

Supplementary Material

Investigation of diffusion and binding properties of uranium in the diffusive gradients in thin-films technique

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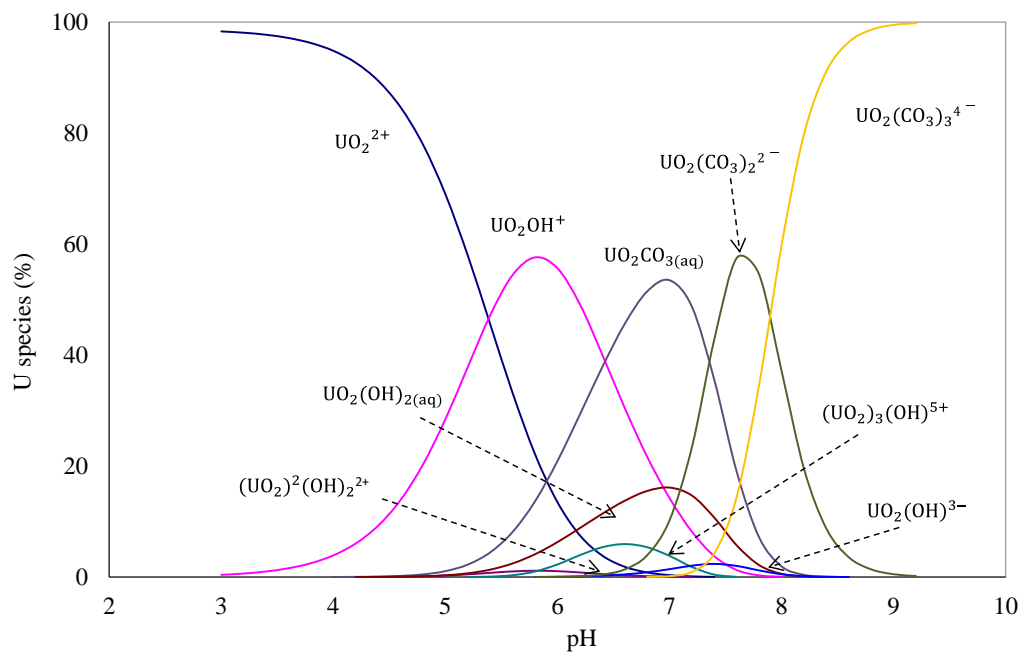


Figure S1. Uranium speciation in a solution containing $50 \mu\text{g L}^{-1}$ total dissolved U in equilibrium with air ($I = 0.01\text{M}$, $p\text{CO}_2 = 0.038\%$) modelled using vMINTEQ 3.0.

