Electronic Supplementary Information for:

Curbing chlorine disinfection byproduct formation a biomimetic FeTAML iron oxidation catalyst.

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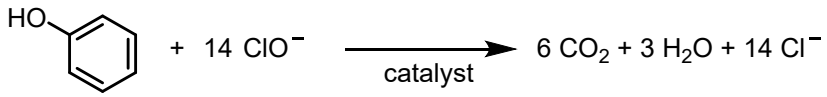
Table of Contents

Total Mineralisation of Phenol



Scheme S1. The total mineralisation of phenol driven by hypochlorite.

Purity of FeTAML

"[Fe(TAML)]$^{-}$" was used as supplied by GreenOx Catalysts Inc., who advised that residual sodium, chloride, water and isopropanol (^{i}PrOH) were also present, with an approximate "molecular weight" of 650 g mol^{-1}. The concentration of [Fe(TAML)(OH$_2$)]$^{-}$ stock solutions were thus determined from their absorbances at 366 nm ($\varepsilon_{366\,nm}$ = 6600 M^{-1} cm^{-1}). The amount of ^{i}PrOH in the "[Fe(TAML)]$^{-}$" was measured by ^{1}H NMR (500 MHz, D_2O) as follows. "[Fe(TAML)]$^{-}$" (13.94 mg) and dimethyl sulfone (1.44 mg, 15.3 mmol) were dissolved in 12 mL of d_2-water. The ^{1}H NMR (500 MHz) spectrum of this solution was then acquired (see Figure S1), and was dominated by singlets at δ 1.06 ((C$\underline{H_3}$)$_2$CHOH, 8.58 H) and at δ 3.02 ((C$\underline{H_3}$)$_2$SO$_2$, 6 H) assigned to the methyl groups of ^{i}PrOH and Me_2SO_2, respectively, and a broad signal at δ 3.91 ($Me_2C\underline{H}OH$, 1.27 H) also assigned to ^{i}PrOH. The amount of ^{i}PrOH in the "[Fe(TAML)]$^{-}$" sample could then be determined by comparison of the relative integrals against the Me_2SO_2 internal standard, as shown in Table S1.

Table S1. Mass and mass % of ^{i}PrOH in "[Fe(TAML)]$^{-}$" from ^{1}H NMR (500 MHz, D_2O) spectroscopy using Me_2SO_2 as an internal standard.

Species	δ / ppm	I	I / N$_{equiv}$	n / mmol	m / mg	Mass %
Me_2SO_2	3.02	6.00	1	15.3	1.44	100
^{i}PrOH	3.91	1.27	1.27	19.4	1.17	8.4
	1.06	8.58	1.43	21.9	1.32	9.5

Where: I = the integral normalised against Me_2SO_2; I / N$_{equiv}$ is the normalised integral, I, divided by the number of equivalent H atoms per molecule of analyte. For Me_2SO_2, n and m were determined from the mass of pure Me_2SO_2 dissolved (1.44 mg, 15.3 mmol). For ^{i}PrOH, n was given by the product of I / N_{equiv} and the number of moles of Me_2SO_2 standard, and converted to a mass, m, using the MW = 60.1 g / mol. The Mass % was calculated simply by dividing the m_{iPrOH} by the total mass of "[Fe(TAML)]$^{-}$" (13.94 mg).

The amount of ^{i}PrOH impurity in "[Fe(TAML)]$^{-}$" was measured by ^{1}H NMR (500 MHz, D_2O), using dimethyl sulfone (1.44 mg, 15.3 mmol) as an internal standard. The integral of the signal at δ 3.02 was normalised to six (the number of equivalent ^{1}H environments in Me_2SO_2). Thus the number

of moles of ^{i}PrOH could be determined after dividing the normalised integrals assigned to ^{i}PrOH by the number of equivalent H atoms in ^{i}PrOH ($I_{3.91}$ / 6 or $I_{1.06}$ / 1) and then multiplying by the number of moles of Me_2SO_2 standard added (15.3 mmol). These values were converted to masses (1.17 mg calculated from δ 3.91, or 1.32 mg from δ 1.06), to give a range of between 8.4–9.5% ^{i}PrOH impurity (by mass) in the supplied "[Fe(TAML)]$^{-}$".

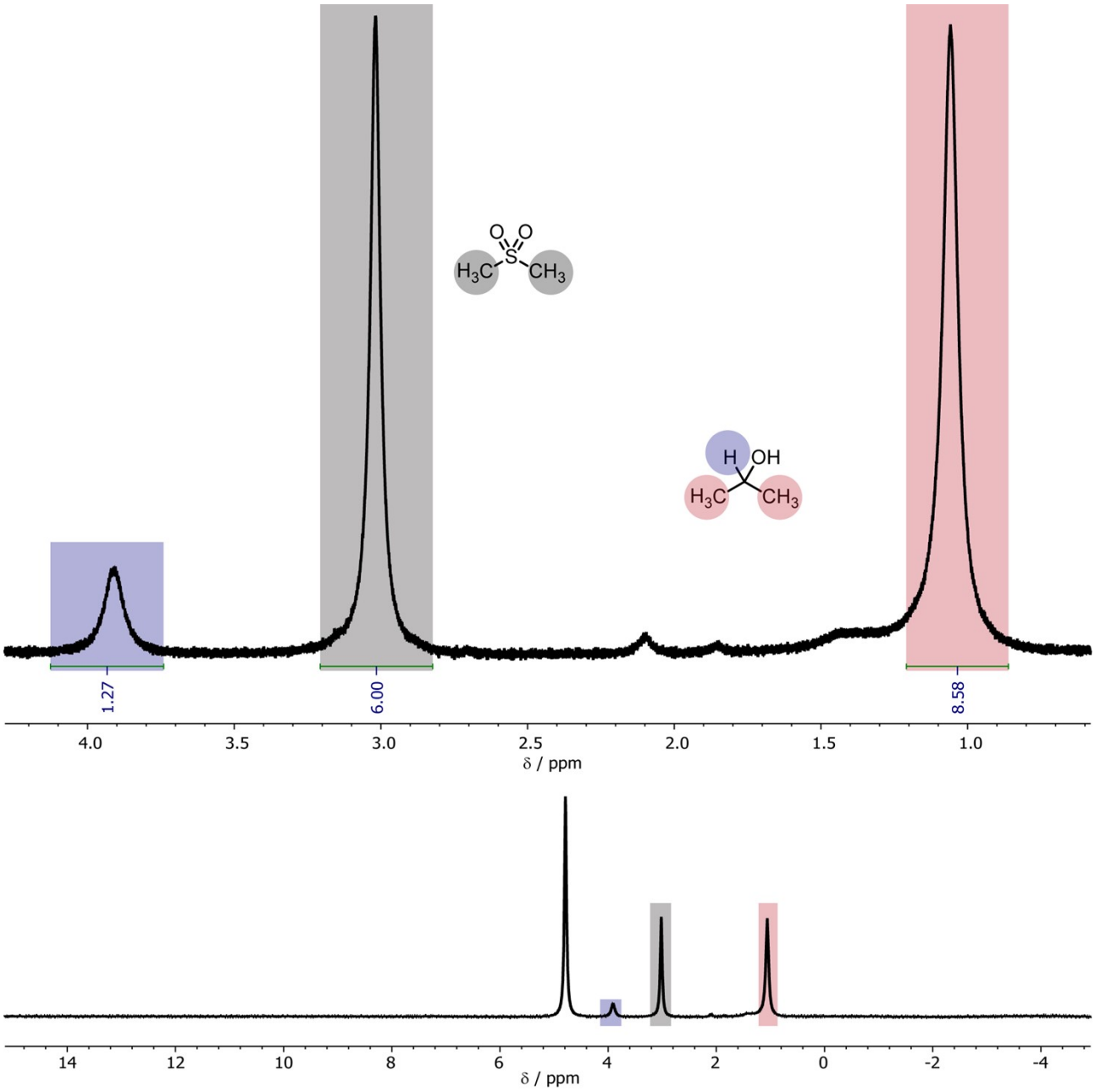


Figure S1. ^{1}H NMR (500 MHz, D_2O) spectrum of "[Fe(TAML)]$^{-}$" (13.94 mg) and dimethyl sulfone (1.44 mg, 15.3 mmol), with an expansion showing signals from the Me_2SO_2 standard and ^{i}PrOH impurity shown above.

Additional experimental details

We have previously shown how MIMS can conveniently monitor the formation of halophenols and trihalomethanes during chlorine treatment of water spiked with phenol.[1] During these previous studies, we demonstrated that the instrument responses were sensitive to the nature of the water media. In order to control for any variability in the quality of the tap water used, blank experiments on freshly prepared phenol stock solutions were always performed (see Figure S6) prior to experiments with [Fe(TAML)], and the instrument responses of key analytes (Cl_3PhOH, $CHCl_3$ and $CHBrCl_2$) were calibrated from injections of certified standards at the conclusion of experiments every day. Across the four replicates the variance and reproducibility can be assessed by the variance in the maximum concentrations of the analytes, summarised in Table S2 below (and compared to a similar comparison across seven replicates published previously,[1] albeit with different data processing protocols).

