Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass spectrometry

Sebastien Allard[a,], Jeffrey W.A. Charrois[a], Cynthia A. Joll[a], and Anna Heitz[a]*

[a] Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia

Correspondence to: Dr. S. Allard, Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, GPO Box U1987 Perth, Western Australia 6845, Australia.

Phone: 61 08 9266 7949

E-mail: s.allard@curtin.edu.au

Abstract

Trihalomethanes are predominantly formed during disinfection of water via reactions of the oxidant with natural organic matter. Even though chlorinated and brominated trihalomethanes are the most widespread organic contaminants in drinking water, when iodide is present in raw water iodinated trihalomethanes can also be formed. The formation of iodinated trihalomethanes can lead to taste and odour problems and is a potential health concern since they have been reported to be more toxic than their brominated or chlorinated analogues. Currently, there is no published standard analytical method for I-THMs in water. The analysis of 10 trihalomethanes in water samples in a single run is challenging because the iodinated trihalomethanes are found at very low concentrations (ng/L range), while the regulated chlorinated and brominated trihalomethanes are present at much higher concentrations (above μg/L). An automated headspace solid phase microextraction technique, with a programmed temperature vaporizer inlet coupled with gas chromatography mass spectrometry, was developed for routine analysis of 10 trihalomethanes i.e. bromo- chloro- iodo-trihalomethanes in water samples. The carboxen/polydimethylsiloxane/divinylbenzene fiber was found to be the most suitable. The optimisation, linearity range, accuracy and precision of the method are discussed. The limits of detection range from 1 ng/L to 20 ng/L for iodoform and chloroform, respectively. Matrix effects in treated groundwater, surfacewater, seawater, and secondary wastewater were investigated and it was shown that the method is suitable for the analysis of trace levels of iodinated trihalomethanes in a wide range of waters. The method developed in the present study has the advantage of being rapid, simple and sensitive. A survey conducted throughout various process stages in an advanced water recycling plant showed the presence of iodinated trihalomethanes at ng/L levels.

Keywords: iodinated trihalomethanes, solid-phase microextraction, iodinated disinfection by-products, iodoform, programmed temperature vaporizer, headspace analysis.

1. Introduction

Iodo-trihalomethanes (I-THMs) are disinfection by-products (DBPs) formed during the oxidative treatment of iodide (I^-) containing waters. Early concerns about I-DBPs arose from their association with medicinal taste and odour in drinking water during the late 1980's [1]. The taste and odour threshold of iodoform (CHI_3) is in the range of 0.02-5 μg/L, and when exceeded can lead to organoleptic problems and consumer complaints [1,2]. Recently, new concerns about human health risks were raised by Plewa *et al.* (2004), who reported that I-DBPs are more genotoxic and mutagenic than their regulated chlorinated and brominated analogues, highlighting iodoorganic compounds should be considered when evaluating drinking water exposures [3,4]. Currently, there is no published standard analytical method for I-THMs in water. Given the recent research interest into I-DBPs, increased occurrence monitoring and research into formation reactions, an improved analytical method that allows the simultaneous quantification of chloro-,bromo-,and iodo-THMs will be of great use to the water quality community.

Iodide is oxidised into hypoiodous acid (HOI) at near neutral pH by disinfectants used in water treatment such as chlorine (HOCl), monochloramine (NH_2Cl) and ozone (O_3). HOI can react with organic compounds including natural organic matter (NOM) producing iodinated disinfection by-product such as I-THMs [5] or be further oxidised to iodate (IO_3^-) [6], which is a desired non-toxic sink of iodine in drinking water [7]. The formation of iodoform is significantly influenced by the disinfectant and its concentration. In the case of chlorine, both iodate and iodoform can be produced. Chloramination or the presence of ammonia during chlorination favours the formation of iodinated organic compounds because monochloramine can oxidize I^- to HOI but cannot further oxidize HOI to IO_3^- [6,8]. Therefore, I-THMs are gaining increasing attention as unregulated DBPs especially in areas where monochloramine is used as a disinfectant [4,9-12].

