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Analysis of halonitriles in drinking water using solid-phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

Halonitriles are a class of nitrogen-containing disinfection by-products (DBPs) that have been reported to be more toxic and carcinogenic than the regulated DBPs. While haloacetonitriles (HANs) are often measured in drinking waters, there is little information on the formation, characteristics, and occurrence of other, higher molecular weight halonitriles. Halopropionitriles and halobutyronitriles have been predicted to be highly toxic and carcinogenic, and may have sufficient potency and selectivity to account for epidemiological associations of chlorinated and chloraminated water with adverse health effects. This paper reports on the development, optimisation, and validation of a simple, robust, and sensitive analytical method for the determination of halonitriles in waters, as well as the application of the method to study the formation and characteristics of halonitriles. This is the first reported method development for analysis halopropionitriles and halobutyronitriles, and the first study on their formation and occurrence as DBPs in drinking waters. The new method uses headspace solid-phase microextraction to extract the halonitriles from water, which are then analysed using gas chromatography–mass spectrometry (HS SPME/GC–S). The method demonstrated good sensitivity (detection limits: 0.9–80 ng L^{-1}) and good precision (repeatability: 3.8–12%), and is linear over three orders of magnitude. Matrix effects from raw drinking water containing organic carbon (4.1 mg L^{-1}) were shown to be negligible in the analysis of halonitriles. The optimised method was used to study the stability and persistence of halonitriles in aqueous samples, and the formation and occurrence of halonitriles in waters. Results from laboratory-scale disinfection experiments showed that haloacetonitriles were formed in chlorinated and chloraminated samples, but 2,2-dichloropropionitrile was only measured in chloraminated samples. Results from surveys of several drinking water distribution systems confirmed the laboratory findings.

1. Introduction

The use of disinfectants in drinking water treatment leads to the formation of disinfection by-products (DBPs), some of which have been associated with a number of adverse human health effects such as bladder and colon cancers [1]. As a result of the public health concern associated with DBPs, the concentrations of some DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs) in drinking water are regulated. However, recent advances in the fields of toxicology and epidemiology have shown that some emerging, non-regulated DBPs are more toxic and carcinogenic than the regulated DBPs.

Nitrogen-containing DBPs (N-DBPs) are among the emerging DBPs that present a greater toxicological risk than the regulated DBPs [2]. N-DBPs are represented by a variety of chemical classes, including halonitriles, with haloacetonitriles (HANs) being the most commonly measured and studied sub-group to date [3]. There are nine species of brominated and/or chlorinated HANs that can form in drinking waters: monochloroacetonitrile (MCAN), monobromoacetonitrile (MBAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), trichloroacetonitrile (TCAN), tribromoacetonitrile (TBAN), dibromochloroacetonitrile (DBCAN) and bromodichloroacetonitrile (BDCAN). The most commonly measured HANs in chlorinated and chloraminated waters are DCAN, TCAN, BCAN, and DBAN [4]. The cytotoxicity and genotoxicity of some HANs have been found to be significantly higher than those of the THMs or HAAs [5,6]. Four HANs, MCAN, DCAN, TCAN, and BCAN have been reported to be direct-acting mutagens [7]; BCAN and DBAN were found to initiate tumours when applied to mouse skin [8]; while DCAN and TCAN have been found to cause adverse effects on foetal development [9]. Other halonitriles, such as halopropionitriles

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and halobutyronitriles, have also been qualitatively identified as DBPs [10]. However, there is little information on the formation, characteristics, and occurrence of these halonitriles as DBPs. Halopropionitriles and halobutyronitriles have been predicted to be highly toxic and carcinogenic by quantitative structure–activity relationship (QSAR) and quantitative structure–toxicity relationship (QSTR) analyses, with chronic lowest observed adverse effect levels (LOAELs) of less than 1 mg/kg per day [11]. These LOAEL values suggest that they have sufficient potency and selectivity to account for epidemiological associations of chlorinated and chloraminated water with adverse health effects, and thus their occurrence in potable waters needs further study [11].

In order to investigate the occurrence and the behaviour of halopropionitriles and halobutyronitriles as DBPs, a robust and sensitive analytical method is required. Based on chemical and physical characteristics of halonitriles, gas chromatography–mass spectrometry is appropriate for the analysis of these compounds. Several extraction and pre-concentration methods are available to achieve the required sensitivity, including liquid–liquid extraction (LLE), closed-loop stripping analysis (CLSA), and solid phase microextraction (SPME). Traditionally, LLE has been the method of choice for sample preparation, hence many standard methods for the analysis of DBPs utilise LLE. The most commonly used method for the analysis of four species of HANs (DCAN. DBAN, BCAN, and TCAN), the US EPA Method 551, utilises LLE to extract and concentrate these analytes. However, LLE is time consuming, labour intensive, and often uses large volumes of high purity, toxic solvents [12]. CLSA is potentially a very sensitive method for the analysis of halonitriles due to the very high pre-concentration factor that can be achieved by this method. However, it is labour intensive, and time consuming, and low recoveries of HANs with CLSA have been reported [13]. SPME offers an attractive alternative to LLE and CLSA, since it is a simple, fast, and solvent-free method that involves minimal sample handling and is easily automated. SPME combines sampling and pre-concentration into one step through absorption or adsorption of the analytes from the sample matrix onto a fibre coated with polymeric materials, and allows direct transfer of the analytes into a GC inlet via thermal desorption [14]. An SPME-based method for the analysis of six species of HANs has been reported previously [15], which has good sensitivity and precision. Therefore, SPME was selected as the extraction and pre-concentration method for the analysis of halonitriles.

The objectives of this study were to develop and optimise a method for extraction and quantification of halonitriles, in particular halopropionitriles and halobutyronitriles, at ng L^{-1} concentrations. Using this newly developed analytical method, we also investigated the stability and persistence of halonitriles in aqueous samples to determine conditions that best preserve these compounds. We also studied the formation of halonitriles in laboratory-scale disinfection experiments, and their occurrence in drinking water distribution systems. For these purposes, eight species of halonitriles, for which analytical standards were available, were selected as representatives: six species of HANs (MCAN, MBAN, DCAN, DBAN, BCAN, and TCAN), 2,2-dichloropropionitrile (2,2-DCPN), and 2,2-dibromobutyronitrile (2,2-DBBN). Although HANs were included, the focus of this study was on the longer chain halonitriles, 2,2-DCPN and 2,2-DBBN, and the method was optimised for maximum recovery of these compounds. This is the first report of analytical method development and validation for 2,2-DCPN and 2,2-DBBN, and the first study on the stability of these compounds in aqueous solutions and their formation and occurrence as DBPs in drinking waters.

