

Oxidation of Cr^{III} to Cr^{VI} During Chlorination of Drinking Water

*Dana Lindsay, Kevin J Farley, Richard F. Carbonaro**

Department of Civil & Environmental Engineering, Manhattan College, Riverdale, NY 10471

* Corresponding author

Electronic Supplementary Information

Chromium Stability Regions

An E_h -pH diagram is shown in Figure S1 to show the stability regions for chromium. Data used to construct the diagram is presented in Table S1. A total chromium of 100 μM to match what was used in experiments. The diagram shows that Cr^{III} is insoluble over the pH regime employed in experiments, precipitating as $\text{Cr}(\text{OH})_3(\text{s,amorphous})$. Thus, the Cr^{III} nitrate salt used in experiments is expected to precipitate during reaction time courses. Precipitation is known to occur slowly, due to the slow rate of ligand exchange exhibited by Cr^{III} . For this reason, Cr^{III} nitrate stock solutions were prepared fresh within one hour of each experiment (see Experimental Methods section for more details). Cr^{III} -EDTA is known to remain soluble over the entire pH range investigated.¹

Cr^{VI} is not expected to form solid precipitates with the components of the reaction medium (either DDW or NYC tap water). The dominant forms of Cr^{VI} at near-neutral pH are HCrO_4^- and CrO_4^{2-} .

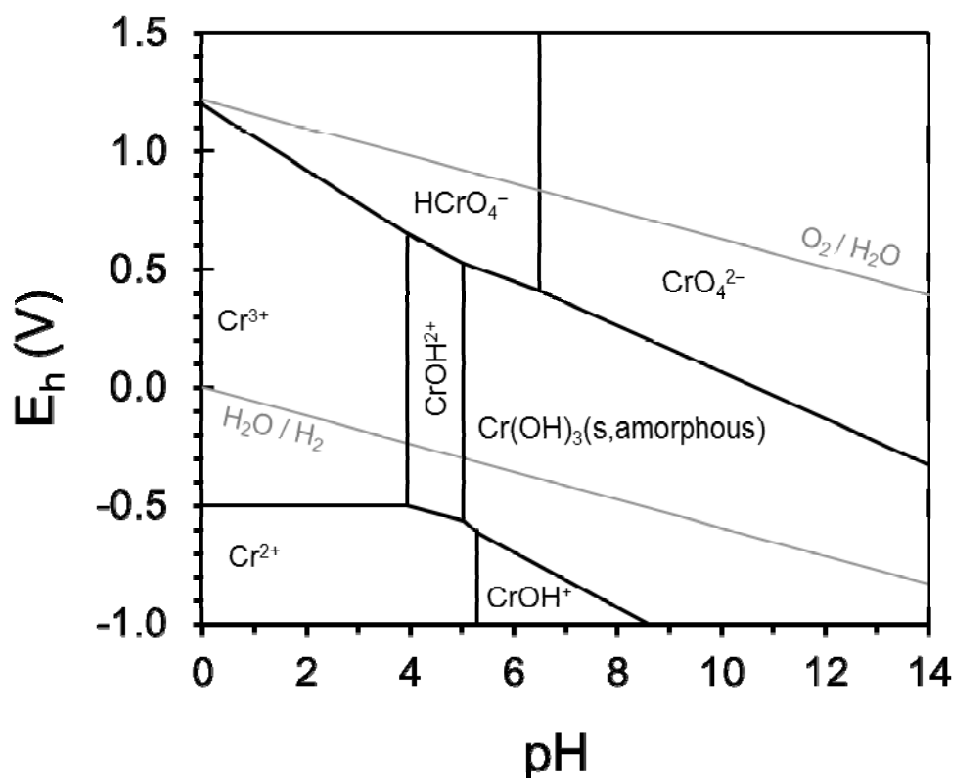


Figure S1: Eh-pH diagram for chromium. The total chromium used to create the figure was 100 μM to match what was used in experiments. Thermodynamic data used to create the diagram is shown in Table S1.