The analysis of the iodo-trihalomethanes along with the regulated chlorinated and brominated trihalomethanes in water samples in a single run is challenging, because the iodinated trihalomethanes are found at very low concentrations (ng/L range), while the regulated chlorinated and brominated trihalomethanes are present at much higher concentrations (above the μg/L range) [4,5,9,13,14]. One of the most common and sensitive extraction techniques is liquid-liquid extraction (LLE). However, this method requires some sample preparation, uses a lot of solvent and is time-consuming. An alternative method to

extract and concentrate analytes is the use of solid-phase microextraction (SPME). SPME is a solvent-free concentration technique based on the adsorption of the analytes onto a fiber coated with an adsorbent phase. The fiber can be either introduced into the headspace (HS) of a vial or straight into a liquid sample, until a distribution equilibrium of the analytes has been reached between the sample and the fiber coating. This method has the advantage of being rapid, sensitive, simple (sample preparation usually only involves salt addition) and can be fully automated. Since SPME was first introduced [15], it has been successfully applied to a wide range of volatile analytes, including for extraction of the four regulated THMs [16-20]. The most commonly used SPME fiber for the analysis of regulated THMs is the carboxen/polydimethylsiloxane (CAR/PDMS) [16-18]. Several methods have been reported in the literature for the quantification of regulated THMs [14,21-24], with the majority employing gas chromatography (GC) with either electron capture detection (ECD) or mass spectrometry (MS). Recently, Charrois (2011) reviewed DBPs analytical methods including I-THMs [25]. Cancho *et al*. (1999) studied the efficiency of different extraction methods for the analysis of I-THMs and found that LLE was the most sensitive [13]. In fact, LLE is currently the primary method used for the analysis of I-THMs in water [4,5,9,11]. Only one article reported the use of SPME for extraction of I-THMs from drinking water so far [26]. Cancho *et al*. (2000) reported that the carbowax/divinylbenzene (carbowax/DVB) fiber coupled with GC/ECD provides similar precision to LLE-GC/ECD methods for the analysis of I-THMs [13]. A HS SPME-GC/MS method was also developed using the CAR/PDMS fiber for the analysis of dichloroiodomethane ($CHCl_2I$) and bromochloroiodomethane (CHBrClI) in blood samples [27].

The aim of the present study was to develop a simple and sensitive method allowing the simultaneous analyse of 10 THMs species (including the four regulated chlorinated and brominated THMs and six iodinated THMs) in water samples. To address this challenge, the polarity and the pore size of 5 SPME fiber coatings were compared in order to select the most suitable fiber. A HS SPME procedure, using a programmed temperature vaporizer inlet (PTV) coupled with a cryogenic trap during GC-MS analysis, was then optimised and the limits of detection (LOD), repeatability, reproducibility and linearity range were determined. Thus, we report here the first analytical method for the simultaneous detection of these 10 THMs in water at ng/L levels. Our improved method considerably enhances the repeatability, reproducibility

and recovery of all analytes compared to existing techniques. Finally, real samples from a wastewater treatment plant were analysed and I-THMs were detected at ng/L levels in real samples. This method improves and optimizes the current state-of-the-art analytical techniques for detection of THMs in water.

2. Experimental

2.1. Chemicals and materials

Methanol (HPLC-grade; MeOH) was aquired from Thermo Fisher (Scoresby, Victoria, Australia). 1,2-dibromopropane, iodoform (CHI_3), chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) were purchased from Sigma-Aldrich (Castle Hill, NSW, Australia) at the highest purity. Iodo-trihalomethanes (I-THMs), (bromodiiodomethane ($CHBrI_2$), (CHBrClI), chlorodiiodomethane ($CHClI_2$), dibromoiodomethane ($CHBr_2I$), ($CHCl_2I$)) were purchased from Orchid Cellmark (New Westminster, BC, Canada). Sodium sulfate (Na_2SO_4) was purchased from Sigma Aldrich (Castle Hill, NSW, Australia). SPME fibers as follows were obtained from Supelco (Castle Hill, NSW, Australia): carboxen/polydimethylsiloxane (CAR/PDMS; 85 μm), polydimethylsiloxane (PDMS; 100 μm), polydimethylsiloxane/divinylbenzene (PDMS/DVB; 65 μm), carboxen/polydimethylsiloxane/divinylbenzene (DVB/CAR/PDMS; 50/30 μm), Carbowax/DVB (70 μm). Fibers were initially conditioned in accordance to the supplier's instructions.

2.2. Standard solutions

A stock standard solution containing each THM at 1 g/L was prepared in MeOH. An intermediate concentration (10 mg/L) THM standard solution was prepared in MeOH. Solutions were stored in the dark at -20^{o}C for a maximum of one month. Working standard solutions were prepared daily in ultra pure water. The internal standard (IS) solution (1,2-dibromopropane) was prepared in MeOH at a concentration of 5 mg/L. The THM standards used for calibration and samples were spiked with 10 μL of internal standards solutions to achieve a concentration of 5 μg/L.

2.3. GC-MS conditions

A Gerstel MPS2 multifunction autosampler was used to perform automated SPME injections. The autosampler was coupled to a programmed temperature vaporizer (PTV) inlet (CIS-4; Gerstel, Baltimore, MD, USA). Experiments were carried out with a Agilent 6890N GC interfaced with a Agilent 5975 Network Mass Selective Detector. The separation was carried out on a 30 m x 0.25 mm ID ZB-5 (Phenomenex®) column with a film thickness of 1 μm.

