Occurrence and Determination of Haloacetic Acids in Metro Manila Drinking Water

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ABSTRACT

Haloacetic acids are found in chlorinated water with high organic matter content. An analytical method based on a US EPA method for measuring these compounds in water is described. The optimized method used diethyl ether as extraction solvent with sulphuric acid-methanol as esterification agent and subsequent detection by gas chromatography-electron capture detection. Evaluation of this method showed that it was linear in the concentration range of 10 to 150 μg L^{-1} and the method detection limits were from 17 to 57 μg L^{-1}. Although the method demonstrated low recoveries (16 to 43%), it is useful in the quantitative determination of monochloroacetic acid as well as the qualitative determination of other haloacetic acids in water. Drinking water samples taken from different areas in Metro Manila serviced by the local treatment plants were analysed using the method. Monochloroacetic acid, monobromoacetic acid, and bromochloroacetic acid were detected in these samples. Monochloroacetic acid was quantified and found in concentrations ranging from 19 to 157 μg L^{-1}. In most of the water samples, the concentration of monochloroacetic acid exceeded the US EPA maximum allowable total concentration of 60 μg L^{-1} for the five haloacetic acids (monochloro-, dichloro-, trichloro-, monobromo-, and dibromoacetic acids) in drinking water. This initial study established the occurrence of potentially harmful haloacetic acids in the local drinking water supplies.

Keywords: haloacetic acids; disinfection by-products; drinking water; chlorination

INTRODUCTION

Maintaining a safe and high quality drinking water is a common goal all over the world. Drinking water sources can be surface water, such as rivers and lakes, or groundwater for those that have rich water tables. In most countries, the disinfection method of choice is chlorination due to the efficacy of this process against waterborne illnesses and the relative ease in maintenance and operation of the necessary equipment (Nieuwenhuijsen et al., 2000; Kaur et al., 2004). Chlorination as a disinfection process was introduced in the 19th century when there were deaths due to typhoid, cholera, dysentery, and other diseases caused by waterborne bacteria (Lee et al., 2001). Chlorination of drinking water is effective in preventing deaths from these diseases because chlorine is a good primary and residual disinfectant. In the early 1970s however, the presence of disinfection by-products (DBPs) in drinking water was reported (Lee et al., 2001). Trihalomethanes (THMs) were detected in drinking water as a result of the reaction of chlorine with humic substances that are present in the source water (Hozalski et al., 2001). This raised concerns because chloroform, one of the THMs, is classified as a probable human carcinogen (Nikolaou et al., 2004).

The detection of THMs in drinking water led to the development of more rigorous water treatment processes and also paved the way to the development of methods that are suitable for the

determination of these substances even at low concentrations. Recent technological advances also provided more options for research on drinking water quality. Thus, other DBPs like haloacetonitriles (HANs), haloacetic acids (HAAs) and their brominated analogues have been detected. The brominated analogues are formed when bromine is present in the raw source water (Cowman & Singer, 1996; Hozalski et al., 2001; Hua et al., 2006). Of the different DBPs, the HAAs are gaining interest from researchers. Unlike the THMs and HANs, HAAs are not volatile. Thus, measures like allowing the water to stand or boiling before consumption do not guarantee removal of the HAAs. Moreover, the identified HAAs are regarded to be more toxic than the volatile DBPs (Takino et al., 2000). Some studies have reported that HAAs are probable causes of cancers targeting the reproductive organs (Nieuwenhuijsen et al., 2000).

The HAAs that have been detected in relatively high concentrations are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). Together, the total concentration of these HAAs is regulated as total for HAA5 for the allowed maximum contaminant level. The US Environmental Protection Agency (EPA) regulates these compounds and allows a maximum value of 60 $\mu g\ L^{-1}$ for total HAA5 in drinking water (USEPA DBP rule). Other countries also monitor the levels of the total concentration of HAA5 and four other minor HAAs known to occur in drinking water. Together, these are termed HAA9 that includes the HAA5 as well as bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA), (Cowman & Singer, 1996; Hua et al., 2006). The European Union monitors the level of THMs in drinking water and is now considering regulating the HAA contaminant levels.

