

RESEARCH ARTICLE

An experimental laboratory reactor for quantitative kinetic studies of disinfection byproduct formation using membrane inlet mass spectrometry

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Rationale: The type and quantity of environmentally problematic disinfection byproducts (DBPs) produced during chlorination of water depend on the natural organic matter and organic contaminants that raw water contains, and on the operational conditions of the drinking water treatment process. There is a need for a fast and quantitative method that determines which DBPs are produced and monitors the chemical dynamics during a drinking water treatment.

Methods: A small experimental chemical reactor (50 mL) was mounted directly onto the membrane inlet interface of a membrane inlet mass spectrometer (MIMS). In this setup, the membrane was the only separation between the reaction mixture in the chemical reactor and the open ion source of the mass spectrometer 2 cm away. Water samples to be chlorinated were placed in the reactor and the chlorination reaction was initiated by injection of hypochlorite. The formation of intermediates and products was monitored using either full-scan mass spectra or selected ion monitoring of relevant ions.

Results: An algorithm for analyte quantification was successfully developed for analysis of the complex mixtures of phenol (a model for waterborne organic compounds), chlorinated intermediates and trihalomethane products which simultaneously pass the membrane into the mass spectrometer. The algorithm is based upon the combined use of standard addition and an internal standard, and all analytes could be quantified at nanomolar concentrations corresponding to realistic water treatment conditions. Experiments carried out in the temperature range 15–60°C showed that the reaction dynamics change with operational parameters, for example in tap versus deionized water.

Conclusions: We have successfully shown that an experimental laboratory reactor directly interfaced with a MIMS can be used for quantitative monitoring of the chemical dynamics during a water treatment. This technique could provide rapid assistance in the optimization of operating parameters for minimizing DBP production.

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1 | INTRODUCTION

The supply of clean drinking water is a global challenge as described in the sixth of the United Nations' seventeen Global Goals. In many developing countries access to freshwater is the largest problem, whereas the dominating problem in other countries is biologically and chemically contaminated water resources (surface water, groundwater and wastewater). The contaminants are typically heavy metals, solvents, dyes, pesticides, pharmaceuticals and personal care products.^{1,2} A recent review of European occurrence of emerging contaminants³ showed that pharmaceuticals were detected in 31 out of 39 studies. Similarly, a new global study⁴ investigating the occurrence of 61 selected pharmaceuticals in river water found 51 of them in at least one study and 14 were found in rivers on all continents except Antarctica.

In most countries, raw water needs to be disinfected before it can be consumed. The disinfectants used typically are chlorine, chloramine, chlorine dioxide, UV and ozone, with chlorine as the globally most used disinfectant due to its lower cost and high efficiency against most pathogens.⁵ A side effect of the disinfection process is the production of harmful disinfection byproducts (DBPs) such as halomethanes, haloacetic acids, haloamines, nitrosamines, haloaldehydes and haloaromatics.^{6,7} Many of these DBPs are known to be carcinogens, mutagens and toxicants.^{8,9}

The type and concentration of DBPs produced from a raw water resource are very hard to predict. They depend on the complex network of possible chemical reactions taking place between the disinfectant and organic compounds in the water originating from natural organic matter (NOM), pollutants and the compounds released from killed pathogens. In addition, operational conditions such as dose, contact time, temperature, pH and ammonium and metal concentrations in the raw water have an influence upon the outcome of the reactions.⁵ For these reasons the optimization of drinking water treatment technology is difficult. There is an urgent need for simple methods that can follow the chemical dynamics during drinking water treatment. DBPs must be identified along with the circumstances that influence their production. We show here that membrane inlet mass spectrometry (MIMS) is a good candidate for such a method.

The detection of common DBPs such as trihalomethanes, organic and inorganic haloamines and halogen-containing aldehydes, ketones and aromatics by MIMS has been demonstrated,¹⁰⁻¹⁵ and it has been implemented for onsite surveillance of DBPs (trihalomethanes and haloamines) in swimming pools.^{16,17} In these studies, water samples for analysis were transported to a MIMS instrument and then analyzed using a flow-through type of membrane inlet.¹⁸

Kinetic studies of water disinfection have also been performed and a review covering the use of MIMS for direct chemical measurements has been published.¹⁹ In these studies, a chemical reactor was typically set up and connected to the MIMS instrument using a water-circulating system where sample water is continuously extracted from the reactor and then pumped through the membrane inlet before it is recirculated to the reactor or discharged.²⁰⁻²⁵ This

approach works well when proper care is taken to limit contact between sample water and plastics (apart from the MIMS membrane) in the whole circulating system to avoid memory effects.²¹ Another difficulty with this setup is quantification since it is well known^{26,27} that the occurrence and intensity of MIMS signals depend heavily on both the matrix and the external calibration which should be done in water with composition similar to that of the reacting liquid.

