Supporting Information (SI)

Temperature-dependent luminescence spectroscopic investigations of uranyl(VI) complexation with the halides F^- and Cl^-

M. Demnitz[1], S. Hilpmann[1], H. Lösch[1], F. Bok[1], R. Steudtner[1], M. Patzschke[1], T. Stumpf[1], N. Huittinen[1]*

[1)]*Helmholtz-Zentrum Dresden-Rossendorf e.V., Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany*

*Corresponding author :

Nina Huittinen
email : n.huittinen@hzdr.de
phone : +49 351 260 2148
fax : +49 351 260 3553

Tables S1–S8

Conditional stability constants in Table 2 in the main text were calculated by using published NEA TDB values.[1] Reaction schemes in that review included the reaction of the free uranyl(VI) with 1 to 4 fluoride forming the various uranyl(VI) fluoride complexes. To obtain stepwise fluoride complexation of the uranyl(VI) the log*K** values from the NEA TDB were averaged and subtracted from each other e.g. log*K** [UO_2^{2+}+2 F^- ⇌ UO_2F_2] – log*K** [UO_2^{2+}+ F^- ⇌ UO_2F^+] = log*K** [UO_2F^++ F^- ⇌ UO_2F_2]. The error range of the literature log*K** was calculated by using two times the standard deviation of the literature values.

Table S1: Published conditional complexation constants at an ionic strength of around 1 M and used methods for the uranyl(VI) fluoride complexes.

Complex	Reaction	log*K**	Method	Temperature	Literature
UO_2F^+	UO_2^{2+} + F^- ⇌ UO_2F^+	4.55±0.05	Quinhydrone electrode	20 °C	Ahrland et al.[2]
		4.66±0.10	NMR	25 °C	Vdovenko et al.[3]
		4.54±0.05	Quinhydrone electrode Ion selective electrode	25 °C	Ahrland et al.[4]
		4.52±0.06	Ion selective electrode	25 °C	Ishiguro et al.[5]
		4.56±0.05	Ion selective electrode	21 °C	Sawant et al.[6]
		4.60±0.02	Spectrophotometry	25 °C	Tian et al.
UO_2F_2	UO_2^{2+} + 2 F^- ⇌ UO_2F_2	7.89±0.05	Quinhydrone electrode	20 °C	Ahrland et al.[2]
		7.98±0.05	Quinhydrone electrode Ion selective electrode	25 °C	Ahrland et al.[4]
		7.90±0.06	Ion selective electrode	25 °C	Ishiguro et al.[5]
		8.07±0.04	Spectrophotometry	25 °C	Tian et al.
$UO_2F_3^-$	UO_2^{2+} + 3 F^- ⇌ $UO_2F_3^-$	10.46±0.05	Quinhydrone electrode	20 °C	Ahrland et al.[2]
		10.41±0.05	Quinhydrone electrode Ion selective electrode	25 °C	Ahrland et al.[4]
		9.96±0.07	Ion selective electrode	25 °C	Ishiguro et al.[5]
		10.34±0.06	Ion selective electrode	21 °C	Sawant et al.[6]
		10.78±0.04	Spectrophotometry	25 °C	Tian et al.
$UO_2F_4^{2-}$	UO_2^{2+} + 4 F^- ⇌ $UO_2F_4^{2-}$	11.81±0.05	Quinhydrone electrode	20 °C	Ahrland et al.[2]
		11.81±0.05	Quinhydrone electrode Ion selective electrode	25 °C	Ahrland et al.[4]
		10.94±0.12	Ion selective electrode	25 °C	Ishiguro et al.[5]
		11.92±0.14	Spectrophotometry	25 °C	Tian et al.

Table S2: Published conditional complexation constants at an ionic strength of around 1 M and used methods for the uranyl(VI) chloride complexes.