Table S2. Maximum concentrations of analytes during replicate blank experiments.

Analyte	Maximum Observed / μM				
	28/10/2021	9/11/2021	16/11/2021	17/3/2022	Larsen *et al.*, 2022[1]
ClPhOH	4.3	3.9	3.8	2.5	3.9 ± 0.1
Cl_2PhOH	4.2	3.6	3.5	2.5	3.4 ± 0.2
Cl_3PhOH	18	17	17	17	12.5 ± 0.7
CHX_3	0.48	0.97	0.91	0.93	3.1 ± 0.4

The reactions in this study were monitored at 40 °C. Unsurprisingly, we have demonstrated previously that the reaction outcomes are temperature dependent,[1] although reactions conducted at 15 °C, 25 °C and 40 °C appear to follow similar profiles (with slower rates at lower temperatures), with an initial buildup of Cl_3PhOH which then slowly decays. Different chemistry was observed at 60 °C, with the rapid formation of Cl_3PhOH which, unlike under colder conditions, did not react any further. While we would have preferred to perform these reactions at lower temperatures more reminiscent of real treatment conditions, our setup struggled to maintain stable temperatures below 40 °C.

Signal Overlap: Corrected Instrument Response (Φ_i)

Except for the trichlorophenols (the largest molecular ion at *m/z* 196), substituting Φ_i with the signal intensity (I_i) at the *m/z* ratio corresponding with the major ion formed during electron ionization (EI) for each compound was generally unsuitable, as fragmentation of heavier species (*e.g.,* through the loss of halides) resulted in (small) contributions to signal overlap (see Figure S2).

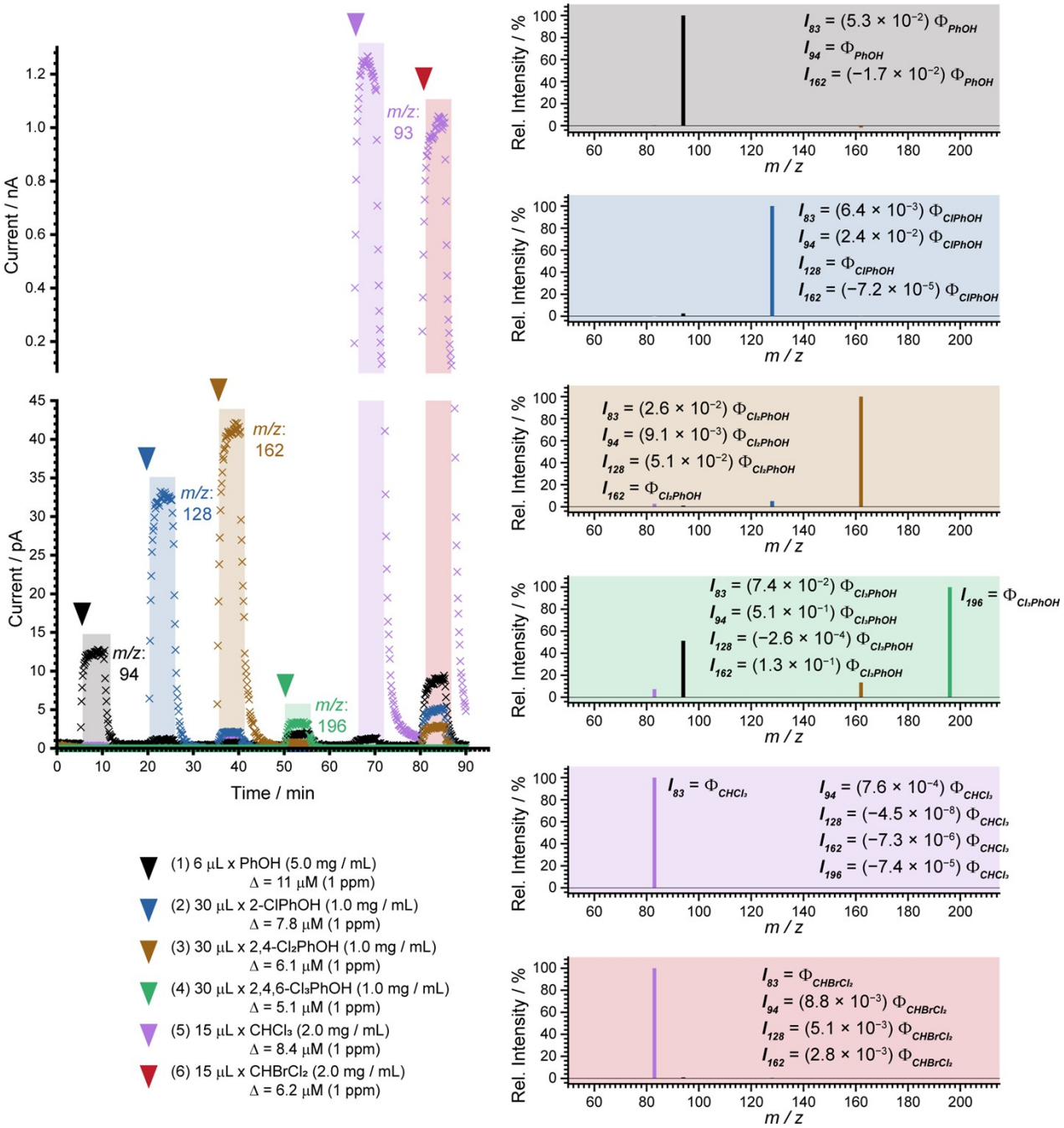


Figure S2. Left: Background subtracted raw MIMS signals at *m/z* 83 (purple), 94 (black), 128 (blue), 164 (brown) and 196 (green) following injections of certified standards into 30 mL of tap water, as labelled. After the MIMS responses stabilised, the reaction chamber was emptied and washed with fresh tap water (5 × 30 mL) before the injection of the next standard. On the right are shown the maximum signals recorded at the selected *m/z* ratios during each injection.

The most abundant *m/z* ratio for each compound were monitored throughout all measurements conducted during this work. The relative intensities at the five *m/z* ratios of interest for each compound were thus measured during calibrations of each individual analyte at 1 mg / L shown in Figure S2, and are given below in Table S3.

Table S3. Relative intensities (%) of major ionic fragments from MIMS following injections of PhOH (6 μL × 5.0 mg / mL), 2-chlorophenol (30 μL × 1.0 mg / mL), 2,4-dichlorophenol (30 μL × 1.0 mg / mL), 2,4,6-trichlorophenol (30 μL × 1.0 mg / mL), chloroform (15 μL × 2.0 mg / mL), and bromodichloromethane (15 μL × 2.0 mg / mL) into tap water (see Figure S2).

m/z	PhOH	2-ClPhOH	2,4-Cl_2PhOH	2,4,6-Cl_3PhOH	$CHCl_3$	$CHBrCl_2$[a]
83	5.3	0.64	2.6	7.4	**100**	**100**
94	**100**	2.4	0.91	51	7.6×10^{-2}	0.88
128	0	**100**	5.1	-2.6×10^{-2}	-4.5×10^{-6}	0.51
162	−1.7	-7.2×10^{-3}	**100**	13	-7.3×10^{-4}	0.28
196	-	-	-	**100**	-7.4×10^{-3}	-

From these measurements, two limiting conditions (χ_{CHCl3} = 0 or 1) were considered, and five simultaneous equations were constructed for each to relate the contributions of each species (Φ_i) to an observed signal at each of the *m/z* ratios of interest (I_i), equations S1A…S5A for χ_{CHCl3} = 1, or S1B…S5B for χ_{CHCl3} = 0.