To circumvent the uncertainties associated with a reactor using a water circulation system for MIMS analysis, the reactor can be mounted directly on a membrane inlet mass spectrometer^{26,28} so that the membrane constitutes a part of the reactor wall. Permeating analytes pervaporate directly into the ion source of the mass spectrometer or are connected to it via a very short tube. In the experimental laboratory reactor (ELR) presented here, analytes vaporize directly from the vacuum side of the membrane into an open ion source. This setup minimizes vacuum effects caused by interactions between analytes and metal surfaces inside the vacuum manifold^{25,29,30} and enhances the vaporization of semi-volatile organic compounds from the membrane inside the mass spectrometer via direct radiational heating from the filament. The setup also makes it possible to perform quantification by direct standard addition into the reacting liquid.

To demonstrate the potential of our ELR-MIMS setup for kinetic studies of water treatment processes and optimization of drinking water treatment technologies, we have chosen chlorination of phenol as a model system. Chlorination is globally the most common disinfectant method and phenol is a common model compound for DBP formation from NOM and many contaminants present in raw water. Further, the chlorination chemistry of small aromatics has been described^{5,31-35} and MIMS monitoring of phenol chlorination without quantification has previously been published²³ together with a suggested schematic of the reaction mechanism.

2 | EXPERIMENTAL

2.1 | Chemicals

With exception of the experiment comparing the kinetics of phenol disinfection in deionized water (18.2 MΩ cm, Milli-Q, Millipore) and in local tap water, all experiments were performed in tap water to simulate real conditions. All solutions were prepared using certified standards as pure solids (200 mg of 2-chlorophenol and 200 mg of 2,4-dichlorophenol) or dissolved in methanol (phenol, 5000 mg/L; 2,4,6-trichlorophenol, 1000 mg/L; chloroform, 2000 mg/L; and bromodichloromethane, 2000 mg/L) purchased from VWR Denmark. Sodium hypochlorite (5% active chlorine) was also purchased from VWR Denmark.

We chose to use drinking water directly from the tap for these studies to demonstrate the potential of the ELR-MIMS setup under as natural conditions as possible. Danish drinking water is based upon groundwater supplied to the consumer without any chemical treatment and we used water directly from a tap at the University of

Southern Denmark, Odense. The water is supplied by the local waterworks (Vandcenter Syd A/S) and biannually it publishes an extensive accredited characterization of the water on its homepage.³⁶ Important parameters for this study are pH 7.5, NOM content of 1.9 mg/L, bromide concentration around 100 µg/L and none (< 0.01 µg/L) of more than 50 regularly occurring organic contaminants and degradation products in the water.

2.2 | Description of ELR–MIMS setup

The mass spectrometer used in this study was a PrismaPro quadrupole mass spectrometer (Pfeiffer Vacuum, Asslar, Germany) with an open ion source and a mass range m/z 0–300. The quadrupole was mounted in a vacuum chamber in such a way that the open ion source was directly adjacent to the vacuum flange to which the ELR was attached on the opposite side (Figure 1). A detailed diagram of a similar membrane interface–ion source connection has previously been published.³⁷ In this setup the only barrier between the reaction liquid of the ELR and the open ion source of the mass spectrometer is a polydimethylsiloxane sheet membrane, 125 µm thick (Technical Products Inc., Decatur, GA, USA). Analyte molecules from the ELR liquid permeate the membrane and evaporate into the vacuum of the mass spectrometer from the membrane assisted by heavy illumination from the ion source's filament.³⁸ The membrane area exposed to reaction liquid is a 5 mm diameter sheet supported by a 100 µm thick stainless steel plate with a dense network of 0.5 mm holes.

The ELR (Figure 1) is made of stainless steel and has a chemical reaction chamber with a capacity of 50 mL. A typical experiment is conducted with 30 mL of reaction liquid, in which case the magnetically stirred reaction liquid creates a conical liquid surface and

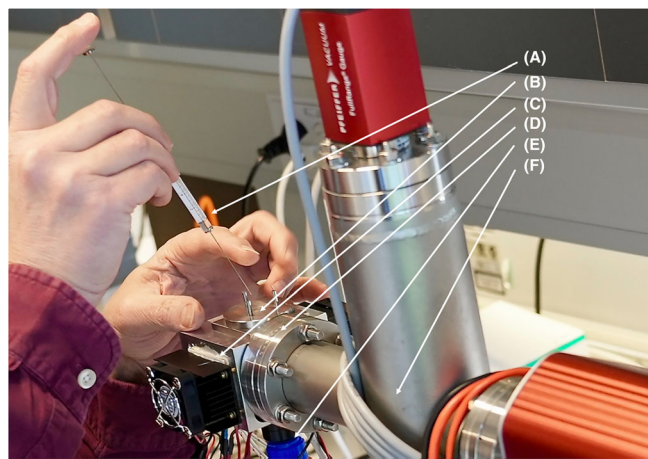


FIGURE 1 ELR–MIMS setup for kinetic studies of disinfection processes. a, Hamilton syringe for reactant and hypochlorite injection; b, closed 50 mL chemical reactor; c, Peltier elements for reactor thermostating (12–75°C), vacuum interface with membrane inlet; e, magnetic stirrer; f, quadrupole mass spectrometer [Color figure can be viewed at wileyonlinelibrary.com]