Urbansky (2000) have discussed various methods that have been reported for the analysis of HAAs and noted that most of these methods use gas chromatography coupled with electron capture detection (GC-ECD) or mass spectrometry (GC-MS). The HAAs have to be derivatized to esters before GC analysis. The US EPA Standard Method 552.2 is generally the method used for the determination of HAAs (Hodgeson et al., 1990). This method employs an extraction step using methyl tert-butyl ether (MTBE) and esterification using diazomethane. The use of MTBE is now minimized, if not avoided, because this is also a contaminant of interest due to its possible toxicity. The use of diazomethane, on the other hand, has special requirements and has inherent hazards. Modifications to the US EPA method using other extraction solvents and derivatizing agents have been reported in several studies. One such modified procedure used acidic methanol to derivatize the HAAs and subsequent microextraction step (Cancho & Ventura, 2005). Another method used in situ derivatization using dimethyl sulfate with solid phase microextraction and GC-MS for determination (Sarrion et al., 2000).

For our study, the US EPA Method 552.2 was modified by using diethyl ether as extraction solvent. The extracts were derivatized with a sulphuric acid-methanol mixture and the subsequent determination was performed using GC-ECD. The modified method was applied in the analysis of HAAs in drinking water samples taken from selected areas in Metro Manila. We present here an available and accessible method for HAAs analysis as well as a relevant finding on the occurrence of HAAs in the tap water samples in Metro Manila. This is the first report that reveals the presence of three HAAs (MCAA, MBAA, and BCAA) in the local drinking water supply.

MATERIALS AND METHODS

Sampling

The drinking water samples were collected from a total of 31 sampling sites from different cities in Metro Manila serviced by the local water treatment plants. Figure 1 shows the collection sites. These sites were the same sampling sites for the study on volatile DBPs reported earlier (Rodriguez *et al*., 2006). Prior to sampling, 1.5 g of NH_4Cl (Merck, Germany) was placed in thoroughly washed and dried 1 L glass bottles. Samples were collected directly from the tap into the glass bottles after allowing it to flow for 1 min, filled to the brim, and immediately refrigerated at 4°C prior to analysis. Extraction and analysis were done between one day and fourteen days after sample collection.

Figure 1. Location of sampling sites in some cities in Metro Manila (numbers indicate the sampling sites listed in Table 2). [Metro Manila map modified from http://mapsof.net/uploads/static-maps/metro_manila _political_map.png]

Extraction

The extraction procedure was a modification to the US EPA Standard Method 552.2. Extraction was carried out by adding 30 ml aliquot of the water samples to 40-ml Teflon-faced vials (Daigger, IL, USA) containing 3 g of copper sulphate (JT Baker, NJ, USA) and 10 g of acidified sodium sulphate (Merck, Germany) prepared as reported earlier (Rodriguez *et al*., 2006). The surrogate standard 2,3-dibromopropionic acid (Aldrich, WI, USA) was spiked (spike level equivalent to 600 µg L^{-1} in the final extract) and 2.5 ml of concentrated sulphuric acid (Merck, Germany) was added to adjust the pH of the samples to about 0.5. The pH should be low enough to ensure that the HAAs are in the acid form. Diethyl ether (JT Baker, NJ, USA) was then added (3 ml for 30 ml sample) and the vials were then shaken mechanically for 1 h. After shaking, the samples were allowed to stand for 5 min and then 2 ml of the diethyl ether layer of the samples were transferred to 5 ml Supelco conical vials with Teflon face.

Derivatization

The diethyl ether extracts were dried using a gentle stream of nitrogen gas to about 0.5 ml each. Then, 0.5 ml of 10% sulfuric acid in methanol solution was added to methylate the haloacetic acids. The vials were then placed in a water bath kept at 70°C for 2 h. After heating, the extracts were cooled before adding 2 ml of diethyl ether and 1 ml of 10% sodium bicarbonate solution to neutralize the excess sulphuric acid. These were shaken mechanically for 5 min and allowed to stand. Finally, 1 ml aliquots were transferred from the diethyl ether layer of the derivatized extracts to 2 ml vials (Shimadzu, Japan). To these extracts, an internal standard mix composed of fluorobenzene and 3-bromo-1-chloropropane (Supelco, Bellefonte, USA) was added prior to GC-ECD analysis.