$$I_{83} = (5.3 \times 10^{-3})\Phi_{PhOH} + (6.4 \times 10^{-3})\Phi_{ClPhOH} + (2.6 \times 10^{-2})\Phi_{Cl_2PhOH} + (7.4 \times 10^{-2})\Phi_{Cl_3PhOH} + \Phi_{CHCl_3} \quad \text{(S1A)}$$

$$I_{94} = \Phi_{PhOH} + (2.4 \times 10^{-2})\Phi_{ClPhOH} + (9.1 \times 10^{-3})\Phi_{Cl_2PhOH} + (5.1 \times 10^{-1})\Phi_{Cl_3PhOH} + (7.6 \times 10^{-2})\Phi_{CHCl_3} \quad \text{(S2A)}$$

$$I_{128} = \Phi_{ClPhOH} + (5.1 \times 10^{-2})\Phi_{Cl_2PhOH} + (-2.6 \times 10^{-4})\Phi_{Cl_3PhOH} + (-4.5 \times 10^{-8})\Phi_{CHCl_3} \quad \text{(S3A)}$$

$$I_{162} = (-1.7 \times 10^{-2})\Phi_{PhOH} + (-7.2 \times 10^{-5})\Phi_{ClPhOH} + \Phi_{Cl_2PhOH} + (1.3 \times 10^{-1})\Phi_{Cl_3PhOH} + (-7.3 \times \quad \text{(S4A)}$$

$$I_{196} = \Phi_{Cl_3PhOH} + (-7.3 \times 10^{-5})\Phi_{CHCl_3} \quad \text{(S5A)}$$

$$I_{83} = (5.3 \times 10^{-3})\Phi_{PhOH} + (6.4 \times 10^{-3})\Phi_{ClPhOH} + (2.6 \times 10^{-2})\Phi_{Cl_2PhOH} + (7.4 \times 10^{-2})\Phi_{Cl_3PhOH} + \Phi_{CHBrCl_2} \quad \text{(S1B)}$$

$$I_{94} = \Phi_{PhOH} + (2.4 \times 10^{-2})\Phi_{ClPhOH} + (9.1 \times 10^{-3})\Phi_{Cl_2PhOH} + (5.1 \times 10^{-1})\Phi_{Cl_3PhOH} + (8.8 \times 10^{-3})\Phi_{CHBrCl_2} \quad \text{(S2B)}$$

$$I_{128} = \Phi_{ClPhOH} + (5.1 \times 10^{-2})\Phi_{Cl_2PhOH} + (-2.6 \times 10^{-4})\Phi_{Cl_3PhOH} + (5.1 \times 10^{-3})\Phi_{CHBrCl_2} \quad \text{(S3B)}$$

$$I_{162} = (-1.7 \times 10^{-2})\Phi_{PhOH} + (-7.2 \times 10^{-5})\Phi_{ClPhOH} + \Phi_{Cl_2PhOH} + (1.3 \times 10^{-1})\Phi_{Cl_3PhOH} + (2.8 \times 1 \quad \text{(S4B)}$$

$$I_{196} = \Phi_{Cl_3PhOH} \tag{S5B}$$

These sets of equations are better expressed as matrices [***A***] (χ_{CHCl3} = 1) and [***B***] (χ_{CHCl3} = 0), which convert the contributions of each species (Φ_i) into signal intensities (I_i) according to equations S6A and S6B, respectively.

$$[A]\begin{pmatrix}\Phi_{PhOH}\\ \Phi_{ClPhOH}\\ \Phi_{Cl_2PhOH}\\ \Phi_{Cl_3PhOH}\\ \Phi_{CHCl_3}\end{pmatrix} = \begin{bmatrix}I_{83}\\ I_{94}\\ I_{128}\\ I_{162}\\ I_{196}\end{bmatrix} \tag{S6A}$$

$$[A] = \begin{bmatrix} 5.3\times10^{-3} & 6.4\times10^{-3} & 2.6\times10^{-2} & 7.4\times10^{-2} & 1 \\ 1 & 2.4\times10^{-2} & 9.1\times10^{-3} & 5.1\times10^{-1} & 7.6\times10^{-4} \\ 0 & 1 & 5.1\times10^{-2} & -2.6\times10^{-4} & -4.5\times10^{-8} \\ -1.7\times10^{-2} & -7.2\times10^{-5} & 1 & 1.3\times10^{-1} & -7.3\times10^{-6} \\ 0 & 0 & 0 & 1 & -7.4\times10^{-5} \end{bmatrix}$$

$$[B]\begin{pmatrix}\Phi_{PhOH}\\ \Phi_{ClPhOH}\\ \Phi_{Cl_2PhOH}\\ \Phi_{Cl_3PhOH}\\ \Phi_{CHBrCl_2}\end{pmatrix} = \begin{bmatrix}I_{83}\\ I_{94}\\ I_{128}\\ I_{162}\\ I_{196}\end{bmatrix} \tag{S6B}$$

$$[B] = \begin{bmatrix} 5.3\times10^{-3} & 6.4\times10^{-3} & 2.6\times10^{-2} & 7.4\times10^{-2} & 1 \\ 1 & 2.4\times10^{-2} & 9.1\times10^{-3} & 5.1\times10^{-1} & 8.8\times10^{-3} \\ 0 & 1 & 5.1\times10^{-2} & -2.6\times10^{-4} & 5.1\times10^{-3} \\ -1.7\times10^{-2} & -7.2\times10^{-5} & 1 & 1.3\times10^{-1} & 2.8\times10^{-3} \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

Inverting [***A***] and [***B***] gives [***A***]$^{-1}$ and [***B***]$^{-1}$, respectively, which were then used (equations S7A and S7B) to calculate the corrected instrument responses (Φ_i) from the intensities at ***m/z*** 83, 94, 128, 162 and 196 observed in the MIMS.

$$[A]^{-1}\begin{pmatrix}I_{83}\\ I_{94}\\ I_{128}\\ I_{162}\\ I_{196}\end{pmatrix} = \begin{bmatrix}\Phi_{PhOH}\\ \Phi_{ClPhOH}\\ \Phi_{Cl_2PhOH}\\ \Phi_{Cl_3PhOH}\\ \Phi_{CHCl_3}\end{bmatrix} \tag{S7A}$$

$$[A]^{-1} = \begin{bmatrix} -8.0\times10^{-4} & 1 & -2.4\times10^{-2} & 7.8\times10^{-3} & -5.1\times10^{-1} \\ 8.8\times10^{-7} & -8.5\times10^{-4} & 1 & -5.1\times10^{-2} & 7.5\times10^{-3} \\ -1.6\times10^{-5} & 1.7\times10^{-2} & -3.3\times10^{-4} & 1 & -1.4\times10^{-1} \\ 7.4\times10^{-5} & -4.2\times10^{-7} & -4.7\times10^{-7} & -1.9\times10^{-6} & 1 \\ 1 & -5.7\times10^{-3} & -6.3\times10^{-3} & -2.5\times10^{-2} & -6.8\times10^{-2} \end{bmatrix}$$

$$[B]^{-1}\begin{pmatrix} I_{83} \\ I_{94} \\ I_{128} \\ I_{162} \\ I_{196} \end{pmatrix} = \begin{bmatrix} \Phi_{PhOH} \\ \Phi_{ClPhOH} \\ \Phi_{Cl_2PhOH} \\ \Phi_{Cl_3PhOH} \\ \Phi_{CHCl_3} \end{bmatrix} \qquad \text{(Eq. S7B)}$$

$$[B]^{-1} = \begin{bmatrix} -8.6\times10^{-3} & 1 & -2.4\times10^{-2} & 7.7\times10^{-3} & -5.1\times10^{-1} \\ -4.9\times10^{-7} & -8.3\times10^{-4} & 1 & -5.1\times10^{-2} & 7.9\times10^{-3} \\ -3.0\times10^{-5} & 1.7\times10^{-2} & -3.1\times10^{-4} & 1 & -1.4\times10^{-1} \\ 0 & 0 & 0 & 0 & 1 \\ 1 & -5.7\times10^{-3} & -6.3\times10^{-3} & -2.5\times10^{-2} & -6.8\times10^{-2} \end{bmatrix}$$

Calibration of Sensitivities (S_i)

The sensitivity of PhOH, S_{PhOH}, was determined by the change in steady state Φ_{PhOH} after the initial injection of PhOH (Δ[PhOH] = 16 μM) according to equation S8:

$$S_{PhOH} = \Delta\Phi_{PhOH} / (1.6 \times 10^{-5})\ \text{A M}^{-1} \qquad \text{(Eq. S8)}$$

Sensitivities for 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol ($S_{2\text{-}ClPhOH}$, $S_{2,4\text{-}Cl2PhOH}$, and $S_{2,4,6\text{-}Cl3PhOH}$, respectively) were similarly determined by monitoring their corrected instrument responses ($\Phi_{2\text{-}ClPhOH}$, $\Phi_{2,4\text{-}Cl2PhOH}$, and $\Phi_{2,4,6\text{-}Cl3PhOH}$, respectively) following 50 μL additions of "Phenol Mix #1" (VWR Chemicals, 0.5 mg / mL of each compound). Sensitivities for chloroform and bromodichloromethane (S_{CHCl3} and $S_{CHBrCl2}$) were determined by monitoring the corrected instrument response at *m / z* 83 (Φ_{CHX3}) following 3 μL injections of certified standard solutions (2 mg / mL). The sensitivities used throughout this work are summarized in Table S4 (and see Figure S3), and are generally consistent with previous, independent measurements.[1]

Table S4. Sensitivities (S_i) of the six compounds of interest from *in situ* calibrations in 30 mL of tap water at pH 7–8 and 40 °C.