a fast flow of liquid passing by the membrane surface to reduce the boundary layer in front of it. The reaction chamber is isolated from the surrounding air with a lid penetrated by three stainless steel tubes (2 mm inner diameter). One tube was used to inject chemicals into the reaction liquid, whereas the other two tubes can be used to pass a continuous stream of gases through the headspace, thereby ensuring a well-defined headspace gas composition. This makes it possible to perform quantitative measurements of gas evolution and consumption as described elsewhere.³⁹ In the present studies the seal was kept closed during the experiments. To thermostat the ELR, two Peltier elements (Peltier cooler module ET-161-12-08-E, European Thermodynamics Limited) were mounted on the side of the reactor, which made it possible to control the temperature of the reaction liquid between 15 and 70°C.

2.3 | Experimental procedure

With an expected content of 2 ppm NOM in tap water, we chose to perform our demonstration studies of the ELR–MIMS system using a substrate (phenol) concentration of 1.5 ppm (16 µM) and a chlorination agent (hypochlorite) at a concentration of 8.3 ppm (160 µM). The hypochlorite concentration is slightly higher than that used in a typical chlorination process (5 ppm maximum, WHO guidelines⁴⁰) but ensures surplus chlorine to react with the phenol while still being close to normal operational conditions.

The experiments were conducted following the same protocol. First 30 mL of tap water was filled into the ELR, the reactor was closed by the lid and stirring started. After a few minutes, when the reactor had reached thermal equilibrium, selected ion monitoring (SIM) of the six ions used for quantitation was started. Except for the experiments investigating the importance of temperature, all experiments were carried out at 40°C, which makes it possible to observe the whole chlorination process within our intended maximum 1 h total analysis time for an experiment. A Gantt chart illustrating the experimental timeline is presented in Table 1.

2.4 | Choosing ions for monitoring reactants, intermediates and products

The most abundant intermediates produced from phenol during chlorination are monochlorophenols (MCPs), dichlorophenols (DCPs) and trichlorophenols (TCPs) with 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol as the most abundant isomers.³⁴ All isomers permeate through the membrane into the mass spectrometer simultaneously and this complicates quantification. MIMS cannot distinguish between isomers in a mixture of chlorophenols. We chose to use the most abundant isomers for calibration and estimated that this gives an inherent error in concentrations of ±15% for the three chlorophenols caused by small differences in isomer permeation through the membrane, and in ionization and fragmentation. Further, the issue of overlapping electron ionization mass spectra must be

TABLE 1 Gantt chart illustrating the experimental timeline

Timeline (min)	0 to 5	5 to 10	10 to 50	50 to 55	55 to 60
Activity	Pure water. Background signals recorded	Phenol injected and the last 40 s used for calibration of phenols	Reaction started by injection of hypochlorite and the reaction monitored to the end	Chloroform standard injected and peak rise (m/z 83) used for calibration	Bromodichloromethane standard injected and peak rise (m/z 127) used for calibration

considered. Based upon database spectra (NIST Chemistry webbook⁴¹) we found that the overlap between the phenols is relatively small if the nominal mass of the molecules is used for quantification. That is, m/z 94 for phenol (no overlap), m/z 128 for MCP (5% overlap from DCP), m/z 162 for DCP (9% overlap from TCP) and m/z 196 for TCP (no overlap).

Trihalomethanes are also produced from phenol, and we observed the production of trichloromethane (TCM; chloroform) and bromodichloromethane (BDM) during the chlorination process. BDM is problematic since it has the same nominal mass as DCP (m/z 162), and its fragment ions show small peak overlaps with all other compounds except TCP. We chose to use the fragment at m/z 127 to quantify BDM since this ion is only overlapped a little with other compounds (MCP and DCP) in solution. The abundance of BDM at m/z 127 was then used to correct for BDM peak overlap with the other molecules. A potential overlap from dibromochloromethane was experimentally excluded as described later. TCM was quantified using m/z 83 since the relative abundance of its characteristic ions at the molecular ion region was too low for quantification. Despite both TCM and BDM having their most abundant ion at m/z 83, the peak overlap correction from BDM using m/z 127 worked very well as demonstrated later.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of standard experiment

Figure 2 shows the results of an experiment (raw data) where a solution of 16 μM phenol in tap water was chlorinated using the protocol described in Table 1. The six characteristic ions discussed above were monitored during the reaction using SIM. The SIM data show that upon addition of hypochlorite, the substrate phenol is rapidly transformed into MCP followed by a transformation of MCP into DCP and further DCP into TCP. TCM production is seen already from the start and the signal continues to increase throughout the experiment, whereas BDM appears later. At time 3550 s a standard of TCM (1.7 μM change in final concentration) was injected into the reaction medium for calibration of TCM and a corresponding rise in signal was observed for m/z 83. At time 3700 s a standard of BDM (1.2 μM change in final concentration) was injected into the reaction for calibration of BDM and a corresponding rise in signal was observed for m/z 127. Here a large parallel increase in signal for m/z 83 was also observed showing the effect of BDM overlap upon the TCM ion.

