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Determination of Monochloroacetic Acid in Swimming Pool Water by Ion Chromatography-Conductivity Detection

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ABSTRACT

In this study, an analytical method involving ion chromatography with conductivity detection was developed and optimized for the determination of monochloroacetic acid in swimming pool water. The ion chromatographic method has a detection limit of 0.02 mg L^{-1} and linear range of 0.05 to 1.0 mg L^{-1} with correlation coefficient of 0.9992. The method is reproducible with percent RSD of 0.052% (n=10). The recovery of monochloroacetic acid spiked in different water types (bottled, tap and swimming pool water) ranged from 28 to 122%. In dilute solutions, chloride and bromide were simultaneously analyzed along with monochloroacetic acid using the optimized method. Chloride and bromide have detection limits of 0.01 to 0.05 mg L^{-1}, respectively. The usefulness of the ion chromatographic method was demonstrated in the analysis of monochloroacetic acid in swimming pool water samples. In such highly-chlorinated samples, an Ag/H cartridge was used prior to the ion chromatographic determination so as to minimize the signal due to chloride ion. Monochloroacetic acid was detected in concentrations between 0.020 and 0.093 mg L^{-1} in three of the six swimming pool water samples studied. The presence of monochloroacetic acid in the swimming pool water samples suggests the possible occurrence of other disinfection by-products in these waters.

Keywords: Monochloroacetic acid, chloride, bromide, water, ion chromatography

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INTRODUCTION

Water is important in sustaining life. To safeguard human and ecological health, contaminants must be absent or kept at the minimum possible levels. Because water is used for human consumption, the highest quality of water should thus be maintained. It is common to disinfect water by ozonation or chlorination to prevent the spread of disease. However, disinfection by-products are unintentionally produced during water treatment. When bromide-containing water is treated using ozone, the potentially carcinogenic bromate may be formed (von Gunten and Hoigne 1994, WHO 2008). Chlorination of water containing naturally-occurring organic matter, on the other hand, results in the formation of a variety of disinfection by-products (Liang and Singer 2003, Richardson and others 2007). Chlorine species such as HOCl and OCl^- react with humic and fulvic substances in water to form the regulated disinfection by-products including haloacetic acids and trihalomethanes. Haloacetic acids are more soluble in water and are reported to be as potentially harmful as the commonly-analyzed trihalomethanes (Nieuwenhuijsen and others 2000, Richardson and others 2007, Plewa and others 2010, Pals and others 2011). The US EPA regulates five haloacetic acids in drinking water, which are collectively known as HAA5. Monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acids constitute the HAA5 and these have a total allowable limit of 60 ug L^{-1} in drinking water (US EPA 2009). The 2007 Philippine National Standards for Drinking Water (PNSDW) drawn from the World Health Organization (WHO) register of standard values for disinfection by-products include three haloacetic acids namely: monochloroacetic acid at 0.02 mg L^{-1}, dichloroacetic acid at 0.05 mg L^{-1}, and trichloroacetic acid at 0.2 mg L^{-1} (PNSDW 2007, WHO 2008). Of these compounds, only dichloroacetic acid is categorized as Group B or possibly carcinogenic to humans by the International Agency for Research on Cancer (WHO IARC 2004). Nevertheless, monochloroacetic acid and trichloroacetic acid have been reported to exhibit cytotoxicity, genotoxicity, mutagenicity and teratogenicity in animal studies (Liang and Singer 2003, Plewa and others 2010, Pals and others 2011).

Water is important not only for drinking but also for bathing and cleaning. Likewise, it is essential in recreational activities such as swimming, diving or water aerobics. Swimming in pools, for example, provides exercise, relaxation, therapy and wellness to man. For hygiene and health protection, swimming pool water is usually disinfected. It has been shown that microorganisms can thrive in swimming pools and cause outbreak of disease (Friedman and others 1999, Leoni and others 1999). Chlorination is the disinfection method of choice for swimming pools because of the residual effects of chlorine. In some countries like Germany, it is recommended to maintain chlorine levels of 0.3 to 0.6 mg L^{-1} or higher to safeguard the wellbeing

of the swimmers (Uhl and Hartmann 2005). Chlorinated swimming pool water has more organic matter than chlorinated drinking water because of continuous inputs from the swimmers. As a consequence, disinfection by-products including haloacetic acids are formed in swimming pools. Likely, recirculation or reuse of this water may result in disinfection by-products accumulation. Lee and others (2010) demonstrated that haloacetic acids represent over 60% of the disinfection by-products found in swimming pool waters in Korea which were treated with chlorine, ozone-chlorine, or electrochemically-generated mixed oxidants. In their chlorinated water samples, haloacetic acids were measured at 14.1 to 636 ug L^{-1} concentrations. Catto and others in 2012 reported haloacetic acids in water from two swimming pools in Canada with concentrations of less than the limit of detection (<LOD) to 201.0 ug L^{-1}. In Swiss swimming pool waters, the haloacetic acids ranged from 0.9 to 240 ug L^{-1} where the concentrations of monochloroacetic acid alone were 11-117 ug L^{-1} (Berg and others 2000). Haloacetic acids in water samples from swimming pools in Portugal were detected in concentrations between 0.1 and 72.9 ug L^{-1} (Sa and others 2000). The monochloroacetic acid in these samples ranged from 0.6 to 13.2 ug L^{-1}.