	S_i / A M^{-1}	S_i / S_{PhOH}
PhOH	$(2.2 \pm 0.2) \times 10^{-7}$ [2.35×10^{-7}][a]	1
2-ClPhOH	$(1.120 \pm 0.005) \times 10^{-6}$ [1.11×10^{-6}][a]	5.1 ± 0.5
2,4-Cl_2PhOH	$(9.3 \pm 0.1) \times 10^{-7}$ [1.04×10^{-6}][a]	4.2 ± 0.4
2,4,6-Cl_3PhOH	$(7 \pm 2) \times 10^{-8}$ [9.08×10^{-8}][a]	0.3 ± 0.1
$CHCl_3$	$(3.8 \pm 0.2) \times 10^{-5}$ [4.42×10^{-5}][a]	170 ± 25
$CHBrCl_2$	$(2.9 \pm 0.5) \times 10^{-5}$	132 ± 35

[a] data in square brackets from Larsen *et al.*.[1] Uncertainties in S_i / S_{PhOH} ($\sigma_{Si\ /\ S(PhOH)}$) were propagated according to $\sigma_{Si\ /\ S(PhOH)} = (\sigma_{Si} / Si + \sigma_{S(PhOH)} / S_{PhOH})$

(S_i / S_{PhOH}).

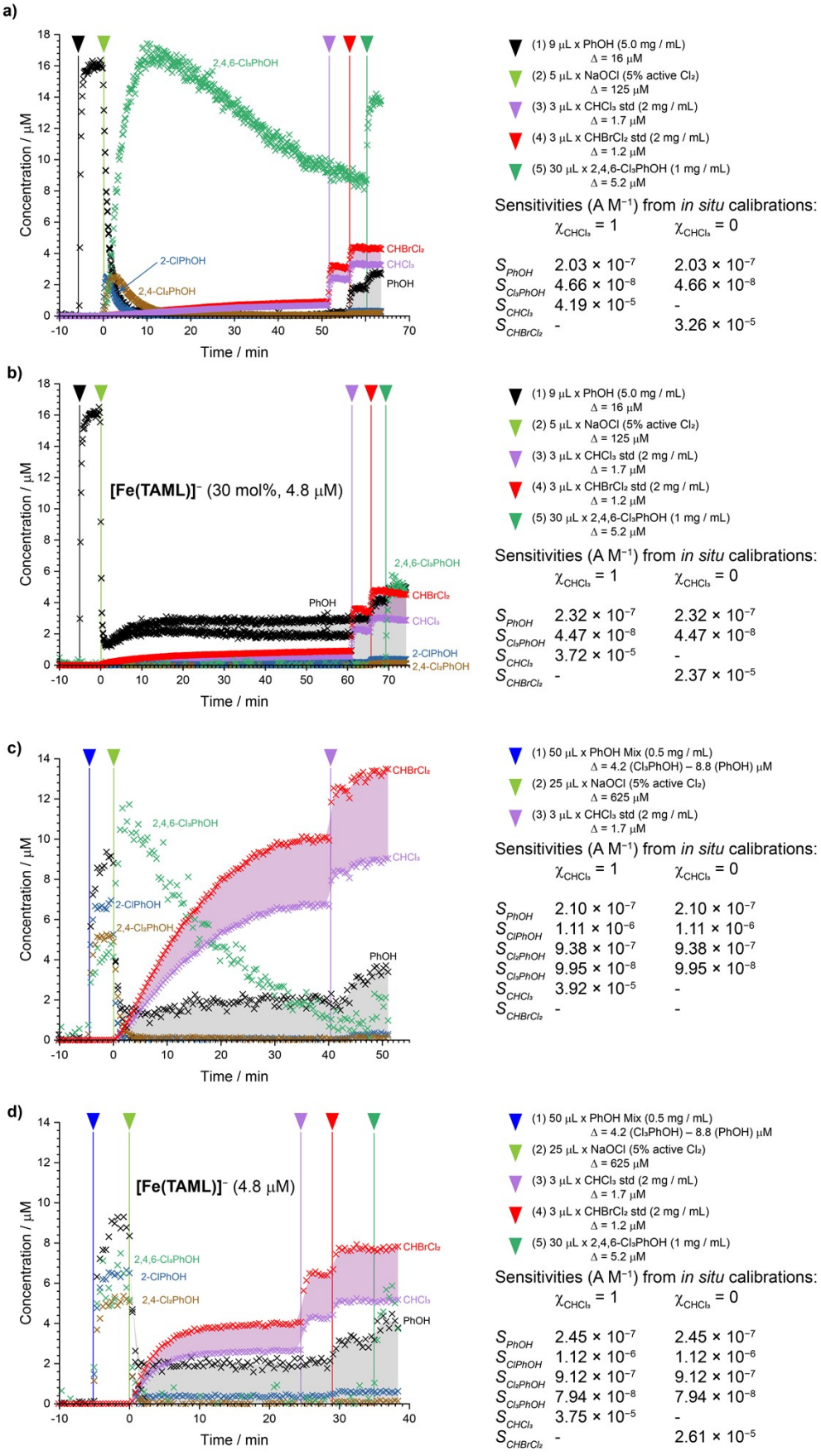


Figure S3. *In situ* sensitivity calibration experiments. Injections were into 30 mL of tap water at 40 °C.

Calibration protocol

The overall protocols used to convert raw MIMS data into concentration (ranges) are thus depicted in Figures S4 and S5.

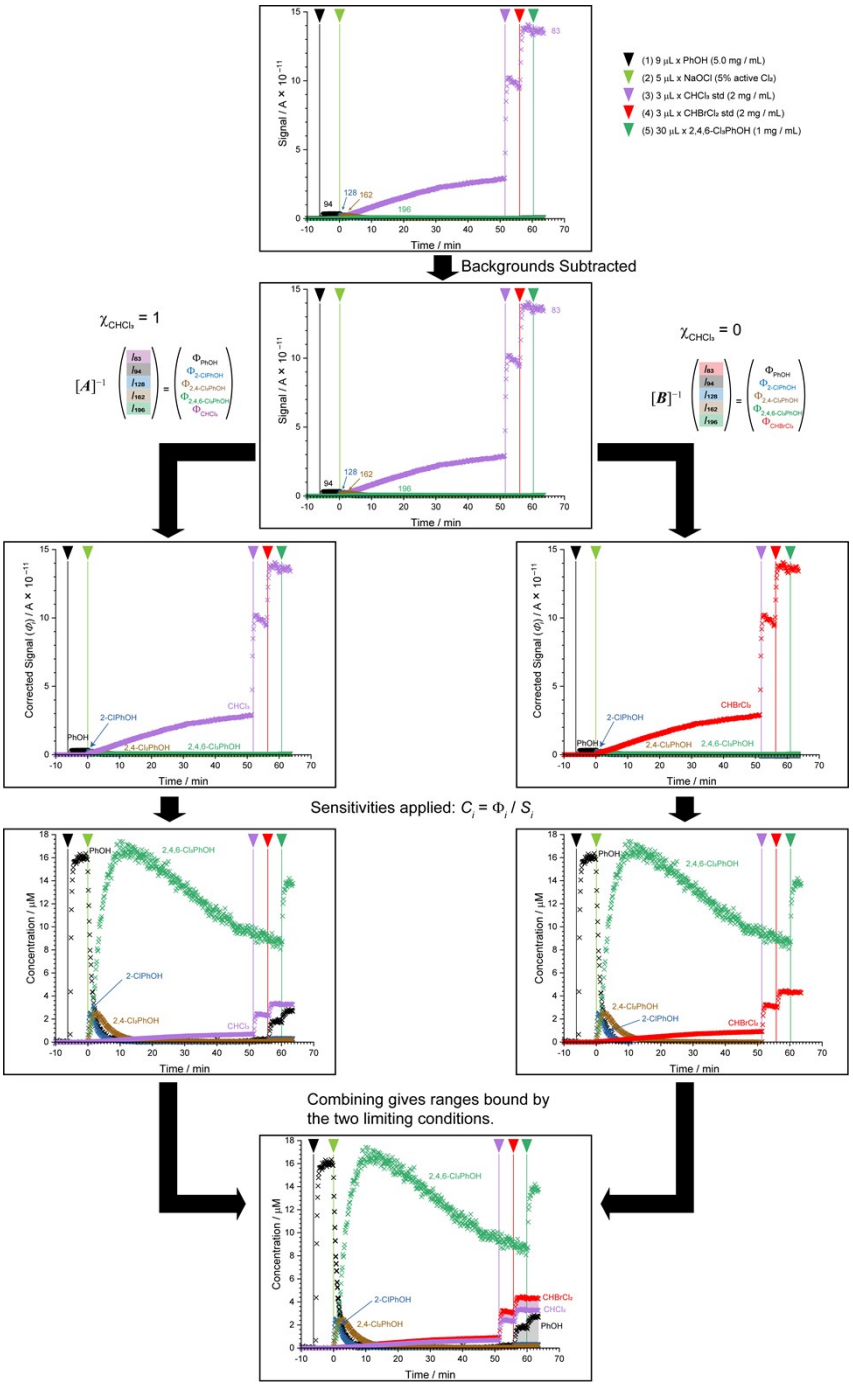


Figure S4. Calibration workflow for an uncatalyzed reference experiment. Solid arrows within the plots represent injection of phenol (black), sodium hypochlorite (bright green), chloroform (purple), bromodichloromethane (red) or 2,4,6-trichlorophenol (green). The corrections for signal overlap and sensitivities for each of the two limiting conditions (χ_{CHCl3} = 0 or 1) were calculated in parallel as shown, then combined to give concentration ranges.