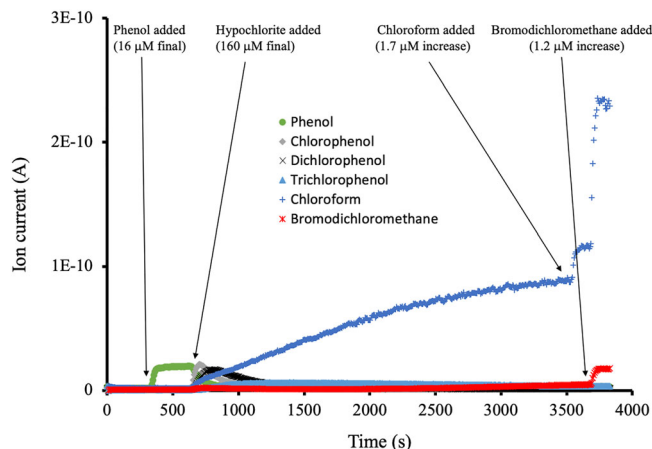


FIGURE 2 Raw data from a typical experiment where tap water spiked with phenol (16 μM) is disinfected using hypochlorite (160 μM) and monitored using SIM [Color figure can be viewed at wileyonlinelibrary.com]

Figure 3 shows mass spectra (raw data) recorded at 90, 215, 820 and 2700 s after the addition of hypochlorite to the solution to start the chlorination of phenol. These times were chosen because they reflect the times of maximum signal for MCP (m/z 128), DCP (m/z 162), TCP (m/z 196) and TCM (m/z 83). After 90 s a significant part of the phenol has been chlorinated and m/z 128 (MCP) is the most abundant ion in the spectrum. Further chlorination to DCP was also observed by an abundant m/z 162 ion and to a lesser degree further chlorination to TCP at m/z 196. The remaining phenol was still observed at m/z 94. Already at this point a significant signal from TCM is seen at m/z 83. A small signal at m/z 127 indicates that BDM could be present and cause an overlap to the chloroform signal, but, as discussed later, this peak is overlap originating from MCP and DCP. After 215 s the relative abundances of ions from the chlorophenols have changed. DCP (m/z 162) is now the most abundant chlorophenol, whereas the relative abundance of MCP has reduced and that of TCP has increased significantly. TCM (m/z 83) is now the most abundant ion in the spectrum. The ion at m/z 127 is reduced, which emphasizes that the signal seen at m/z 83 in the early phase is due to TCM and it is not affected by overlap from BDM at this stage.

The spectrum recorded after 820 s of reaction is completely dominated by TCM at m/z 83 (note change in scale). Still no significant ion at m/z 127 (BDM) is observed. Phenol (m/z 94) and MCP (m/z 128) are almost gone. TCP (m/z 196) is now the most abundant chlorophenol and its presence gives rise to a set of

