Application of automated solid-phase microextraction to determine haloacetonitriles, haloketones, and chloropicrin in Canadian drinking water

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ABSTRACT

An automated headspace solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC-MS) method was developed to monitor the occurrence of selected haloacetonitriles (HANs), haloketones (HKs), and chloropicrin (CP) in drinking water supplies. The method was rapid with analysis time of 30 min, including extraction and chromatographic run. Chemical ionization (CI) was used to increase the sensitivity of the method for the HKs. SPME fibers with seven different coatings including commercial polyacrylate (PA), carbowax/divinylbenzene (CW/DVB), polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carboxen/polydimethylsiloxane (CAR/PDMS), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), and a novel custom-made polydimethylsiloxane/divinylbenzene-N-vinylpyrrolidone (PDMS/DVB-NVP) were evaluated. The DVB/CAR/PDMS fiber was found more suitable for the range of the analytes and the novel PDMS/DVB-NVP fiber more efficient for the brominated acetonitriles under the experimental conditions. Method detection limits (MDLs) for the chlorinated acetonitriles and CP varied between 2 and 40 ng/L and for the brominated acetonitriles and HKs between 100 and 180 ng/L. Relative standard deviations (RSD %) of measurements were 4–7%. The method was applied in parallel with a liquid–liquid extraction gas chromatography electron capture detection (LLE-GC-ECD) method (EPA Method 551.1) to the analysis of drinking water samples from eight Canadian water treatment and distribution systems. The results generated by the two methods showed good agreement.

Key words | Canadian drinking water analysis, chloropicrin, disinfection by-products (DBPs), haloacetonitriles, haloketones, solid-phase microextraction (SPME)

INTRODUCTION

Disinfection of drinking water by chlorination is among the most successful public health measures ever implemented to control pathogens and protect the public from waterborne diseases. However, chemical disinfection itself results in the formation of many disinfection by-products (DBPs) in drinking water by the reaction of disinfectants (chlorine, chloramines, chlorine dioxide, and ozone) with naturally occurring organic matter in water. Since the first discovery of DBPs in the 1970s (Bellar et al. 1974; Rook 1974), toxicological and epidemiological studies have identified potential adverse health effects (developmental, reproductive, and carcinogenic) of some DBPs (Weisburger 1977; Bull et al. 1985; Muellner et al. 2007; USEPA-ICR 2009).

The predominant by-products that result from the chlorination of drinking water are trihalomethanes and haloacetic acids, which have been regulated in many countries. In addition to these, haloketones (HKs) and nitrogenous
disinfection by-products (N-DBPs) such as haloacetonitriles (HANs) and halonitromethanes can be formed in drinking water (Zhang et al. 2000; Yang et al. 2007). The levels of HANs and other N-DBPs in treated waters are often increased when chloramine is used as a disinfecting agent, or when nitrogen-containing compounds of natural origin are present in source waters (Richardson et al. 2007; Lipscomb et al. 2009). Compared to carbon-based DBPs (i.e., DBPs without a nitrogen), the N-DBPs are more chemically reactive and thus potentially more toxic (Richardson et al. 2007). As a result, the US Environmental Protection Agency (EPA) has cited the N-DBPs, including HANs, as research priorities (Weinberg et al. 2002) and encouraged further toxicology studies, as well as development of new techniques for measurement and monitoring of these analytes in drinking water. Health Canada has also recently approved a drinking water guideline for a N-DBP, N-nitrosodimethylamine (NDMA), at a maximum acceptable limit of 40 ng/L (Health Canada 2010).

The common HAN compounds found in drinking water are trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) (Krasner et al. 1989). These, along with the commonly observed HKs, 1,1-dichloro-2-propanone (1,1-DCP) and 1,1,1-trichloro-2-propanone (1,1,1-TCP), and trichloronitromethane (chloropicrin (CP)) were included in US EPA Information Collection Rule (USEPA-ICR 1996) and may be regulated in the future.