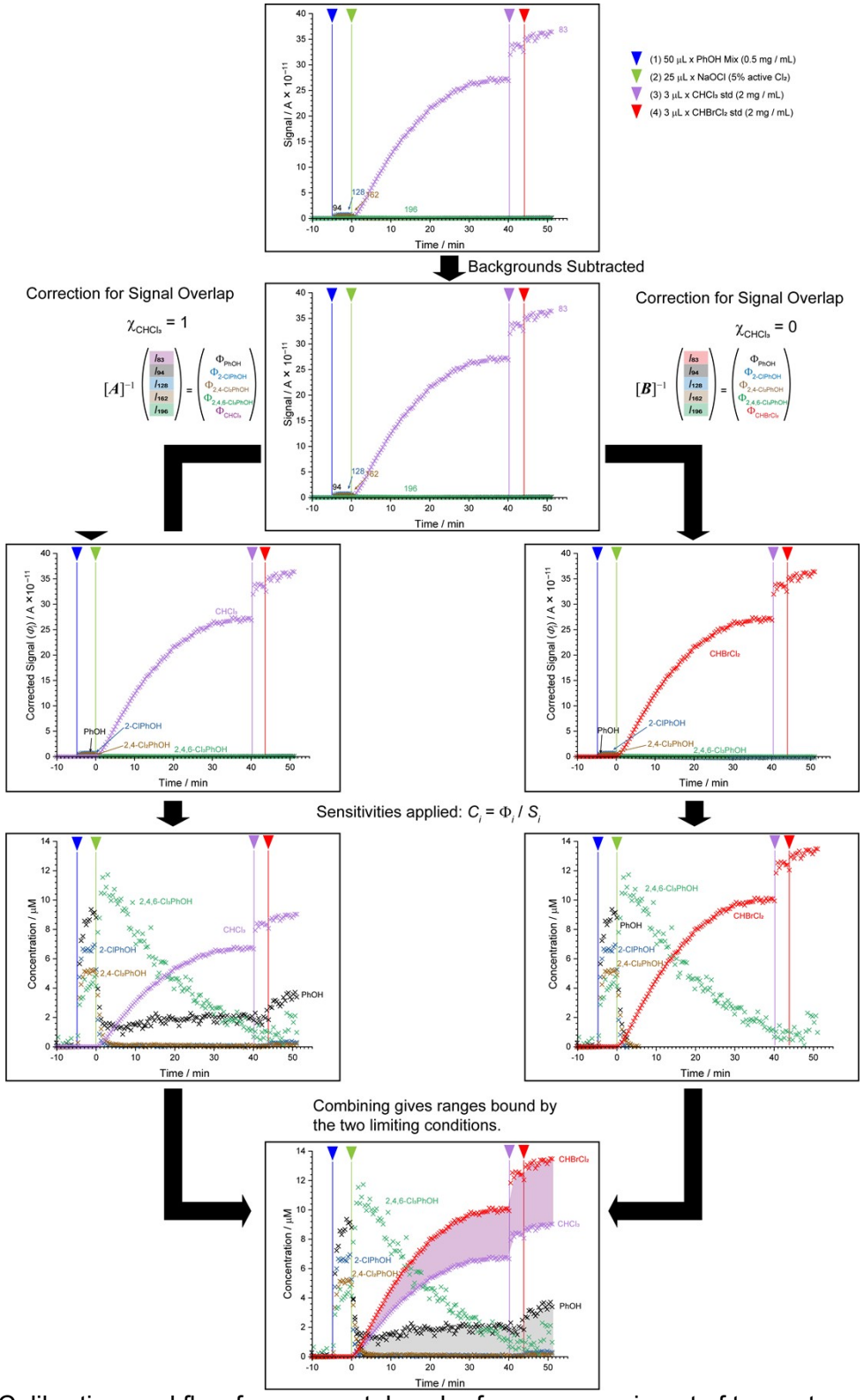


Figure S5. Calibration workflow for an uncatalyzed reference experiment of tap water contaminated by a mixture of phenols. Solid arrows within the plots represent injection of Phenol Mix #1 (VWR Chemicals, blue), sodium hypochlorite (bright green), chloroform (purple), bromodichloromethane (red) or 2,4,6-trichlorophenol (green). The corrections for signal overlap and sensitivities for each of the two limiting conditions (χ_{CHCl3} = 0 or 1) were calculated in parallel as shown, then combined to give concentration ranges.

Estimation of Uncertainties

Where sensitivities were calibrated by injection of internal standards at the conclusion of a given experiment, the standard error from Table S4 for that analyte (σ_i) was used to estimate a 95% confidence interval (95% CI = ±2 σ_i). Where relative sensitivities (S_i / S_{PhOH}) were used instead, then the relative errors for the analyte and phenol (σ_{Si} / S_i and $\sigma_{S(PhOH)}$ / S_{PhOH}, respectively) were combined to propagate the standard error in S_i / S_{PhOH} ($\sigma_{(Si\ /\ S(PhOH))}$) according to equations S9 and S10.

$$\sigma_{Si\ /\ S(PhOH)} = (\sigma_{Si} / Si + \sigma_{S(PhOH)} / S_{PhOH})\ (S_i / S_{PhOH}) \qquad \text{(Eq. S9)}$$

$$95\%\ \text{CI} = \pm 2\ \sigma_{Si\ /\ S(PhOH)} \qquad \text{(Eq. S10)}$$

For trihalomethane concentration, a range bound by the upper limit of the 95% CI for [$CHBrCl_2$] and the lower limit of the 95% CI for [$CHCl_3$] was used to conservatively estimate a 95% CI.