Optimal GC-MS conditions were determined, as measured by maximum sensitivity, baseline separation of analytes and Gaussian peak shapes. Using a cryogenic trap cooled with liquid CO_2, the GC inlet was operated in splitless mode at -20°C to permit trapping of the analytes at the head of the column. The oven temperature program was as follows: -20 °C for 7.65 min, then increased at a rate of 50°C/min to 80°C held at 80°C for 6 min, then ramped to 220°C at 10°C/min, held at 220°C for 1 min, then ramped to 300°C at 50°C/min and held at 300°C for 3 min (total run time = 35 min) . Helium was used as the carrier gas at a constant flow of 0.7 mL/min. The optimised conditions gave a good separation of the chromatographic peaks for the analysis of the 10 THMs and the IS (**Figure 1**).

Detection of analytes was carried out using a mass spectrometer in electron impact (EI) ionisation mode at 70 eV. The mass spectrometer quadrupole temperature was set at 150°C and the mass spectrometer source at 230°C. For improved sensitivity, the compounds were quantified in selected ions monitoring (SIM) mode and split into 2 groups. In the first group, 13 mass to charge ratios (m/z) were selected, and in the second group 9 m/z, all with a dwell time of 40 ms. Appropriate monitoring ions were selected using the signal-to-noise (S/N) of the major fragments obtained during analysis of the pure compounds (**Table 1**). The compounds were identified using their retention times, comparison of the mass spectra data of pure compounds with the Wiley275 and NIST2005 databases and specific diagnostic ion fragments of each component. For each compound several monitoring ions were selected, one for quantification and the others for confirmation. The ratio between the peak area corresponding to the fragment having the highest signal to noise ratio (and not the highest peak area value) and the peak area of the internal standard 1,2-dibromopropane was used for quantification.

2.4. SPME procedure

Amber vials (20 mL) were filled with aliquots of standard solution (10 to 17 mL) containing the 10 analytes or a sample and the internal standard. Anhydrous sodium sulfate previously heated at 400^{o}C for 4 hours was added to each sample (up to 5.5 g). The samples were also incubated at different temperatures and different time ranges to evaluate the volatilisation of the analytes into the headspace. The SPME fiber was suspended in the headspace of the vial to allow the adsorption of the analytes. Adsorption time was varied from 15 to 60 min and the fiber was introduced into the injector for desorption. Desorption times between 2 and 6 min were tested. The selected values of the optimized variables were as follow: 10 ml of sample, 5.5 g of sodium sulphate, 15 min extraction time at 70^{o}C, and 8 min desorption time using the PTV inlet (Section 3.1.2).

2.5. Statistical analysis

Calibration standards for each analyte were from 10 ng/L to 100 µg/L: given this large range of concentrations and since the correlation coefficient (R^2) value is mostly driven by the high concentration standards, the linear regression of each calibration curves was subject to 4 statistical tests using SigmaPlot 10.0. A R^2 value > 0.99, a normality test to check the error distribution and the presence of outlying influential points, a Durbin-Watson statistic test to check if there is a correlation in the residuals to avoid the violation of linearity as in the case of a straight line fitted to data which are growing exponentially and a constant variance test. The linearity range was thus defined according to positive results for all these tests.

2.6 Survey of 10-THMs in an advanced water recycling plant

Samples were collected from an Advanced Water Recycling Plant (AWRP) in Perth, Australia that treats secondary treated wastewater by ultrafiltration (UF), reverse osmosis (RO) and UV disinfection, to produce approximately 5 ML/day of recycled water, recharged to local aquifer as part of a groundwater replenishment trial. In the AWRP, secondary wastewater undergoes chloramination before UF to minimize RO membrane fouling. Samples were taken of secondary wastewater, as well as after chloramination, UF and reverse osmosis to monitor changes in THMs through the AWRP. In order to test the method with additional challenging matrices, primary

wastewater (after clarification) from the wastewater treatment plant, and RO reject water was also tested.

Samples were collected in 1L amber glass bottles, and treated with sodium sulphite (24 mg/L) as a preservation agent. Sample bottles were kept cool (in an ice box) and transported back to the laboratory for analysis, or refrigerated in the dark at 4°C until the time of extraction, which was typically within 24 hours.