The conventional methods for sample preparation, pre-concentration and quantification of volatile chlorinated by-products in drinking water are based on liquid–liquid extraction (EPA Method 551.1) or purge and trap (EPA Method 524.2) followed by gas chromatography (GC) separation with electron capture (ECD) or mass spectrometry (MS) detection (Hodgeson & Cohen 1990; Munch 1995). Although reliable, the liquid–liquid extraction method is time-consuming, labor-intensive and uses toxic solvents (e.g., methyl-tert-butyl ether (MTBE) in EPA Method 551.1). The purge and trap method is more sensitive, but it has a few shortcomings including possibility of losses of very volatile compounds, foaming of sample, cross-contamination in the purging vessel, and the cost associated with the technique. Simpler methods have also been used, including direct aqueous injection (Wolska et al. 1998) and headspace method (Golfinopoulos et al. 2001); however, they have the disadvantage of lower sensitivity.

Solid-phase microextraction (SPME) is the newest approach in the analysis of volatile chlorinated by-products in drinking water. The technique is simple, rapid, sensitive, and solvent-free. Ease of automation of the entire analytical procedure and low sample volume requirement are other advantages of this technique. SPME has been successfully applied to analysis of THMs in water (Stack et al. 2000; Cho et al. 2003; San Juan et al. 2007; Niri et al. 2008). Scimenti et al. (2002) reported an automated headspace SPME-GC-ECD method for the determination of several DBPs at 12 water treatment plants in the USA. Antoniou et al. (2006) described a manual headspace SPME-GC-ECD method for the determination of chlorinated volatile organic compounds in water and municipal wastewater, evaluating four SPME fibers. Although a wider range of DBPs were analyzed, the total analysis times of these two methods were both above 80 min. In this study, a faster automated HS-SPME-GC-MS method was optimized for the determination of seven target DBPs. Six different commercial SPME fibers along with a new custom-made one were evaluated and the optimized method was applied to the analysis of real samples. Source and drinking water samples from eight water treatment and distribution systems in Canada were analyzed in parallel by the optimized HS-SPME-GC-MS method in the University of Waterloo (Waterloo, ON) and a liquid–liquid extraction gas chromatography electron capture detection (LLE-GC-ECD) method equivalent to EPA Method 551.1 (Williams et al. 1997) in Health Canada Laboratories (Ottawa, ON). The results obtained by the two methods were compared.

### EXPERIMENTAL

#### HS-SPME-GC-MS method

**Chemicals and supplies**

A 2,000 μg/mL halogenated volatiles mixed analytical standard (EPA 551B) [TCAN, DCAN, BCAN, DBAN, CP, 1,1-DCP, 1,1,1-TCP] in acetone was purchased from Supelco (Bellefonte, USA). Secondary stock solutions in the range...
0.01–20 μg/mL were prepared in acetone and stored at 4 °C in amber vials in a refrigerator. Standard aqueous solutions for external calibration were freshly prepared for each set of water samples, prior to analysis, by spiking 5 μL of the appropriate stock solutions into 5 mL of blank water. Natural spring water (ozonized), verified to be free of target analytes and interfering compounds, from Hichinbrooke, QC, bottled by Labrador Laurentienne Inc. (Anjou, QC), was used for blanks and as matrix for fortified samples. The pH of the blank water was adjusted to 4.5 using 0.1 N HCl. Nano-pure water was obtained from a Barnstead/Thermodyne water system (Dubuque, USA). Acetone (analytical grade), methanol for chemical ionization (CI) (analytical grade), headspace vials (10 mL) and the commercial SPME fibers used in the study (polyacrylate (PA) 85 μm, carbowax/divinylbenzene (CW/DVB) 70 μm, polydimethylsiloxane (PDMS) 100 μm, polydimethylsiloxane/divinylbenzene (PDMS/DVB) 65 μm, carboxen/polydimethylsiloxane (CAR/PDMS) 75 μm, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30/μm) were all purchased from Supelco. Oasis HLB particles (30 μm) for the custom-made fiber were purchased from Waters (Mississauga, Canada). Bulk PDMS was provided by Dow Corning Co. (Midland, USA). Helium for GC was ultra-pure and supplied by Praxair (Kitchener, Canada).