Table S1: Thermodynamic data employed to create Eh-pH Diagram

Redox Reactions	E⁰ (V)
$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- = \text{Cr}^{3+} + 4\text{H}_2\text{O}$	1.20 ²
$\text{Cr}^{3+} + \text{e}^- = \text{Cr}^{2+}$	-0.50 ²
Solubility Reactions	Log K
$\text{Cr}(\text{OH})_3(\text{s,amorphous}) + 2\text{H}^+ = \text{CrOH}^{2+} + 2\text{H}_2\text{O}$	5.78 ³
Deprotonation Reactions	
$\text{H}_2\text{CrO}_4(\text{aq}) = \text{HCrO}_4^- + \text{H}^+$	0.2 ⁴
$\text{HCrO}_4^- = \text{CrO}_4^{2-} + \text{H}^+$	-6.51 ⁴
$\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$	-3.95 ⁵
$\text{CrOH}^{2+} + \text{H}_2\text{O} = \text{Cr}(\text{OH})_2^+ + \text{H}^+$	-5.55 ⁵
$\text{Cr}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Cr}(\text{OH})_3(\text{aq}) + \text{H}^+$	-8 ⁶
$\text{Cr}(\text{OH})_3(\text{aq}) + \text{H}_2\text{O} = \text{Cr}(\text{OH})_4^- + \text{H}^+$	-11.5 ³

Figures S2 and S3 are referred to in the text.

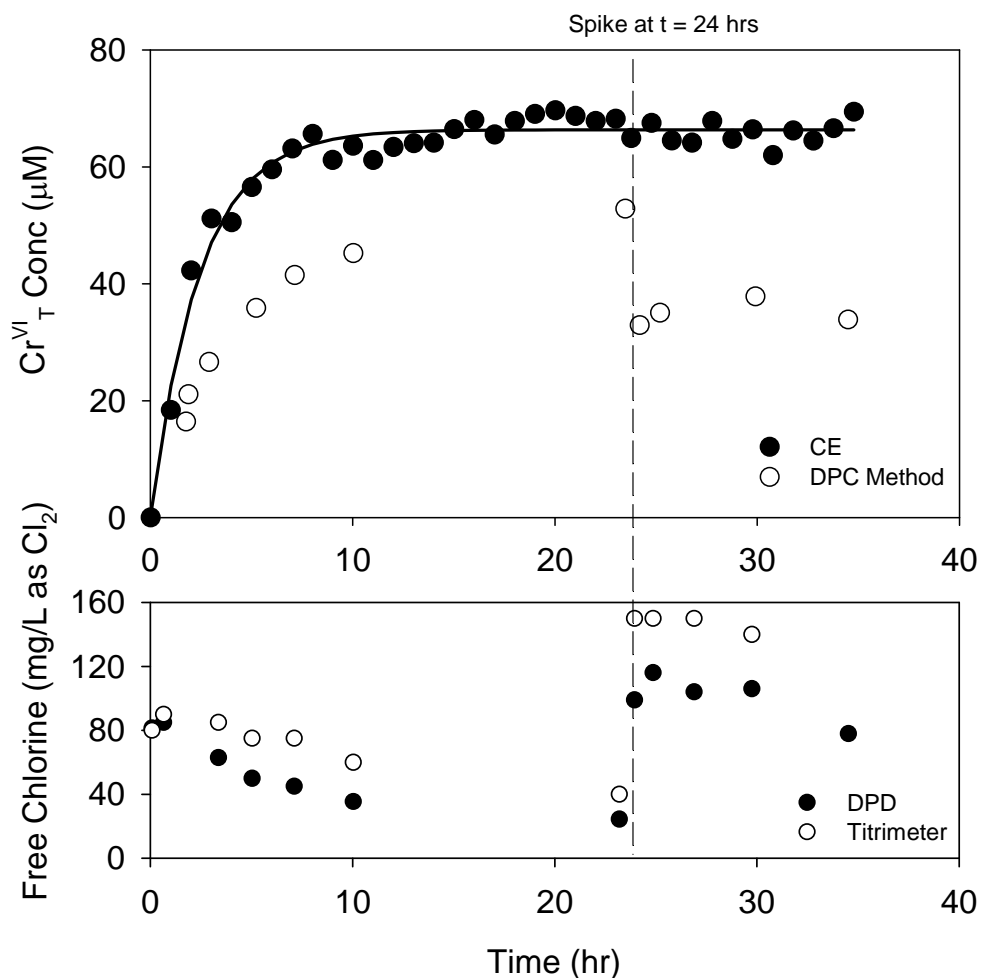


Figure S2: Top: Cr^{VI}_T concentration measured on the CE and using the DPC colorimetric test for Cr^{VI} on the DU 800 Spectrophotometer. Bottom: Free chlorine concentration measured by the DPD spectrophotometric method and titrimeter methods.