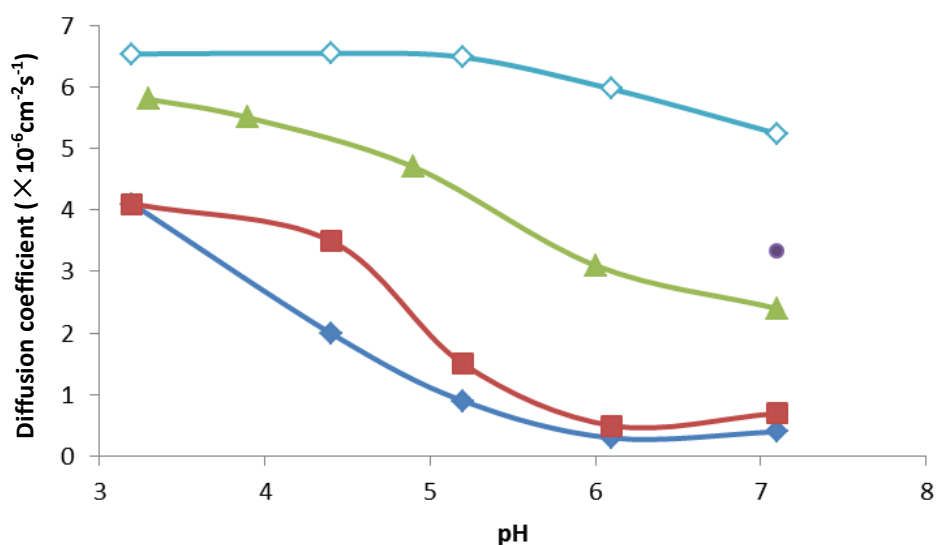


Figure S2. Diffusion coefficients measured using a diffusion cell in this work as a function of pH, with initial U concentration of 1 mg L^{-1} (red squares) and $500 \text{ } \mu\text{g L}^{-1}$ (blue diamonds). Green triangles denote the D values obtained from the experiment of Li et al. (2006). The open diamonds are diffusion coefficients of U in water calculated using ν MINTEQ 3.0 to predict the species distribution and theoretical simulations for D values of each species (Kerisit et al. 2010). The purple circle denotes the diffusion coefficient obtained in 1 mg L^{-1} uranium solution using a conditioned cell (the lower value than expected could be due to possible precipitation of U in 1 mg L^{-1} solution at pH 7). All the values have been converted to $25 \text{ } ^\circ\text{C}$.

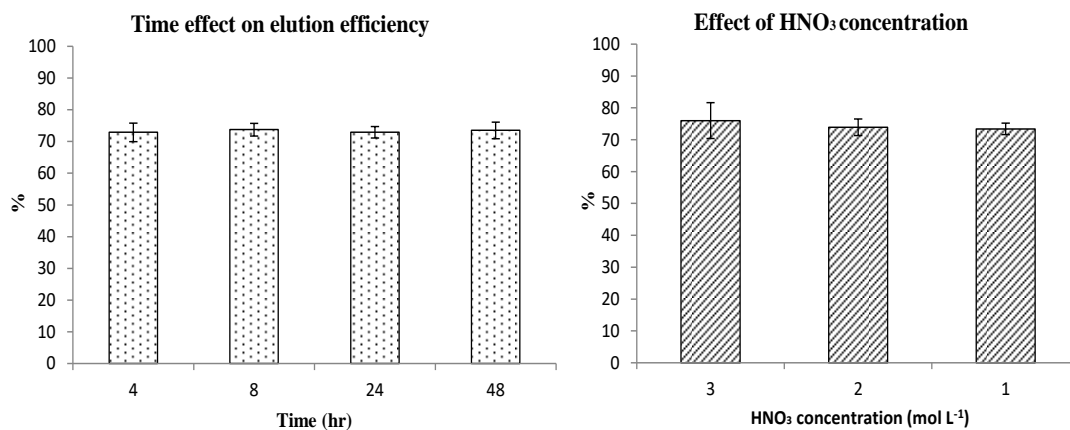


Figure S3. The left columns show the effect of elution time on elution efficiency from a Chelex resin gel at pH 6. The right columns show the effect of HNO₃ concentration on elution efficiency at pH 6. The error bars are the standard deviations from three replicate deployments.

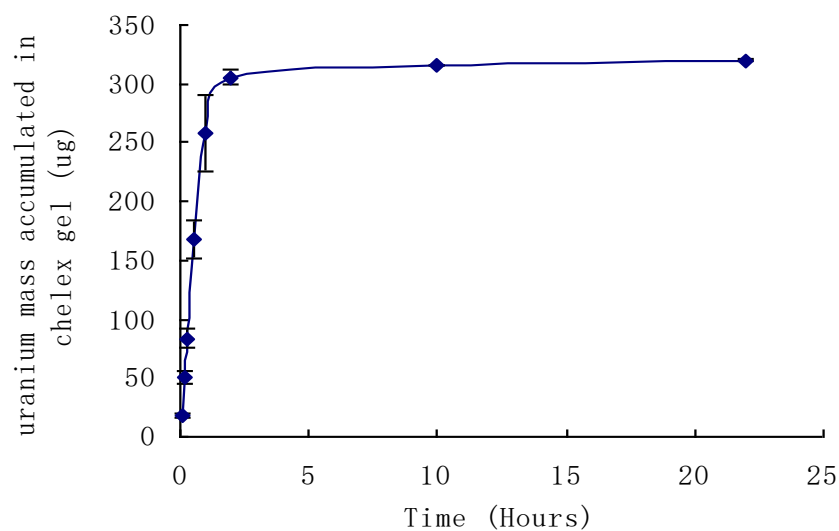


Figure S4. Effect of immersion time on uranium uptake by Chelex gel discs of 4.9 cm² at pH 5.9 with an initial uranium concentration of 20 mg L⁻¹. Error bar refers to standard deviations (n = 3).