Instrumentation and analysis

A Varian 3800 gas chromatograph coupled with a 4000 ion trap MS detector (Varian, Mississauga, Canada) was used. Automated analyses were performed using a CTC Analytics CombiPAL autosampler equipped with SPME agitator (Zwingen, Switzerland) and Cycle Composer software (Version 1.4.0). The injection port was equipped with a SPME insert and was kept splitless during injection. The chromatographic separation was carried out on a RTX-5 amine capillary column (30 m × 0.25 mm × 0.25 μm) from Restek (Bellefonte, PA, USA). The column was initially set at 40 °C for 1 min, ramped at 20 °C/min to 200 °C and held for 1 min) giving a total GC run of 10 min. The helium carrier gas flow rate was constant at 1 mL/min.

The mass spectrometer was operated in the electron ionization (EI) and the CI modes with automatic switching. The EI segments were set for five analytes: TCAN, DCAN, CP, BCAN, DBAN. The CI segments were set for 1,1-DCP and 1,1,1-TCP with methanol as the CI reagent. Identification of analytes was carried out using full SCAN fragmentation (40–250 m/z) and the mass spectra library of the National Institute of Standard and Technology (NIST, USA). Selected ion storage mode was employed for final analyses and the identity of analytes was confirmed by their characteristic ions and the retention times. The ion trap, manifold, and transfer line temperatures were set at 170, 50 and 220 °C, respectively. The EI energy was 70 eV and the emission current was 10 μA. Spectra were recorded using the automatic gain control (AGC) function with a target value of 20,000 for EI and 5,000 for CI. Data acquisition was started after 2 min. The method detection limits (MDLs) were determined using spiked water samples at 4, 10 and 100 ng/L for TCAN, CP, and DCAN, respectively, 200 ng/L for BCAN and DBAN, and 300 ng/L for 1,1-DCP and 1,1,1-TCP. Scanning electron microscopy was performed on a LEO 1530 field emission SEM (Carl Zeiss NTS GmbH, Germany) using 10 nm of gold deposition on the surface before the microscopy.

SPME procedure

All SPME fibers were conditioned before use, according to the manufacturer’s instructions. The desorption temperature for each fiber was set at 5 °C below the maximum operating temperature recommended by the manufacturer. The polydimethylsiloxane/divinylbenzene-N-vinylpyrrolidone (PDMS/DVB-NVP) fiber was conditioned (30 min) at 250 °C and desorbed at the same temperature. Headspace extractions (automated) were performed in triplicate using 5-mL samples and/or calibration standards in 10-mL vials at 30 °C for 15 min. The agitation speed was 500 rpm and the incubation and desorption times were 5 and 2 min, respectively.

LLE-GC-ECD method

Chemicals and supplies

Disinfectant by-products mix (EPA 551B) (TCAN, DCAN, BCAN, DBAN, CP, 1,1-DCP, 1,1,1-TCP) 1 mg/mL, in acetone was purchased from Accustandard (Newhaven, CN, USA). The surrogate standards (dibromomethane and
1,2-dibromopropane) and the recovery standard (1,3-dibromo-
propylene) were purchased from Sigma-Aldrich Canada
(Oakville, ON) and solutions of 1 mg/mL were prepared
in acetone. A mixed solution of 10 mg/L dibromomethane
and 50 mg/L 1,2-dibromopropane was then prepared in
MTBE. MTBE (99.0%), preservative-free, was purchased
from Burdick & Jackson, Honeywell International Inc.
(Muskegon, MI). Anhydrous sodium sulfate (baked at
400 °C for 3 hours) and sodium chloride, biological grade,
containing minimal bromide ion (assayed at 0.001%) were
purchased from Fisher Scientific (Fair Lawn, NJ). Deionized
water (18 M Ω·cm) was obtained from Millipore Super-Q
system. Purified water was prepared by the distillation of
Super-Q water over KMnO₄ and H₂SO₄. Natural spring
water (ozonized), verified to be free of target analytes and
interfering compounds, from Hichinbrooke, QC, bottled by
Labrador Laurentienne Inc. (Anjou, QC), was used for
blanks and as matrix for fortified samples. Blank water pH
was adjusted to 4.5 using 0.1 N HCl. Ascorbic acid from
Fisher Scientific (Fair Lawn, NJ) was used to prepare a
0.114 M solution (0.500 mg/25 mL) in purified water. This
solution was used to quench residual chlorine at the time
of sample collection. Hydrochloric acid (HCl) 36.5–38%
was purchased from EMD Chemicals (Gibbstown, NJ) and
diluted using purified water. A 0.1-N solution of HCl was
used to adjust the pH of water samples to 4.5–5 in the
field and also to adjust the pH of the natural spring water
used for blanks. All gases were ultra-pure grade.