Haloacetic acids in drinking water are commonly analyzed using US EPA Method 552.2. This method involves solvent extraction with methyl tert-butyl ether (MTBE), methylation with 10% sulphuric acid in methanol, and determination by gas chromatography-electron capture detection or GC-ECD. Studies on the analysis of haloacetic acids in swimming pool water are also carried out using US EPA Method 552.2 (Lee and others 2010, Catto and others 2012). Berg and others (2000) used diazomethane to derivatize the haloacetic acids before determination by gas chromatography-mass spectrometry or GC-MS. Sa and others (2012), on the other hand, used dimethyl sulphate for derivatization and headspace solid phase microextraction followed by GC-ECD. Electrophoresis has also been demonstrated to be an alternative method for haloacetic acids analysis particularly in drinking water. Haloacetic acids may be extracted by solid-phase extraction (SPE) and determined by capillary electrophoresis with diode array detection (Martinez and others 1998), capillary electrophoresis with contactless conductivity detection (Kuban and others 2012) or microchip capillary electrophoresis with capacitatively coupled contactless conductivity detection (Ding and Rogers 2010). Capillary zone electrophoresis with direct UV detection and contactless conductivity detection was used by Lopez-Avila and others (2003). Carrero and Rusling (1999) demonstrated the use of high pressure liquid chromatography and an electrochemical detector coated with a film of nafion and dido-decyldimethylammonium bromide in haloacetic acids determination. Ion chromatography or IC is another technique for haloacetic acids analysis. Direct injection ion chromatography and mass

spectrometry (MS) were used to determine trace levels of haloacetic acids in drinking water (Matthew and others 2009). Solid-phase extraction followed by ion-pair liquid chromatography with electrospray ionization-mass spectrometry was also used to study haloacetic acids in different water samples including tap, river and swimming pool waters (Loos and Barcelo 2001, Prieto-Blanco and others 2012). Sun and Gu (2007) used ion chromatography with suppressed conductivity to determine haloacetic acids in chlorinated hospital effluents.

Monochloro-, monobromo- and bromochloroacetic acids were reported to be detected in Metro Manila drinking water samples (Rodriguez and Espino 2010). Only monochloroacetic acid was quantified and it was found to be in 19-157 ug L^{-1} concentrations. The analytical method was a modified US EPA Method 552.2 in which diethyl ether was used as extraction solvent instead of MTBE, resulting in low recoveries. This preliminary study demonstrated that haloacetic acids may be formed in the water supplies in Metro Manila. It was thus deemed that haloacetic acids may also occur in recreational waters such as in swimming pools where expectedly the water source would come from the main distribution lines of the drinking water supply.

The aim of this present study was to develop and optimize an ion chromatographic-conductivity detection method for monochloroacetic acid in swimming pool water. If detected in the water samples, monochloroacetic acid may serve as a marker for the occurrence of disinfection by-products including the other priority haloacetic acids.

EXPERIMENTAL METHOD

Chemicals and Solvents

Chloride and bromide analytical standards, both labeled IC standard in 100 mL of 1000 µg mL^{-1}, were purchased from Fluka (Buchs, Switzerland). The monochloroacetic acid analytical standard (99.9% chloroacetic acid, 1000 mg/ampule) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The seven calibration solutions of these standards were in the range of 0.05 to 1 mg L^{-1}. All solutions were prepared in Absolute® distilled water (Asia Brewery Inc., Philippines).

The mobile phase was a mixture consisting of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ prepared by dissolving appropriate amounts of $NaHCO_3$ and Na_2CO_3 (J.T. Baker, Philipsburg, NJ, USA) in distilled water. The 100 mM H_2SO_4 regenerant solution used in the anion conductivity suppressor device was prepared from 18 M H_2SO_4 solution (Labscan, Bangkok, Thailand).

Ordinary tap water, swimming pool water and bottled water (Summit® and Evian® bottled drinking water purchased from a local supermarket) were used in spiking and recovery experiments.

Sample Collection and Preparation

Surface water samples were taken from six Quezon City swimming pools in August 19-28, 2012. These pools are rectangular in shape and small to medium in size, typical of swimming pool facilities in Metro Manila. These were generally filled with chlorinated water from the tap. The water samples were collected in clean 500-mL PET bottled water containers; headspace was avoided during collection. The containers were then sealed, covered on the outside with paper, and brought immediately to the laboratory for analysis. The samples were filtered through 125 mm Whatman Grade No. 40 filters (Whatman, NJ, USA). For chloride and bromide determination, the samples were diluted 20 to 150 times with distilled water to appropriate concentrations such that the analytes can be measured against the calibration solutions. Before injection into the ion chromatograph, the samples were filtered using 0.45 um nylon syringe filters (Whatman, NJ, USA). For monochloroacetic acid determination, undiluted swimming pool water samples were passed through 2.5 cc Dionex II OnGuard Ag/H cartridges (Thermo Scientific, Waltham, MA, USA). Prior to use, the cartridges were conditioned with 15 mL distilled water. Eight milliliters of the samples were passed through the cartridges. The first 6 mL fractions were discarded, while the last 2 mL fractions were used for monochloroacetic acid analysis.