3. Results and discussion

3.1. Optimization of the HS SPME procedure for extraction of THMs from water samples.

3.1.1 SPME fiber coating evaluation

The choice of SPME coating is a key factor for achieving optimal extraction efficiencies, resolution and detection limits. Several SPME fibers are used to analyse the regulated THMs: 85 μm CAR/PDMS [16-18], 100 μm PDMS [28], 65 μm PDMS/DVB [20] and 50/30 μm DVB/CAR/PDMS [19]. The 75 μm CAR/PDMS [27], 7 and 100 μm PDMS [26], and 65 μm Carbowax/DVB [26] are the only fibers tested for I-THMs. In this study, all five of these SPME fibers were tested in order to determine the optimum sensitivity for all 10 THMs. Ultra pure water (10 mL) spiked at a concentration of 10 μg/L of each THM and 1,2-dibromopropane at 5 μg/L were analysed. The extraction time was 15 min at 40^{o}C and the desorption time was 2 min at 220^{o}C in splitless mode for all fibers. As shown in **Figure 2** the extraction efficiency is strongly dependent of the nature of the SPME fiber as well as the molecular size of the compounds. Clearly the non-polar PDMS coating is not efficient for adsorbing THMs, as the area counts of both chlorinated and iodinated THMs, except for iodoform, were lower than for the other fibers in our analytical conditions. Previous studies [16-18] reported the CAR/PDMS fiber to be the best option for the analysis of chlorinated and brominated THMs. However, we observed that as the molecular weight of the target molecule increased, the efficiency of the CAR/PDMS decreased and the PDMS/DVB fiber became more efficient at sorbing the analytes (**Figure 2**). Furthermore, the PDMS/DVB fiber was the most efficient at sorbing the analytes for I-THMs. This

behaviour can be explained by the mesoporous pore size of the DVB coating with an average diameter of 17 Å, which are fairly large compared to the CAR micropores with an average diameter of 10 Å. The extraction of the compounds by the fiber is mainly governed by physical retention of the analytes into the pores and not by chemical retentions such as polar or nonpolar interaction. As the atomic radius of the halogens increases in the order chlorine (0.97 Å), bromine (1.12 Å) and iodine (1.32 Å) the molecular size and the volume (**Table 1**) of the corresponding THMs also increases. Since the I-THMs have larger volumes than the corresponding Cl- and Br- THMs, the I-THMs need larger pores for adsorption onto the fiber. The pore diameter of the fiber should be twice the size of the analyte [29], in the case of CHI_3 the cross section of the molecule is 6.20 Å, which makes it difficult to accommodate within the micropores. In contrast $CHCl_3$ has a cross section of 4.77 Å, which is ideal for the CAR/PDMS fiber. Adsorption predictions based on molecular volume and fiber pore sizes were confirmed experimentally. For example, with iodoform; the PDMS fiber gave a better extraction efficiency compared to the CAR/PDMS because the pores of the CAR/PDMS are too small for the iodoform molecules, thus nonpolar-nonpolar interactions from the PDMS fiber led to a higher adsorption of the compounds in this case. The results from the CAR/PDMS/DVB fiber also support this prediction. The CAR/PDMS/DVB fiber is a mix of mesoporous and microporous pores. As shown in **Figure 2** the CAR/PDMS/DVB fiber exhibited an intermediate behaviour with a lower sensitivity for the low molecular weight compounds compared to the CAR/PDMS, and a lower sensitivity for the high molecular weight compounds compared to the PDMS/DVB. On the other hand, the intermediate molecular weight analytes ($CHBr_2I$, $CHClI_2$) were well extracted and this fiber perfectly fitted the purpose of this study. The CAR/PDMS/DVB was therefore selected as a compromise between the smaller and the heavier THMs allowing for the simultaneous analysis of 10 THMs species. The CAR/PDMS/DVB was further compared to the carbowax/DVB used by Silva *et al.*(2006) for the analysis of $CHCl_2I$ and CHBrClI [27]. The extraction efficiency obtained using the carbowax/DVB fibre was found to be ten times lower than the CAR/PDMS/DVB for all THMs (**Figure SI1**) indicating that polarity is not the main mechanism for the retention of the THMs. Hence, the CAR/PDMS/DVB fiber was used in subsequent experiments.