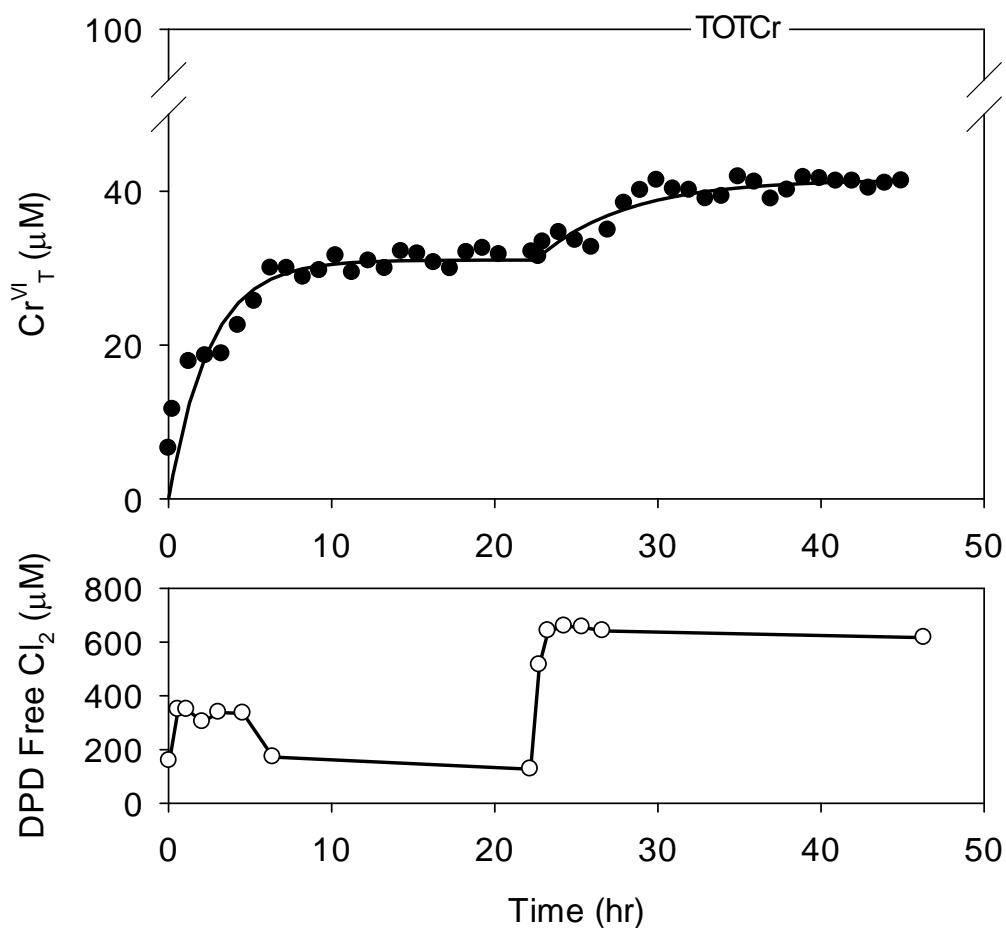


Figure S3: Results from a double spike experiment in DDW using 100 μM $\text{Cr}(\text{NO}_3)_3$ with two spikes of 30 mg/L as Cl_2 .

Thermodynamic Calculations Involving Cr^V and HOCl

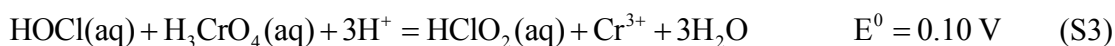
Assuming chlorine functions as a two electron oxidant, Cr^V is produced. The redox potential for the Cr^V/Cr^{III} half reaction in acidic solution can be written as the following ⁷:



where H₃CrO₄(aq) represents the fully-protonated Cr^V oxoanion. The 2 electron oxidation of hypochlorous acid to chlorous acid is the following:



Coupling Equation S1 and S2 yields a reaction which represents the oxidation of hypochlorous acid to chlorous acid:

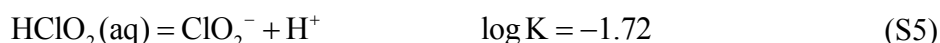


which is favorable under standard conditions. Equation S3 includes the chemical forms most relevant in acidic (pH ~ 0) conditions. Calculation of E for the conditions employed in this study (pH ~7) is complicated by the fact that the pK_a values of the Cr^V oxo anion are unknown.