Other possible disinfection byproduct endpoints

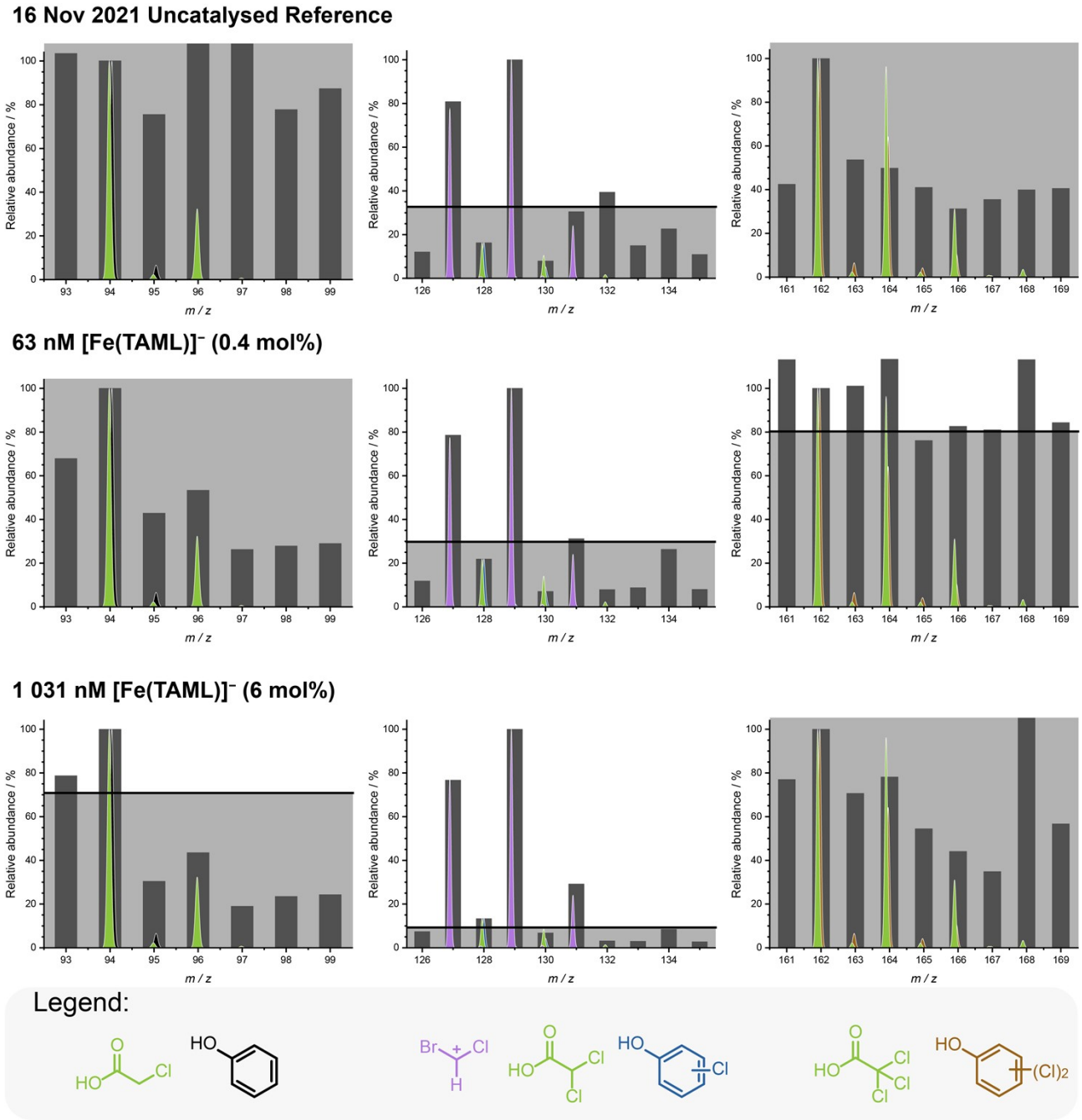


Figure S6. Normalised expansions of the raw membrane inlet mass spectra (dark grey bars) collected 1 hour after water contaminated with phenol (16 μM) was treated with NaOCl (8 molar equivalents, 130 μM) at pH 7–8 and 40 °C, with concentrations of $[Fe(TAML)]^-$ as indicated. Simulated isotopic distributions for phenol, chlorophenols, chloroacetic acids and the $[CHBrCl]^+$ cation are shown as gaussian distributions according to the legend. The background levels recorded for each experiment at *m / z* 94, 128 or 162 are represented by a black horizontal line in the relevant expansion, with the region below shaded grey.

Calibrated Output

Background uncatalyzed controls

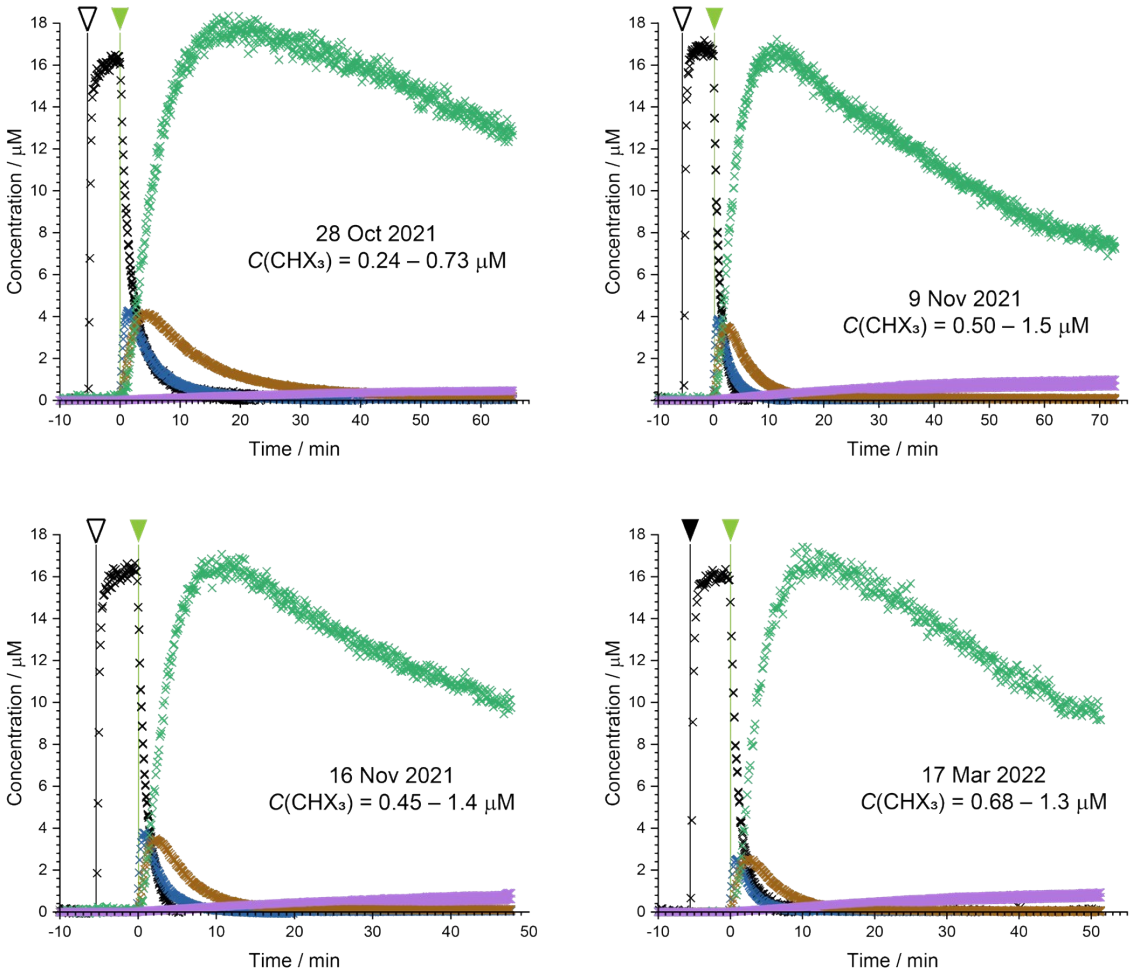


Figure S7. Calibrated background MIMS spectra of tap water (30 mL, pH 7–8) after injections of phenol (hollow black triangles: 150 μL × 3.2 mM in water, or solid black triangle: 9 μL × 53.1 mM in methanol) and NaOCl (8 molar equivalents, 5 μL × 0.76 M, green triangle) at 40 °C on different days as indicated. 95% CI's (from propagating uncertainties of relative sensitivites) for trihalomethane concentrations are given.
× Phenol, × chlorophenols, × dichlorophenols, × trichlorophenols, × trihalomethanes. Data collected after the calibration injections have been omitted for clarity (see Figure S2 for representative examples).

Other Control Experiments

Additional controls are presented below in Figure S8. As shown on the top panels of Figure S8, adding half an equivalent of isopropanol (which is a known contaminant in the "[Fe(TAML)]$^{-}$ " as supplied) did not change the profiles of the uncatalyzed reactions of phenol with sodium hypochlorite. The presence of an additional half equivalent of isopropanol also had no noticeable effect on the

[Fe(TAML)]$^-$ catalysed reactions of phenol and hypochlorite (which resulted in less trihalomethane formation, 0.59 μM *cf.* 0.84 μM for the uncatalyzed reactions, and no build-up of chlorophenols).

Prior to these experiments, the membrane inlet mass spectrometer had been re-tuned, and so sensitivities were recalibrated (see Table S5) by a series of injections of certified standards (see Figure S2 and Table S5). The sensitivities of each compound were improved by ~ an order of magnitude after the re-tuning of the instrument, but the relative sensitivities of each compound (S_i / S_{PhOH}) remained consistent with previous measurements.

Table S5. Sensitivities (S_i) of the six compounds of interest from *in situ* calibrations in 30 mL of tap water at pH 7–8 and 40 °C.

	S_i / A M^{-1}	S_i / S_{PhOH}
PhOH	$(1.17 \pm 0.04) \times 10^{-6}$ [$(2.2 \pm 0.2) \times 10^{-7}$][a]	1 ± 0.03 [1.0 ± 0.1][a]
2-ClPhOH	4.2×10^{-6} [$(1.120 \pm 0.005) \times 10^{-6}$][a]	3.8 [5.1 ± 0.5][a]
2,4-Cl_2PhOH	6.7×10^{-6} [$(9.3 \pm 0.1) \times 10^{-6}$][a]	6.1 [4.2 ± 0.4][a]
2,4,6-Cl_3PhOH	6.0×10^{-7} [$(7 \pm 2) \times 10^{-8}$][a]	0.55 [0.3 ± 0.1][a]
$CHCl_3$	$(1.2 \pm 0.1) \times 10^{-4}$ [$(3.8 \pm 0.2) \times 10^{-5}$][a]	130 ± 15 [170 ± 25][a]
$CHBrC_{l2}$	$(1.2 \pm 0.2) \times 10^{-4}$ [$(2.9 \pm 0.5) \times 10^{-5}$][a]	110 ± 22 [132 ± 35][a]

[a] data in square brackets from Table S4. Where sensitivities were calibrated over replicate injections, standard errors are shown and the uncertainty in S_i / S_{PhOH} ($\sigma_{Si\ /\ S(PhOH)}$) were propagated according to $\sigma_{Si\ /\ S(PhOH)} = (\sigma_{Si} / Si + \sigma_{S(PhOH)} / S_{PhOH})\ (S_i / S_{PhOH})$.