3.1.2 Optimization of desorption conditions

In SPME-GC, the analytes are transfered onto the GC column after thermal desorption from the SPME fiber. The fiber is introduced into the heated GC injection port to volatilise the analytes before separation by the GC column, therefore the injection port temperature and the time of desorption are important parameters and are among several factors that can affect the sensitivity of the analysis. Desorption temperature is limited by the stability of the fiber and the analytes. Significant thermal degradation of iodoform was observed by Frazey *et al.* (1998) for temperatures above 200°C [30]. In this study, therefore desorption temperatures of 160°C, 180°C , 200°C and 220°C in splitless mode were evaluated. The responses were found to be relatively similar at each temperature except for the highest molecular weight compounds ($CHBrI_2$ and CHI_3) where an increased response was observed from 160°C to 200°C and a similar response for 220°C (**Figure SI2**). Considering the thermal stability limitations of iodoform, the injector temperature was fixed at 200°C. When low temperatures were used, analytes were not all efficiently removed from the fiber, resulting in carry-over due to an incomplete desorption of the analytes. To prevent carry-over, different desorption times were investigated. Desorption times from 2 to 6 min were evaluated, with no significant differences in analyte response (**Figure SI3**) and no carry-over of the analytes observed in ultra pure water. However, when matrix effects were investigated (section 3.2.2), some carry-over was observed, likely due to the saturation of the SPME fiber by matrix constituents. As previously explained, we were limited by the thermal stability of the I-THMs for the injector temperature and a longer time of desorption had little effect.

In order to overcome this problem a PTV inlet was then used, which allows application of a temperature gradient program for the injector. The initial injector temperature was 160°C, held for 3 min, then the temperature was slowly increased at 1 °C/s until 270°C. At this time the split vent was opened and the SPME fiber kept in the injector for 3 min at 270°C for rapid regeneration. The use of the PTV injector increased the desorption time of the analytes, however it did not affect the quality of the chromatographic separation since the analytes are trapped at -20°C at the top of the GC column. It also avoided thermodegradation and allowed the complete desorption of all analytes. A great improvement in terms of reproducibility and recovery of analytes was achieved with the use of a PTV inlet.

3.1.3 Optimization of the sample volume

Headspace SPME is based on the equilibrium of analytes among the three phases of the system; the aqueous solution, the headspace (the gas phase) and the SPME coating (the solid phase). The analytes partition between the aqueous and gas phases leading to an equilibrium and thus the concentration of analytes in the headspace is dependent on the headspace volume. The sample volume was varied from 10 mL to 17 mL (**Figure SI4**) in the 20 mL amber vial. For the analysis of almost all THMs an equal volume of solution and headspace was found to give the highest response except for the low molecular weight species ($CHCl_3$ and $CHCl_2Br$) for which a lower headspace volume (12 to 15 mL of sample) was better. This is in agreement with Cho *et al.* (2003), who found a greater relative response when decreasing the headspace volume only for the low molecular weight regulated THMs [17]. A sample volume of 10 mL was then used for the experiments and analysis.

3.1.4 Optimization of the extraction time

In order to evaluate the extraction efficiency of the fiber, the extraction time was varied from 15 to 30 min (**Figure SI5**). Only a slight improvement in the relative response was observed for the 30 min extraction, especially for the higher molecular weight analytes. Several studies have reported the same behaviour with an equilibrium time longer than 30 min for the high molecular weight compounds [20,26,30]. Although the maximum sensitivity obtainable using SPME is achieved at equilibrium conditions, a proportional relationship has already been demonstrated between the amount of analytes adsorbed into the SPME and its initial concentration in the sample [31]. Thus the analytes could be quantified in non-equilibrium conditions. Shorter extraction times may therefore be used to decrease analysis time at the expense of some sensitivity, and in the current study, an extraction time of 15 min was selected for the following experiments and analysis.

3.1.5 Optimization of extraction temperature and salt addition

The addition of salt increases the ionic strength of the solution and results in a variation of the gas/liquid equilibrium, which increases the relative volatility of the analytes in the headspace [32,33]. As shown in **Figure 3** (only 6 THMs are presented to highlight the trend of the results), the extraction efficiency of all analytes increased with the salt concentration even above the salt saturation of the solution, except for the

lower molecular weight THMs ($CHCl_3$ and $CHCl_2Br$) where a maximum was found around 2.5 g. Extraction efficiency was still increasing above 5.5 g, but because the salt concentration had exceeded its saturation point, it was fixed at 5.5 g.

Increasing the temperature during the adsorption period increased the extraction rate for higher molecular weight compounds but also had the adverse effect of decreasing the sensitivity for smaller compounds. Experiments in which the extraction temperature was varied from 30°C to 70°C showed that the response of the small molecules ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$) decreased with increasing temperature (**Figure 4**). However, a clear trend of increasing response for all other analytes with increasing temperature was observed. San Juan *et al.* (2007) showed that the bromoform was better extracted at 70°C (compared to 40°C) because it was the heaviest and least volatile of the THMs they examined and also the least soluble in water [20]. Our results supported this finding, i.e., an improvement of the extraction efficiency was observed when increasing the temperature from 30°C to 70°C for the heavier, less volatile and less soluble compounds like CHI_3 (solubility = 0.1 g/L). Therefore, an extraction temperature of 70°C was selected to maximize the response of the larger molecular weight I-THMs which are likely to be present at lower concentrations than the Cl- and Br-THMs.