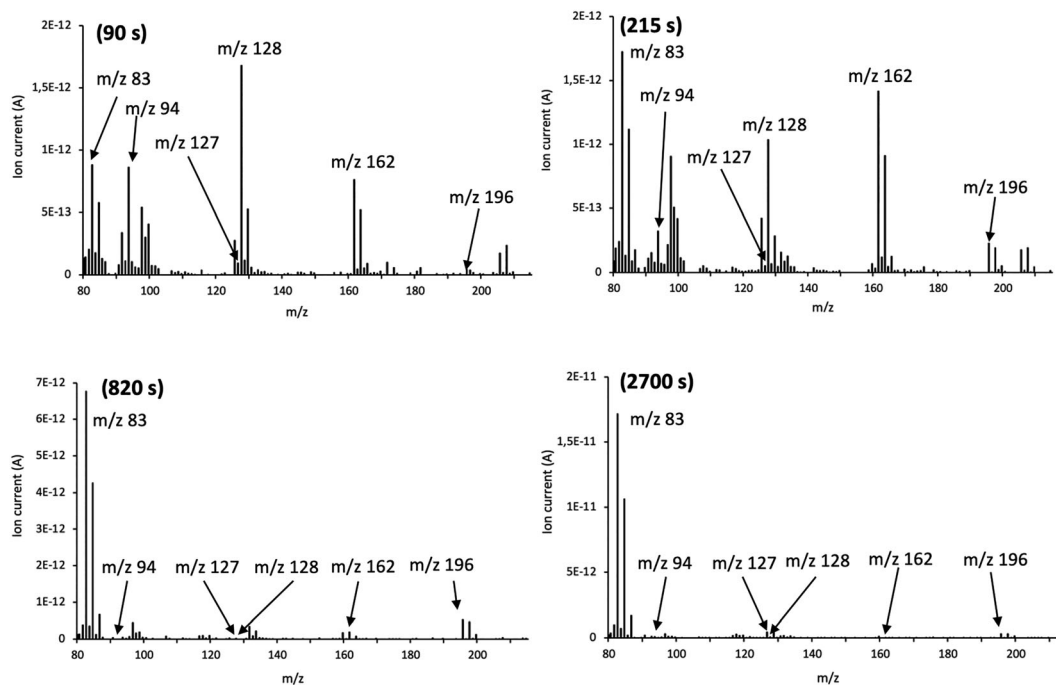


FIGURE 3 Mass spectra recorded 85, 215, 820 and 2700 s after the addition of hypochlorite. The ions used for quantification of phenol (m/z 94), MCP (m/z 128), DCP (m/z 162), TCP (m/z 196), TCM (m/z 83) and BDM (m/z 127) are shown in the spectra. The y-axes show the intensities of raw data without any calibration

fragments at m/z 160, 162 and 164. These fragments overlap with DCP ions at m/z 162, 164 and 166. Based upon the relative abundance of the isotopes, where m/z 162 is larger than m/z 160, it can be concluded that there is still some DCP present in the reaction mixture. In the spectrum recorded after 2700 s of reaction the abundance of m/z 83 has increased further (note change of scale), but this time the signal does not just originate from TCM. A significant set of ions at m/z 127, 129 and 131 has appeared with relative isotopic abundances corresponding to that expected from the CHBrCl^+ fragment from BDM. Compared to previous spectra the abundance of m/z 127 has increased by a factor of almost 10. The ions at m/z 127, 129 and 131 could also originate from dibromochloromethane, but the absence of a molecular ion cluster at m/z 206, 208, 210 and 212 excludes this possibility. At this point in the reaction, both TCM and BDM are present in the reaction mixture. Apart from residual TCP, none of the chlorophenols are left in the reaction mixture.

We have not been able to detect further chlorination to tetra- and pentachlorophenol as previously reported by Rios et al²³ even after a prolonged reaction of 7200 s. This difference is probably related to the use by Rios et al of much higher concentrations (hypochlorite 2500 mg/L and phenol 500 mg/L) than ours (8.3 and 1.5 mg/L). During our experiments, we did not observe ions in the mass spectra indicating production of brominated chlorophenols as has been reported by others.³³

As a result of the above discussed spectra, spectra recorded of pure substances dissolved in tap water as well as database spectra from NIST, we arrived at the following algorithms for correcting overlap between signals from the various substances.

Analyte	m/z used	Formula for overlap-corrected signals
2,4,6-Trichlorophenol	196	$I_{196,\text{corrected}} = I_{196}$
2,4-Dichlorophenol	162	$I_{162,\text{corrected}} = I_{162} - (I_{196} \times 0.09) - (I_{127} \times 0.03)$
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	$I_{127,\text{corrected}} = I_{127} - (I_{162} \times 0.03) - (I_{128} \times 0.04)$

In practice the overlap between signals was measured using spectra recorded of the pure compounds using the ELR-MIMS system. This calibration could be reused for weeks but must be redone following any tuning of the mass spectrometer parameters or filament replacement.

3.2 | Quantification

Table 2 presents a comparison of measured signals and sensitivities for all compounds at 1 ppm in tap water and in deionized water. The sensitivity parameters in Table 2 could be reused for weeks unless any change of the mass spectrometers operational parameters have been made or the membrane has been renewed. When dissolved in tap water the relative sensitivity between the compounds differs by a

TABLE 2 Comparison of ELR–MIMS sensitivities for the compounds investigated in this study when dissolved in tap water and in deionized water

Analyte	Concentration in ppm (μM)	m/z	Measured signal (A) ^a		Sensitivity (A/ μM)		Relative sensitivities using phenol in tap water as reference	
			Tap water	Deionized water	Tap water	Deionized water	Tap water	Deionized water
Phenol	1 (10.6)	94	2.50×10^{-12}	2.40×10^{-12}	2.35×10^{-13}	2.26×10^{-13}	1.0	0.96
2-Chlorophenol	1 (7.8)	128	8.60×10^{-12}	2.40×10^{-12}	1.11×10^{-12}	3.09×10^{-13}	4.7	1.37
2,4-Dichlorophenol	1 (6.1)	162	6.40×10^{-12}	1.04×10^{-12}	1.04×10^{-12}	1.70×10^{-13}	4.4	0.75
2,4,6-Trichlorophenol	1 (5.1)	196	4.60×10^{-13}	1.60×10^{-13}	9.08×10^{-14}	1.05×10^{-14}	0.39	0.047
Chloroform	1 (8.4)	83	3.70×10^{-10}	2.90×10^{-10}	4.42×10^{-11}	3.46×10^{-11}	190	150
Bromodichloromethane	1 (6.1)	127	1.50×10^{-11}	1.30×10^{-11}	2.46×10^{-12}	2.13×10^{-12}	10	9.4

^aIon current measured in amperes.

factor of up to 500 (190/0.39), whereas in deionized water it differs by a factor of up to 3200 (150/0.047). When shifting from tap water to deionized water the sensitivity of phenol is almost unaffected, that of the trihalomethanes slightly reduced and that of the chlorophenols significantly reduced. The reduction in sensitivity is a factor of 3.4, 5.9 and 8.3 for 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol respectively. This behavior is caused by the increasing hydrophobicity of the chlorophenols with the number of chlorine atoms. The more hydrophobic the compound the more it is pushed out of salt-containing water into the hydrophobic silicone membrane. This experiment clearly shows the importance of matrix effects in MIMS and the need for calibration using standards dissolved in a solution as like the reaction liquid as possible. Ideally, standard addition directly into the reaction liquid should be used.