Complex	Reaction	log*K**	Method	Temperature	Literature
UO_2Cl^+	$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+$	-0.10±0.11	Electromotive force	20 °C	Ahrland et al.[7]
		-0.30±0.26	Spectrophotometry	20 °C	
		-0.42±0.04	Spectrophotometry	25 °C	Davies et al.[8]
		1.64	Spectrophotometry	25 °C	Hefley et al.[9]
		-0.05	Electromotive force	25 °C	Ohashi et al.[10]
		-0.60	Mole volume determination	RT	Jedináková et al.[11]
		-0.31±0.10	Spectrophotometry		Awasthi et al.[12]
UO_2Cl_2	$UO_2^{2+} + 2\ Cl^- \rightleftharpoons UO_2Cl_2$	-1.76±0.30	Spectrophotometry	25 °C	Awasthi et al.[12]

Table S3: Used logK^0 values for PHREEQC calculations.

Reaction equation	log*K*°	Reference
$H^+ + F^- \rightleftharpoons HF(aq)$	3.173	13, 14
$HF(aq) + F^- \rightleftharpoons HF_2^-$	0.587	13, 14
$UO_2^{2+} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+$	−5.25	15, 16
$UO_2^{2+} + 2\ H_2O \rightleftharpoons UO_2(OH)_2(aq) + 2\ H^+$	−12.15	15, 16
$UO_2^{2+} + 3\ H_2O \rightleftharpoons UO_2(OH)_3^- + 3\ H^+$	−20.25	15, 16
$UO_2^{2+} + 4\ H_2O \rightleftharpoons UO_2(OH)_4^{2-} + 4\ H^+$	−32.4	15, 16
$2\ UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2(OH)^{3+} + H^+$	−2.7	15, 16
$2\ UO_2^{2+} + 2\ H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2\ H^+$	−5.62	15, 16
$3\ UO_2^{2+} + 4\ H_2O \rightleftharpoons (UO_2)_3(OH)_4^{2+} + 4\ H^+$	−11.9	15, 16
$3\ UO_2^{2+} + 5\ H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5\ H^+$	−15.55	15, 16
$3\ UO_2^{2+} + 7\ H_2O \rightleftharpoons (UO_2)_3(OH)_7^- + 7\ H^+$	−32.2	15, 16
$4\ UO_2^{2+} + 7\ H_2O \rightleftharpoons (UO_2)_4(OH)_7^+ + 7\ H^+$	−21.9	15, 16
$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+$	0.17	15, 16
$UO_2^{2+} + 2\ Cl^- \rightleftharpoons UO_2Cl_2(aq)$	−1.1	15, 16
$UO_2^{2+} + F^- \rightleftharpoons UO_2F^+$	5.16	15, 16
$UO_2^{2+} + 2\ F^- \rightleftharpoons UO_2F_2(aq)$	8.83	15, 16
$UO_2^{2+} + 3\ F^- \rightleftharpoons UO_2F_3^-$	10.9	15, 16
$UO_2^{2+} + 4\ F^- \rightleftharpoons UO_2F_4^{2-}$	11.84	15, 16

Table S4: Used ε parameters (SIT) for PHREEQC and logK^0 calculations.

Species i,j	ε(i,j)	Reference
Na^+, HF_2^-	−0.11	[13, 14]
Na^+, ClO_4^-	0.01	[15, 16]
Na^+, Cl^-	0.03	[15, 16]
Na^+, F^-	0.02	[15, 16]
UO_2^{2+}, Cl^-	0.46	[15, 16]
UO_2^{2+}, ClO_4^-	0.46	[15, 16]
UO_2Cl^+, Cl^-	0.22	[15, 16]
UO_2Cl^+, ClO_4^-	0.33	[15, 16]
UO_2F^+, Cl^-	0.04	[15, 16]
UO_2F^+, ClO_4^-	0.28	[15, 16]
Na^+, $UO_2F_3^-$	−0.14	[15, 16]
Na^+, $UO_2F_4^{2-}$	−0.3	[15, 16]
$UO_2(OH)^+$, Cl^-	−0.003	[15, 16]
$UO_2(OH)^+$, ClO_4^-	−0.06	[15, 16]
Na^+, $UO_2(OH)_3^-$	−0.09	[15, 16]

Table S5: Determined LI-factors for the uranyl(VI) fluoride complexes in solution at 25 °C; pH = 2; I = 1 M.