3.2 Testing Method performance

3.2.1 SPME linearity, detection limits, precision and accuracy

In order to evaluate the accuracy of the developed HS SPME-GC/MS method for drinking water purposes, the linear range, detection limits, precision and accuracy for each compound were determined. Linearity was studied over 4 orders of magnitude, using 14 concentration levels between 10 ng/L and 100 μg/L for each analyte. This was because I-THMs are likely to be found at ng/L to low μg/L levels [13,34] whereas the regulated THMs are usually found at higher concentrations, usually several μg/L. The linearity was examined by plotting calibration curves of the ratio of the peak areas of the THMs to the peak areas of the internal standard versus the concentration of each analyte. The linear range and the correlation coefficient R^2 relative to each compound are reported in **Table 2**. Linearity was investigated up to 100 μg/L, however, for the highest molecular weight compounds, the calibration curves became exponential at the higher

concentration. This behaviour could not be accounted for by an overloading of the fiber since the opposite slope was observed. Even if a substantial decrease of the IS area was observed for the highest concentration due to a competition for adsorption on the fiber, it does not explain the increasing area relative to the theoretical area arising from the calibration curves. This may mean that for low molecular weight compounds and for the IS, the equilibria between analytes and SPME phase were constant over the whole concentration range tested but that the high molecular weight compounds were preferentially adsorbed at high concentrations. As shown in **Table 2**, the linearity ranges cover at least two orders of magnitude corresponding to the expected concentration of I-THMs (< μg/L) and regulated THMs (> μg/L). Method limits of detection (LOD) and quantification (LOQ) were calculated respectively as the concentration equivalent to *S/N* = 3 and *S/N* = 10 [35] using a 100 ng/L standard for the I-THMs and 1 μg/L for the other THMs by manual *S/N* calculation on unsmoothed chromatograms. LOD ranged from 1 ng/L for CHI_3 to 20 ng/L for $CHCl_3$. Accordingly, LOQs ranged between 4 ng/L for CHI_3 and 68 ng/L for $CHCl_3$ (**Table 2**). Our results demonstrate that the proposed HS SPME-GC/MS method is suitable for measuring THMs at ng/L levels.

The precision of the method was evaluated by determination of the repeatability and reproducibility. The repeatability refers to the analysis of 8 samples in one day and the reproducibility refers to the analysis of a total of 12 samples over 3 different days. **Table 2** shows excellent repeatability ranging from 1 to 9% for a standard of 5 μg/L which is representative of the expected concentrations of regulated THMs. For a lower concentration of 100 ng/L, corresponding to an expected concentration for I-THMs, the repeatability was still very good ranging from 3 to 13% RSD (except for $CHCl_3$ where a RSD of 23% was found because of the high volatility of this analyte), with an average of 10% for the I-THMs. The reproducibility for a standard concentration of 100 ng/L ranged from 10 to 16% RSD (**Table 2**).

3.2.2 Effect of different water matrices

Optimisation of the conditions for desorption of the analytes from the SPME fiber was required in order to minimize potential matrix effects given the large range of concentrations studied. When the ten THM analytes were spiked into real waters and desorption of the analytes from the SPME fiber was conducted at a constant desorption temperature of 200^0C, very low recoveries were obtained. With application of the PTV inlet to apply a temperature gradient program for the desorption process, the recoveries were greatly

enhanced. Standard additions of 1 μg/L were carried out with 4 different waters, a drinking water sourced from groundwater (tapwater), from surfacewater, from a desalination plant and a chloraminated secondary wastewater. The response from all of these samples were compared to a similar standard addition into ultra pure water. Good recoveries (87% to 103% for tapwater, 85% to 98% for surface water, 84% to 96% for seawater and 85% to 91% for secondary wastewater) were obtained for all I-THMs standards from the 4 water-types tested, indicating that matrix effect were negligible for the analysis, even in secondary wastewater.

3.2.3 Analysis of 10-THMs in water samples from an advanced water recycling plant

The optimized HS SPME-GC/MS method was used to quantify the 10 THMs throughout various stage in an advanced water recycling plant in Western Australia. The concentrations of total chlorine, DOC and the 10 THMs are shown in **Table 3**. Previous research has indicated that some disinfection by-products, including THMs, can form within membrane treatment, specifically as a result of the chloramination step protecting RO membranes from excessive biofouling. The behaviour of the regulated THMs is comparable to other studies of disinfection by-products in MF/RO plants in Western Australia [36].