**Instrumentation**

A Varian CP-3800 gas chromatograph equipped with dual
programmable injectors and ECD detectors was used. A DB-
5 capillary column (30 m × 0.25 mm × 1 μm) was used as
the main column and the confirmatory column was a
DB-1 (50 m × 0.25 mm × 1 μm), both Agilent J&W columns
from Agilent Technologies (Santa Clara, CA). Helium
carrier gas flow and nitrogen make-up gas flow for the
ECD were set at 1 and 30 mL/min, respectively. Injector
temperature program was from 80 to 240 °C at a rate of
140 °C/min. Column oven temperature was initially set at
50 °C (hold 4 min), ramped at 1.5 °C/min to 65 °C (hold
1 min); ramped at 5 °C/min to 120 °C (hold 5 min), and
finally ramped at 10 °C/min to 200 °C (hold 5 min). The
conditions were the same for both columns. The MDLs for
all analytes were determined using spiked water samples
at 200 ng/L.

**LLE extraction**

Samples were removed from cold storage and allowed to sit
at ambient temperature for about 30 min. Twelve milliliters
of each water sample were removed using a disposable pip-
ette and 3 mL of extracting solvent (MTBE) containing a
known concentration of the two surrogate standards 1,2-
dibromomethane (surrogate standard 1), 1,3-dibromopro-
pane (surrogate standard 2) were immediately added.
Sodium chloride (16 g) was added to each bottle. Bottles
were capped, shaken for 2 × 1.5 min and then allowed to
stand for 30 min for phase separation. The MTBE extract
was transferred to a 4-mL vial, calibrated at 3.0 mL and
diluted to the calibration mark with pure MTBE. Drying
salt (Na₂SO₄, about 0.1 g) was added and the vial was vor-
texed to allow thorough mixing. Then, 15 μL of the
recovery standard solution (50 ng/μL) was added to obtain
250 pg/μL in the final extract. Extracts were thoroughly
mixed by vortexing and stored in labeled vials at cold
room temperature (about 4 °C) until analysis by GC.

**Water samples**

Samples were collected from eight public water treatment
plants and distribution systems in the winter of 2010 by
Health Canada. Water samples were collected and stabil-
ized under the same protocol for SPME and LLE analysis.
The samples were collected in 65-mL amber bottles pre-
loaded with 0.2 mL ascorbic acid solution (0.114 M) as a
quencher and enough 0.1 N HCl solution to bring the
sample to pH 4.5–5. The required HCl amount was predeter-
mined by titration for each water sample. The bottles were
filled with no headspace from the water tap after running
water for at least 5 min. Water samples were packed in
ice-filled coolers and sent to both participating laboratories
at the University of Waterloo and Health Canada for analy-
sis by SPME-GC-MS and LLE-GC-ECD methods,
respectively. Samples were analyzed less than 4 days after
collection. Stability studies conducted previously by Health
Canada show that water samples stabilized according to
this protocol and kept in a cold, dark room are stable for at least 14 days (unpublished results).