Phenol as the substrate is present in the aqueous solution at a well-defined concentration (16 μM) at the beginning of the experiment and prior to the addition of hypochlorite. TCM and BDM were quantified by adding standards (final concentration changes of 1.7 and 1.2 μM respectively) into the reaction liquid at the end of the experiment. We did not quantify the chlorinated intermediates (MCP, DCP and TCP) based upon direct standard addition since this could involve uncertainties caused by fast reactions of the added standards with residual hypochlorite in the solution. Instead, these intermediates were quantified using the initial phenol signal as an internal standard and their relative sensitivity towards phenol from Table 2.

The data treatment for quantification was performed in three steps:

1. The measured ions were corrected for their background signals.
2. The background-subtracted signals were then corrected for potential peak overlaps from other ions in the solution.
3. The concentration of the individual molecules was calculated using the calibration methods described above.

Figure 4 shows the quantification of the same experiment as shown in Figure 2. Several differences are observed. Firstly, the concentrations

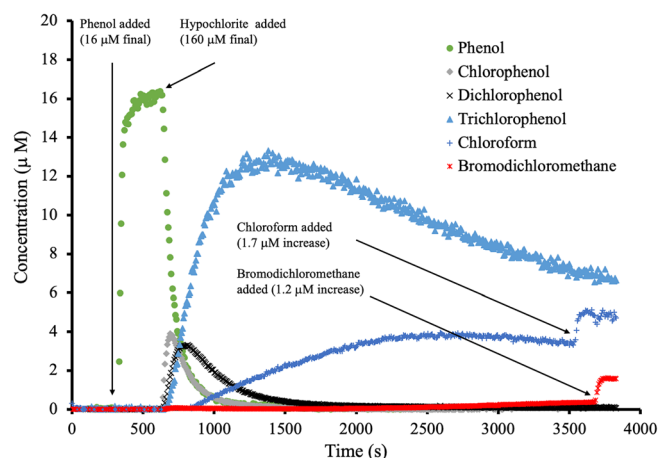


FIGURE 4 Quantification of a typical experiment (same experiment as in Figure 2) where tap water spiked with phenol (16 μM) is disinfected using hypochlorite (160 μM) [Color figure can be viewed at wileyonlinelibrary.com]

of MCP and DCP at their maximum are less than 4 μM , which is just 25% of the initial phenol concentration (16 μM) in contrast to the impression of almost equal concentrations given by the raw data used in Figure 2. Secondly, the concentration of TCP reaches 12 μM (75% of the original phenol concentration). This is in sharp contrast to the impression of its low concentration using raw data and is a result of the 10 times lower sensitivity for TCP than for MCP and DCP. With respect to TCM and BDM, the actual concentrations are much lower (<4 μM) than those indicated by their very abundant signals. This is the result of the extreme high sensitivity for the two compounds as compared to the phenols. The most interesting observation is that TCM in the quantified data (Figure 4) reaches a maximum after approximately 2000 s of reaction (time 2600 s in the figures), whereafter it declines. The decline in TCM is mirrored in an appearance of BDM. This maximum is not observable using raw data (Figure 2) since both TCM and BDM have m/z 83 as their most

abundant ion. It is well known that there is an equilibrium between hypochlorite and hypobromite in water containing bromide and this equilibrium results in a replacement of a chlorine atom in TCM with a bromine atom.³ Our tap water contains around 100 µg/L of bromide. This concentration corresponds to 1.25 µM, which is just above the 1.20 µM maximum BDM concentration measured in Figure 4 and illustrates the efficiency of the chemical replacement of chlorine with bromine in chlorinated water. The efficiency of the peak overlap algorithms is clearly shown when the BDM standard is added at time 3700 s. The BDM signal at m/z 127 rises as expected, whereas only a small disturbance at the time of injection is observed in the TCM signal (m/z 83) despite the peak overlap.