Even though the iodide concentration in the secondary effluent was below 10 μg/L, I-THMs were still detected. $CHCl_2I$, $CHClI_2$ and $CHBrI_2$ were detected at low concentrations ranging from 2 to 13 ng/L. $CHClI_2$ and $CHBrI_2$ were detected in the primary wastewater, while $CHCl_2I$, $CHClI_2$ and $CHBrI_2$ were detected at the post-UF sample. While I-THMs may be expected to have been detected in the post-chloramination sample, it is hypothesized that the contact time with chloramine before sampling was too short for formation of these compounds. Despite the formation of I-THMs within the advanced water recycling plant, RO removed a large proportion of the THMs including the I-THMs, and other DOC. This is also confirmed by the elevated concentrations of THMs found in the RO reject sample.

4. Conclusions

A new HS SPME-GC/MS method was developed for simultaneous analysis of 10 THMs (4 regulated, chlorinated and brominated and 6 unregulated, iodinated) for the first time. Of the five SPME fibers tested, the CAR/PDMS/DVB fiber was selected because this fiber was able to efficiently extract compounds over a wide molecular weight range. After optimisation of the HS SPME parameters and the use of a PTV inlet, detection limits ranging from 1 ng/L for iodoform to 20 ng/L for chloroform were obtained, with a linearity range of at least two orders of magnitude. Good recoveries (84% to 103%) were obtained of THMs that had been spiked into a wide range of treated waters, demonstrating that the method is applicable for analysis of real water samples and that matrix effects were negligible. The occurrence of I-THMs is important for water utilities because of their very low odour threshold, their toxicity and their potential human health effects. We applied this method for determination of I-THMs at ng/L levels at an advanced water recycling plant. Although the detected levels of the regulated THMs were much lower than their typical concentrations in drinking water, simultaneous detection of Cl-, Br- and I-THMs at these low levels can provide insights on the chemistry of halogenated disinfection by-product formation in the process under study. This method is an improvement to existing analytical methods for the analysis of Cl-, Br-, I-THMs because no solvents are used, it is simple, fast and automated and there is no sample pre-treatment required.

5. Acknowledgments

The authors would like to acknowledge funding and support from the Australian Research Council, the Water Corporation, Water Quality Research Australia (WQRA) and GHD Pty Ltd. Technical support from Andrew Chan and Geoff Chidlow at the Curtin Water Quality Research Centre is also gratefully acknowledged.

References

[1] R.C. Hansson, M.J. Henderson, P. Jack, R.D. Taylor, Water Res. 21 (1987) 1265.

[2] A. Bruchet, K. N' Guyen, J. Mallevialle, C. Anselme, Proceedings of AWWA Annual Conference (1989) 125.

[3] M.J. Plewa, E.D. Wagner, S.D. Richardson, A.D. Thruston Jr, Y.T. Woo, A.B. McKague, Environ. Sci. Technol. 38 (2004) 4713.

[4] S.D. Richardson, F. Fasano, J.J. Ellington, F.G. Crumley, K.M. Buettner, J.J. Evans, B.C. Blount, L.K. Silva, T.J. Waite, G.W. Luther, A.B. McKague, R.J. Miltner, E.D. Wagner, M.J. Plewa, Environ. Sci. Technol. 42 (2008) 8330.

[5] Y. Bichsel, U. von Gunten, Environ. Sci. Technol. 34 (2000) 2784.

[6] Y. Bichsel, U. Von Gunten, Environ. Sci. Technol. 33 (1999) 4040.

[7] H. Burgi, T. Schaffner, J.P. Seiler, Thyroid 11 (2001) 449.

[8] N. Karpel Vel Leitner, J. Vessella, M. Dore, B. Legube, Environ. Sci. Technol. 32 (1998) 1680.

[9] J.G. Pressman, S.D. Richardson, T.F. Speth, R.J. Miltner, M.G. Narotsky, E.S. Hunter Iii, G.E. Rice, L.K. Teuschler, A. McDonald, S. Parvez, S.W. Krasner, H.S. Weinberg, A.B. McKague, C.J. Parrett, N. Bodin, R. Chinn, C.F.T. Lee, J.E. Simmons, Environ. Sci. Technol. 44 (2010) 7184.

[10] S.D. Richardson, Anal. Chem. 82 (2006) 4742.

[11] E.M. Smith, M.J. Plewa, C.L. Lindell, S.D. Richardson, W.A. Mitch, Environ. Sci. Technol. 44 (2010) 8446.

[12] H. Gallard, S. Allard, R. Nicolau, U. Von Gunten, J.P. Croue, Environ. Sci. Technol. 43 (2009) 7003.