GC-ECD determination and quantitation

The instrument used for this study was a Shimadzu GC8A equipped with a ^{63}Ni for electron capture detection. The carrier gas was nitrogen at 5 ml min^{-1} flow and the column used was ZB 624 (cyanopropylphenylmethylpolysiloxane, 30m × 0.53mm id × 3.00µm ft) from Phenomenex, Torrance, USA. Using a 10-µL syringe (Hamilton, USA), 3 µL of the extracts were manually injected. The analyses were carried out in these conditions : split mode (1:10) injection; 120°C column temperature for isothermal separation; 160°C injector temperature; 160°C detector temperature. These isothermal parameters were the settings for optimum separation of the methylated HAAs.

The haloacetic acids were quantified against calibration standard solutions prepared using the methylated standards spiked in diethyl ether. Internal standard correction was performed to account for loses during the analysis.

RESULTS AND DISCUSSION

Optimization of extraction & derivatization

The haloacetic acids included in this study were MCAA, DCAA, MBAA, TCAA, BCAA, and DBAA. The method for the haloacetic acid analysis was optimized by first converting the standard haloacetic acid mix to the methylated form. Briefly, the HAAs were spiked in ultrapure water, ensured to be in their acid forms by adding concentrated sulphuric acid to achieve a pH of 0.5. The HAAs were subsequently extracted using 3 ml of diethyl ether, the HAAs were derivatized to the methylated forms by adding 10% H_2SO_4 in methanol, and then a second diethyl ether extraction was performed.

The second extraction process may be carried out by neutralizing the excess H_2SO_4 in methanol with $NaHCO_3$ prior to addition of the extraction solvent. However, it was observed that splattering occurs during the addition of the bicarbonate solution which may result to loss of the analytes. A parallel analysis was carried out wherein the diethyl ether was added prior to neutralization of the excess acid. Extra care was observed during the addition of the bicarbonate after diethyl ether was added because the neutralization of the excess acid resulted in the evolution of gas. The recoveries of all analytes were significantly increased when diethyl ether was added before neutralization of the excess acid with sodium bicarbonate. Loses due to the splattering may be minimized by the presence of the solvent. Adding diethyl ether at this point may have hindered loses because the HAAs are already in the methylated form thus interaction of the analytes with the solvent is already favored.

For the HAA analysis, an internal standard solution composed of fluorobenzene and 2-bromo-1-chloropropane was used. However, only absolute recoveries against 2-bromo-1-chloropropane can be calculated because the peak for fluorobenzene co-eluted with the diethyl ether peak. Separation of the HAAs was excellent using the isothermal GC-ECD parameters, the retention times of the analytes are given in Table 1. The run time of each analysis was 18 min which was the optimum GC run time due to the isothermal oven temperature. Improving the run time, i.e., shortening of time, leads to closely positioned peaks which is less favorable.

Method performance

Using the optimized method, recoveries of HAAs spiked in ultrapure water at 10 to 150 μg L^{-1} concentrations were determined. Recoveries were calculated using commercially available methylated HAA standard solutions. Our results show that in this concentration range, the response of all HAAs with increasing concentration was linear having correlation coefficients of 0.997 to 0.999. Table 1 lists the absolute recoveries of HAAs at 50.0 μg L^{-1} spike level. TCAA was not recovered nor detected even at higher spike concentrations. For this particular HAA, the optimized method is not applicable. The percent absolute recoveries of the five other haloacetic acids ranged from 16.4 to 42.9 at 50.0 μg L^{-1} concentration in water; the standard deviations ranged from 4.15 to 12.6. These recoveries are low compared to those reported using the EPA standard method (comparison shown in Table 1) where all HAAs have relatively good recoveries. However, it should be noted that for the EPA method, the derivatization was done using diazomethane and the extraction by MTBE. Diazomethane derivatization is excellent for MCAA and TCAA analysis because of the difficulty of methylating these compounds. Diazomethane and MTBE were not tried in this study because handling of these chemicals requires special set-up and equipment.