3.3 | Reproducibility

The reproducibility of the experiments was tested by analyzing seven replicas of the phenol disinfection process. It was very high with standard deviations in maximum recorded concentrations and the time to reach that being 3.9 ± 0.1 µM after 72 ± 9 s, 3.4 ± 0.2 µM after 168 ± 16 s, 12.5 ± 0.7 µM after 736 ± 56 s and 3.1 ± 0.4 µM after 2000 ± 200 s for MCP, DCP, TCP and TCM respectively. A maximum concentration for BDM cannot be given since the concentration kept rising slowly throughout the experiment after its appearance was registered at 1188 ± 110 s. After 2700 s of reaction the concentration of BDM measured was 0.2 µM. A cycle of MID data was recorded every 7.2 s which sets the lowest limit for the deviation in peak appearance time in good agreement with observations for MCP (± 9 s) and DCP (± 16 s), whereas TCP (± 38 s), TCM (± 140 s) and BDM (± 170 s) had larger deviations. This is expected since the maximum concentrations are reached at times when they change slowly, and hence a small uncertainty in concentration can translate into a large uncertainty in time.

3.4 | Detection limits and response times

The ability to analyze analytes at a suitable low concentration is an important part of an analytical method and for online monitoring the response time should be shorter than the lifetime of the transients

involved. Table 3 presents measured detection limits and response times for the analytes involved in these chlorination experiments. Except for TCP (detection limit of 0.3 µM), all the involved molecules participating in phenol degradation reactions have detection limits lower than 1% (0.16 µM) of the substrate's concentration making it possible to detect even low-concentration intermediates in the reaction cascades. The membrane response times are about 55 s for the compounds. This is well below the lifetime of the chemical transients observed for all involved compounds except for the initial transformation of phenol into MCP. The half-time for disappearance of phenol is 70 s and MCP reaches its maximum concentration at this same time. These transients are too close to the measured 10–90% rise times and this initial step proceeds probably faster than the data show. Future work will focus upon finding a way of mounting a thinner membrane in the setup without losing the advantages of being able to radiate the vacuum side of the membrane with light and heat from the filament.

3.5 | Importance of water type

Figure 5 shows the monitoring of chlorination of phenol (16 µM) carried out in deionized water using 160 µM hypochlorite. Some significant differences as compared to the same process carried out in tap water are seen. The reactions proceed at a much slower rate and practically no production of TCM (*ca* 0.05 µM) or BDM (<0.012 µM) was observed. The time to reach maximum MCP, DCP and TCP concentrations increased from 56 to 91 s, from 270 to 385 s and from 690 to more than 3600 s respectively. The low TCM concentration probably reflects an even further reduced reaction rate than that observed for the phenol halogenations, since its production requires additional reaction steps starting with the breakdown of a halogenated aromatic ring. The absence of BDM was expected since deionized water does not contain significant concentrations of bromide that can react with hypochlorite and form hypobromite.³³

The dynamics of the process is also changed. Maximum concentrations for MCP and DCP increased from 2.6 to 6.9 µM and from 2.7 to 3.9 µM respectively, when the reaction was performed in deionized water. TCP did not reach a maximum, not even after 2 h.

TABLE 3 Detection limits and response times

Compound	Ion used for quantification (m/z)	Detection limit ^a in ppm (µM)	Response time ^b (s)
Phenol	94	0.015 (0.16)	55
MCP	128	0.005 (0.04)	55
DCP	162	0.006 (0.04)	60
TCP	196	0.060 (0.30)	55
TCM	83	0.002 (0.016)	40
BDM	127	0.002 (0.012)	60

^aDetection limits were based upon a signal-to-noise ratio of 3.

^bResponse times were based upon 10–90% rise times following an abrupt concentration change.

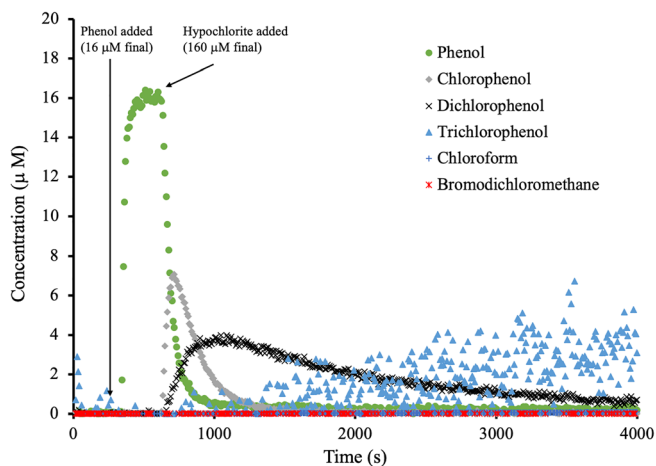


FIGURE 5 Chlorination of phenol carried out in deionized water. Apart from the reaction being carried out in deionized water instead of in tap water as in all other experiments, the experimental conditions were the same [Color figure can be viewed at wileyonlinelibrary.com]

Here the TCP concentration reached 6.8 μM , which is still lower than the 12.5 μM concentrations reached after 690 s in the parallel tap water studies. The very noisy TCP signal is a result of the 10 times lower sensitivity for TCP in deionized water than in tap water and we were measuring at the detection limit of TCP in deionized water.