Complex	UO_2^{2+}	UO_2F^+	UO_2F_2	$UO_2F_3^-$	$UO_2F_4^{2-}$
LI-factor	1.00	0.86	1.60	1.50	1.40

Table S6: Wavenumbers of the first and the second peak of the deconvoluted spectra and their difference (v_s).

Component	Peak I [cm^{-1}] (E)	Peak II [cm^{-1}] (S_1)	Difference [cm^{-1}], (v_s)
UO_2^{2+}	20445.7	19577.1	868.6
Species 1 (UO_2F^+)	20181.6	19331.1	850.5
Species 2 (UO_2F_2)	20088.4	19241.9	846.5
Species 3 ($UO_2F_3^-$)	19996.0	19157.1	838.9
Species 4 ($UO_2F_4^{2-}$)	19751.1	18925.1	826.1

Table S7: Determined K_d and K_s values from the $K_d + K_s$ and K_dK_s terms of the linear fit of equation S1.

Temperature	K_d [M^{-1}]	K_s [M^{-1}]
1 °C	1150 ± 104	426 ± 45
15 °C	2073 ± 352	447 ± 106
25 °C	1942 ± 424	720 ± 197
35 °C	1788 ± 184	969 ± 109
45 °C	1724 ± 102	995 ± 63

Table S8: Determined K_d values and the lifetimes of the uranyl(VI) aquo ion with the calculated k_q at 1 to 45 °C.

Temperature	K_d [M^{-1}]	τ_0 [ns]	k_q [$M^{-1}s^{-1}$]
1 °C	1150	10190	1.13E+08
15 °C	2073	3420	6.06E+08
25 °C	1942	1670	1.16E+09
35 °C	1788	860	2.08E+09
45 °C	1724	470	3.67E+09

Figures S1–S10

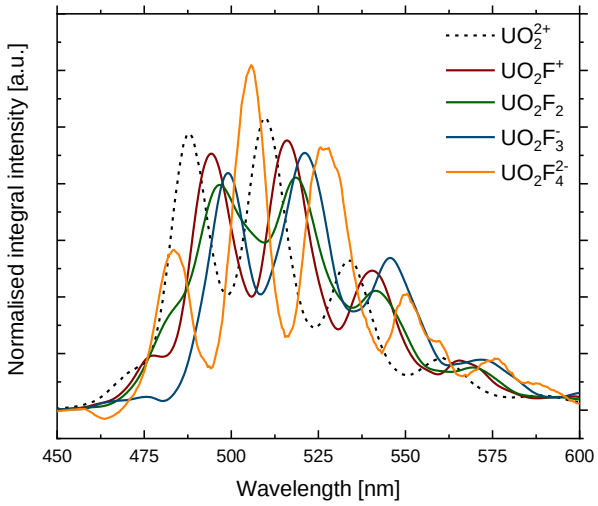

Figure S1: Single luminescence component spectra of UO_2^{2+}, UO_2F^+, UO_2F_2, $UO_2F_3^-$ and $UO_2F_4^{2-}$ at [F] = 0 – 0.175 M; $-\log[H^+]$ = 2; I = 1 M; T = 25 °C.