RESULTS AND DISCUSSION

Analytes’ description and properties

The DBPs studied in this research were a group of seven analytes including selected HANs, HKs, and CP. Table 1 presents the analytes’ description, acronym, Chemical Abstracts Service Registry Number (CASRN), and physical properties including molecular weight (MW), boiling point (b.p.), solubility in water, Henry law constant (H) and log of octanol-water partition coefficient (log \( K_{ow} \)). The value of the Henry law constant serves as a measure of volatility of analyte while the log \( K_{ow} \) provides an indication of the preference of the compound for the organic phase (lipophilic compounds) or the water phase (hydrophilic compounds). As can be seen from the table, the analytes exhibit different volatility, lipophilicity, and solubility in water, which affect their extraction from water.

Selection of fiber

To select the most appropriate fiber for the extraction of the analytes, fibers with seven different coatings including PA, CW/DVB, PDMS, PDMS/DVB, CAR/PDMS, DVB/CAR/PDMS, and a custom-made PDMS/DVB-NVP were tested. Figure 1 presents the relative extraction efficiencies of the analytes by the various fibers for 15 min extraction time. As shown, the commercial DVB/CAR/PDMS fiber was more suitable for the range of analytes under the experimental conditions. The CAR/PDMS fiber was found to be 40% more efficient for the extraction of DCAN and 1,1-DCP compared with the DVB/CAR/PDMS fiber. The custom-made PDMS/DVB-NVP fiber was 80% more efficient for the extraction of the brominated acetonitriles (DBAN and BCAN). This fiber was prepared by coating a stainless steel wire (0.005″) with a thin film of PDMS diluted in hexane, covering it with the Oasis HLB particles through shaking inside a small vial, and fixing the particles by PDMS thermal curing. Figure 2 shows the SEM image of the custom-made PDMS/DVB-NVP fiber. Based on the overall results and the versatility of the DVB/CAR/PDMS, this fiber was selected for the rest of the experiments.

Extraction temperature

The extraction temperature 30°C was selected based on volatility of analytes and our previous SPME studies. While increasing temperature is beneficial for headspace extraction of semi-volatiles, it does not significantly improve the extracted amount of volatile species, and rather, results in a decrease in the partition coefficient between fiber and headspace and loss of sensitivity.

Extraction time

Figure 3 illustrates the effect of extraction time on the extraction of the analytes from water for the headspace SPME. To obtain the time profile, extraction times of 15 s, 1 min,
Figure 1 | Comparison of different SPME fibers for the headspace extraction of analytes; 20 μg/L spiked water samples at 30 °C for 15 min.

Figure 2 | SEM image (×95 magnification) of the custom-made PDMS/DVB-NVP fiber.
2 min, 4 min, 8 min, 16 min, 30 min, 60 min, and 120 min were examined using 20 μg/L spiked water samples. The equilibration times varied between 4 min for TCAN to more than 120 min for DBAN. Based on the results and considering the GC run time, a 15 min extraction time was found to be a good compromise allowing good sensitivity for all analytes.

Desorption time

Desorption time and possible carryover of the analytes on the DVB/CAR/PDMS fiber were tested at the injection temperature of 265 °C. Since the analytes are very volatile, they are easily desorbed from the fiber. The optimum desorption time was found to be 2 min leading to complete removal of all analytes from the fiber without carryover.

Chemical ionization

During the optimization procedure it was found that significant background interference impacted the ability of the method to quantify 1,1-DCP and 1,1,1-TCP at low ppb levels in EI mode. At the same time, it was noticed that the major ion fragment on the EI spectra of these analytes was \( m/z = 43 \) with an almost total absence of molecular ion. Therefore, CI with methanol as the reagent was considered as an option to improve the sensitivity. Since an ion trap collects ions over relatively long periods, collisions between analyte and reagent ions are increased. The increased collisions facilitate the possibility of using liquid reagents such as methanol because only low concentrations are needed. For the CI technique, no optimization was performed; rather the instrument was used under the established manufacturer default conditions. Figures 4 and 5 compare the detection of 1,1-DCP and 1,1,1-TCP for 50 μg/L spiked water samples under EI and CI modes. As shown, the application of CI considerably improved the signal-to-noise ratio and the sensitivity of the method for these two analytes, with the molecular ions M⁺ becoming significantly abundant. Therefore, CI with methanol was considered as part of the optimized method and a multi-segment acquisition approach was employed with automatic switching between the ionization modes. The time segments and instrumental conditions for operation of the mass spectrometer are presented in Table 2. Also, a typical chromatogram from HS-SPME-GC-MS analysis of a spiked water sample containing all analytes at 5 μg/L is shown in Figure 6.
Analytical parameters and sample analysis