The observed differences are not a surprise, since it is well known that the presence of metal ions in water affects the disinfection process.⁵ The tap water used contains a large amount of known as well as unknown metal ions³⁶ and we expect that some of these ions may act as catalysts in the reaction and thereby accelerate the reaction as compared to that observed with deionized water. Some metal ions might be released from the stainless steel walls in the reactor because of interaction with the aggressive hypochlorite, but these metal ions will be present for both tap and deionized water experiments. The pH can also play a significant role for the reaction dynamics. The pH of our tap water is around 7.5, whereas that of the deionized water is around 6. During our experiments, pH fluctuations were measured to be within ± 0.2 . There is no doubt that this will play an important role for DCP and TCP, which have $\text{p}K_a$ values of around 7.4 and 6.0 respectively. Since the chlorination reaction is expected to happen via the phenolate ions this could explain the slower reactions observed in deionized water, since less phenolate will be present in the reaction mixture at pH 6 than at pH 7.5. Further, the tap water used contains up to 2 mg/L NOM. We had expected NOM to compete with phenol for the hypochlorite and thus slow down the degradation rate of phenol in tap water as compared to the reaction in deionized water; however, we observed the opposite. Blind experiments carried out with tap water without the addition of phenol showed production of trihalomethanes of about 1/6 of that observed when phenol is added. The trihalomethane formation kinetics was the same.

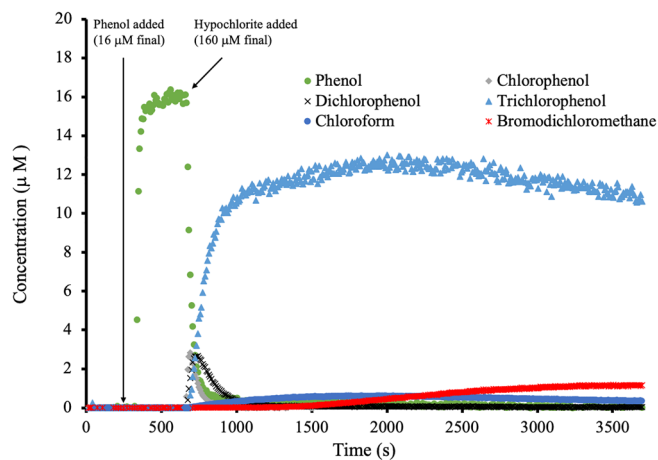


FIGURE 6 Chlorination of phenol carried out at 60°C. Apart from the temperature, the reaction conditions were the same as those in Figure 4 [Color figure can be viewed at wileyonlinelibrary.com]

3.6 | Influence of temperature upon reaction dynamics

To investigate the influence of temperature we performed the standard experiment at 15, 25, 40 and 60°C. When the temperature within the ELR rises, two independent parameters can affect the observed reaction dynamics: the actual chemical reaction dynamics and the transport dynamics of the organic molecules pervaporating through the membrane. Typically, MIMS signals from organic compounds increase with temperature and the membrane response time become faster. Not surprisingly, the time needed to reach maximum concentration of the compounds decreased significantly the higher the temperature. At 15 and 25°C the reaction proceeded with similar dynamics to that shown in Figure 4 (40°C). That is, the time scale is simply compressed when the temperature increases, and relative ratios of the intermediates stay the same. However, a maximum concentration for TCM and the appearance of BDM production were not observed within the 45 min of reaction time available to fulfill our 1 h criterion for a complete experiment. A different reaction dynamic was observed at 60°C (Figure 6). It appeared as if the reaction quickly proceeded with chlorination of phenol, MCP and DCP until a high 12 μM concentration of TCP was reached. Then, in contrast to the experiments at lower temperatures the concentration of TCP at 60°C stayed almost constant throughout the rest of the 45 min of reaction time. If the dynamics was to be the same at 60°C as that observed at 15, 25 and 40°C, then the TCP concentration should have dropped fast towards zero shortly after the plateau. It appears as if the reaction has stopped apart from a continued transformation of TCM into BDM. This behavior is not compatible with a membrane pervaporation effect and must somehow be connected to the chemical reaction dynamics, but this will need further studies for an explanation. For this reason, we ran the experiments at 40°C, where it is possible to characterize the chlorination process under varying conditions within an hour without losing the dynamics observed at lower temperatures.

4 | CONCLUSIONS

With phenol as a model substrate for water chlorination we have demonstrated that a small ELR–MIMS system can be used for real-time and quantitative monitoring of the chemical dynamics during a drinking water treatment process and for determining which and when DBPs are produced, and under what circumstances. Using this system, we demonstrated that the dynamics of the phenol chlorination were much slower when performed in deionized water as compared to natural tap water and it was unaffected by temperature between 15 and 40°C. In contrast, a large difference was observed at 60°C where the reaction cascade appeared to stop at TCP. By performing test experiments at 40°C, we were able to fulfill our success criterion of a complete chlorination experiment performed within 1 h.

For quantification of phenol, its chlorophenol intermediates and trihalomethanes, we developed an algorithm for quantification based upon a combination of standard addition and an internal standard. Using this algorithm, the compounds could all be quantified at nanomolar concentrations in tap water.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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