of U(VI) in the presence of dissolved Ca²⁺ (Table 2). Calcium ion may compete with U(VI) for cation-exchange sites and further broaden the U(VI) peak, causing U(VI) to elute within the first eight to twenty-five 10-ml fractions as opposed to the first eight to twenty-two 10-ml fractions. When separations are performed with lower concentrations of Ca²⁺ (0.01 M and 0.03 M), U(VI) elutes within eight to twenty-two 10-ml fractions and the recovery of U(VI) is greatly improved.

3.3. The mechanism for the elution order of U(IV) and U(VI)

The elution order for this separation is not intuitive. One would anticipate U(IV) to elute after U(VI) because the U(IV) ion has a greater valence and smaller size than the U(VI) ion (which exists as the UO₂²⁺ ion). However, U(IV) ion generally forms more stable inorganic complexes than U(VI) ion [18]. Both U(IV) and U(VI) form several strong, highly soluble oxalate complexes (Table 3) but at low pH, the UO₂²⁺ ion is the dominant U(VI) species in solution and it is not expected to form soluble complexes with oxalate [19,20]. At high concentrations of dissolved oxalate, U(IV)-oxalate complexes should dominate U(IV) solution speciation.

Table 3
The U formation constants

Reaction	log K
U ⁴⁺ + H ₂ O ↔ UOH ³⁺ + H ⁺	-1.0
U ⁴⁺ + 2H ₂ O ↔ U(OH) ₂ ²⁺ + 2H ⁺	-2.0
U ⁴⁺ + 3H ₂ O ↔ U(OH) ₃ ⁺ + 3H ⁺	-5.0
U ⁴⁺ + 4H ₂ O ↔ U(OH) ₄ + 4H ⁺	-9.0
U ⁴⁺ + 5H ₂ O ↔ U(OH) ₅ ⁻ + 5H ⁺	-13.0
UO ₂ ²⁺ + H ₂ O ↔ UO ₂ OH ⁺ + H ⁺	-5.2
UO ₂ ²⁺ + 2H ₂ O ↔ UO ₂ (OH) ₂ + 2H ⁺	-12.0
UO ₂ ²⁺ + 3H ₂ O ↔ UO ₂ (OH) ₃ ⁻ + 3H ⁺	-20.0
UO ₂ ²⁺ + 4H ₂ O ↔ UO ₂ (OH) ₄ ²⁻ + 4H ⁺	-33.0
2UO ₂ ²⁺ + H ₂ O ↔ (UO ₂) ₂ OH ³⁺ + H ⁺	-2.8
2UO ₂ ²⁺ + 2H ₂ O ↔ (UO ₂) ₂ (OH) ₂ ²⁺ + 2H ⁺	-5.6
3UO ₂ ²⁺ + 4H ₂ O ↔ (UO ₂) ₃ (OH) ₄ ²⁺ + 4H ⁺	-11.9
3UO ₂ ²⁺ + 5H ₂ O ↔ (UO ₂) ₃ (OH) ₅ ⁺ + 5H ⁺	-15.5
3UO ₂ ²⁺ + 7H ₂ O ↔ (UO ₂) ₃ (OH) ₇ ⁺ + 7H ⁺	-31.0
4UO ₂ ²⁺ + 7H ₂ O ↔ (UO ₂) ₄ (OH) ₇ ⁺ + 7H ⁺	-21.9
U ⁴⁺ + C ₂ O ₄ ²⁻ ↔ UC ₂ O ₄ ²⁺	8.6
U ⁴⁺ + 2C ₂ O ₄ ²⁻ ↔ U(C ₂ O ₄) ₂	16.9
U ⁴⁺ + 3C ₂ O ₄ ²⁻ ↔ U(C ₂ O ₄) ₃ ²⁻	22.7
U ⁴⁺ + 4C ₂ O ₄ ²⁻ ↔ U(C ₂ O ₄) ₄ ⁴⁻	27.7
UO ₂ ²⁺ + C ₂ O ₄ ²⁻ ↔ UO ₂ C ₂ O ₄	4.6
UO ₂ ²⁺ + 2C ₂ O ₄ ²⁻ ↔ UO ₂ (C ₂ O ₄) ₂ ²⁻	8.7
UO ₂ ²⁺ + 3C ₂ O ₄ ²⁻ ↔ UO ₂ (C ₂ O ₄) ₃ ⁴⁻	12.0
U ⁴⁺ + NO ₃ ⁻ ↔ UNO ₃ ³⁺	-0.3
UO ₂ ²⁺ + NO ₃ ⁻ ↔ UO ₂ NO ₃ ⁺	0.1

Stability constants for U-oxalate species from Zakharova and Moskvina [19]; Mikaye and Nurnberg [20].

Stability constants for U-nitrate species from Arhland [21] and references therein.

Stability constants for U(IV)-hydrolysis species from Lemire and Tremaine [23].

Stability constants for U(VI)-hydrolysis species from Grenthe et al. [24].