2. Materials and methods

2.1. Chemicals and materials

Organic solvents (methanol and acetonitrile) were of HPLC grade purity and obtained from Mallinckrodt. Organic compounds (ascorbic acid) and inorganic reagents (KH_2PO_4, Na_2HPO_4, NaOH, HNO_3, $(NH_4)_2SO_4$) were of analytical grade purity, and were used without further purification. Analytical grade anhydrous sodium sulphate was baked at 400 °C for 4 h prior to use to remove organic impurities. Commercially available halonitrile standards were of analytical grade purity, and were used without further purification. Monochloroacetonitrile (MCAN), monobromoacetonitrile (MBAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), and trichloroacetonitrile (TCAN) were obtained from Aldrich as neat standards. Bromochloroacetonitrile (BCAN) was obtained from AccuStandard® as a solution in acetone (5 mg mL^{-1}). 2,2-Dichloropropionitrile (2,2-DCPN) was purchased from Labo Test OHG as a neat standard. 2,2-Dibromobutyronitrile (2,2-DBBN) was synthesised from butyronitrile and *N*-bromosuccinimide following an adaptation of the procedures reported by Merckx and Bruylants [16] and Couvreur and Bruylants [17]. 1,2-Dibromopropane-d_6 used as internal standard in the analysis of halonitriles was obtained from CDN Isotopes. Technical grade sodium hypochlorite (12.5%, w/v) used in the disinfection experiments was obtained from APS Ajax. Two types of SPME fibres (Supelco) were evaluated: 75 μm carboxen-polydimethylsiloxane (CAR-PDMS) and 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS).

2.2. Standard solutions

A stock standard solution (2000 ng μL^{-1}) of each halonitrile was prepared in methanol. Working standard solutions containing a mixture of eight halonitriles at the desired concentration range were prepared by dilution of the stock solutions with methanol. A stock solution of 1,2-dibromopropane-d_6 in methanol (1000 ng μL^{-1}) was prepared as an internal standard solution. The working internal standard solution (25 ng μL^{-1}) was prepared by dilution of the stock solution with methanol.

2.3. Headspace SPME/GC–MS method development and optimisation

The retention time, purity, and experimental mass spectra of the two longer chain halonitriles (2,2,-DCPN and 2,2-DBBN) were initially determined by GC–MS analysis of the organic solution of each compound (via direct liquid injection). The GC–MS conditions for the analysis of halonitriles by HS SPME/GC–MS were then optimised using aqueous solutions of a mixture of halonitriles at concentrations ranging between 20 and 50 μg L^{-1}.

The following factors were considered for the optimisation of the HS SPME/GC–MS procedure: salt concentration, sample volume, sample pH, extraction time and temperature, and desorption temperature. HS SPME of halonitriles was performed using a Gerstel MPS2 Autosampler interfaced with a Hewlett Packard 6890N GC and a Hewlett Packard 5973N MSD. Halonitriles were desorbed from the SPME fibre in the injector port of the GC at 200 °C, under splitless injection mode. GC separation of the halonitriles was carried out using helium as the carrier gas (constant flow of 1.1 mL/min; average velocity 37 cm/s), and a 30 m × 0.25 mm ID ZB-5MS (Phenomenex®) column with a film thickness of 1 μm. The GC oven temperature was programmed as follows: 0 °C for 1 min, heated at 5 °C/min to 200 °C, then increased to 300 °C at 15 °C/min and held for 5 min. A cryogenic unit using liquid CO_2 was used

to cool the oven temperature to 0 °C. The MSD was operated in electron impact (EI) mode (70 eV), and routine analyses were carried out in Selected Ion Monitoring (SIM) mode. Optimisation of the HS SPME/GC–MS method focused on the two longer chain halonitriles: 2,2-DCPN and 2,2-DCBN.

2.4. Analytical method validation

Validation of the HS SPME/GC–MS procedure for the analysis of halonitriles involved evaluation of blank analyses and matrix effects, determination of the precision (repeatability and reproducibility) and sensitivity (detection and determination limits) of the method, and assessment of the linear range of calibration.

2.5. Investigation on the stability of longer chain halonitriles

The effects of several key factors on the stability of halonitriles during storage were investigated at low (0.1 ng L^{-1}) and high (10 μg L^{-1}) concentrations: temperature, pH, presence of chlorine residual, and preservation agent. Aqueous solutions of halonitriles were prepared using high purity water (MilliQ). These solutions were subjected to a pre-determined set of conditions during storage. At days 0, 1, 4, 7, and 14, the concentrations of halonitriles in the samples were measured using HS SPME/GC–MS. The storage time for 'day 0' samples was negligible.

2.6. Sample collection

Untreated water samples were collected from a drinking water reservoir in the Southwest of Western Australia. The samples were transported in amber glass Winchesters (4 L) and stored at 4 °C upon arrival at the laboratory. These samples were used for bench-scale chlorination and chloramination experiments.

The study of the occurrence of halonitriles in drinking water samples involved collection of water samples from selected water treatment plants and distribution systems. Samples were collected in 60 mL vials containing preservation agent (1 g; a mixture of KH_2PO_4 (198 g), Na_2HPO_4 (2.0 g), and ascorbic acid (0.24 g)) which served to quench disinfectant residual and preserve the sample by maintaining the sample pH at 5. Field and trip blanks were also collected in these sampling events to monitor contamination during sampling. Field blanks consisted of sealed vials containing high purity water that were opened and re-sealed at each sampling location. Trip blanks comprised sealed vials containing high purity water that were transported to each site during the sampling trip but were not opened. All samples were analyzed within 2 days of sampling. Water samples from a water treatment plant in western Canada were also collected. The samples were transported to Western Australia, along with a trip blank. The samples were analysed within 3 days of arrival in Western Australia.

2.7. Disinfection experiments

Chlorine dosing solution was prepared by dilution of commercially available sodium hypochlorite solution (12.5%, w/v). Monochloramine dosing solution was prepared following the method described by Cowman and Singer [18]. The untreated water samples (containing 13.1 mg L^{-1} dissolved organic carbon) were subjected to chlorination (30 mg L^{-1} Cl_2) and chloramination (20 mg L^{-1} as Cl_2). Chlorine and chloramine doses were selected to provide disinfectant residuals of 3–5 mg L^{-1} at the end of the experimental period. Chlorination experiments were conducted at pH 7, while chloramination experiments were at pH 8. Phosphate buffers were used for pH adjustments. The experiments were carried out at 20 °C, for 72 h. In each experiment, at various times up to 72 h (t = 1, 24, and 72 h), the residual disinfectant in a subsample of the reaction solution was quenched with a slight excess of aqueous ascorbic acid solution (aliquots of 40 g L^{-1} solution), and the sample was then analysed for eight species of halonitriles.

3. Results and discussion

3.1. Optimisation of GC–MS conditions for the analysis of longer chain halonitriles

The mass spectra of the longer chain halonitriles were not available in published mass spectral databases, therefore the experimental mass spectra of these halonitriles were initially obtained by GC–MS analysis of the organic solution of each compound (via direct liquid injection). Fig. 1 illustrates the mass spectra of the two longer chain halonitriles: 2,2-DCPN and 2,2-DBBN, obtained in SCAN mode. Further analyses of halonitriles were carried out in selected ion monitoring (SIM) mode, using the most abundant characteristic mass ions of each halonitrile, in order to optimise the sensitivity and selectivity of the method. Table 1 gives the characteristic mass (m/z) ions included in the GC–MS analysis for the two longer chain halonitriles, as well as for the HANs.