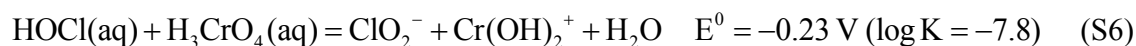
The other species in Reaction S3 can be converted to their relevant forms using protonation equilibria. For Cr³⁺, the dominant species is Cr(OH)₂⁺. The relevant reaction is the following:



Equation S3 can also be adjusted to include chlorite ion by considering the proton dissociation reaction:



Combination of S3, S4 and S5 yields the following reaction which represents the oxidation of hypochlorous acid to chlorite ion:



which is unfavorable under standard conditions. Note that S6 is independent of pH. Calculation of E for the conditions employed in this study can be accomplished using the following:

$$E \text{ (in V)} \approx -0.23 - \frac{0.0592}{2} \log \left(\frac{[\text{ClO}_2^-][\text{Cr(OH)}_2^+]}{[\text{HOCl(aq)}][\text{H}_3\text{CrO}_4(\text{aq})]} \right) \quad (\text{S7})$$

Using typical concentrations of $[\text{HOCl(aq)}] = 200 \mu\text{M}$, $[\text{Cr(OH)}_2^+] = 10 \mu\text{M}$ and assuming that $[\text{ClO}_2^-]$ is equal to $1 \mu\text{M}$, a concentration of $\text{H}_3\text{CrO}_4(\text{aq})$ of 1 M is required to make Equation S7 favorable. This suggests that Cr^{V} is not a strong enough oxidant at neutral pH to oxidize HOCl to chlorite ion.

Characterization of NYC Tap Water

NYC Tap water was characterized in a subset of experiments and analyzed for TOC, free chlorine and pH as it flowed through a manifold containing online water quality instruments. Readings were taken from the manifold immediately after the water was collected (Table S2).

Table S2: Analysis of NYC tap water prior to addition of Cr^{III} and chlorine			
Experiment ⁽¹⁾	TOC (mg/L)	Free Cl ₂ (mg/L as Cl ₂)	pH
1	1.74	0.61	7.35
2	1.74	0.45	6.98
3	1.71	0.60	7.32
4	1.70	0.58	6.99
5	1.77	0.57	7.02
6	1.72	0.52	6.95
7	1.74	0.61	7.35
11	1.67	0.62	7.33
12	1.64	0.57	7.11
13	1.68	0.64	7.17
14	1.73	0.56	7.18
15	1.63	0.54	7.13
16	1.63	0.54	7.13
17	1.69	0.50	7.15
18	1.69	0.47	7.03
19	1.75	0.50	7.08
20	1.75	0.50	7.08

(1) Experiment numbers correspond with results in Table 1

Quality Assurance/Quality Control

CE calibration standards were prepared by dissolving pre-weighed amounts of K₂CrO₄ in DDW. To assure accurate Cr^{VI} measurements, the CE Cr^{VI} calibration solutions were standardized by measuring total dissolved chromium (Cr_T) by using Flame-AAS. Figure S4 shows a) the calibration curve for the Cr^{VI} AAS standards (absorbance versus Cr_T) and b) a comparison of the measured and nominal Cr^{VI} concentrations of the CE standards. The excellent agreement between measured and nominal Cr^{VI} concentrations confirms that the concentration of Cr^{VI} in the CE standards are accurate.