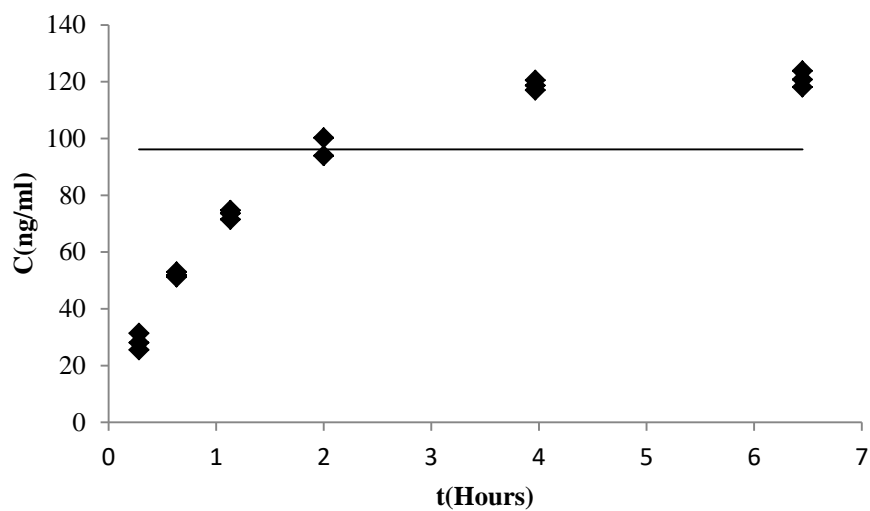


Figure S5. Concentration of U measured by DET devices (with an APA diffusive gel and without a binding gel) exposed for different times to a 100 ng mL^{-1} U solution at pH 7.4. The solid line denotes the solution concentration.

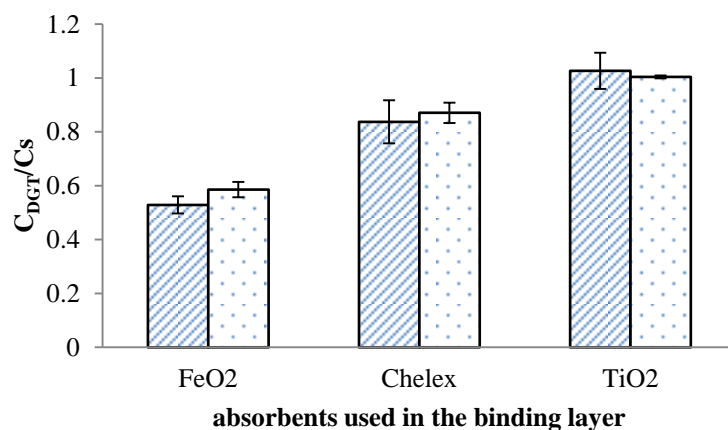


Figure S6. Ratio of the DGT measured concentration to the concentration in solution. DGT deployments of 6 hours were performed at two different pH (hashed fill denotes pH 5.8, dotted denotes pH 6.4) using three absorbents. C_{DGT} was calculated using the measured solution concentration and D_U ($5.26 \pm 0.17 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) measured by the DGT method II loaded with Metsorb binding gel at pH 7.2. Errors bars show the standard deviations for 3 deployments. The B values used for FeO2 DGT, Chelex DGT and Metsorb DGT are 0.64, 0.86 and 1.00 respectively.