The calibration curves for all the compounds were established in concentration ranges varying between 0.01 and 20 $\mu$g/L. The correlation coefficients ($R^2$) were satisfactory exceeding 0.9925 (Table 3). The precision of the measurements (relative standard deviations, RSD %) at 2 $\mu$g/L spike level for three replicates ranged from 4 to 7% indicating good repeatability of the method. The MDLs were determined as three times the standard deviation of eight replicates at low concentrations close to the analytes’ detection limits. The MDL for all analytes, including those obtained by the LLE-GC-ECD method, are shown in Table 3. The SPME MDLs for TCAN and CP were lower and for DCAN comparable with those of the LLE method. The MDL values for the rest of the analytes were higher then those obtained by the LLE-GC-ECD method.

The HS-SPME-GC-MS optimized method was applied for analysis of the selected DBPs in real drinking water samples from eight public water treatment and distribution systems in Canada. These samples were collected as part of the National Survey of Disinfection By-Products and Selected Emerging Contaminants in Canadian Drinking Water, 2009–2010. Table 4 describes the characteristics of the water samples, including pH, turbidity, temperature, and total chlorine, as well as disinfection process and population at the region of each water treatment plant. The sites included in Table 4 were randomly selected among the 65 sites of the survey to have samples...
Figure 5 | GC-MS chromatogram and MS spectrum of 1,1,1-TCP for 50 μg/L spiked water samples; EI (top) and CI (bottom). Molecular ion not observed in EI mode, signal-to-noise ratio significantly increased in CI mode.

Table 2 | Operation conditions of the mass spectrometer in selected ion storage mode with automatic switching between EI and CI

<table>
<thead>
<tr>
<th>MS segment</th>
<th>Time range (min)</th>
<th>Ionization mode</th>
<th>Characteristic ions (m/z)(^a)</th>
<th>Mass ranges (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00–2.00</td>
<td>Off</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>2.00–2.75</td>
<td>EI</td>
<td>108, 82, 84, 110</td>
<td>81–84, 107–111</td>
</tr>
<tr>
<td>3</td>
<td>2.75–2.93</td>
<td>EI</td>
<td>74, 76, 82, 84</td>
<td>73–77, 81–84</td>
</tr>
<tr>
<td>5</td>
<td>3.29–3.59</td>
<td>EI</td>
<td>117, 82, 84, 119</td>
<td>81–84, 116–120</td>
</tr>
<tr>
<td>6</td>
<td>3.59–3.80</td>
<td>EI</td>
<td>74, 76, 118, 120</td>
<td>73–77, 117–120</td>
</tr>
<tr>
<td>8</td>
<td>4.40–10.00</td>
<td>EI</td>
<td>118, 79, 81, 120</td>
<td>78–82, 117–121</td>
</tr>
</tbody>
</table>

\(^a\)Quantification ion in italic.
analyzed by two different analytical methods in order to validate the methods. For each water system five samples were collected, representing the raw water source before the treatment plant (R), the treated water at the end of the treatment process (T), and three samples at progressively distant points in the distribution system with increasing residence time (D1, D2, D3). Table 5 shows the results of sample analysis for the occurrence of the selected DBPs by the HS-SPME-GC-MS and the LLE-GC-ECD methods. For most of the water treatment systems, the plant-treated water samples (T) have lower DBPs than the distributed samples (D1, D2, D3). This can be attributed to the fact that in the absence of hydrolysis, higher residence time in an active, oxidizing matrix (free chlorine-containing drinking water) leads to higher concentrations of DBPs in the distribution system samples than the treated samples collected immediately after the treatment plants. For comparison of the results obtained by the two methods, a scattered plot was derived by pooling the data in Table 5. As illustrated in Figure 7, there is good correlation ($R^2 = 0.9217$) between the results obtained by the two methods.

