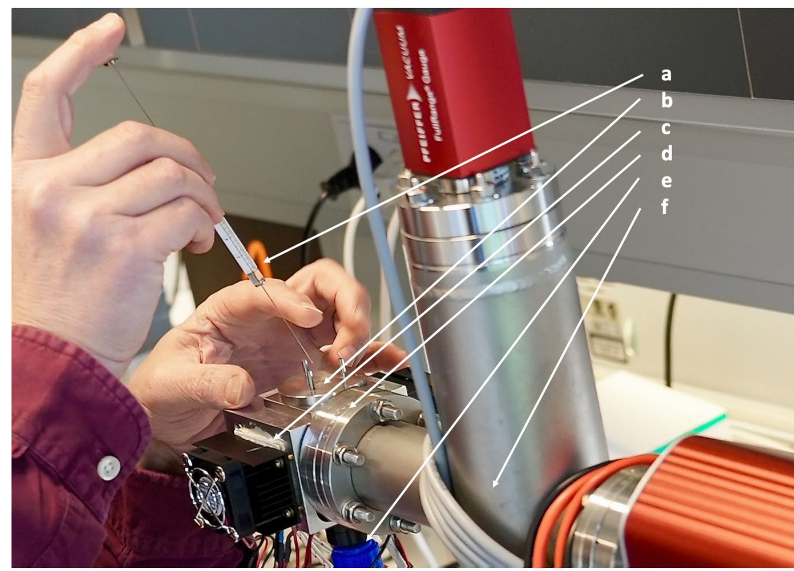
Investigation of disinfection byproduct formation during advanced water treatment using a transportable chemical reactor membrane inlet mass spectrometer

James N. McPherson[1], Freja T. Larsen[2] Christine J. McKenzie[2] and Frants R. Lauritsen[2]

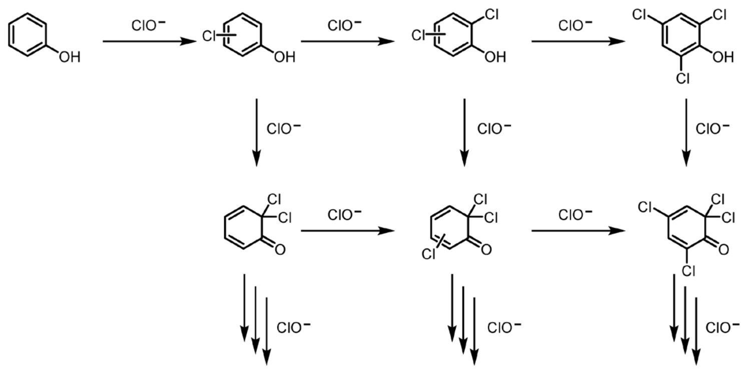
[1]Technical University of Denmark, Denmark, [2]University of Southern Denmark, Denmark
Correspondence: Frants R. Lauritsen, email frl@sdu.dk