[13] B. Cancho, F. Ventura, M. Galceran, A. Diaz, S. Ricart, Water Res. 34 (2000) 3380.

[14] R.S. Zhao, W.J. Lao, X.B. Xu, Talanta 62 (2004) 751.

[15] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.

[16] C.V. Antoniou, E.E. Koukouraki, E. Diamadopoulos, J. Chromatogr. A 1132 (2006) 310.

[17] D.H. Cho, S.H. Kong, S.G. Oh, Water Res. 37 (2003) 402.

[18] A.D. Guimaraes, J.J. Carvalho, C. Goncalves, M.D.F. Alpendurada, Int. J. Environ. Anal. Chem. 88 (2008) 151.

[19] A. Lara-Gonzalo, J.E. Sanchez-Uria, E. Segovia-Garcia, A. Sanz-Medel, Talanta 74 (2008) 1455.

[20] P.M. San Juan, J.D. Carrillo, M.T. Tena, J. Chromatogr. A 1139 (2007) 27.

[21] S.M. Pyle, D.F. Gurka, Talanta 41 (1994) 1845.

[22] A.D. Nikolaou, T.D. Lekkas, S.K. Golfinopoulos, M.N. Kostopoulou, Talanta 56 (2002) 717.

[23] N. Vora-adisak, P. Varanusupakul, J. Chromatogr. A 1121 (2006) 236.

[24] J. Kuivinen, H. Johnsson, Water Res. 33 (1999) 1201.

[25] J.W.A. Charrois, in: Encyclopedia of Analytical Chemistry, Robert A. Meyers (Eds.), Analysis of Emerging Disinfection By-Products in Drinking Water, Chichester,2011,.pp.205.

[26] B. Cancho, F. Ventura, M.T. Galceran, J. Chromatogr. 841 (1999) 197.

[27] L.K. Silva, M.A. Bonin, B. McKague, B.C. Blount, J. Anal. Toxicol. 30 (2006) 670.

[28] M.A. Stack, G. Fitzgerald, S. O'Connell, K.J. James, Chemosphere 41 (2000) 1821.

[29] J. Pawliszyn, Solid phase microextraction: theory and practice, Wiley-VCH Inc., New York, 1997.

[30] P.A. Frazey, R.M. Barkley, R.E. Sievers, Anal. Chem. 70 (1998) 638.

[31] J. Ai, Anal. Chem. 69 (1997) 1230.

[32] F.A. Banat, F.A. Abu Al-Rub, J. Simandl, Chem. Eng. Technol. 22 (1999) 761.

[33] H. Takamatsu, S. Ohe, J. Chem. Eng. Data 48 (2003) 277.

[34] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, A.D. Thruston Jr, Environ. Sci. Technol. 40 (2006) 7175.

[35] I. Kristiana, A. Heitz, C. Joll, A. Sathasivan, J. Chromatogr. A 1217 (2010) 5995.

[36] P. Van Buynder, R. Lugg, C. Rodriguez, M. Bromly, J. Filmer, P. Blair, M. Handyside, S. Higginson, N. Turner, O. Lord, P. Taylor, K. Courtney, C. Newby, A. Heitz, K. Linge, J. Blythe, J. Busetti, S. Toze, Premier's Collaborative Research Program (2005-2008): 'Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment' Department of Health, Perth, 2009

Figure captions

Figure 1: Chromatographic separation of 10 trihalomethane (THM) species using headspace solid-phase microextraction GC/MS analysis. THMs: 10 μg/L.; Total ion chromatogram collected in selected-ion monitoring mode; Column: 30 m x 0.25 mm ID ZB-5 Internal standard: 1,2-dibromopropane. Figure 2: Extraction efficiencies of the CAR/PDMS, PDMS/DVB, CAR/PDMS/DVB and PDMS solid-phase microextraction (SPME) fibers normalized to the area count of the fragment m/z 127, and comparison of average fiber coating pore sizes with trihalomethane (THM) molecular weights.

Figure 3: Effect of the addition of sodium sulfate salt on the extraction efficiency of 10 trihalomethanes (THMs). Only six THMs are presented to clarify the trend of the results. Salt concentration from 0 to 0.55 g/mL, THMs : 10 μg/L, desorption temperature: 220^{o}C, extraction temperature: 40^{o}C, desorption time: 2 min, sample volume: 10 mL, adsorption time: 15 min.

Figure 4: Effect of the extraction temperature on the extraction efficiency of 10 trihalomethane (THMs). Sodium sulfate salt concentration 0.25 g/mL, THMs : 1 μg/L, desorption temperature: 200^{o}C, extraction temperature from 30 to 70^{o}C, desorption time: 2 min, sample volume: 10 mL, adsorption time: 15 min.