Optimisation of the GC–MS method tested the effect of the initial temperature of the GC oven and the GC temperature program. Initial temperatures of 35 °C, 10 °C, and 0 °C and initial heating rates of 8 °C/min, 5 °C/min, and 3 °C/min were evaluated (results not presented). Gaussian peak shapes for each halonitrile analyte were obtained using an initial GC oven temperature of 0 °C. Baseline separation of all analytes was achieved with a heating rate of 5 °C/min.

3.2. Optimisation of HS SPME procedure for the analysis of longer chain halonitriles

The development of the headspace (HS) SPME procedure for the analysis of longer chain halonitriles involved consideration and optimisation of the following factors: fibre type, sample pH, salt addition, sample volume, extraction temperature, extraction time, desorption temperature, and desorption time. The range of values evaluated for each factor (i.e. variable) and the corresponding HS SPME parameters (i.e. fixed parameters) are given in Table 2. Experiments to evaluate these factors were conducted using aqueous mixtures of halonitriles (5 μg L^{-1} in MilliQ water) in Teflon-lined screw cap vials (20 mL).

3.2.1. Fibre selection

Two different types of SPME fibres were evaluated in this study, in order to assess their sensitivity and selectivity in the extraction of halonitriles: 75 μm CAR-PDMS fibre and 50/30 μm DVB-CAR-PDMS fibre. These fibres were selected because previous studies have demonstrated that they were effective in extracting nitriles, including HANs, from aqueous solutions [15,19,20]. In this study, the 50/30 μm DVB-CAR-PDMS fibre was found to extract the two longer chain halonitriles more efficiently than the 75 μm CAR-PDMS fibre, as demonstrated by the higher GC–MS responses (based on peak area) achieved when using this fibre (results not presented). Therefore, the 50/30 μm DVB-CAR-PDMS fibre was used in subsequent method optimisation stages.

3.2.2. Salt addition

For SPME carried out in HS mode, the addition of salt to aqueous samples containing neutral organic molecules such as halonitriles has been shown to increase the amount of analyte extracted by the SPME fibre [21]. In order to evaluate the effect of salt addition on the extraction efficiency of halonitriles, various amounts of sodium sulphate were added to the sample (0–40%, w/v), while

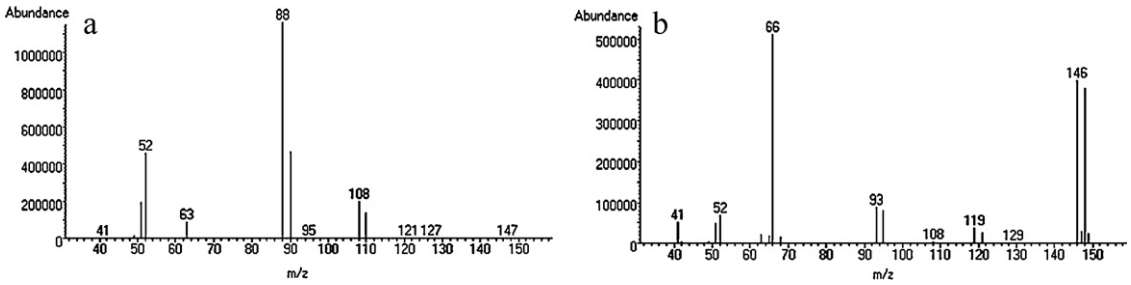

Fig. 1. Experimental mass spectra of the two longer chain halonitriles: (a) 2,2-DCPN and (b) 2,2-DBBN, obtained by GC–MS analysis of the organic solution of each compound in electron impact (EI) mode, via direct liquid injection.

Table 1
Characteristic mass ions (*m*/*z*) of halonitriles selected for GC–MS analysis in SIM mode.

Compound	Characteristic mass ions (m/z)
Chloroacetonitrile (MCAN)	48[a], 50, 75[b], 77
Bromoacetonitrile (MBAN)	79, 81, 119[a], 121[b]
Dichloroacetonitrile (DCAN)	47, 74[a], 76, 82[b], 84
Dibromoacetonitrile (DBAN)	79, 81, 91, 93, 118[a], 120[b], 197, 199, 201
Bromochloroacetonitrile (BCAN)	74[a], 76[b], 118, 120
Trichloroacetonitrile (TCAN)	74, 76, 108[b], 110[a]
2,2-Dichloropropionitrile (2,2-DCPN)	50, 52, 88[a], 90, 108[b], 110
2,2-Dibromobutyronitrile (2,2-DBBN)	66[b], 93, 95, 119, 120, 146[a], 148

[a] Mass ion used for quantification.
[b] Mass ion used for confirmation of analyte identity.

other parameters were kept constant. The addition of salt clearly increased the extraction efficiency of the analytes, by up to 4-fold (Fig. 2). Overall, the addition of 30%, w/v of salt was found to optimise extraction (based on peak area) of the halonitriles. An increase in the addition of salt to 40%, w/v had an adverse effect on the recovery of analytes, possibly due to the presence of undissolved salts, resulting in the sorption of analytes to the particles.

3.2.3. Sample pH

In order to investigate the effect of pH on the HS SPME of the two longer chain halonitriles, the pH of the sample was adjusted to pH 4, 5, 6, and 7 (using dilute sulphuric acid solution or dilute sodium hydroxide solution) prior to extraction. The stability of HANs is influenced by pH and most HANs are stable in weakly acidic conditions [22]. The optimum pH for the analysis of 2,2-DCPN and 2,2-DBBN was found to be pH 6 (Fig. 3).

3.2.4. Sample volume

For HS SPME of volatile compounds, the volume of the gaseous phase needs to be minimized to achieve high sensitivity, since these compounds accumulate in the HS [20]. The effect of sample volume in the analysis of halonitriles was examined by varying the sample volume (8, 10, 12, and 15 mL) in the 20 mL vial. All other parameters were kept constant. For the analysis of the longer chain halonitriles, a sample volume of 12 mL, which corresponded to a HS volume of approximately 8 mL, gave the highest response for both analytes.