The esterification agent used in this study was used by Xie (2001) in the analysis of HAAs where liquid-liquid microextraction with acidic methanol derivatization was employed. Xie reported recoveries that ranged from 81 to 144% but the determination of the analytes was done by GC-MS, suggesting that acidic methanol esterification with sensitive analytical determination could provide better detection. The same results were obtained by Domino *et al.* (2004) who compared various methods for HAA determination. In their study, they noted that a higher boiling solvent such as tertiary-amyl methyl ether can improve extraction efficiency of HAAs and that extraction efficiency can also be improved by increasing the amount of sodium sulphate added. Barron & Paull (2006) also studied

Table 1. Percent recoveries and MDL of the modified method and the US EPA method

HAAs	Retention Time[a] (min)	% Absolute Recovery[b], Modified Method	MDL, Modified Method (µg L-1)[c]	% Absolute Recovery, EPA Method 552.2[d]	MDL, EPA Method 552.2, (µg L-1)[d]
MCAA	6.09	16.4	16.9	94.7	0.27
DCAA	7.95	25.9	22.8	84.7	0.24
MBAA	8.3	42.9	38	102	0.2
TCAA	8.3	nd	nd	93	0.08
BCAA	11.96	42.3	50.5	86.9	0.25
DBAA	17.67	42.6	56.8	95.4	0.07

nd = not detected using the modified extraction and derivatization method

[a] Column used: cyanopropylphenylmethylpolysiloxane, 30 m × 0.53 mm id × 3.00 µm ft; N_2 carrier gas at 5 ml min^{-1} flow rate

[b] n = 3; calculated at 50 µg L^{-1} spike level

[c] n = 7; at 50 µg L^{-1} spike level

[d] Reference : Hodgeson, et al., 1990

HAAs and used microbore ion chromatography with suppressed conductivity coupled to electrospray ionization mass spectrometric detection. They reported recoveries ranging from 13 to 84% for the HAAs they studied. Kou *et al*. (2004) who used supported liquid membrane microextraction with HPLC-UV detection reported extraction efficiencies of 3.89 to 39.6% for the HAAs they analysed. Another determination procedure was reported by Liu *et al*. (2004) where hydrophilic anion-exchange column with steep gradient sodium hydroxide addition and inductively coupled plasma mass spectroscopy as detector were used. For their method, the recoveries of the HAAs are in the range of 92 and 104%. The methods above that reported relatively good recoveries use mass spectrometric detection which provides sensitivity that outperforms other detection methods.

In the present study, the method detection limit (MDL) for each haloacetic acid was determined using the optimized method. The standard HAAs in the acid form were spiked in ultrapure water (concentration equal to 50.0 µg L^{-1} in the final extract), extracted, derivatized and analyzed by GC-ECD. Seven replicates were performed and the MDL for each HAA was calculated using the standard deviation of the measurements and the equation (adapted from the US EPA method by Williams & Maillard, 1997):

$$MDL = 3.143 \times SD \quad (for\ n = 7) \qquad (1)$$

where MDL is a statistical estimate of the detection limit that is equal to the standard deviation multiplied by the student's t-value at 99% confidence level. MDL values calculated for the HAAs studied are relatively high (given in Table 1) which means that if the actual concentration of a target HAA in the water sample is below the MDL, the actual level will not be statistically quantified. MDL values obtained using the optimized method and the EPA standard method are given in Table 1. The difference in the MDL values is attributed to the different extraction and derivatization procedures used in the two methods. The optimized method presented in this study, thus, requires further modifications aimed at lowering the detection limits.

Analysis of drinking water samples

The occurrence and levels of HAAs in actual drinking water samples were studied using the optimized method. Although the other HAAs were detected in the samples, only MCAA was quantified and its concentrations are shown in Table 2. The MCAA concentrations were calculated against external calibration solutions prepared by using commercially available methylated standards in diethyl ether. MCAA in the water samples ranged from 19 to 157 µg L^{-1}. These values correspond to corrected values of 98 to 958 µg L^{-1} when the recovery of the method is taken into account. The corrected values indicate that the levels of MCAA alone exceeded the suggested maximum guideline value allowable for total HAA5 concentration (60 µg L^{-1}, US EPA). MBAA and BCAA were detected in the samples but were found in levels below MDL values.