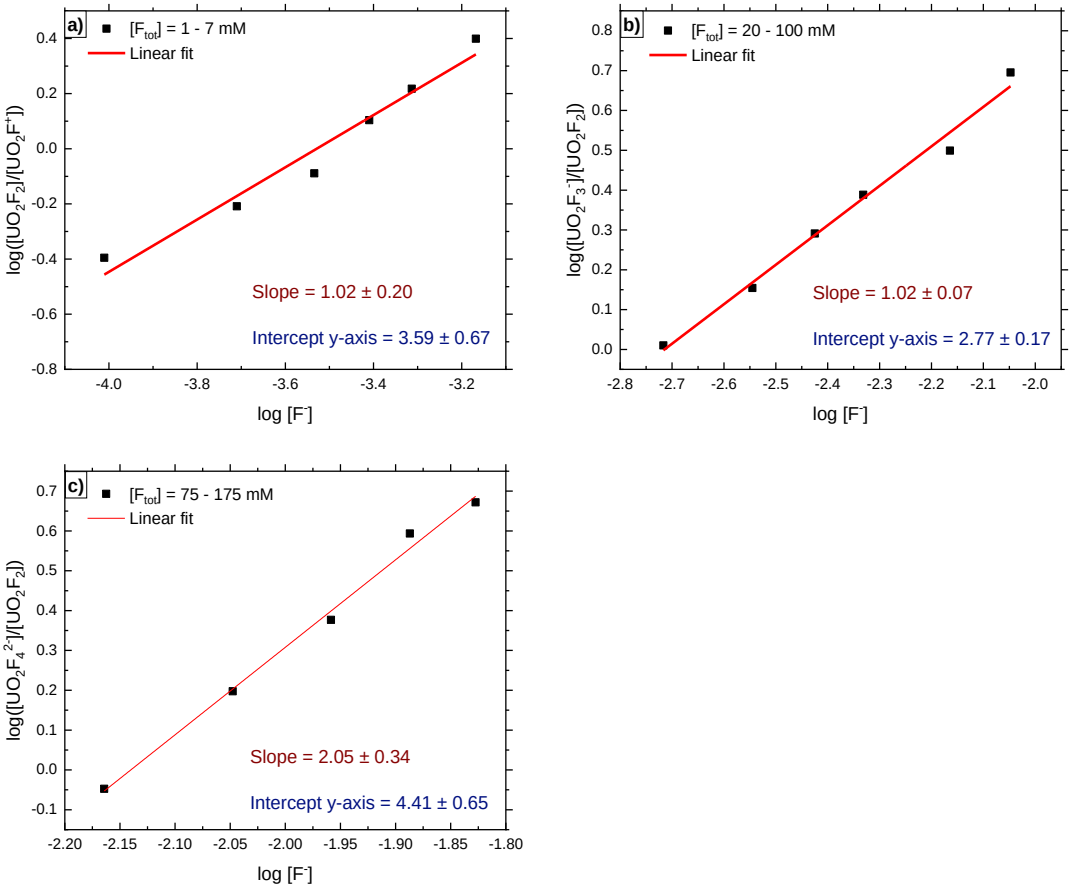

Figure S2: Slope analysis for the a) UO_2F_2, b) $UO_2F_3^-$ and c) $UO_2F_4^{2-}$ complexes according to equation (3).

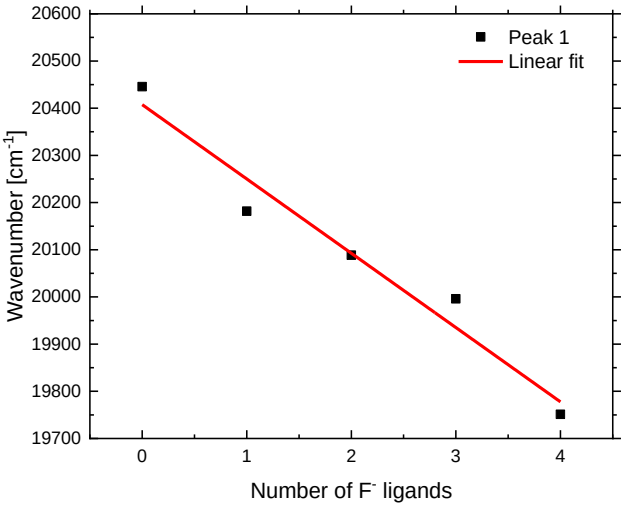

Figure S3: Linear fit of the first peak position (E) versus the number of F^- ligands in the uranyl(VI) fluoride complex.