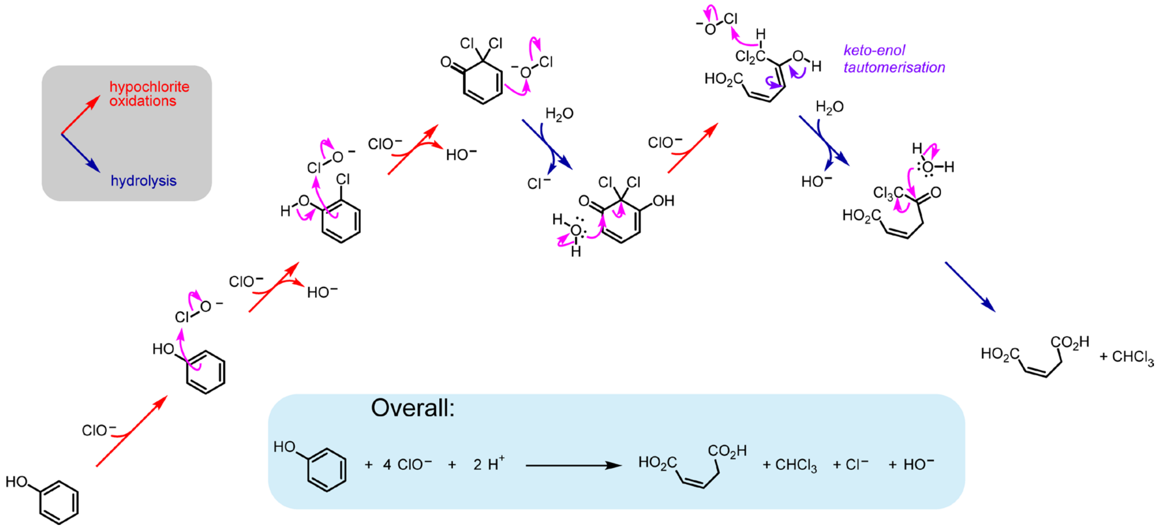


HEMS Workshop, Florida, 2022

DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

Disinfection of the model compound phenol using hypochlorite

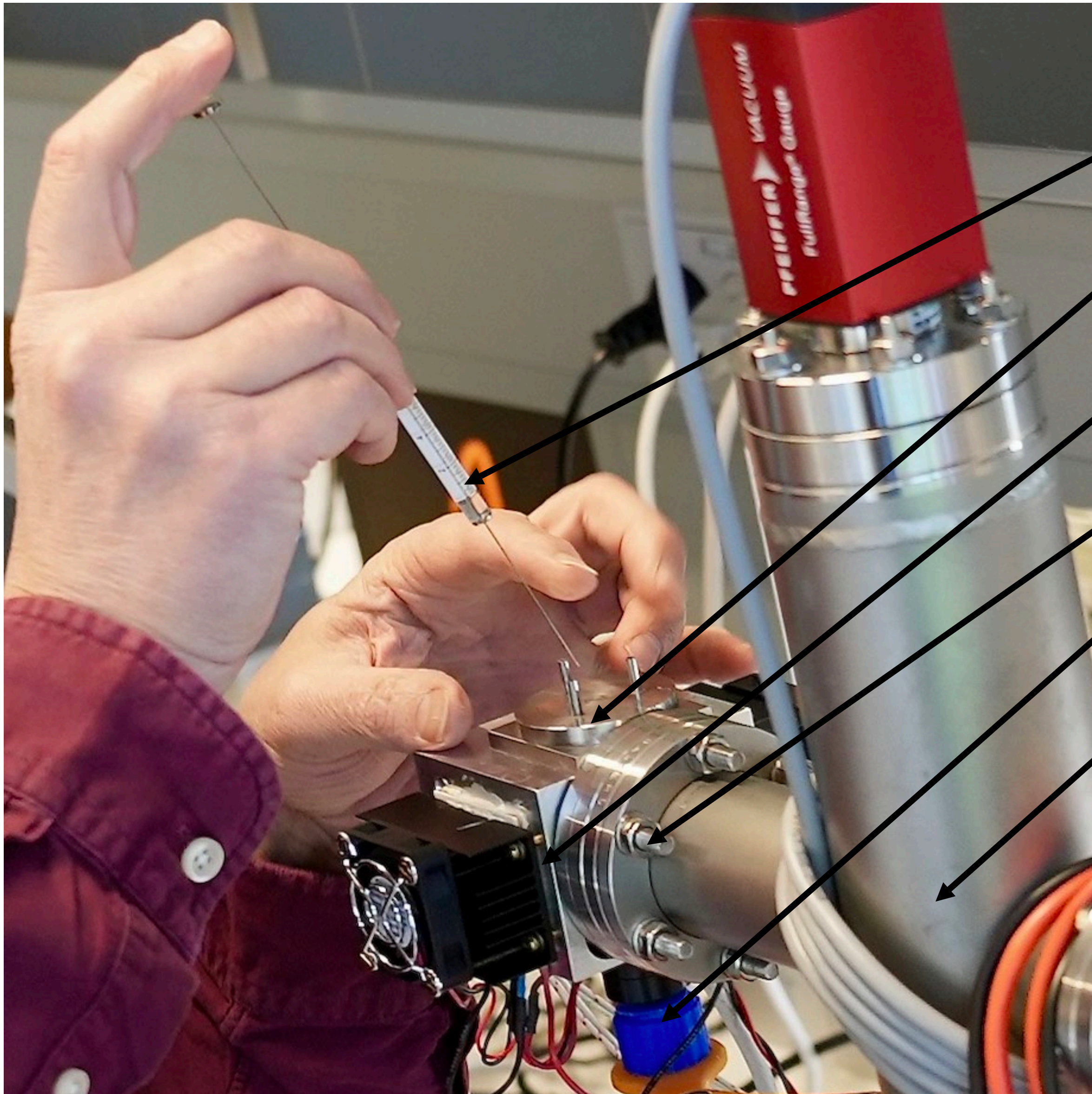




HEMS Workshop, Florida, 2022

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

The experimental laboratory reactor



Hamilton syringe for injection of phenols and hypochlorite

Closed 50 ml chemical reactor

Peltier elements for reactor thermosetting (12-75 ^{o}C)

