Supporting Information

Investigation of the Electrophoretic Mobility of the Actinides Th, U, Np, Pu, and Am in Different Oxidation States

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Figure S1. a) Schematic cross section of the MiraMist CE nebulizer used in the present study. b) Details of the tip of the nebulizer in cross-section and top view with the respective gas and liquid flows. These figures are from Willberger¹ and are based on the Burgener Research Operating Instructions Manual.²



Figure S2. Coupling system between CE and ICP-MS as used for the actinide mobility measurements.

 Table S1. Parameters for the CE-ICP-MS system during measurements.

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system	Agilent 7100 ce (Agilent Technologies, Santa Clara, California, USA)			
voltage	25 kV			
current	10–20 μA			
	fused-silica capillaries,			
capillary	inner diameter: 50 μm,			
	length: 76 cm			
cample introduction	hydrodynamic,			
sample introduction	8 s with 100 mbar			
background	1 M acetic acid,			
electrolyte	рН 2.4			
temperature control	25 °C			
Coupling device				
nebulizer	Mira Mist CE (Burgener Research, Mississauga, Canada)			
spray chamber	Scott-type			
	1.25% HNO₃ and 10% ethanol,			
make-up solution	5 ppb Y, Rh, Ce and Bi as			
	internal standard,			
	flow rate: 5 $\frac{\mu L}{min}$			
	Ar,			
carrier gas	flow rate: 0.86–1.15 $\frac{L}{min}$			
	Ar,			
make-up gas	flow rate: 0.28–0.77 $\frac{L}{min}$			
ICP-MS				
	Agilent 7500 ce (Agilent			
system	California, USA)			
plasma power	1550 W			
detection mode	time-resolved analysis			
dwell time	100 ms			

Capillary electrophoresis

Calculation of the acetate speciation of the metal ions and the resulting mean effective charge q_{eff}

The calculations were conducted with the program Visual MINTEQ (version 3.1)³. The pH value and the concentrations of the different components were set as follows based on the experimental conditions used in this work.

c(acetate) = 1.0 Mc(metal ion) = $5 \cdot 10^{-7} \text{ M}$ pH = 2.38

Based on the stability constants given in the literature, a species distribution of the different metalacetate complexes was calculated. The stability constants (at zero ionic strength) are taken from the ThermoChimie database⁴ for the actinides U(IV), Np(IV), Pu(III), Pu(IV), and Pu(VI), from the NIST database⁵ for Eu(III), and from Willberger et al.⁶ for Th(IV), U(VI), Np(V), and Am(III), respectively.

Eu(III): $log(\beta_1) = 2.77$, $log(\beta_2) = 4.71$, $log(\beta_3) = 5.52$ Pu(III): $log(\beta_1) = 2.85$, $log(\beta_2) = 5.06$ Am(III): $log(\beta_1) = 3.70$, $log(\beta_2) = 5.35$, $log(\beta_3) = 6.45$

Th(IV): $log(\beta_1) = 4.73$, $log(\beta_2) = 8.92$, $log(\beta_3) = 12.16$, $log(\beta_4) = 12.96$, $log(\beta_5) = 14.39$

 $U(IV): log(\beta_1) = 5.64, log(\beta_2) = 9.81$

Np(IV): $log(\beta_1) = 5.83$, $log(\beta_2) = 10.00$

Pu(IV): $log(\beta_1) = 5.93$, $log(\beta_2) = 10.09$

Np(V): $log(\beta_1) = 1.56$

U(VI): $log(\beta_1) = 3.01$, $log(\beta_2) = 5.27$, $log(\beta_3) = 6.82$ Pu(VI): $log(\beta_1) = 2.87$, $log(\beta_2) = 4.77$, $log(\beta_3) = 6.19$

Knowing the distribution of the different species, an effective charge q_{eff} of the respective ion was calculated as the weighted average charge taking into account all species according to the following formula.

$$q_{\rm eff} = \frac{\sum_i q_i \cdot a_i}{100},\tag{Eq. S1}$$

where q_i is the charge of the species and a_i is the corresponding fraction in percent.