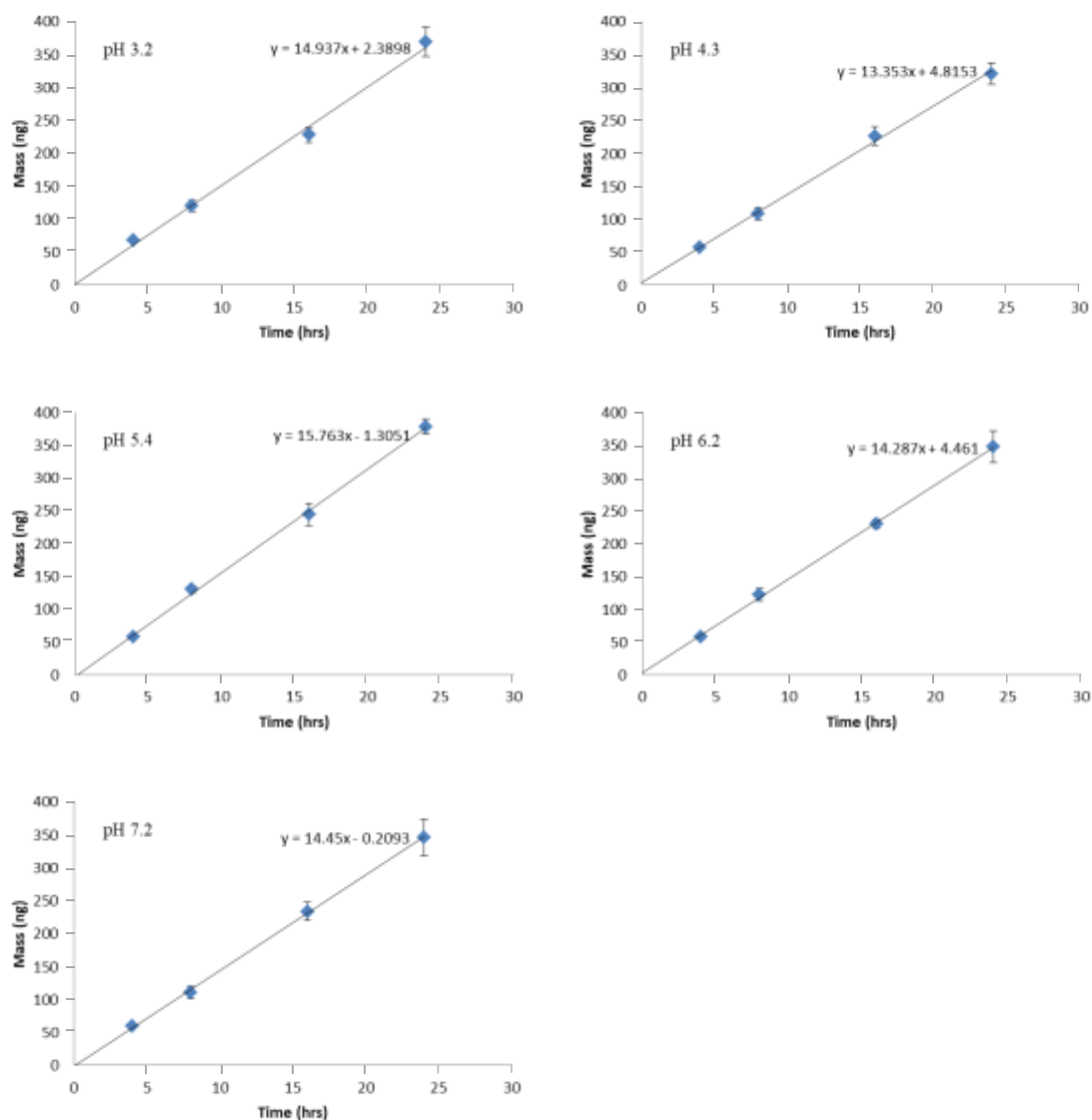


Figure S7. Mass measured by DGT versus time for various deployment times in 8 L of 0.01 M NaNO_3 solution containing $\sim 25 \mu\text{g L}^{-1}$ of uranium at different pH values from 3.2 to 7.2. Standard deviations are presented as error bars ($n = 3$). The D_{Ueff} values calculated using equation 5 at corresponding pH are 4.86 ± 0.24 (pH 3.2), 4.45 ± 0.13 (pH 4.3), 5.01 ± 0.18 (pH 5.4), 4.67 ± 0.07 (pH 6.2) and 4.58 ± 0.09 (pH 7.2) at the unit of $10^{-6} \text{cm}^2 \text{s}^{-1}$.