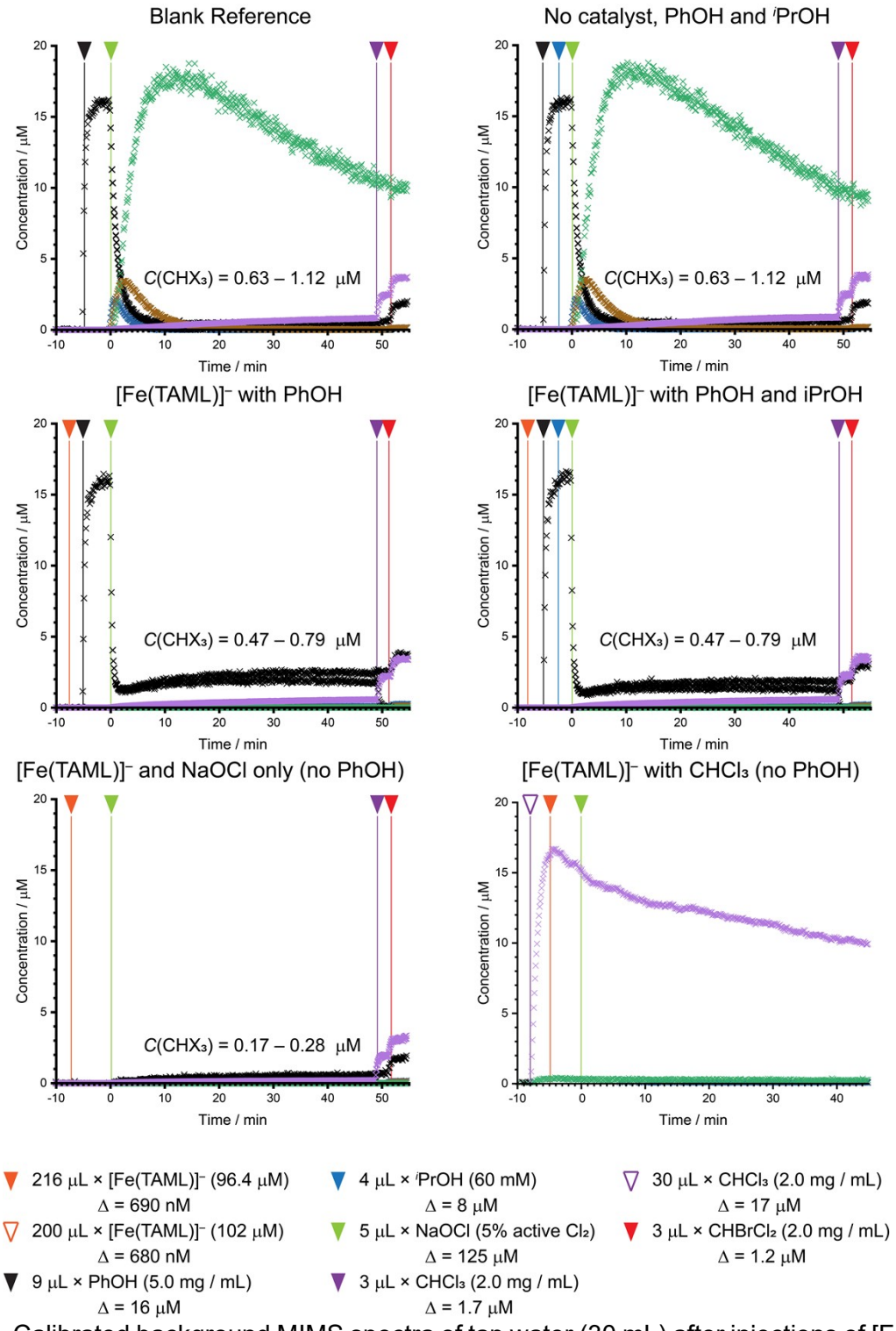


Figure S8. Calibrated background MIMS spectra of tap water (30 mL) after injections of $[Fe(TAML)]^-$ (orange triangles: 216 μL × 96.4 μM, or hollow orange triangle: 200 μL × 102 μM), phenol (solid black triangles: 9 μL × 53.1 mM in methanol), isopropanol (blue triangles: 4 μL × 60 mM), NaOCl (green triangles: 5 μL × 0.76 M), $CHCl_3$ (purple triangles: 3 μL × 16.7 mM, or hollow purple triangle: 30 μL × 0.76 M) and $CHBrCl_2$ (red triangles: 3 μL × 12.2 mM) at pH 7–8 and 40 °C. 95% CI's (from replicate injections of $CHCl_3$ and $CHBrCl_2$ standards) for trihalomethane concentrations are given. × Phenol, × chlorophenols, × dichlorophenols, × trichlorophenols, × trihalomethanes.

Reactions with [Fe(TAML)]⁻ catalyst present

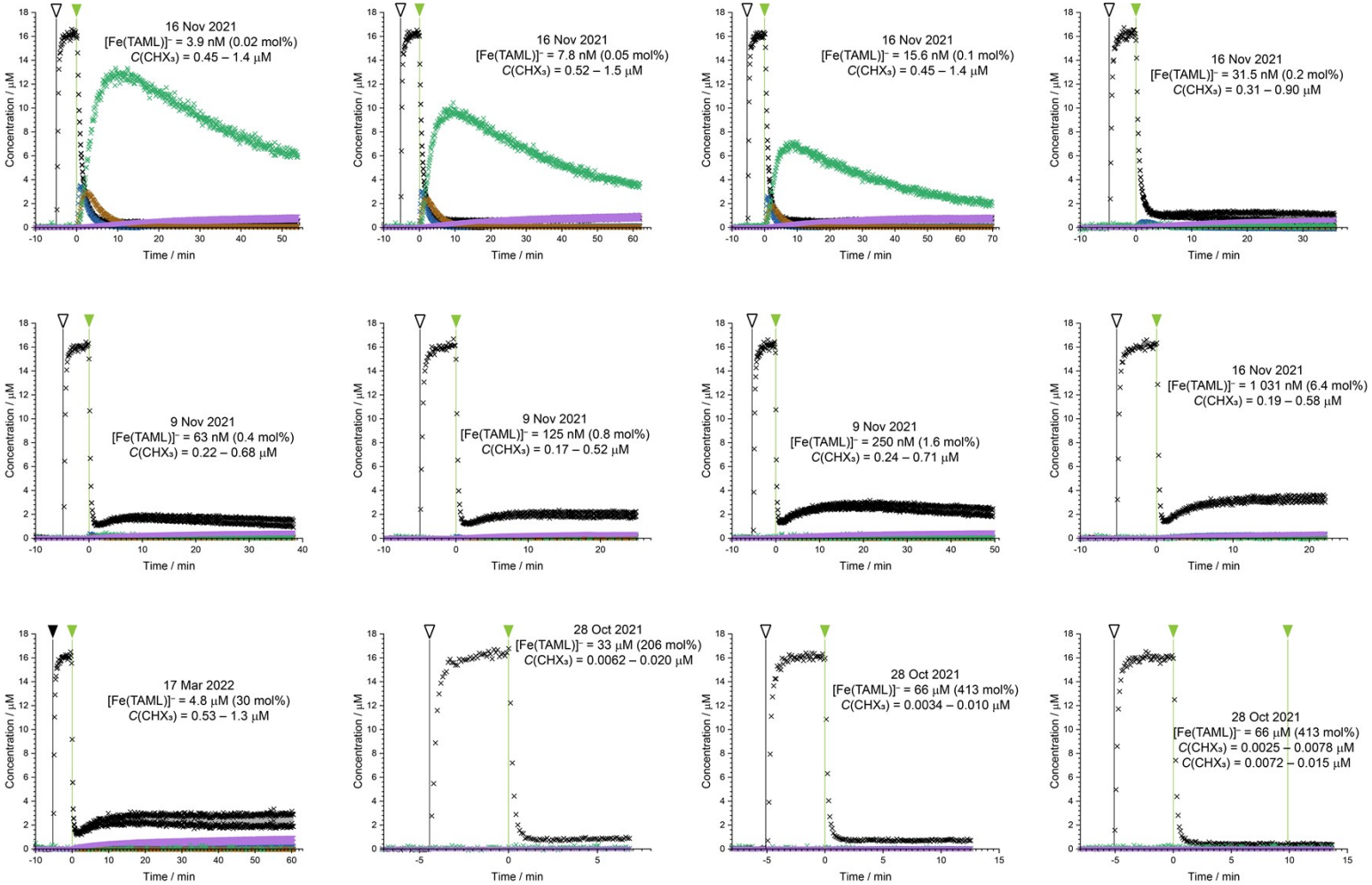


Figure S9. Calibrated MIMS spectra of dilute aqueous solutions of [Fe(TAML)]⁻ after injections of phenol (hollow black triangles: 150 μL × 3.2 mM in water, or solid black triangle: 9 μL × 53.1 mM in methanol) and NaOCl (8 molar equivalents, 5 μL × 5% active chlorine, green triangle) at pH 7–8 and 40 °C on different days as indicated. 95% CI's (from propagating uncertainties of relative sensitivities) for trihalomethane concentrations are given.