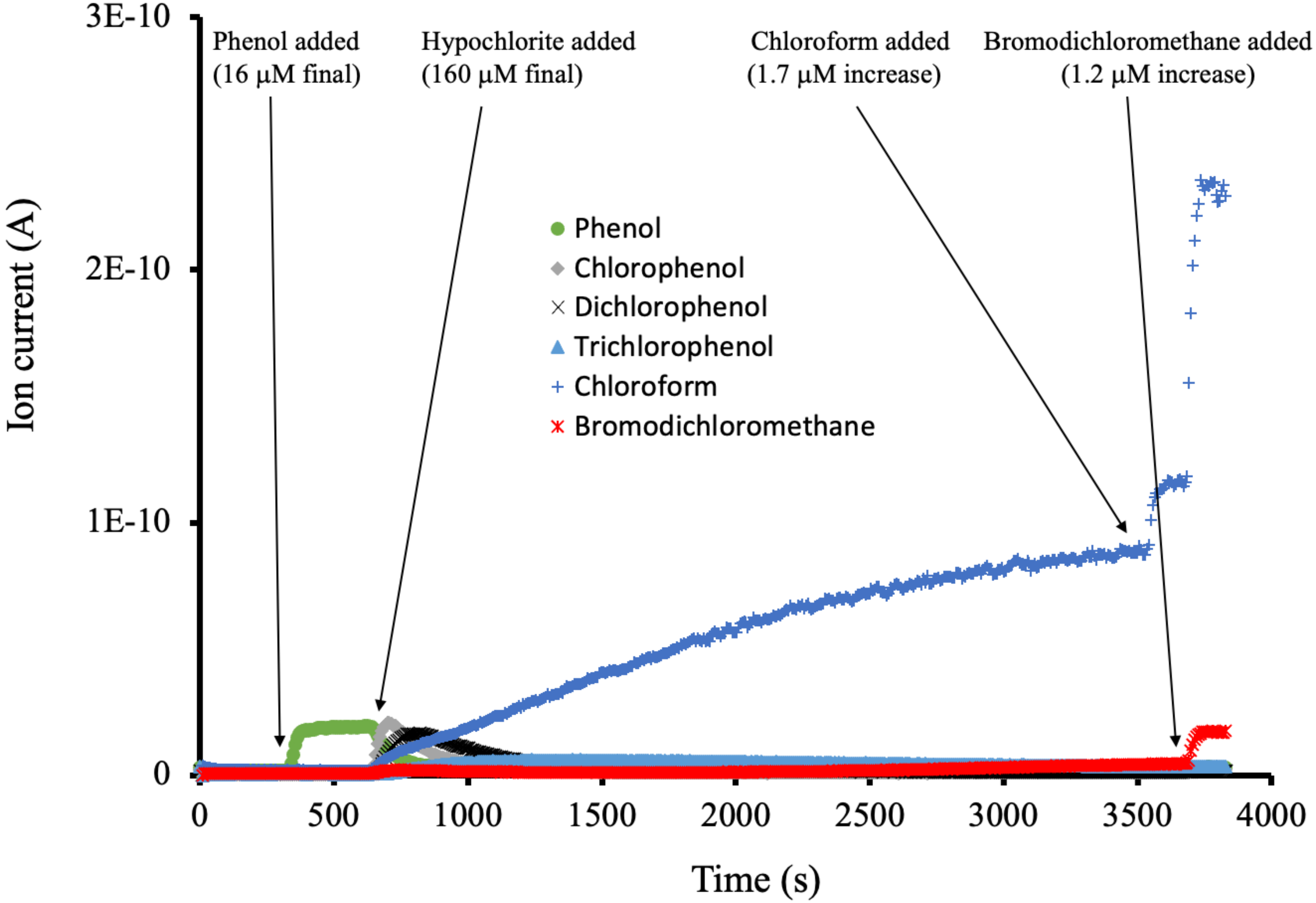
Vacuum interface with membrane inlet

Magnetic stirrer

Quadrupole mass spectrometer

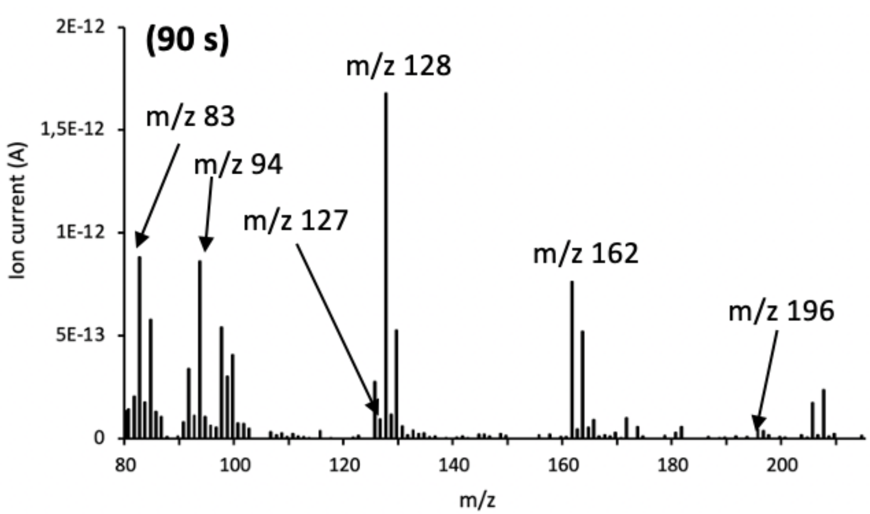
SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