Table 2. Concentrations (values in parenthesis are standard deviations) of monochloroacetic acid in drinking water samples from various sampling sites in Metro Manila

Sampling Location No.	Sampling Site[a]	MCAA Concentration, mg L^{-1} [b]	
		Actual[c]	Corrected[d]
1	UPD A	24 (4)	144 (22)
2	UPD B	20 (5)	121 (28)
3	UPD C	25(5)	152 (31)
4	UPD D	19 (4)	98 (28)
5	UPD E	nd	nd
6	UPD F	30 (4)	113 (25)
7	Marikina City A	46 (4)	278 (27)
8	Marikina City B	56 (4)	343 (21)
9	Marikina City C	96 (4)	588 (26)
10	Manila A	120 (7)	735 (44)
11	San Juan A	74 (3)	451 (20)
12	San Juan B	101 (10)	614 (61)
13	Mandaluyong City A	154 (19)	941 (114)
14	Mandaluyong City B	75 (11)	457 (68)
15	Muntinlupa City A	nd	nd
16	Muntinlupa City B	157 (12)	958 (71)
17	Makati City A	128 (24)	778 (146)
18	Makati City B	152 (5)	928 (28)
19	Pasig City A	112 (12)	683 (71)
20	Pasig City B	71 (15)	434 (91)
21	Caloocan City A	81(13)	494 (80)
22	Quezon City A	96 (24)	583 (150)
23	Quezon City B	55 (22)	336 (133)
24	Quezon City C	68 (6)	412 (35)
25	Quezon City D	97 (1)	590 (9)
26	Quezon City E	86 (14)	523 (82)
27	Quezon City F	86 (10)	524 (61)
28	Quezon City G	91 (11)	553 (66)
29	Quezon City H	89 (6)	541 (39)
30	Valenzuela City A	71 (3)	433 (16)
31	Valenzuela City B	97 (12)	589 (74)

nd= not detected
[a] Sampling sites A,B, etc. are different households from the same city; UPD samples were collected in February 2003; other samples were collected in December 2002 to June 2003
[b] n=3
[c] actual = quantified concentrations using standard calibration solutions
[d] corrected = concentrations corrected for recovery of MCAA at 50 μg L^{-1}

These findings prompt a need to study the formation, reduction or possible removal of HAAs in the local water supplies. There is also a need to improve the extraction recoveries and detection limits of the method by considering other analytical techniques. The use of alternative extraction solvents and derivatization reagents can be explored. MTBE and diazomethane may still be the best extraction solvent and derivatization reagent, respectively. However, hazards precaution, correct handling, and proper waste disposal should be in place. Other determination techniques such as the use of ion chromatography (IC), high pressure liquid chromatography (HPLC) or GC with MS detection may prove useful in studying HAAs as contaminants in the drinking water supplies in Metro Manila.

CONCLUSIONS

The modified method for analysing haloacetic acids in drinking water described in this study was evaluated in terms of linearity, recovery, and method detection limits. The use of diethyl ether as solvent for extraction and a sulphuric acid-methanol mixture as methylating agent were explored. The optimized method showed linear correlation for a wide concentration range but suffers from low recoveries and high detection limits. Application of the optimized method to analyse actual water samples detected three HAAs (MCAA, MBAA, and BCAA) in the drinking water supplies in Metro Manila. The method was successful in the quantitative determination of MCAA where its concentrations in most of the water samples analysed were above the 60 μg L^{-1} maximum contaminant level recommended by the US EPA for total HAA5 in drinking water. This study offers an available method that can be used to quantify MCAA and qualitatively determine other HAAs present in the local drinking water supplies.

Modifications such as the use of IC-, HPLC- or GC-MS and the use of other extraction solvents and derivatization reagents are suggested to improve the performance of the method. An improved method may be used to study the formation and possible control of HAAs found to occur in the drinking water in Metro Manila where to date, these compounds are not routinely monitored for public safety.

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