3.2.5. Extraction temperature

In HS SPME, the extraction temperature affects both sensitivity and extraction kinetics. The optimum extraction temperature for the analysis of the longer chain halonitriles was determined by observing the variation in the responses of these analytes (based on peak areas), when only the extraction temperature was varied (30 °C, 40 °C, and 50 °C). Similar responses for both halonitriles were observed at extraction temperatures of 30 °C and 40 °C (less than 5% variations); while at 50 °C, the responses for 2,2-DCPN and 2,2-DBBN were reduced by 50% and 25%, respectively. The trend observed in this optimisation process reflects the interactions between the thermodynamic and kinetic aspects of SPME, whereby the extraction yield increases with increasing temperature due to enhanced mass transfer (i.e. kinetic aspect), and reaches a maximum at a particular temperature, then decreases with increasing temperature due to decreasing distribution constant (i.e. thermodynamic aspect) [23]. A previous study by Kristiana [15] showed that the optimum extraction temperature for HANs was 40 °C. Since

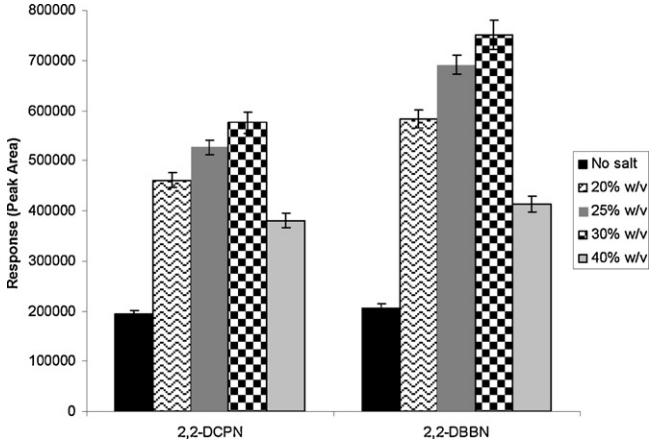

Fig. 2. The effect of salt addition on the extraction of longer chain halonitriles (5 μg L^{-1} in MilliQ water) by HS SPME.

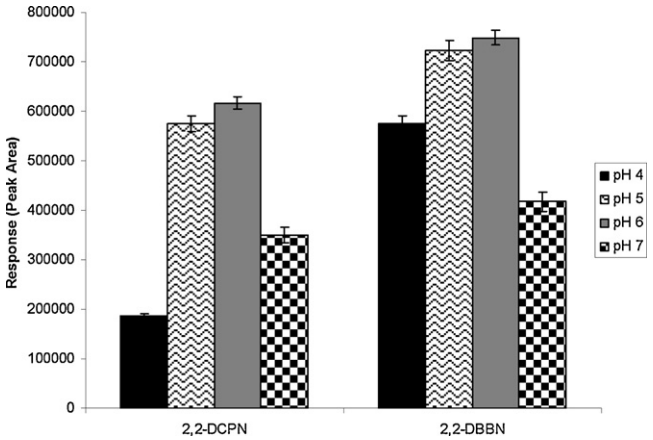

Fig. 3. The effect of sample pH on the extraction of longer chain halonitriles (5 μg L^{-1} in MilliQ water) by HS SPME.

Table 2
Variables evaluated for the optimisation of the HS SPME procedure with the corresponding experimental parameters used.

Parameters	VARIABLES					
	Fibre type	Salt amount	Sample pH	Sample volume	Extraction temperature	Extraction time
Fibre type	75 μm CAR-PDMS 50/30 μm DVB-CAR-PDMS	50/30 μm DVB-CAR-PDMS	50/30 μm DVB-CAR-PDMS	50/30 μm DVB-CAR-PDMS	50/30 μm DVB-CAR-PDMS	50/30 μm DVB-CAR-PDMS
Salt amount	25%, w/v	0, 20, 25, 30, 40% w/v	25%, w/v	25%, w/v	30%, w/v	30%, w/v
Sample pH	5	5	4, 5, 6, 7	6	6	6
Sample volume	10 mL	10 mL	10 mL	8, 10, 12, 15 mL	12 mL	12 mL
Extraction temperature	40 °C	40 °C	40 °C	40 °C	30, 40, 50 °C	40 °C
Extraction time	10 min	10 min	10 min	10 min	10 min	5, 10, 15, 20, 25, 30 min

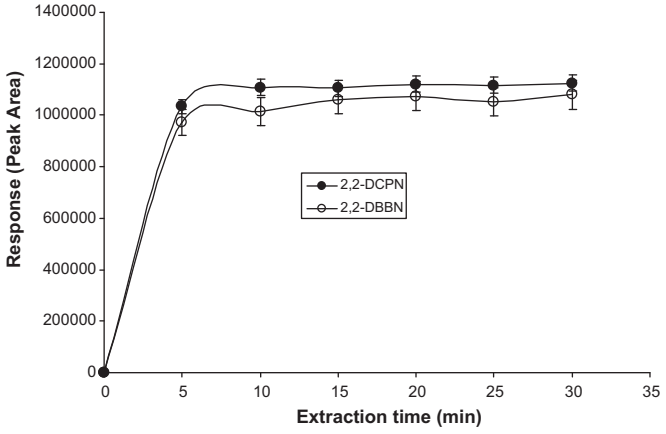

Fig. 4. Extraction time profile of the longer chain halonitriles obtained using optimum extraction conditions (50/30 μm DVB-CAR-PDMS fibre, 30%, w/v of salt, pH 6, sample volume of 12 mL, extraction temperature of 40 °C).

HANs were to be included in the analysis of halonitriles, 40 °C was selected as the extraction temperature for HS SPME of halonitriles.

3.2.6. Extraction time

Extraction time was optimised by evaluating the GC–MS responses corresponding to pre-determined extraction times. The response of 2,2-DCPN was observed to be constant, within experimental error, after an extraction time of 10 min, while the equilibration time for 2,2-DBBN was found to be 15 min (Fig. 4). Considering both analytes, the optimum extraction time for this analysis was determined to be 15 min.

3.2.7. Desorption conditions

Initially, desorption temperatures within the recommended operating temperature for the 50/30 μm DVB-CAR-PDMS fibre (230–270 °C), as specified by the manufacturer, were evaluated. However, thermal degradation of some of the halonitriles was observed at this temperature range, and thus lower desorption temperatures (220 and 200 °C) were tested. The optimum desorption temperature for the two longer chain halonitriles was found to be 200 °C, which was sufficiently low to avoid thermal degradation of analytes. Temperatures lower than 200 °C were not investigated, since a previous study of the analysis of HANs had shown that carryover of analytes was observed at a desorption temperature of 180 °C [19]. A desorption time of 3 min at 200 °C was found to be sufficient to completely desorb all analytes, since no carryover of analytes was observed using this optimum desorption temperature and time.

3.3. Inclusion of haloacetonitriles in HS SPME/GC–MS analysis of halonitriles

Although the focus of this study was to develop and optimise an analytical method for 2,2-DCPN and 2,2-DBBN, the HANs were included in the method, in order to provide more comprehensive information on the formation and occurrence of halonitriles. In this study, six species of HANs (MCAN, MBAN, DCAN, DBAN, BCAN, and TCAN) were included. The optimum conditions for the analysis of the HANs, determined in a separate study [15], were different to those used for analysis of 2,2-DCPN and 2,2-DBBN and it was necessary to compromise on some method parameters, specifically pH and the equilibrium/extraction time. For the analysis of HANs, the optimum pH was 5, compared with pH 6 for the two longer chain halonitriles; and the optimum extraction time was 30 min, compared with 15 min for the two longer chain halonitriles. For the analysis of all of the halonitriles, the extraction time was set

Table 3
Optimum conditions for HS SPME of halonitriles.