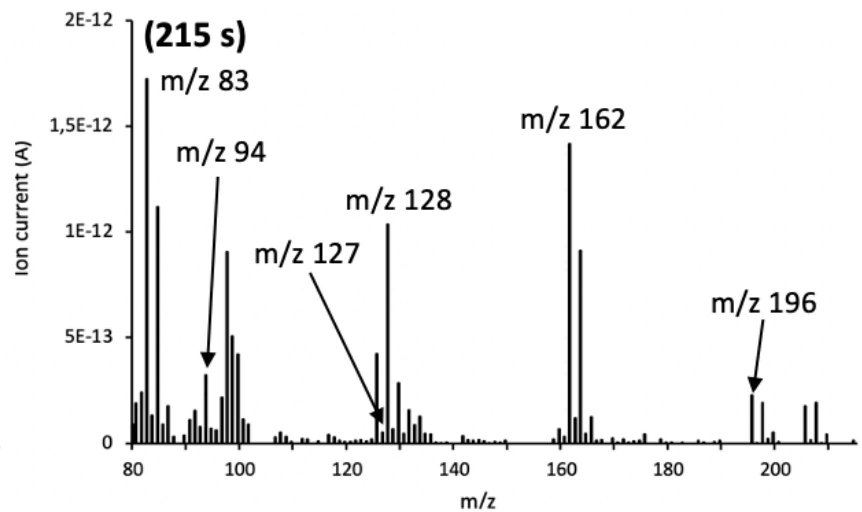
A standard experiment: Raw data

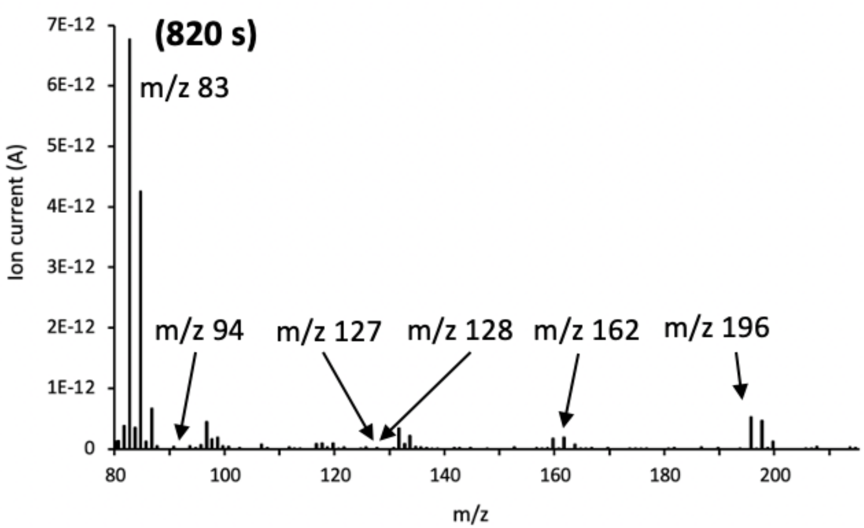


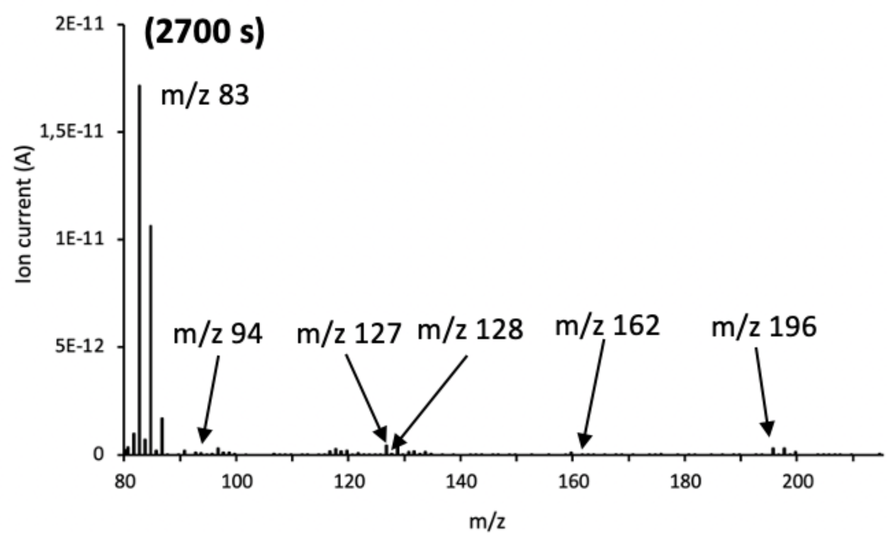
SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