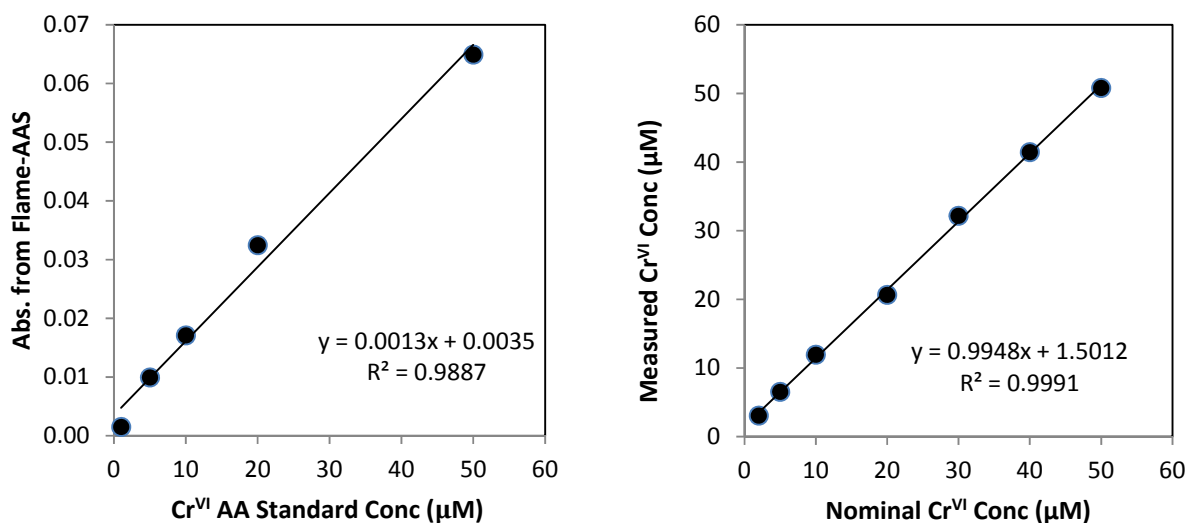


Figure S4. In a) a representative Cr^{VI} calibration curve is shown Flame-AAS and b) a comparison between actual and nominal Cr(VI) concentrations on the AAS.

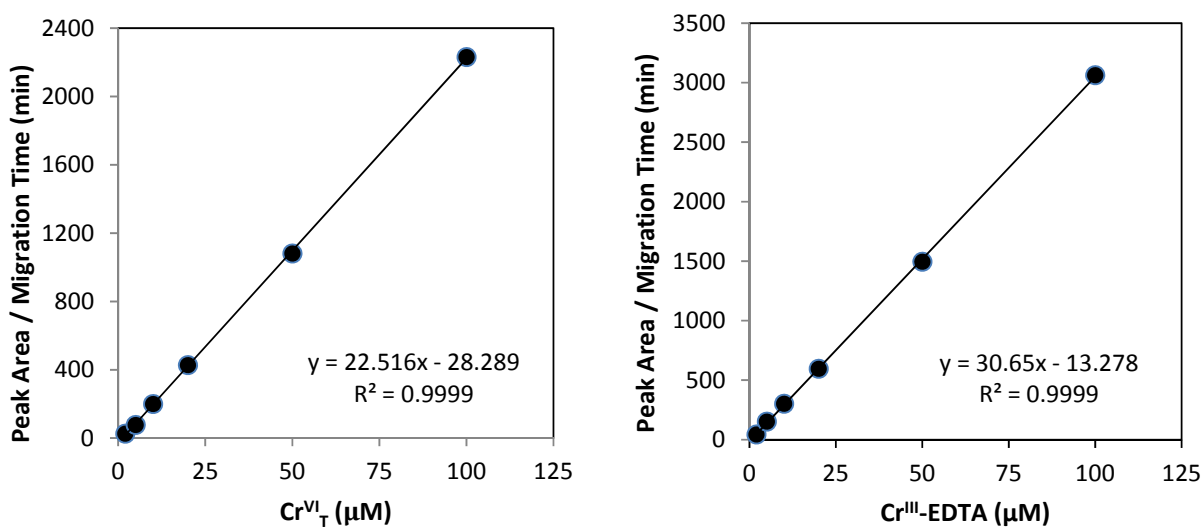


Figure S5. Calibration curves for CE analysis of a) Cr^{VI}_T and b) Cr^{III}-EDTA using a phosphate background electrolyte. See the Methods section for details.

Representative calibration curves for Cr^{VI}_T and Cr^{III}-EDTA are shown in Figure S5. The lowest standard in both cases was 2 µM. This standard yielded a discernible peak for both Cr^{VI}_T and Cr^{III}-EDTA. The relationship between normalized peak area (peak area / migration time) was extremely linear over the range of standard concentrations employed (2 to 100 µM). Standard curves for Cr^{VI}_T were generated each time a Cr^{III} oxidation experiment was performed.

Standard curves for Cr^{III}-EDTA were generated only when it was employed as the starting form of Cr^{III}.

Chlorine spike experiments were performed by adding various doses of NaOCl (20 to 100 mg/L as Cl₂) to individual vials containing DDW and various amounts of Cr^{VI} (Figure S6). Free chlorine was measured using the DPD method within a few minutes of the dose. The linear range of the method is 0.02 to 2.0 mg/L as Cl₂ so samples were diluted accordingly. Chlorine free blanks were used each time a sample was run in accordance with the method. The results indicate that DPD free Cl₂ concentrations were consistently less than the nominal dose. The average ratio of measured to nominal concentration was 0.88 when Cr^{VI}_T was not present. As Cr^{VI}_T increased, the DPD free Cl₂ decreased slightly for the 20 and 50 mg/L Cl₂ doses.