Parameter	Optimum conditions
Fibre type	50/30 μm DVB/CAR/PDMS fibre
Salt amount	30%, w/v
Sample volume	12 mL in 20-mL vial
Sample pH	5
Extraction temperature	40 °C
Extraction time	15 min
Desorption temperature	200 °C

at 15 min and pH 5 was selected as the optimum pH. Although the equilibration time for HANs was longer than 15 min, quantitative analysis of HANs at non-equilibrium conditions was still possible, since automation of the HS SPME procedure allowed agitation and sampling time and conditions to be kept constant. The responses of 2,2-DCPN and 2,2-DBBN (based on peak areas) were only slightly higher at pH 6 than at pH 5 (Fig. 3), therefore the selection of pH 5 did not significantly affect the extraction of the longer chain halonitriles, but improved the extraction of HANs. The conditions selected as optimal for the analysis of all of the halonitriles, including HANs and the longer chain halonitriles, in a single method are listed in Table 3.

For further confirmation, the optimised conditions for HS SPME/GC–MS analysis of halonitriles were used to analyse aqueous solutions containing all eight species of halonitriles. The resulting chromatograms showed that there was no coelution of target analytes, and interferences between the different species of halonitriles were not observed. Moreover, the chromatographic responses of the longer chain halonitriles were not affected by the presence of the six species of HANs, even when the latter were present at significantly higher (up to 100-fold) concentrations, as would be expected in real water samples. This study showed that HANs can be simultaneously analyzed with 2,2-DCPN and 2,2-DBBN.

3.4. SPME fibre selectivity

Significant differences in the analytical responses in HS SPME/GC–MS were observed between the different halonitriles in this study, suggesting that some of the compounds were preferentially sorbed or recovered from aqueous solution. As shown in Fig. 5, chromatograms from HS SPME/GC–MS analyses of aqueous solutions containing all eight species of halonitriles at the same concentrations showed significantly higher responses for the longer chain halonitriles, compared to those of HANs. Among the six HANs species, different magnitudes of responses were also observed, with the following trend: TCAN > DCAN > DBAN ≈ BCAN > MBAN ≈ MCAN. These trends are different to those observed in the GC–MS analysis of an organic solution containing all eight species of halonitriles at the same concentrations (by direct injection), as shown in the Supporting information (Fig. 1), where differences in the responses of the halonitriles were seen due to variations in instrumental responses. In the case of direct injection, the responses were differentiated based on the halogen substituents of the halonitriles, where all eight species of halonitriles had similar molar responses but in terms of relative mass responses (Fig. 1, Supporting information), the four species of chlorinated halonitriles (MCAN, DCAN, TCAN, and 2,2-DCPN) had similar responses which were approximately twice of those of the brominated species (MBAN, DBAN, BCAN, and 2,2-DBBN). However, in HS SPME/GC–MS, some halonitriles seemed to be better volatilised into the headspace than others, resulting in the greater relative responses of these halonitriles. The hydrophilicity, as measured by the octanol–water partition coefficients (K_{ow} or $\log P_{ow}$), of these compounds could explain the observed trend in their relative responses. Compounds with higher K_{ow} are less hydrophilic and thus have higher tendency to be transferred to the headspace. Among the HANs, the trend in the magnitude of their responses closely followed the trend of their K_{ow} values. TCAN, which has the highest K_{ow} value (2.54 at 25 °C), has the highest response. DCAN followed (1.53 at 25 °C), then DBAN (1.30 at 25 °C) and BCAN (1.23 at 25 °C). MCAN (0.14 at 25 °C) and MBAN (0.25 at 25 °C) have the lowest K_{ow} values resulting in their low responses. In addition, there may also be differences in the extent to which the various analytes are adsorbed by the SPME fibre. Based on their K_{ow} values, 2,2-DCPN (1.42 at 25 °C) and 2,2-DBBN (2.18 at 25 °C) should have similar responses to DCAN and TCAN, respectively. However, the magnitude of their responses is significantly higher than these HANs. Compared to the other HANs, 2,2-DCPN and 2,2-DBBN have similar substitution patterns, and they displayed a similar magnitude in response. This suggests that the chemical and physical properties of the SPME fibre coating used in this analysis caused it to be selective towards halonitriles with 2,2-substitution pattern, resulting in the preferential adsorption of these compounds.

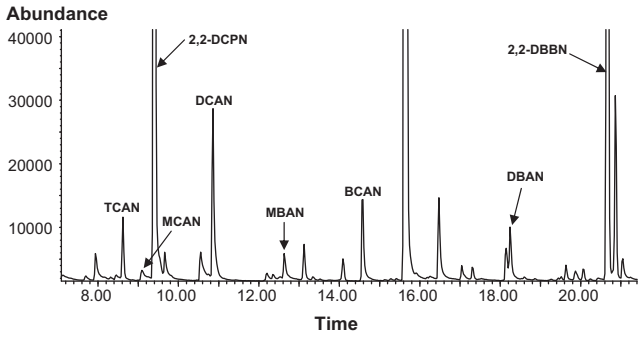

Fig. 5. Chromatogram from HS-SPME/GC–MS analysis of an aqueous mixture containing all eight species of halonitriles (1 μg L^{-1} of each halonitrile).

3.5. Method validation

3.5.1. Analysis of blanks

Analysis of blank samples were carried out to check for interfering peaks as well as to give an indication of the presence of contaminants in the extraction and analysis procedures. Chromatograms of blank samples containing MilliQ water, internal standard, and salt were free from interfering peaks (peaks with the same retention time as the target analytes), indicating that the analytical method was free from interferences.

3.5.2. Matrix effects

For quantification purposes, matrix effects need to be investigated and controlled, since various components of a sample can alter the partitioning between the phases involved in HS SPME [20]. A set of experiments were carried out to simulate possible matrix effects in the analysis of halonitriles in water samples: an untreated local surface water sample (DOC: 4×10 mg L^{-1}) that contained no halonitriles was spiked with a standard solution of halonitriles, at low (20 ng L^{-1}) and high (1 μg L^{-1}) concentrations, and analysed in duplicate using the optimised HS SPME/GC–MS conditions. Good recoveries (90–105%) were obtained for all analytes (Table 4), indicating that matrix effects were negligible using our method, and thus quantification could be done by external calibration if required.

3.5.3. Calibration

Calibration of halonitriles concentrations was achieved by HS SPME/GC–MS analysis of a series of aqueous standards in the range of 2–20,000 ng L^{-1} for each compound. A calibration curve for each

Table 4
Recoveries, linearity, precision, and sensitivity of the HS SPME/GC–MS method for the analysis of halonitriles.