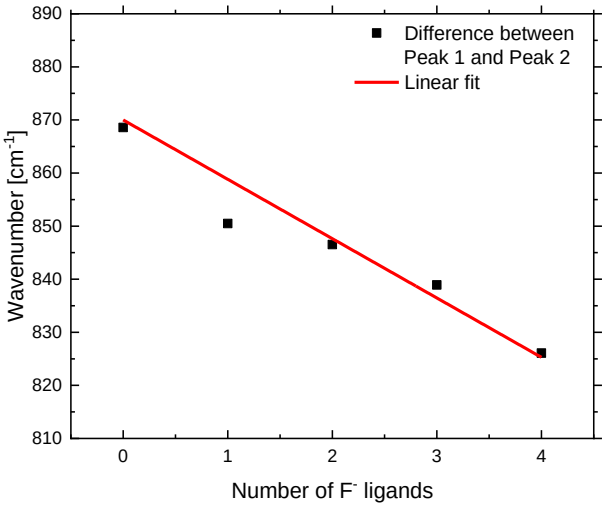

Figure S4: Linear fit of the total symmetric stretch vibration frequency (ν_s) versus the number of F^- ligands in the uranyl(VI) fluoride complex.

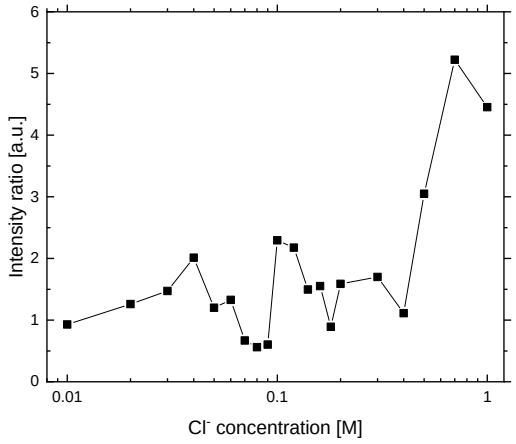

Figure S5: Intensity ratio of uranyl(VI)-chloride samples compared to the uranyl(VI) aquo ion ([Cl] = 0 M) with increasing chloride concentration at [Cl] = 0.01 – 0.1 M; −log[H^+] = 1.4, I = 1.1 M; T = –120 °C.

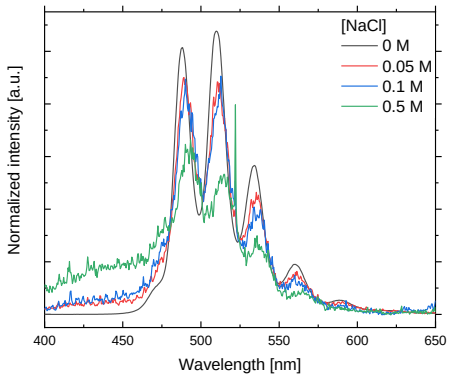

Figure S6: Luminescence spectra of uranyl(VI) ([U] = 0.1 mM) with chloride [Cl] = 0 – 0.05 M at 1 °C; I = 0.5 M; −log[H^+] = 2.5.

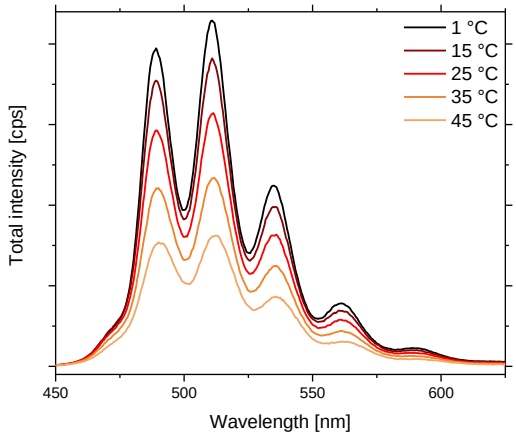

Figure S7: Non-normalized luminescence spectra of uranyl(VI) at [F] = 0.1 mM at 1 – 45 °C (274.15 – 318.15 K). [U] = 0.1 mM, I = 1 M; −log[H] = 2.