![Chromatogram from HS-SPME-GC-MS analysis of a spiked water sample containing the analytes at 5 μg/L.](image)

**Figure 6** | Chromatogram from HS-SPME-GC-MS analysis of a spiked water sample containing the analytes at 5 μg/L.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linear range (μg/L)</th>
<th>Correlation coefficient ($r^2$)</th>
<th>RSD (n = 3)</th>
<th>HS-SPME-GC-MS MDL (ng/L)</th>
<th>LLE-GC-ECD MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloropicrin</td>
<td>0.02–10</td>
<td>0.9959</td>
<td>4</td>
<td>7</td>
<td>40</td>
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<tr>
<td>Trichloroacetonitrile</td>
<td>0.01–20</td>
<td>0.9997</td>
<td>5</td>
<td>2</td>
<td>30</td>
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<tr>
<td>Dichloroacetonitrile</td>
<td>0.10–20</td>
<td>0.9990</td>
<td>4</td>
<td>40</td>
<td>40</td>
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<tr>
<td>Bromochloroacetonitrile</td>
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<td>0.9925</td>
<td>5</td>
<td>160</td>
<td>30</td>
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<td>Dibromoacetonitrile</td>
<td>0.50–20</td>
<td>0.9964</td>
<td>5</td>
<td>130</td>
<td>30</td>
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<td>1,1-Dichloro-2-propanone</td>
<td>0.30–5</td>
<td>0.9970</td>
<td>7</td>
<td>100</td>
<td>30</td>
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<tr>
<td>1,1,1-Trichloro-2-propanone</td>
<td>0.60–10</td>
<td>0.9977</td>
<td>7</td>
<td>180</td>
<td>30</td>
</tr>
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</table>
Table 4 | Site description and characteristics of the Canadian drinking water samples (winter 2010)

<table>
<thead>
<tr>
<th>Site description and characteristic</th>
<th>WTP-36</th>
<th>WTP-46</th>
<th>WTP-49</th>
<th>WTP-53</th>
<th>WTP-54</th>
<th>WTP-55</th>
<th>WTP-59</th>
<th>WTP-60</th>
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<tbody>
<tr>
<td>Total population supplied</td>
<td>5,000</td>
<td>35,000</td>
<td>58,000</td>
<td>70,000</td>
<td>1,421</td>
<td>10,000</td>
<td>700,000</td>
<td>6,000</td>
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<td>Raw water source</td>
<td>River</td>
<td>River</td>
<td>Lake</td>
<td>Lake</td>
<td>Well</td>
<td>Well</td>
<td>River</td>
<td>Lake</td>
</tr>
<tr>
<td>Raw water pH</td>
<td>7.11</td>
<td>8.11</td>
<td>7.35</td>
<td>6.34</td>
<td>6.71</td>
<td>7.69</td>
<td>8.20</td>
<td>7.91</td>
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<tr>
<td>Raw water turbidity</td>
<td>0.13</td>
<td>6.68</td>
<td>0.42</td>
<td>0.63</td>
<td>2.90</td>
<td>0.12</td>
<td>1.46</td>
<td>0.49</td>
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<tr>
<td>Raw water temp</td>
<td>2.5</td>
<td>1.5</td>
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<td>3</td>
<td>6</td>
<td>7</td>
<td>1</td>
<td>1.5</td>
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<tr>
<td>Treated water pH</td>
<td>7.68</td>
<td>7.51</td>
<td>7.56</td>
<td>5.75</td>
<td>7.08</td>
<td>7.61</td>
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<td>Treated water turbidity</td>
<td>0.70</td>
<td>0.12</td>
<td>0.14</td>
<td>0.75</td>
<td>0.62</td>
<td>0.17</td>
<td>0.08</td>
<td>0.06</td>
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<td>5.5</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>6.5</td>
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<td>1.15</td>
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<tr>
<td>Treated water total Cl₂</td>
<td>0.90</td>
<td>1.95</td>
<td>1.34</td>
<td>2.78</td>
<td>0.26</td>
<td>0.65</td>
<td>0.79</td>
<td>0.68</td>
</tr>
<tr>
<td>D1 total Cl₂</td>
<td>0.70</td>
<td>2.10</td>
<td>1.01</td>
<td>1.73</td>
<td>0.36</td>
<td>0.39</td>
<td>0.69</td>
<td>0.65</td>
</tr>
<tr>
<td>D2 total Cl₂</td>
<td>0.65</td>
<td>1.62</td>
<td>0.88</td>
<td>1.46</td>
<td>0.26</td>
<td>0.37</td>
<td>0.88</td>
<td>0.74</td>
</tr>
<tr>
<td>D3 total Cl₂</td>
<td>0.54</td>
<td>1.39</td>
<td>0.39</td>
<td>0.67</td>
<td>0.28</td>
<td>0.38</td>
<td>0.84</td>
<td>0.61</td>
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<tr>
<td>Post-disinfection process</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
<td>Cl₂</td>
</tr>
<tr>
<td>Other disinfection processes</td>
<td>––</td>
<td>O₃, UV</td>
<td>––</td>
<td>––</td>
<td>––</td>
<td>––</td>
<td>UV</td>
<td>–</td>
</tr>
</tbody>
</table>