	2,2-DCPN	2,2-DBBN	MCAN	MBAN	DCAN	DBAN	BCAN	TCAN
% Recovery in raw water samples								
20 ng L^{-1}	90	93	N/A[a]	N/A[a]	92	101	96	95
1 μg L^{-1}	102	102	90	93	97	97	99	105
Typical *r* values	0.988–0.999	0.985–0.999	0.975–0.987	0.979–0.991	0.982–0.998	0.981–0.996	0.986–0.995	0.975–0.985
Repeatability (% RSD)								
20 ng L^{-1}	2.8%	4.5%	N/A[a]	N/A[a]	9.4%	11%	9.4%	4.7%
2 μg L^{-1}	3.8%	5.9%	8.9%	12%	6.8%	7.3%	8.2%	5.4%
Reproducibility (% RSD)								
20 ng L^{-1}	21%	26%	N/A[a]	N/A[a]	22%	23%	22%	18%
2 μg L^{-1}	9.2%	15%	15%	14%	14%	17%	15%	10%
Detection limit (ng L^{-1})	0.5	0.9	29	24	2.8	4.4	3.4	2.2
Determination limit (ng L^{-1})	0.9	2.1	80	63	6.5	10	8.9	5.5

[a] N/A: not applicable, below the detection limit.

halonitrile was obtained by plotting the ratios of the peak areas of the analyte and the internal standard vs. the concentration of the analyte. The internal standard (1,2-dibromopropane-d_6) was used in the analysis of halonitriles in order to compensate for instrumental variation. Linear calibrations with high correlation coefficients (>0.975) were achieved for all halonitriles. The range of correlation coefficient (*r*) values obtained for the calibration of halonitrile concentrations is shown in Table 4, and linearity was achieved over three orders of magnitude.

3.5.4. Method precision

The method precision was evaluated by determining the repeatability and the reproducibility at low (20 ng L^{-1}) and high (2 μg L^{-1}) concentrations for each analyte. Repeatability determinations involved measurement of six replicates consecutively, while reproducibility determinations were six replicates analysed over the course of three days. The results, summarized in Table 4, showed that higher % RSDs were obtained for the reproducibility of the method, which is consistent with the higher variability experienced over the course of several days compared to variations within the same day. Higher % RSDs were also obtained for the precision of the method at low concentration, indicating that the method is more sensitive towards systematic errors at low concentrations.

3.5.5. Method sensitivity

The sensitivity of the analytical method was determined from a series of six 'blank' analyses (MilliQ water containing only internal standard and salt). From these analyses, the spectrum noise over the retention time window of each analyte was integrated, the mean and the standard deviation of these areas of the noise were calculated, followed by conversion of these values to equivalent concentrations of halonitriles using the calibration curves. Detection and determination limits of the method were then calculated using the following formula [24]:

$$\text{Detection limit} = \text{mean concentration} + (3 \times \text{standard deviation})$$

$$\text{Determination limit} = \text{mean concentration} + (10 \times \text{standard deviation})$$

Detection and determination limits in parts per trillion range were obtained for all halonitriles (Table 3), indicating good method sensitivity. This is further demonstrated by the extracted ion chromatograms of each halonitrile, at concentrations near their determination limits, which are shown in the Supporting information (Fig. 2). Some variations in the sensitivity of the method were observed for different species of halonitriles. The highest sensitivity was achieved for 2,2-DCPN, while MCAN and MBAN had similar, yet significantly higher detection limits than other halonitriles. This trend is consistent with the observed differences in relative signal response already discussed in Section 3.4.

3.6. Investigation on the stability of the longer chain halonitriles

HANs have been reported to degrade in the presence of free chlorine residual [22,25], and they have been shown to be more stable in chloraminated systems than in chlorinated systems [4]. Several studies have shown that HANs are chemically unstable, with their stability decreasing with increasing pH [22,25]. Commonly used quenching agents such as sodium sulphite and sodium thiosulphate have been found to degrade HANs [26,27], but the use of ascorbic acid does not significantly affect the stability of HANs [25]. Studies on the stability of the longer chain halonitriles in aqueous solution have not been reported but the factors that affect the stability of HANs are expected to have similar effects on the stability of these compounds. Thus, an investigation was carried out to evaluate the effects of several key factors on the stability of 2,2-DCPN and 2,2-DBBN, including storage temperature, pH, the presence of chlorine residual, and the presence of quenching agent. The stability of the six HANs and the longer chain halonitriles in water at two concentration levels (100 ng L^{-1} and 10 μg L^{-1}) was evaluated over 14 days.

The effect of storage temperature on the stability of the two longer chain halonitriles, at the two concentration levels, is demonstrated (as normalised response) in Fig. 6. Overall, there was no significant difference between samples stored at room temperature and under refrigeration, which suggests that, under these conditions, temperature plays a minor role in the degradation of 2,2-DCPN and 2,2-DBBN. Similar trends were also observed for the six species of HANs (results not shown), where there was no significant difference (at 95% confidence interval) in the GC responses of HANs in samples stored at 22 °C compared to those stored at 4 °C. Therefore, it can be concluded that temperature is not a critical factor in maintaining the stability of halonitriles during storage, as long as it is at or below 22 °C.

HANs are known to degrade with increasing pH [22], but pH did not appear to have any significant effect on the stability of the longer chain halonitriles (Fig. 7). Our study was consistent with previous studies (e.g. Glezer et al. [22]), confirming that the stability of all six species of HANs was adversely affected by increasing pH. For example, TCAN degraded with increasing sample pH (Fig. 7c) and, therefore, halonitriles, especially HANs, need to be preserved at pH 5 during storage.

The presence of chlorine residual did not have any significant effect on the stability of 2,2-DCPN (Fig. 8a), while 2,2-DBBN was found to be relatively stable up to 7 days of storage, but was significantly degraded after 14 days of storage (Fig. 8b). As expected, the six species of HANs were not stable in the presence of chlorine

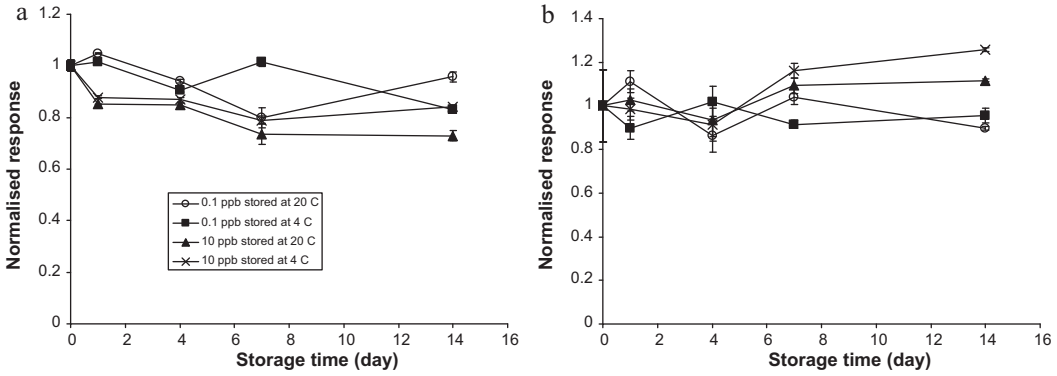

Fig. 6. The effect of storage temperature on the stability of (a) 2,2-DCPN and (b) 2,2-DBBN (normalised response = ratio of chromatographic response measured for each sample to the corresponding chromatographic response measured on day 0).