× Phenol, × chlorophenols, × dichlorophenols, × trichlorophenols, × trihalomethanes. Data collected after the calibration injections have been omitted for clarity (see Figure S2 for representative examples).

Table S6. Observed rate constants and maximum trihalomethane concentrations observed after injections of phenol (150 μL × 3.2 mM in water) and NaOCl (8 molar equivalents, 5 μL × 5% active chlorine) were injected to aqueous solutions of $[Fe(TAML)]^-$ (30 mL, pH 7–8, 40 °C). Plots of all these data are also provided in the Supporting Information.

$[Fe(TAML)]^-$ / nM (ppb)	$[CHCl_3]$ / μM (ppb)	$[CHBrCl_2]$ / μM (/ ppb)	95% CI $[CHX_3]$[j] / μM
0 [28 Oct 21][a]	0.33 (39)	0.48 (78)	0.24 – 0.73
0 [9 Nov 2021][b]	0.69 (83)	1.0 (160)	0.50 – 1.5
0 [16 Nov 21][c]	0.63 (75)	0.91 (150)	0.45 – 1.4
0 [17 Mar 22][d, e]	0.71 (85)	0.93 (150)	0.68 – 1.3
0 [total]	0.33 – 0.71 (39 – 85)	0.48 – 1.0 (78 – 160)	0.24 – 1.5
3.9 (2.5)[c]	0.63 (75)	0.90 (150)	0.45 – 1.4
7.8 (5.1)[c]	0.72 (86)	1.0 (170)	0.52 – 1.5
15.6 (10)[c]	0.62 (74)	0.89 (150)	0.45 – 1.4
31.5 (21)[c]	0.43 (51)	0.62 (100)	0.31 – 0.9
62.5 (41)[b]	0.31 (37)	0.45 (74)	0.22 – 0.68
125 (82)[b]	0.24 (28)	0.34 (56)	0.17 – 0.52
250 (163)[b]	0.33 (39)	0.47 (76)	0.24 – 0.71
1 031 (670)[c]	0.26 (31)	0.38 (62)	0.19 – 0.58
4 800 (3 120)[d, e]	0.58 (69)	0.91 (150)	0.53 – 1.3
33 000 (21 450)[a]	0.0087 (1.0)	0.013 (2.1)	0.0062 – 0.020
66 000 (42 900)[a]	0.0047 (0.57)	0.0069 (1.1)	0.0034 – 0.010
66 000 (42 900)[a, f]	0.0035 (0.42)[g]	0.0051 (0.83)[g]	0.0025 – 0.0078
	0.0074 (0.88)[h]	0.010 (1.7)[h]	0.0072 – 0.015

a: experiment performed on 28/10/2021; ***b***: experiment performed on 9/11/2021; ***c***: experiment performed on 16/11/2021; ***d***: experiment performed on 17/3/2022; ***e***: phenol (9 μL × 53.1 mM) in methanol injected instead of aqueous phenol; ***f***: two additions of NaOCl (2 × 5 μL × 0.76 M); ***g***: after first NaOCl injection; and ***h***: after the second NaOCl injection. ***i***: Uncertainties in the slopes of the linear regressions are provided to provide a lower boundary for the experimental uncertainty—as can be seen from the four duplicate reference experiments, much larger margins are reproduced experimentally. ***j***: 95% CI was bound by subtracting $2\sigma_{CHCl3}$ from $[CHCl_3]$ for the lower limit, and adding $2\sigma_{CHBrCl2}$ to $[CHBrCl_2]$.

Kinetic Analyses

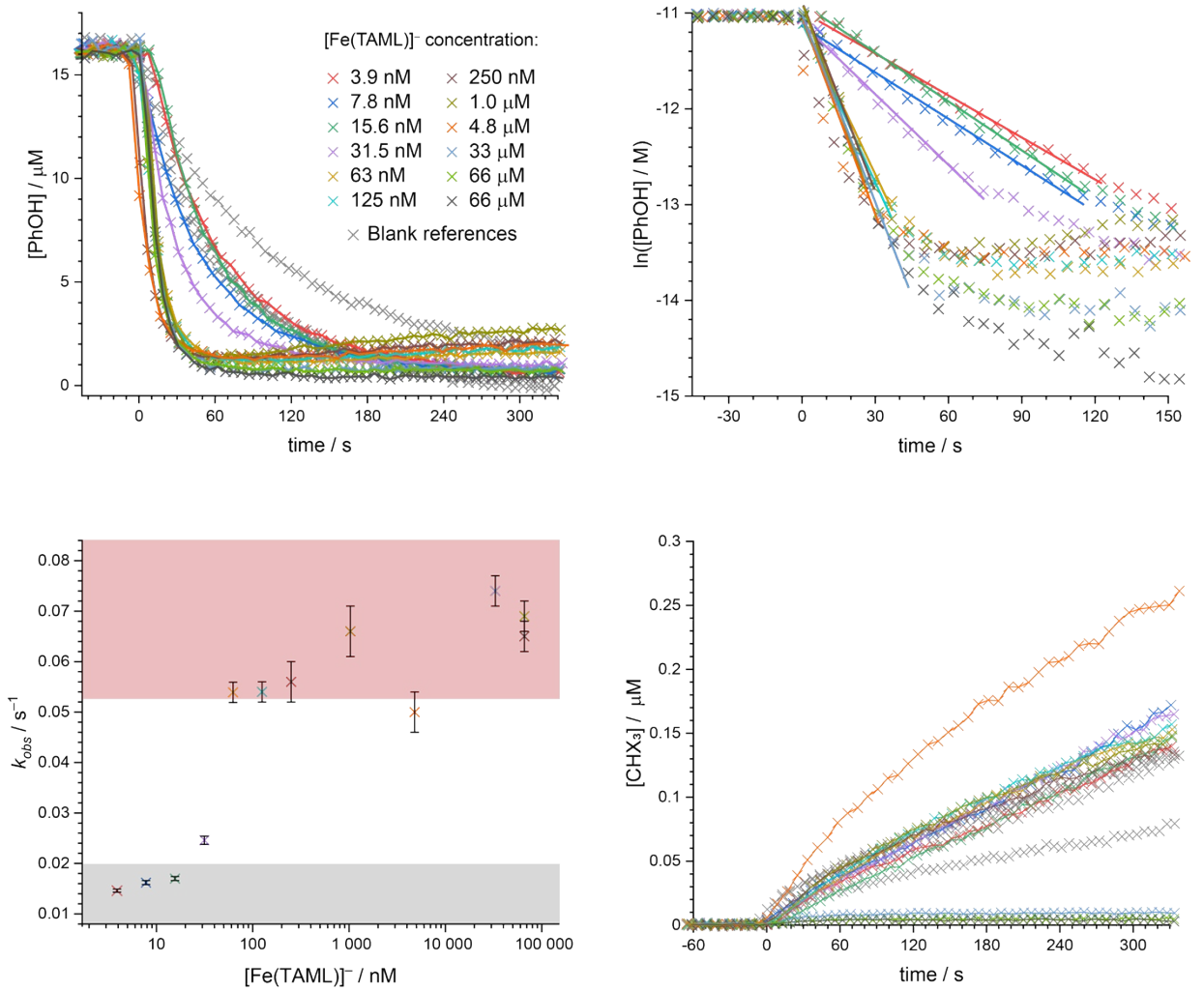


Figure S10. Top left: Change in concentration of phenol over time after the addition of sodium hypochlorite (8 molar equivalents, 130 μM) at different concentrations of [Fe(TAML)]⁻ catalyst over the first 5 and a half minutes. Top right: the natural logarithm of the phenol concentrations are plotted over the first 150 seconds, with fits to the linear regions (before exhaustion of hypochlorite) shown, from which the observed rate constants—which are plotted below (see Table S6)—were obtained. On the plot below, the grey region is bounded by the rate observed for the uncatalyzed background decomposition of phenol, while the red zone represents the response time of the membrane inlet mass spectrometer. Error bars in the bottom plot represent uncertainties in the slopes of the linear regressions to provide a lower boundary for the experimental uncertainty—as can be seen from the four duplicate reference experiments (Table S6), much larger margins are reproduced experimentally. Bottom Right: Change in concentration of trihalomethanes (CHX_3) over time after the addition of sodium hypochlorite (8 molar equivalents, 130 μM) at different concentrations of [Fe(TAML)]⁻ catalyst over the first five and a half minutes.

Reference

(1) Larsen, F. T.; McPherson, J. N.; McKenzie, C. J.; Lauritsen, F. R. An Experimental Laboratory Reactor for Quantitative Kinetic Studies of Disinfection Byproduct Formation Using Membrane Inlet Mass Spectrometry. *Rapid Commun. in Mass Spectrom.* **2022**, *36* (16), e9339. https://doi.org/10.1002/rcm.9339.