The results of these calculations are summarized in Table S2. The acetate ligand is abbreviated as Ac.

Table S2. Species distribution of $5 \cdot 10^{-7}$ M metal ion in 1 M acetic acid at pH 2.38 calculated with Visual MINTEQ³.

Metal ion	Species	Charge q _i	Percentage/%	Effective charge $q_{ m eff}$	
Eu(III)	Eu ³⁺	3	30.9	2.15	
	EuAc ²⁺	2	53.1		
	EuAc ₂ ⁺	1	15.6		
	EuAc₃ (aq)	0	0.4		
	Pu ³⁺	3	23.9	1.75	
Pu(III)	PuAc ²⁺	2	26.9		
	PuAc ₂ ⁺	1	49.2		
	Am ³⁺	3	5.6		
Am(III)	AmAc ²⁺	2	81.5	1 02	
Am(m)	AmAc ₂ ⁺	1	12.3	1.92	
	AmAc₃ (aq)	0	0.6		
	Th ⁴⁺	4	0.0		
	ThAc ³⁺	3	0.3		
	ThAc ₂ ²⁺	2	14.2	1 1 2	
IN(IV)	ThAc₃⁺	1	83.2	1.12	
	ThAc₄ (aq)	0	2.0		
	ThAc₅⁻	-1	0.2		
	U ⁴⁺	4	0	2.02	
	UAc ³⁺	3	2.2		
	UAc ₂ ²⁺	2	93.9		
0(17)	UOH ³⁺	3	0.08		
	U(OH) ₂ ²⁺	2	3.7		
	U(OH)₃⁺	1	0.18		
	Np ⁴⁺	4	0	1.05	
Np(IV)	NpAc ³⁺	3	1.3		
	NpAc ₂ ²⁺	2	54.4		
	NpOH ³⁺	3	0.4	1.96	
	Np(OH) ₂ ²⁺	2	38.7		
	Np(OH)₃⁺	1	5.2		
Pu(IV)	Pu ⁴⁺	4	0		
	PuAc ³⁺	3	43.4	2.33	
	PuAc ₂ ²⁺	2	1.0		
	PuOH ³⁺	3	0.3		
	Pu(OH)2 ²⁺	2	44.6		
	Pu(OH)₃⁺	1	10.7		

Np(V)	NpO ₂ ⁺	1	87.6	0.88	
	NpO ₂ Ac (aq)	0	12.4		
U(VI)	UO2 ²⁺	2	13.7	0.70	
	UO ₂ Ac ⁺	1	47.4		
	UO ₂ Ac ₂ (aq)	0	33.5		
	UO ₂ Ac ₃ -	-1	5.4		
Pu(VI)	PuO ₂ ²⁺	2	22.9	1.01	
	PuO₂Ac ⁺	1	57.3		
	PuO ₂ Ac ₂ (aq)	0	17.7		
	PuO ₂ Ac ₃	-1	2.1		

Estimation of electrophoretic mobilities of non-measurable species

Some instable oxidation states of metal ions are difficult to measure with CE-ICP-MS because they are rapidly oxidized or reduced to more stable species. In the case of Pu(III) it was possible to stabilize it by adding a reducing agent without influencing the migration time of Pu. Unfortunately, some species, for example Np(III), are so instable that it was not possible to stabilize them for the duration of one experiment. Np(III) is oxidized to Np(IV) very rapidly and only a peak with an electrophoretic mobility attributable to the tetravalent species was obtained. The same problem occurred for U(III) and U(V).