Recorded mass spectra during the experiment









Correction for peak overlap

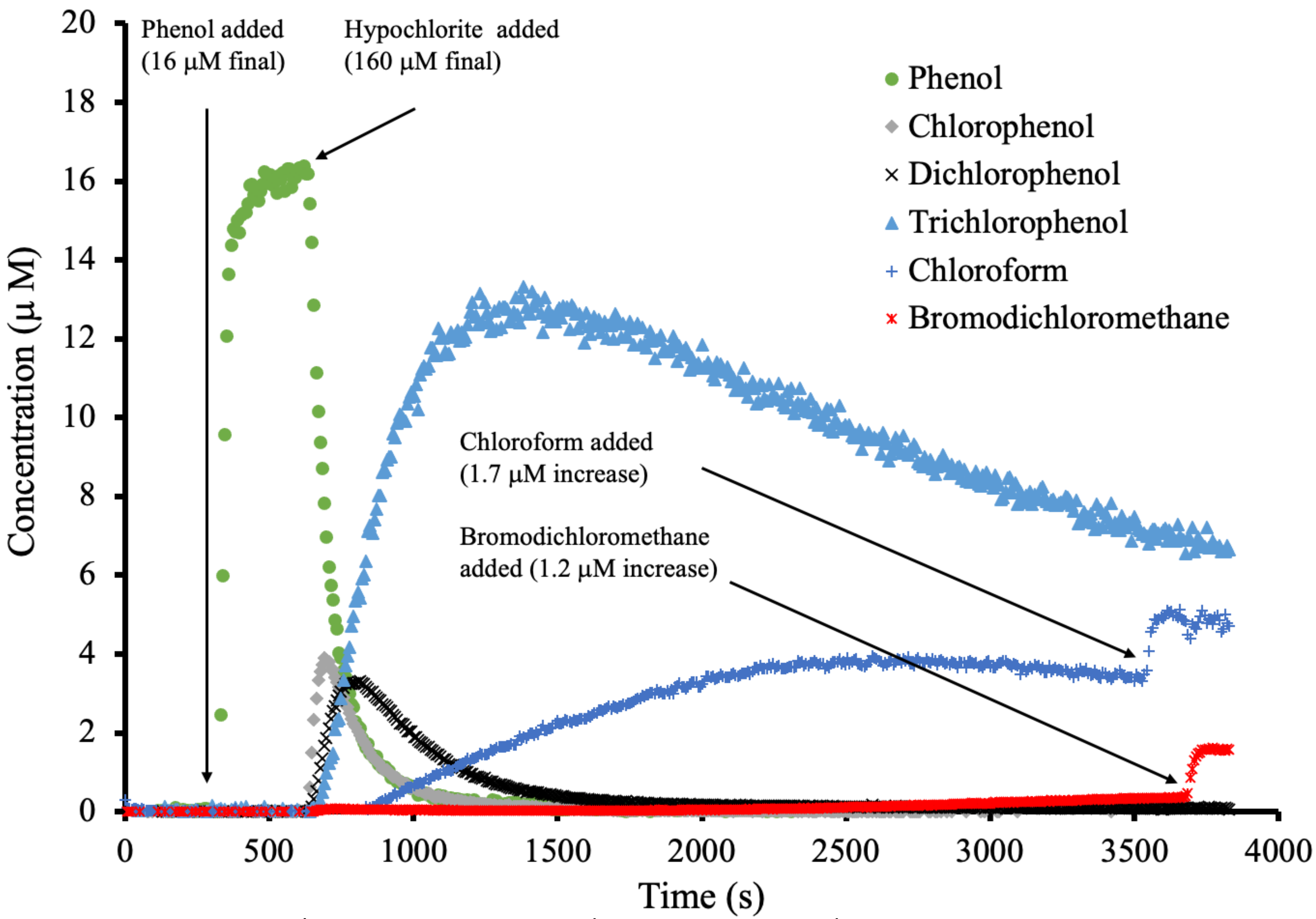
Analyte	*m/z* used	Formula for overlap-corrected signals
2,4,6-Trichlorophenol	196	$I_{196,\text{corrected}} = I_{196}$
2,4-Dichlorophenol	162	$I_{162,\text{corrected}} = I_{162} - (I_{196} \times 0.09) - (I_{127} \bullet 0.03)$
2-Chlorophenol	128	$I_{128,\text{corrected}} = I_{128} - (I_{162} \times 0.05) - (I_{127} \times 0.11)$
Phenol	94	$I_{94,\text{corrected}} = I_{94} - (I_{127} \times 0.09)$
$CHCl_3$	83	$I_{83,\text{corrected}} = I_{83} - (I_{127} \times 9.4)$
$CHBrCl_2$	127	$I_{127,\text{corrected}} = I_{127} - (I_{162} \times 0.03) - (I_{128} \times 0.04)$

Relative sensitivity for the involved analytes

Analyte	Concentration ppm (μM)	m/z	Measured signal A[a]	Sensitivity A/μM	Relative sensitivities using phenol in tap water as reference
Phenol	1 (10.6)	94	2.50×10^{-12}	2.35×10^{-13}	1.0
2-Chlorophenol	1 (7.8)	128	8.60×10^{-12}	1.11×10^{-12}	4.7
2,4-dichlorophenol	1 (6.1)	162	6.40×10^{-12}	1.04×10^{-12}	4.4
2,4,6-trichlorophenol	1 (5.1)	196	4.60×10^{-13}	9.08×10^{-14}	0.39
Chloroform	1 (8.4)	83	3.70×10^{-10}	4.42×10^{-11}	190
Bromodichloromethane	1 (6.1)	127	1.50×10^{-11}	2.46×10^{-12}	10

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

A standard experiment: Quantified



F.T. Larsen, J.N. McPherson, C.J. McKenzie and F.R. Lauritsen.. Rapid Commun. Mass Spectrom. 2022, 36, e9339

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

Detection limits and response times

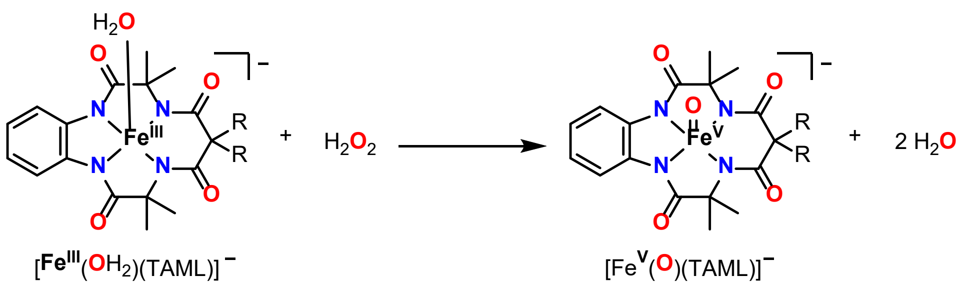
Compound	Ion used for quantification m/z	Detection limit[a] ppb (μM)	Response time[b] s
Phenol	94	15 (0.16)	55
2-Chlorophenol	128	5 (0.04)	55
1,3-dichlorophenol	162	6 (0.04)	60
TCP	196	60 (0.30)	55
TCM	83	2 (0.016)	40
BDM	127	2 (0.012)	60