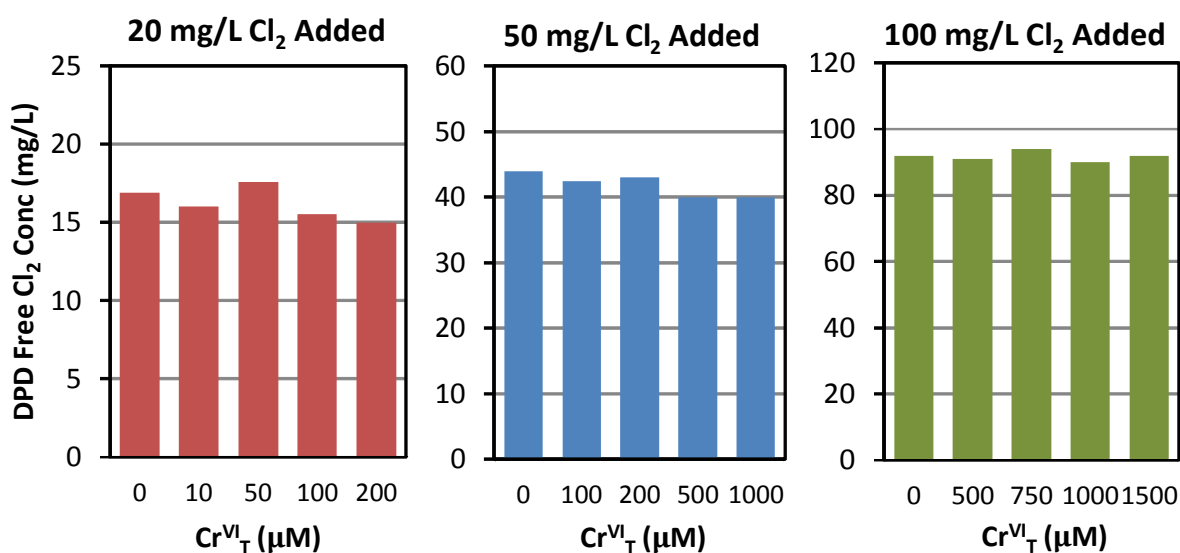


Figure S6. Measured free chlorine using the DPD method for various nominal doses of NaOCl. The categorical axis indicates the amount of Cr^{VI}_T present.

Online water quality instruments (OWQIs) were used as part of a separate study in our laboratory. NYC Tap water was drawn from the manifold containing these instruments and values for TOC free chlorine and pH were recorded (Table S2). The online monitors were calibrated in accordance with manufacturer recommendations, and checked daily against samples of known concentration. The QA/QC limits are shown in Table S3

Parameter	Reporting Units	Accuracy Tolerance
Free chlorine	mg/L as Cl ₂	within ± 0.15 mg/L
pH	pH units	within ± 0.25 units
TOC	mg C/L	within ± 0.25 mg/L

Accuracy and bias of the OWQI sensors was assessed by comparison to grab samples measured using bench top instruments. Two grab samples were collected from the manifold, one immediately after the other. The reading from the OWQI was recorded at the collection time. The water quality parameter was immediately measured in the two grab samples (x_1 and x_2) on bench top instrumentation. Note: If the absolute value of $(x_1 - x_2)$ was greater than the acceptable tolerance (Table S3), two more grab samples were collected and the procedure above was repeated. Accuracy of the OWQI was estimated by computing the difference, Δx , between the average grab sample measurement and the OWQI reading. If the results were outside the acceptable tolerance range for 3 consecutive grab samples, re-calibration of the OWQI was performed.

References

1. R. F. Carbonaro, B. N. Gray, C. F. Whitehead and A. T. Stone, *Geochim. Cosmochim. Acta*, 2008, **72**, 3241-3257.
2. J. W. Ball and D. K. Nordstrom, *Journal of Chemical Engineering Data*, 1998, **43**, 895-918.
3. D. Rai, B. M. Sass and D. A. Moore, *Inorg. Chem.*, 1987, **26**, 345-349.
4. A. E. Martell, R. M. Smith and R. J. Motekaitis, NIST, Editon edn., 2004.
5. R. Tsuchiya and A. Umayahara, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 554-559.
6. U. von Meyenburg, O. Siroky and G. Schwarzenbach, *Helv. Chim. Acta*, 1973, **56**, 1099-1114.
7. J. K. Beattie and G. P. Haight, in *Inorganic Reaction Mechanisms, Part 2 (Progress in Inorganic Chemistry, Vol. 17)*, ed. J. O. Edwards, Wiley, Editon edn., 1972.