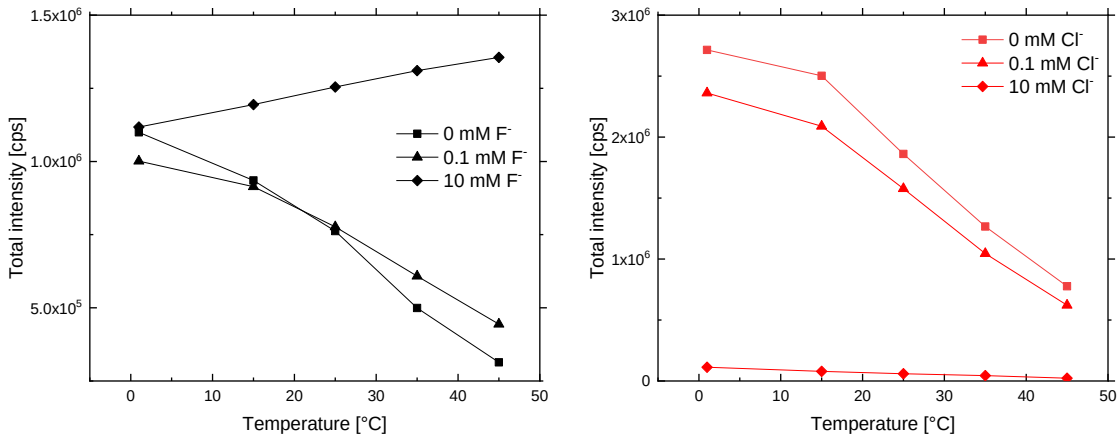

Figure S8: Total luminescence intensity of uranyl(VI) [U] = 0.1 mM with a) fluoride and b) chloride at 0; 0.1 and 10 mM halide concentration at T = 1 – 45 °C.