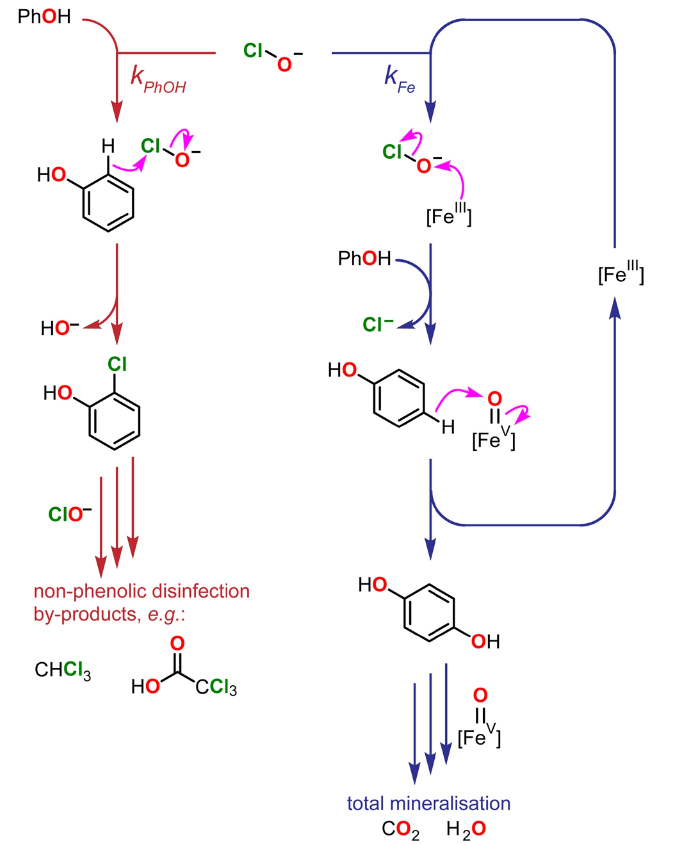
SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

The combined effect of chlorination and use of an oxidative catalyst

As advanced oxidative catalyst we have chosen Collins' $[Fe^{III}(TAML)]^{-}$, which mimics Nature's peroxidases and reacts with oxidants (such as H_2O_2 and OCl^-) to generate reactive iron(V)-oxo species.

Creation of the iron(V)-oxo species

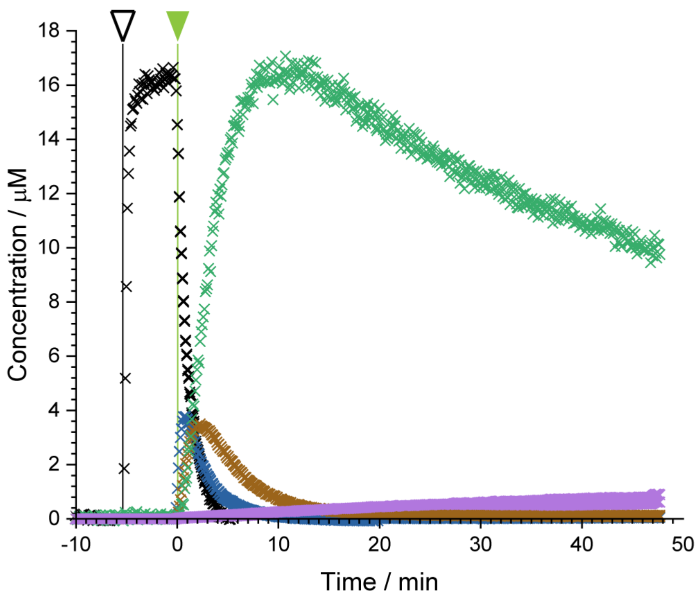




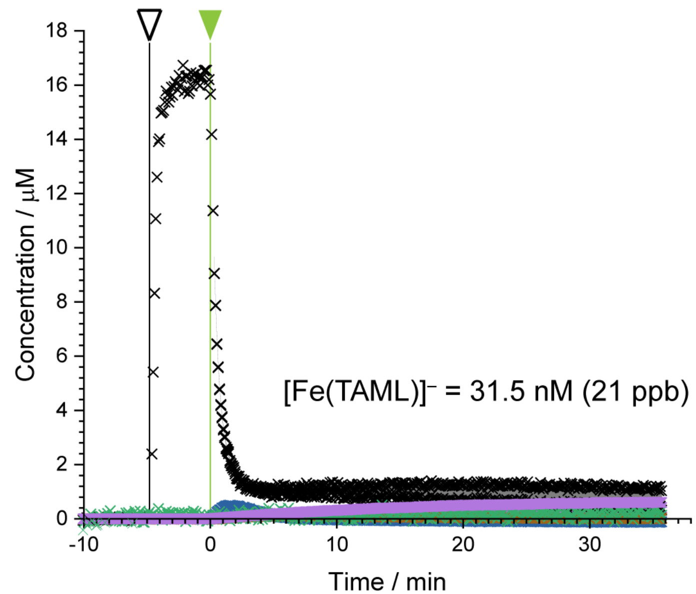
TAML: tetra-amido-N macrocyclic ligand

Chlorination of phenol hypochlorite with and without the oxidative catalyst FeTAML