Nevertheless, it is interesting to know the electrophoretic mobilities for these species. The following systematic approach can be used to estimate μ_{e} . In Table S3 a schema with all investigated actinides and their possible oxidation states is shown. The values written in black are the ones that were determined with CE-ICP-MS. By arranging them in a systematic order as shown below, it is noticeable that the intervals between two corresponding pairs of values for the electrophoretic mobilities are always the same. This is true for both following a row of oxidation states for the same element or a column of elements with the same oxidation states. For example, the difference between Np(IV) and Np(V) is $\Delta \mu_{e}(Np(IV) \rightarrow Np(V)) = 0.67 \cdot 10^{-4} \frac{cm^{2}}{Vs}$, while the difference for the Pu analogues is $\Delta \mu_{e}(Pu(IV) \rightarrow Pu(V)) = 0.69 \cdot 10^{-4} \frac{cm^{2}}{vs}$. Going down the particular oxidation state columns, one can notice that the difference for the Np(IV)/Pu(IV) couple $\Delta \mu_e (Pu(IV) \rightarrow Np(IV)) = 0.46 \cdot 10^{-4} \frac{cm^2}{V_s}$ is identical within the errors with the value for the Np(V)/Pu(V) couple $\Delta \mu_{e}(Pu(V) \rightarrow Np(V)) = 0.44$. $10^{-4} \frac{\text{cm}^2}{\text{Vs}}$. With this one can now assume that the differences in the electrophoretic mobilities are also the same for other pairs of elements or oxidation states. Although Np(III) cannot be measured, one can predict its mobility by comparing the Np(III)/Np(IV) couple with the Pu(III)/Pu(IV) couple. By assuming the difference to be $\Delta \mu_e (Np(III) \rightarrow Np(IV)) = -2.96 \cdot 10^{-4} \frac{cm^2}{V_s}$, which is the same as for $\Delta \mu_{e}(Pu(III) \rightarrow Pu(IV))$, one obtains an electrophoretic mobility of Np(III) of $\mu_{e}(Np(III)) = 4.38 \cdot 10^{-4} \frac{cm^{2}}{V_{s}}$. Since there are no known literature data, this is currently the only possible way to estimate this mobility using experimental results from CE-ICP-MS measurements. With the same procedure, the electrophoretic mobilities of the other elements written in red, i.e., U(III) and U(V), were estimated as $\mu_{e}(U(III)) = 3.25 \cdot 10^{-4} \frac{\text{cm}^{2}}{\text{Vs}}$ and $\mu_{e}(U(V)) = 0.96 \cdot 10^{-4} \frac{\text{cm}^{2}}{\text{Vs}}$ respectively. To confirm that this systematic approach is reasonable, the values written in green in Table S3 are considered. In these cases, the electrophoretic mobilities were estimated first by using before. The estimates are $\mu_{e}(U(IV)) = 0.29 \cdot 10^{-4} \frac{\text{cm}^{2}}{\text{Vs}}$ and the method explained $\mu_{\rm e}({\rm Np}({\rm VI})) = 2.64 \cdot 10^{-4} \frac{{\rm cm}^2}{{\rm Vs}}$. In later experiments, the experimental values were determined as $\mu_{e}(U(IV)) = 0.34 \cdot 10^{-4} \frac{\text{cm}^{2}}{\text{Vs}}$ and $\mu_{e}(Np(VI)) = 2.60 \cdot 10^{-4} \frac{\text{cm}^{2}}{\text{Vs}}$, indicating a good agreement between the estimated and measured values. Consequently, the presented approach seems to provide reliable results and the electrophoretic mobilities in red can be seen as reasonable estimates.

Table S3. Scheme of all investigated actinides and their possible oxidation states.

	electrophoretic mobilities $\mu_{\rm e}$ of the oxidation states / $10^{-4} \frac{\rm cm^2}{\rm Vs}$						
			IV		V		VI
Th			2.18				
U	3.25	-2.91 	0.34*	0.62 →	0.96	0.55 →	1.51
	↓ 1.13		↓ 1.08		↓ 1.13		↓ 1.09
Np	4.38	-2.96 →	1.42	$\xrightarrow{0.67}$	2.09	$\xrightarrow{0.51}$	2.60**
	↓ -0.46		↓ -0.46		↓ -0.44		↓ -0.40
Pu	3.92	-2.96 →	0.96	0.69 →	1.65	0.55 →	2.20
	↓ -0.06						
Am	3.86						

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* sample was diluted in 1 M HCl instead of 1 M acetic acid

** sample was diluted in 1 M HClO₄ instead of 1 M acetic acid

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