Table S1. Distribution of uranium species, expressed as percentages, as a function of pH according to Visual MINTEQ 3.0

50 µg L⁻¹										
pH	UO ₂ ⁺²	UO ₂ OH ⁺	UO ₂ CO ₃ (aq)	(UO ₂) ₂ (OH) ₂ ⁺²	UO ₂ (OH) ₂ (aq)	(UO ₂) ₃ (OH) ⁵⁺	(UO ₂) ₄ (OH) ⁷⁺	UO ₂ (CO ₃) ₂ ⁻²	UO ₂ (CO ₃) ₃ ⁻⁴	Schoepite
3.6	97.13	1.59								
4.6	84.65	13.90	0.21	0.07	0.06					
5.6	33.15	54.43	8.14	1.02	2.46	0.34				
6.6	1.86	30.49	45.61	0.32	13.75	5.95	0.13	1.38		
7.4	0.04	3.76	35.50		10.70	0.45		42.87	4.30	
100 µg L⁻¹										
3.6	97.13	1.59								
4.6	84.59	13.89	0.21	0.13	0.06					
5.6	32.51	53.38	7.99	1.97	2.41	1.28				
6.6	1.64	26.88	40.21	0.50	12.12	16.33	0.62	1.22		
7.4	0.04	3.71	35.02		10.56	1.71	0.06	42.29	4.24	
500 µg L⁻¹										
3.6	97.12	1.59								
4.6	84.12	13.81	0.21	0.66	0.06					
5.6	25.86	42.46	6.35	6.23	1.92	16.09	0.48			
6.6	0.83	13.57	20.31	0.64	6.12	52.57	5.03	0.62		
7.4	0.03	2.90	27.35	0.03	8.25	20.37	2.62	33.03	3.31	
1 mg L⁻¹										
3.6	97.11	1.59		0.02						
4.6	83.55	13.72	0.21	1.30	0.06	0.02				
5.6	20.17	33.11	4.95	7.57	1.49	30.51	1.42			
6.6	0.55	9.10	13.61	0.57	4.10	63.28	8.11	0.41		
7.4	0.02	1.65	15.54	0.02	4.68	14.93	2.18	18.76	1.88	39.08

Table S2. Diffusion coefficients ($\times 10^{-6}$) ($\text{cm}^2 \text{s}^{-1}$) of Co, Cd and U in the restricted gel (D_{RG}^1), open pore gel (D_{APA}^1) and agarose gel (D_{AG}) measured by method 3 using Chelex DGT deployments in 2 L of 0.01 M NaNO_3 solution containing $50 \mu\text{g L}^{-1}$ of uranium and $10 \mu\text{g L}^{-1}$ of Cd and Co assuming a value of B of 0.86 (for uranium only) (D^1) and data from Scally et al. (2006) (D^2). The diffusion coefficients in water, D_{ws} , were taken from the literature for $\text{U}^{1,2}$ and the CRC handbook of thermo-physical and thermochemical data (Lide et al. 1994) for Co and Cd. All data have been corrected to a temperature of 25 °C.

	D_{RG}^1	D_{RG}^2	D_{APA}^1	D_{APA}^2	D_{AG}	D_{ws}
Co	4.21		5.97		7.14	6.99
Cd	4.13	4.34	5.79	6.20	6.95	7.19
U	3.20	–	5.50	–	6.70	6.28

References

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Lide DR, Kehiaian HV (1994) 'Handbook of thermophysical and thermochemical data.' (CRC press)

Scally S, Davison W, Zhang H (2006) Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films. *Analytica Chimica Acta* **558**(1–2), 222–229. doi: 10.1016/j.aca.2005.11.020