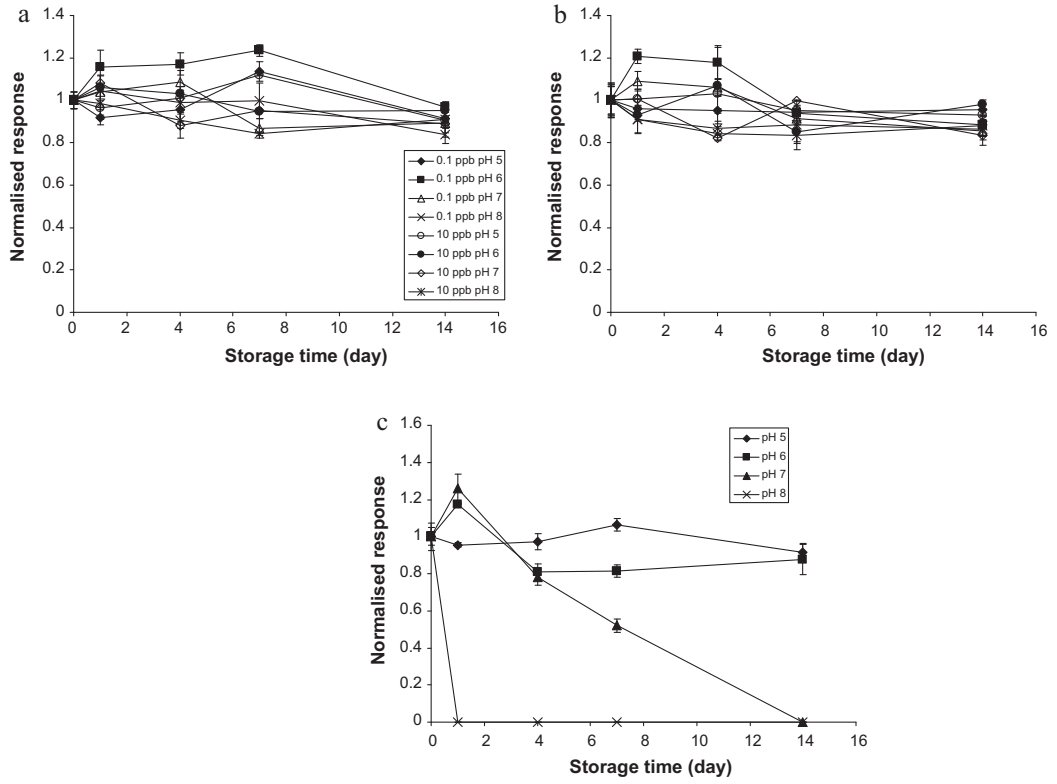

Fig. 7. The effect of pH on the stability of (a) 2,2-DCPN (at 0.1 and 10 μg L^{-1}), (b) 2,2-DBBN (at 0.1 and 10 μg L^{-1}), and (c) TCAN (at 10 μg L^{-1}) in aqueous samples (normalised response = ratio of chromatographic response measured for each sample to the corresponding chromatographic response measured on day 0).

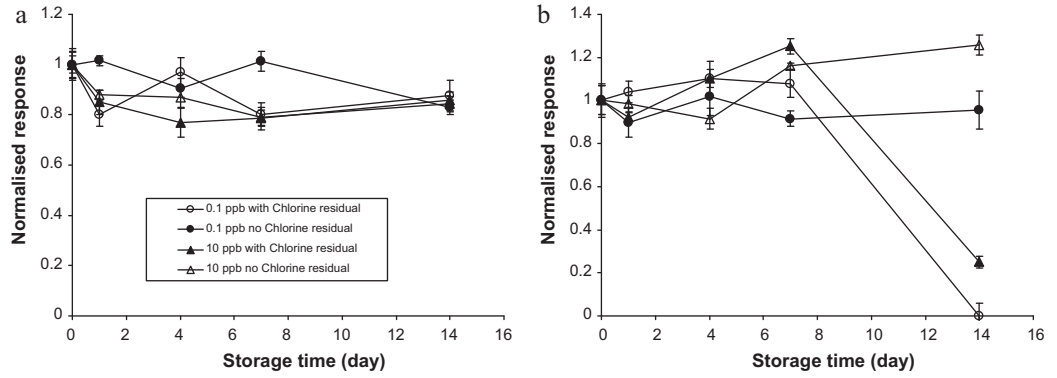

Fig. 8. The effect of the presence of chlorine residual (1–2 mg L^{-1} Cl_2) on the stability of (a) 2,2-DCPN and (b) 2,2-DBBN (normalised response = ratio of chromatographic response measured for each sample to the corresponding chromatographic response measured on day 0).

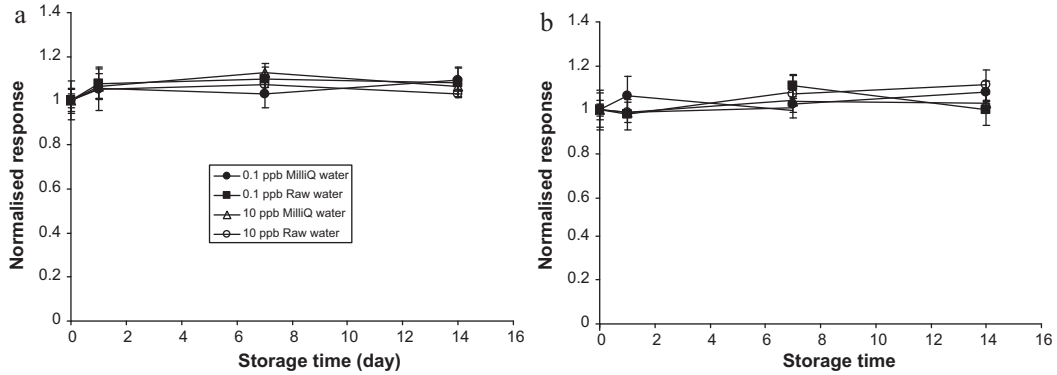

Fig. 9. Variations in the normalised responses of (a) 2,2-DCPN and (b) 2,2-DCBN following the application of the best practice conditions (storage under refrigeration and addition of buffered ascorbic acid as quenching agent) to water samples (normalised response = ratio of chromatographic response measured for each sample to the corresponding chromatographic response measured on day 0).

residual, showing signs of degradation even after one day of storage (results not shown). Overall, the presence of chlorine residual (1–2 mg L^{-1}) was shown to have adverse effects on the stability of halonitriles, and thus chlorine residuals in water samples need to be quenched to preserve halonitriles prior to analysis.