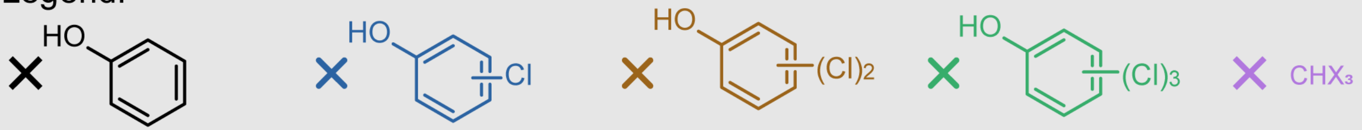
Standard oxidation using hypochlorite



Combined oxidation using both hypochlorite and FeTAML



Legend:

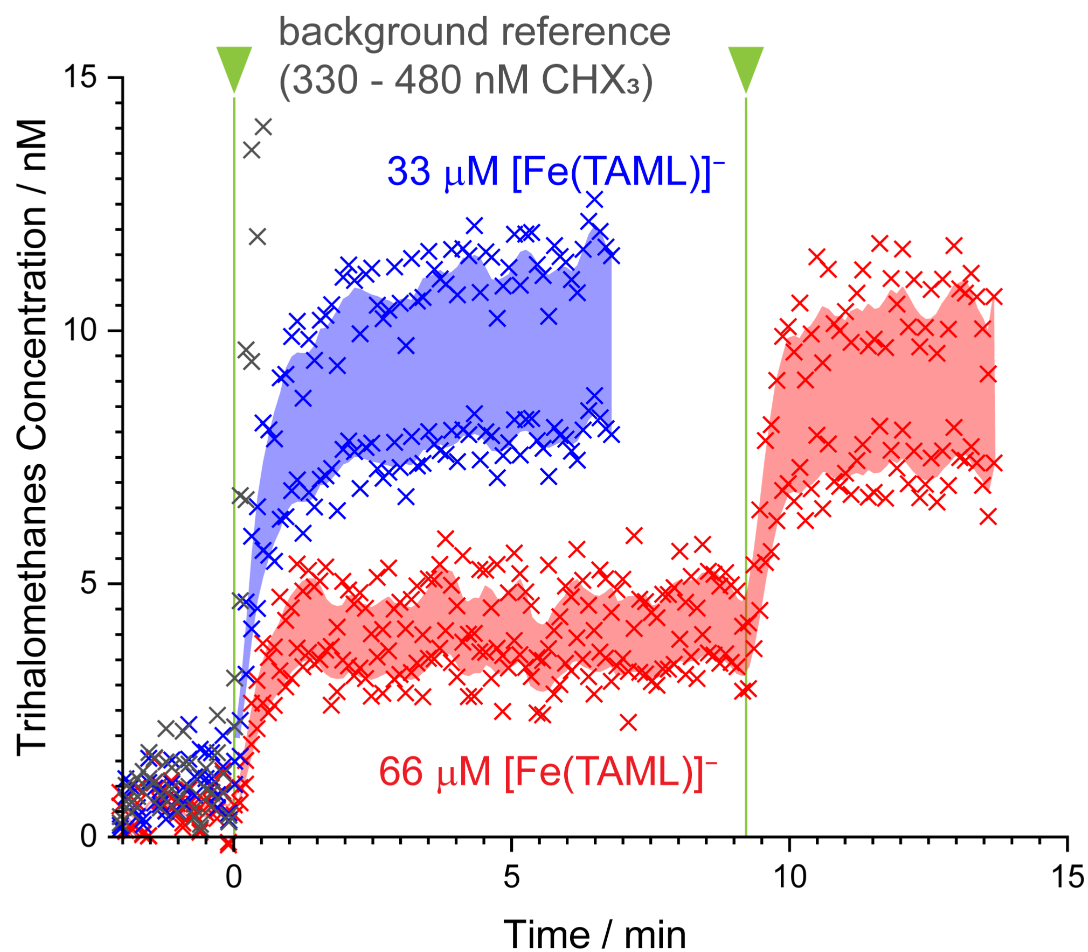


▽ 150 µL × phenol (3.2 mM) in water

▼ 5 µL × NaOCl (0.76 M) in water

SDU DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

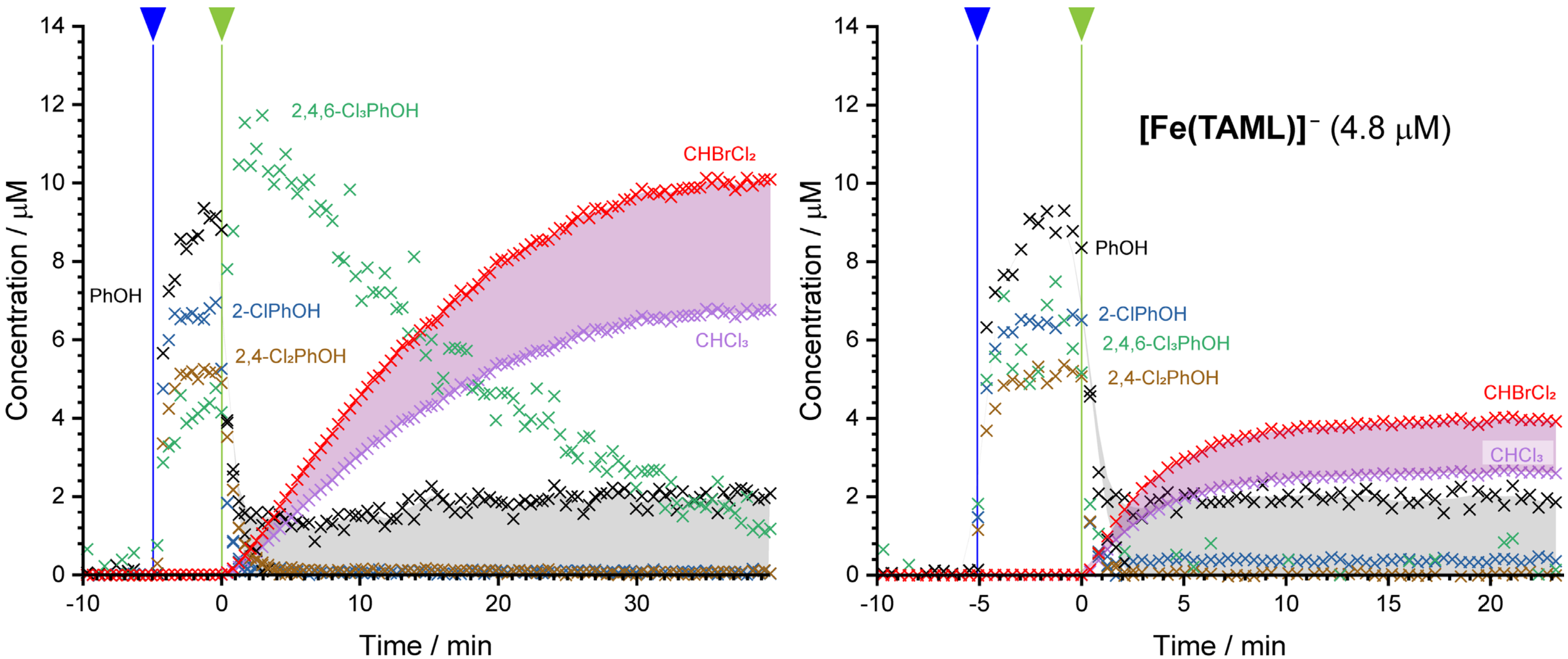
Trihalomethane concentrations after aqueous phenol solutions (16 μM, 30 mL, 40 °C) containing $[Fe(TAML)]^-$ (×: 33 μM, ×: 66 μM, and ×: no catalyst) after injections (green triangles) of NaOCl (160 μM final concentration)



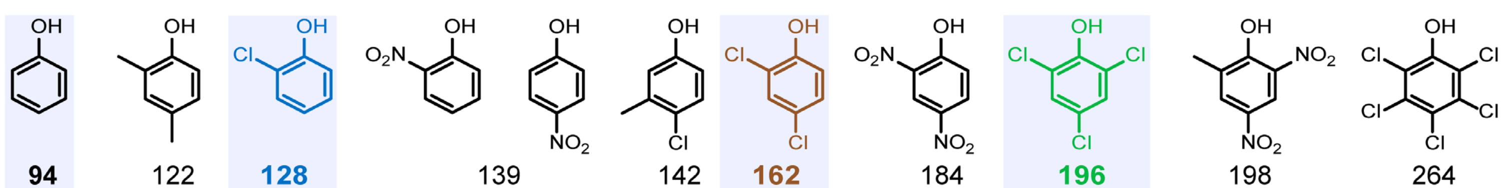
HEMS Workshop, Florida, 2022

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

Monitoring phenol, chlorophenols and trihalomethane concentrations during treatment of water (30 mL) at 40 °C contaminated by phenolic mixture by sodium hypochlorite in the absence (left) and presence (right) of $[Fe(TAML)]^-$.



▼ - 50 μL of 0.5 mg / mL of each (0.275 mg total):



▼ - 25 μL of NaOCl (0.76 M)

HEMS Workshop, Florida, 2022

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY

In conclusion

We have demonstrated that:

- Disinfection reaction of chlorophenols can be monitored quantitatively for phenol substrates, their chlorinated degradation intermediates and trihalomethane disinfection by-products using a combination of standard addition and an internal standard.

- Water treatment using a combination of chlorination and a strong oxidative catalyst leads to a degradation process without formation of chlorinated phenol intermediates and reduced trihalomethane production.

Future research:

Our observation that the chemical composition of raw water (salts, natural organic water and contaminants) has a major influence upon the monitored degradation kinetics will be envestigated further and onsite tests at various water works will be performed to evaluate extrapolation from lab to single site tests as well as from single site to multi-site tests.

SDU
DEPARTMENT OF PHYSICS, CHEMISTRY AND PHARMACY