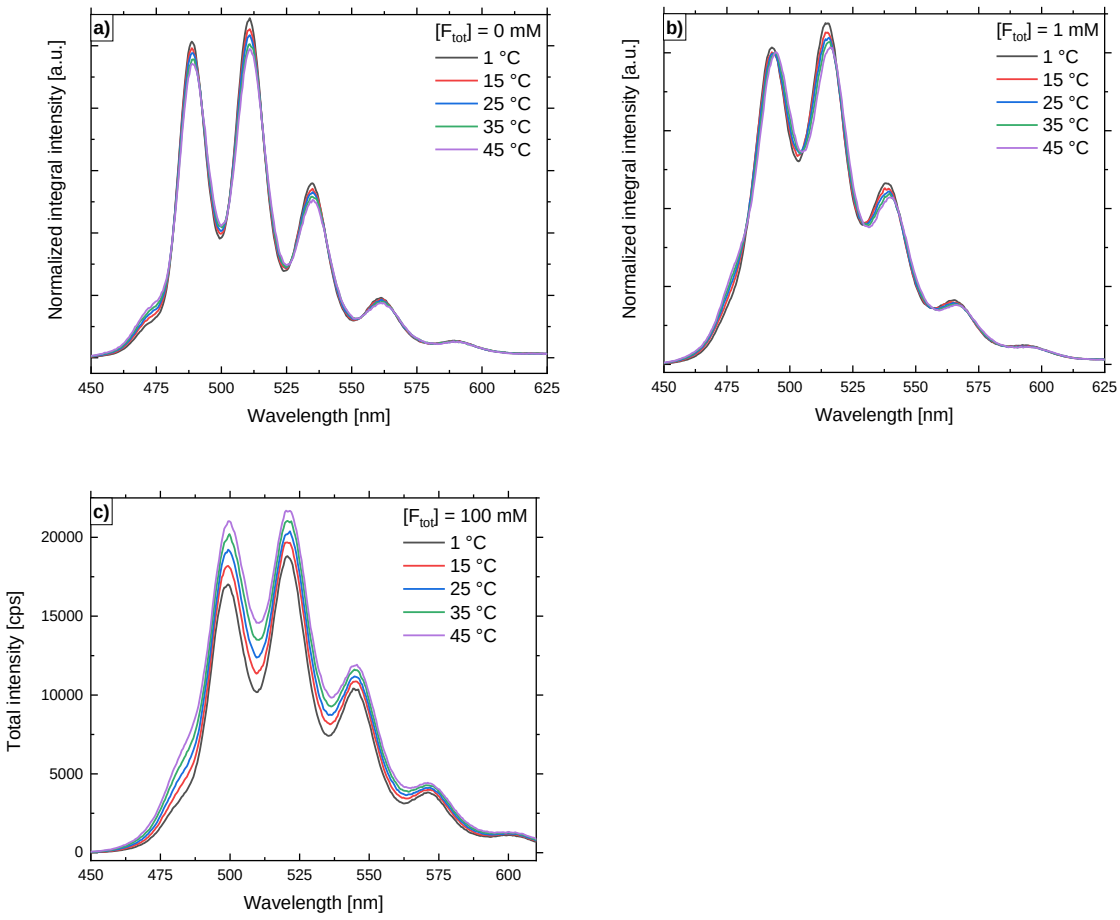

Figure S9: Luminescence spectra of uranyl(VI) ([U] = 0.1 mM) with fluoride a) [F] = 0 mM, b) [F] = 1 mM and c) [F] = 100 mM at 1 – 45 °C; I = 1 M; pH = 2.