WTP: water treatment plant; D1, D2, D3: treated water at three progressively distant locations in distribution system.

*Values in mg/L.

Table 5 | Concentrations (μg/L) of the selected DBPs in Canadian drinking water samples

<table>
<thead>
<tr>
<th>WTP No.</th>
<th>TCAN LLE</th>
<th>SPME</th>
<th>DCAN LLE</th>
<th>SPME</th>
<th>1,1-DCP LLE</th>
<th>SPME</th>
<th>CP LLE</th>
<th>SPME</th>
<th>BCAN LLE</th>
<th>SPME</th>
<th>1,1,1-TCP LLE</th>
<th>SPME</th>
<th>DBAN LLE</th>
<th>SPME</th>
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<tr>
<td>WTP-36-R</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
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<td>0.10</td>
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<td>ND</td>
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</tr>
<tr>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>0.17</td>
<td>0.11</td>
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<td>ND</td>
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<td>0.34</td>
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<td>0.06</td>
<td>ND</td>
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<td>0.43</td>
<td>0.07</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
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<td>ND</td>
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</tr>
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<td>ND</td>
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<td>ND</td>
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<td>1.76</td>
<td>1.10</td>
<td>0.57</td>
<td>0.52</td>
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<td>0.02</td>
<td>2.38</td>
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<td>0.02</td>
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<td>0.02</td>
<td>2.00</td>
<td>2.00</td>
<td>0.78</td>
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<td>ND</td>
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<td>5.71</td>
</tr>
<tr>
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<td>ND</td>
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<td>0.02</td>
<td>3.09</td>
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<td>0.01</td>
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<td>0.20</td>
<td>0.14</td>
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(continued)
CONCLUSION

This study describes a fast automated HS-SPME-GC-MS method for determination of HANs, HKs, and CP in drinking water with good sensitivity at ng/L levels using DVB/CAR/PDMS fiber. The total analysis time including extraction and chromatographic run was 30 min. CI was essential to increase the sensitivity of the MS detection for the HKs. The novel custom-made PDMS/DVB-NVP fiber prepared in this study showed 80% more efficiency for the extraction of the brominated acetonitriles. The method exhibited good linearity in concentration ranges up to 20 μg/L with correlation coefficients exceeding 0.992. The MDLs obtained by the SPME method for the TCAN and CP were lower, the one for DCAN was comparable, and those for brominated acetonitriles and HKs were higher than the MDLs obtained by LLE-GC-ECD. The results for samples collected from eight drinking water systems...
generated by the HS-SPME-GC-MS and LLE-GC-ECD methods showed good agreement, indicating the applicability of the developed SPME method for analysis of these DBPs in drinking water samples.

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