Since a quenching agent is required to eliminate chlorine residual in water samples to preserve halonitriles during storage, the effect of several quenching agents on the stability of halonitriles was also investigated. Previous studies have indicated that ascorbic acid is the most suitable quenching agent for HANs [25]. Therefore, ascorbic acid was used as the quenching agent in this study. The addition of ascorbic acid solution to the water samples reduced the pH of the samples to 4.80, which is close to the ideal storage pH of 5. Phosphate buffer (mixture of KH_2PO_4 and Na_2HPO_4) can be used to fix the pH of samples to 5. A set of experiments was conducted to investigate the effect of ascorbic acid (buffered and non-buffered) on the stability of the eight halonitriles studied. The results showed that there was no significant difference (at 95% confidence interval) in the GC–MS responses of the eight halonitriles in samples stored in the presence of ascorbic acid (non-buffered) compared to those stored in the presence of buffered ascorbic acid. Considering the variety of pH values in water samples, the use of buffered ascorbic acid as quenching agent is preferred, since in waters with relatively high pH, the addition of ascorbic acid on its own may not be sufficient to lower the pH of the water sample to pH ~5.

Investigation of the factors affecting the stability of halonitriles in water samples provided a set of conditions that can be regarded as 'best practice' for sample preservation prior to halonitriles analysis: sample storage under refrigeration, addition of buffered ascorbic acid to quench disinfectant residual and maintenance of the sample pH at pH 5. To complete the investigation on factors affecting the stability of halonitriles in water samples, the effectiveness of these conditions in real water samples was evaluated. The best practice conditions determined in this study were found to be effective in preserving 2,2-DCPN and 2,2-DBBN during storage (Fig. 9). Similar trends were also observed for the six species of HANs. Therefore, these conditions should be applied for sample preservation for halonitriles analysis.

3.7. Formation of halonitriles in chlorination and chloramination

The formation of halonitriles in chlorination and chloramination of a raw (untreated) water sample under laboratory conditions was investigated. DCAN was detected in the chlorinated samples, but not in the chloraminated samples. BCAN and TCAN were detected in the chloraminated samples, but not in the chlorinated samples. The longer chain halonitriles were not detected in any of the chlorinated samples. However, 2,2-DCPN was consistently measured in the chloraminated samples, suggesting that the longer chain halonitriles are more likely to be formed during chloramination than chlorination. The concentrations of 2,2-DCPN increased in the first 24 h, with 100 ng L^{-1} measured at t = 1 h and 115 ng L^{-1} at t = 24 h, then decreased by t = 72 h to 75 ng L^{-1}. The presence of a high concentration of chloramine residual (4.8–12 mg L^{-1}) in the sample during the experimental period may have caused the observed degradation of 2,2-DCPN. The effect of chloramine residual on the stability of halonitriles was not further investigated in this study.

3.8. Occurrence of halonitriles in drinking water distribution system

The occurrence of halonitriles in samples from selected drinking water distribution systems in Western Australia (GF and WN distribution systems) and western Canada (CA) was evaluated using the optimised HS SPME/GC–MS method, with results listed in Table 5. The GF distribution system was chloraminated, while the WN distribution system was chlorinated. CA-1 sample was a raw surface

Table 5
Concentrations (ng L^{-1}) of halonitriles measured in the drinking waters samples collected from water treatment plants and distribution systems.

Sample	Halonitriles (ng L^{-1})[a]				
	2,2-DCPN	DCAN	DBAN	BCAN	TCAN
GF-1	<0.5	870	<4.4	<3.4	10
GF-2	<0.5	120	<4.4	300	<2.2
GF-3	<0.5	350	<4.4	830	<2.2
GF-4	<0.5	330	<4.4	860	<2.2
GF-5	<0.5	60	<4.4	760	<2.2
GF-6	<0.5	120	40	540	<2.2
GF-7	<0.5	260	<4.4	720	<2.2
GF-8	<0.5	500	910	<3.4	5
GF-9	<0.5	540	1260	<3.4	18
GF-10	<0.5	540	1050	<3.4	12
GF-11	<0.5	230	<4.4	570	<2.2
GF-12	<0.5	20	<4.4	<3.4	<2.2
GF-13	<0.5	100	<4.4	<3.4	<2.2
GF-14	<0.5	180	<4.4	650	<2.2
GF-15	<0.5	410	<4.4	190	<2.2
GF-16	<0.5	2950	2520	2100	210
GF-17	<0.5	150	470	190	<2.2
GF-18	<0.5	2650	1770	1510	90
WN-1	<0.5	<2.8	<4.4	<3.4	<2.2
WN-2	<0.5	300	100	600	<2.2
WN-3	<0.5	1400	2300	1700	<2.2
WN-4	<0.5	700	3100	3800	<2.2
CA-1	<0.5	<2.8	<4.4	<3.4	<2.2
CA-2	8	130	<4.4	<3.4	<2.2

[a] Other halonitriles species were measured below the detection limits in all samples; concentrations reported are averages of duplicate measurements.

water sample, while CA-2 sample was collected from a chloraminated distribution system. Four species of HANs were detected in the GF samples (DCAN, BCAN, DBAN, and TCAN), while three species of HANs (DCAN, BCAN, DBAN) were detected in the WN samples. 2,2-DCPN and 2,2-DBBN were not detected in any samples from Western Australia, but 2,2-DCPN was measured in the CA-2 sample, together with DCAN. The results suggest that the abundance of precursor materials of halonitriles (NOM measured as DOC) influenced the formation of halonitriles, especially 2,2-DCPN. For example, in samples collected from Western Australian distribution systems, where the DOC concentrations ranged from 1.8 to 4.3 mg L^{-1}, 2,2-DCPN was not detected (<0.5 ng L^{-1}). However, the CA-2 sample, which had a higher DOC concentration (8.6 mg L^{-1}), contained 2,2-DCPN at 8 ng L^{-1}. 2,2-DCPN was also consistently measured in the laboratory-scale study (Section 3.7) where the DOC concentration in the samples was 13.1 mg L^{-1}.

4. Conclusions

A HS SPME/GC–MS method for the analysis of six species of HANs and two new DBPs, longer chain halonitriles (2,2-DCPN and 2,2-DBBN) was developed, optimised, and validated. The method is rapid and simple with good selectivity, sensitivity, linearity, and precision, free from interferences. It is very likely that the method can also be extended to include the analysis of other longer chain halonitriles which have also been implicated in the QSAR and QSTR analyses (2,2-dibromopropionitrile, 2-bromo-2-chloropropionitrile, 2,2-dichlorobutyronitrile, and 2-bromo-2-chlorobutyronitrile), and this possibility needs to be investigated when standard materials for these compounds become available. The method was used to study the stability and persistence of halonitriles in aqueous samples as well as the formation and occurrence of halonitriles in chlorinated or chloraminated drinking waters. Factors that affect the stability of HANs (pH, presence of chlorine residual) did not appear to affect the stability of the longer chain halonitriles. A 'best practice' procedure for the preservation of water samples to be analyzed for halonitriles was determined from the results of the stability study. This involved the addition of buffered ascorbic acid to water samples, in order to eliminate disinfectant residual as well as to maintain the pH of the sample at 5, and storage of samples under refrigeration. Without preservation, it is recommended that samples be analyzed immediately, to minimize analyte degradation. The method provides a means to investigate the formation and occurrence of halonitriles in source waters and in drinking water distribution systems. Further studies are needed to gain insights into the precursor materials of halonitriles, the conditions that promote their formation, and their occurrence in drinking waters. This new analytical method will assist in these endeavours.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.005.

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