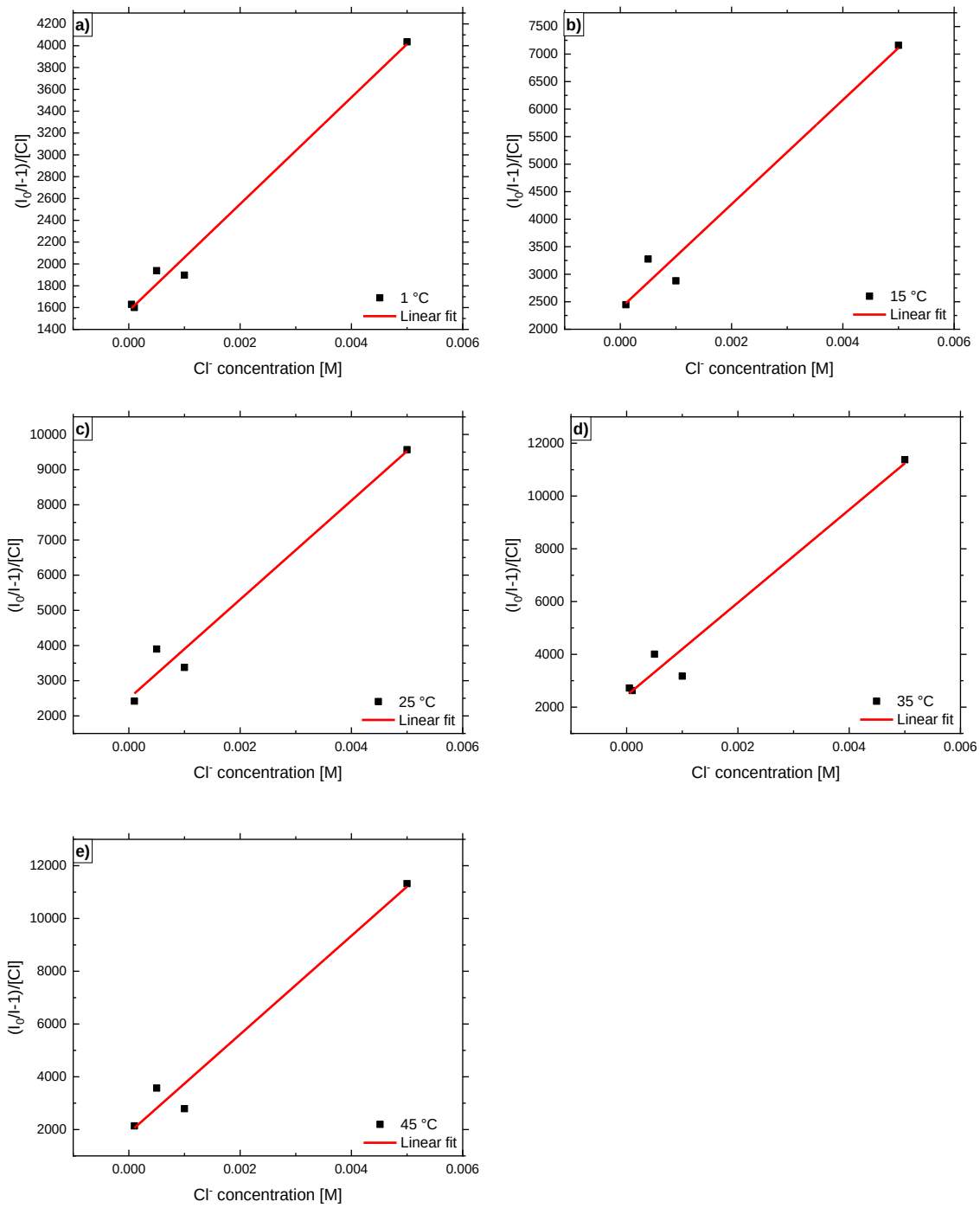

Figure S10: Linear regression of $(I_0/I-1)/[Cl]$ against the chloride concentration at a) 1 °C, b) 15 °C, c) 25 °C, d) 35 °C and e) 45 °C.

Equations S1–S4

$$\frac{I_0}{I} = (1 + K_d \cdot [Q]) \cdot (1 + K_s \cdot [Q]) \tag{S1}$$

$$\left(\frac{I_0}{I} - 1\right) \cdot \frac{1}{[Q]} = (K_d + K_s) + K_d K_s \cdot [Q] \tag{S2}$$

$$\ln(k_q) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(A) \tag{S3}$$

$$\ln\left(\frac{k_q}{T}\right) = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} \tag{S4}$$

References

1. I. Grenthe, J. Fuger, R. J. Konings, R. J. Lemire, A. B. Muller, C. Nguyen-Trung and H. Wanner, *Chemical thermodynamics of uranium*, North-Holland Amsterdam, 1992.
2. S. Ahrland, *Acta Chemica Scandinavica*, 1956, **10**, 705-718.
3. V. M. Vdovenko and O. B. Stebunov, *Sov. Radiochem.*, 1969, **11**, 630-632.
4. S. Ahrland and L. Kullberg, *Acta Chem. Scand.*, 1971, **25**, 3457-3470.
5. S.-i. Ishiguro, C.-F. Kao and H. Kakihana, *Denki Kagaku*, 1977, **45**, 651-653.
6. R. M. Sawant, N. K. Chaudhuri, G. H. Rizvi and S. K. Patil, *Journal of Radioanalytical and Nuclear Chemistry*, 1985, **91**, 41-58.
7. S. Ahrland, *Acta Chemica Scandinavica*, 1951, **5**, 1271-1282.
8. E. Davies and C. Monk, *Transactions of the Faraday Society*, 1957, **53**, 442-449.
9. J. D. Hefley and E. S. Amis, *The Journal of Physical Chemistry*, 1960, **64**, 870-872.
10. H. Ohashi and T. Morozumi, *Electrometric Determination of Stability Constants of Uranyl-Chloride and Uranyl-Nitrate Complexes with pCl-Stat*, Hokkaido Univ., Sapporo, 1967.
11. V. Jedinakova, *Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem. Technol.; (Czechoslovakia)*, 1974, Pages: 113-126.
12. S. P. Awasthi and M. Sundaresan, *Indian Journal of Chemistry Section a-Inorganic Bio-Inorganic Physical Theoretical & Analytical Chemistry*, 1981, **20**, 378-381.
13. I. Grenthe, H. Wanner, I. Forest and O. N. E. Agency, *Chemical thermodynamics of uranium*, North-Holland, 1992.
14. D. Palmer, R. Guillaumont, T. Fanghaenel, V. Neck, J. Fuger, I. Grenthe and M. H. Rand, *Chemical Thermodynamics Vol. 5: Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium*, 2003.
15. E. Giffaut, M. Grivé, P. Blanc, P. Vieillard, E. Colàs, H. Gailhanou, S. Gaboreau, N. Marty, B. Madé and L. Duro, *Applied Geochemistry*, 2014, **49**, 225-236.
16. M. Grivé, L. Duro, E. Colàs and E. Giffaut, *Applied Geochemistry*, 2015, **55**, 85-94.