Using the computer equilibrium speciation program FITEQL [22] and the U formation constants in Table 3, the solution speciation distribution for U(IV) and U(VI) species in the eluent was calculated at 0.38 M ionic strength with the Davies equation (Table 4). The speciation calculations predict that in 0.125 M $\text{H}_2\text{C}_2\text{O}_4$ –0.25 M HNO_3 , the $\text{U}(\text{C}_2\text{O}_4)_4^{4-}$ species dominates U(IV) speciation whereas the free UO_2^{2+} ion, and to some extent, the $\text{UO}_2\text{C}_2\text{O}_4^0$ species are the predominant U(VI) species in solution. This is found to be applicable for the U concentration range of 10^{-5} to 10^{-10} M [for both U(IV) and U(VI)].

An explanation for the elution order may be (1) the relative low affinity of the $\text{U}(\text{C}_2\text{O}_4)_4^{4-}$ species, which does not adsorb to the resin and (2) the strong adsorption of U(VI) (as UO_2^{2+}) to the resin. Assuming that U–oxalate complexation reactions in aqueous solutions are rapid processes, it is likely that U(IV) would elute prior to U(VI). The interference by high concentrations of dissolved Ca^{2+} with the elution of U(VI) may be explained by competition between Ca^{2+} with UO_2^{2+} for exchange sites on the resin.

3.4. Applying the method to natural, high-salinity and high-carbonate waters

The method has been applied to a natural water in contact with reducing sediments. The redox potential of the water from the sediments was -0.05V . At this potential, U(VI) is thermodynamically stable. The sample has the following dissolved constituents 0.030 M Na^+ , 0.004 M Ca^{2+} , 0.008 M Mg^{2+} , 0.002 M K^+ , 0.026 M SO_4^{2-} , 0.007 M Cl^- and a carbonate alkalinity of 0.025 M.

Table 4

The calculated equilibrium percent distribution obtained for the various U(IV) and U(VI) species in the eluent of 0.125 M $\text{H}_2\text{C}_2\text{O}_4$ –0.25 M HNO_3

U(IV) solution species:				
$\text{U}(\text{C}_2\text{O}_4)_4^{4-}$	$\text{U}(\text{C}_2\text{O}_4)_3^{2-}$	$\text{U}(\text{C}_2\text{O}_4)_2^0$	$\text{UC}_2\text{O}_4^{2+}$	UNO_3^{3+}
%				
98.2	1.7	<0.1	<0.1	<0.1
U(VI) solution species:				
UO_2^{2+}	$\text{UO}_2\text{C}_2\text{O}_4^0$	$\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$	$\text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}$	UO_2NO_3^+
%				
82.2	12.9	1.9	0.5	2.9

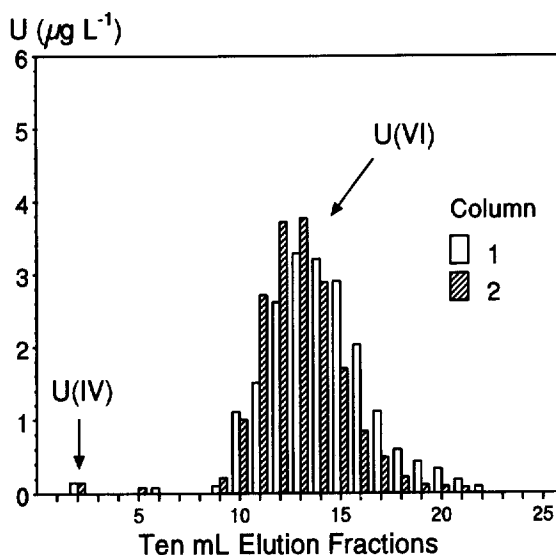


Fig. 2. The elution of 0.19 μg U(VI) in a reducing natural water sample.

A 0.5-ml sample is filtered and diluted with 0.5 ml of 0.25 M $\text{H}_2\text{C}_2\text{O}_4$ –0.55 M HNO_3 that has been equilibrated with a N_2 atmosphere. The additional HNO_3 neutralizes the sample's carbonate alkalinity and helps lower the sample pH. The sample is mixed (by vortexing) one min in a $\text{N}_{2(\text{g})}$ headspace. A 50- μl aliquot is applied to the exchange resin and 25 10-ml elution fractions are collected as described previously (Fig. 2). The elution of U(VI) [$\sim 0.19 \mu\text{g}$ U(VI)] occurs between the 9 and 22 10-ml elution fractions. Although U(IV) was predicted to be the stable U oxidation state, there was little U(IV) in the sample ($<0.1 \text{ ng}$). In addition, a small detectable quantity of U is observed within the fifth and sixth 10-ml elution fractions. This may be due to the

presence of small quantities of U(V) in the natural sample. No peaks are ever observed between the fifth and eighth 10-ml elution fractions when known quantities of U(IV) and U(VI) are separated with this method as in Section 3.1 and Section 3.2 above.

In conclusion, the cation-exchange procedure is less subject to interferences than the DBM chelation method. Because of considerable interferences with dissolved ions, the DBM chelation method is not recommended for U(IV) and U(VI) separations in highly-alkaline, saline waters. The cation-exchange method is subject to interferences from high concentrations of Ca^{2+} , which broaden the U(VI) peak. Lower concentrations of Ca^{2+} have little effect on the recovery of U(VI). The detection of U was greatly aided by the enhanced interface, which enables ICP-MS detection below $1.0 \mu\text{g U l}^{-1}$.

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