The swimming pool water samples were also measured for pH using a Milwaukee pH 600 pocket-sized pH meter (Milwaukee, NC, USA) as well as ultraviolet absorbance at 254 nm using a UV mini 1240 UV-Vis spectrophotometer (Shimadzu, Kyoto, Japan).

Instrumentation

A Metrohm 881 Compact IC Pro (Metrohm AG, Herisau, Switzerland) ion chromatographic system was used. The ion chromatograph was equipped with a sample and eluent degasser, chemical suppressor device, high-pressure pump, six-port injection valve, column heater, and conductivity detector. The ions were separated on an anion column (Metrohm Metrosep A Supp 5-150) with dimensions of 150 mm x 4.0 mm and a stationary phase material containing polyvinyl alcohol plus quaternary ammonium groups. The guard column used was a Metrohm 5 mm x 4 mm Metrosep A Supp 4/5. Samples and standard solutions were introduced into a fixed 20-uL loop using a 10-mL syringe. The 3.2 mM Na_2CO_3 -1.0 mM $NaHCO_3$

mobile phase had a constant flow rate of 0.50 mL min^{-1} which resulted in a total run time of 13 min. Monochloroacetic acid, chloride and bromide elute at 6.3, 7.1 and 10.5 min, respectively. Data acquisition and processing were performed using MagIC Net 2.2 chromatography software.

Analysis and Quantitation

Twenty microliters of the calibration solutions and water samples were injected into the ion chromatograph. Blank solutions (distilled water) were injected at the start of the analysis and after each injection of relatively high concentrations of the analytes to flush the system as well as avoid baseline drift. No peaks were observed at the retention times of the analytes in the blank solutions. The target analytes were separated on the anion analytical column using a 3.2 mM Na_2CO_3-1.0 mM $NaHCO_3$ mobile phase at 25°C. All measurements were done in three replicates. More replicate measurements were done for validation, specifically for recovery and detection limit determinations. Monochloroacetic acid, chloride and bromide in the water samples were quantified by external calibration and linear regression techniques. Data analyses including computations of detection limits, recoveries, concentrations and standard deviations were performed using Excel Microsoft Office 2007.

RESULTS AND DISCUSSION

Ion Chromatographic Determination of Monochloroacetic Acid, Chloride and Bromide

The analytical determination of monochloroacetic acid in water was performed on an anion column and initially using different mobile phases of various proportions of Na_2CO_3 and $NaHCO_3$. At the final conditions of 3.2 mM Na_2CO_3-1.0 mM $NaHCO_3$ mobile phase, 0.5 mL min^{-1} flow and 25°C, monochloroacetic acid eluted at 6.3 min. Monochloroacetic acid is detectable in water solutions containing low concentrations of chloride and bromide. The simultaneous determination of the three analytes is shown in Figure 1 where monochloroacetic acid, chloride and bromide were separately eluted on the anion column at the optimum conditions. The linear range for the determination of these analytes was from 0.05 to 1.0 mg L^{-1} with correlation coefficients, r^2, of 0.9986-0.9993 (Figure 2). The instrument detection limits (IDL) were 0.01, 0.02 and 0.05 mg L^{-1} for chloride, monochloroactic acid and bromide, respectively (Table 1). The repeatability of the determination method was good with percent RSD of 0.052-0.27% for these analytes.

The 0.02 mg L^{-1} detection limit for monochloroacetic acid using this ion chromatographic method is comparable to that of the GC-ECD method developed

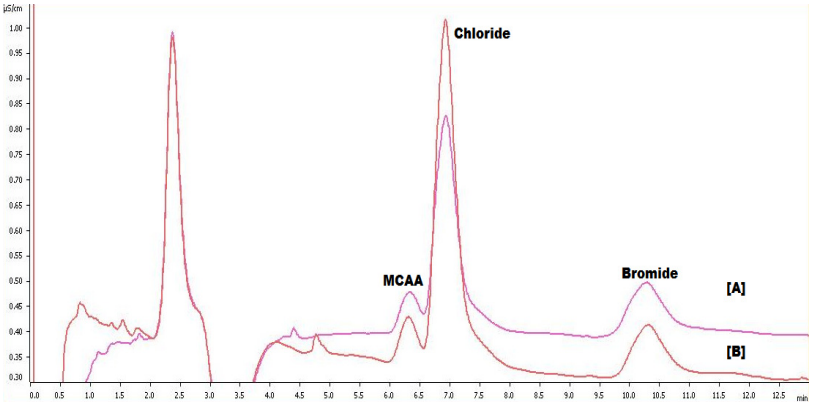

Figure 1. Ion chromatograms of 0.6 mg L^{-1} monochloroacetic acid (MCAA), chloride and bromide spiked in [A] bottled water and [B] tap water. Conditions: 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$ mobile phase, 0.5 mL min^{-1} flow rate, 20 uL injection volume.

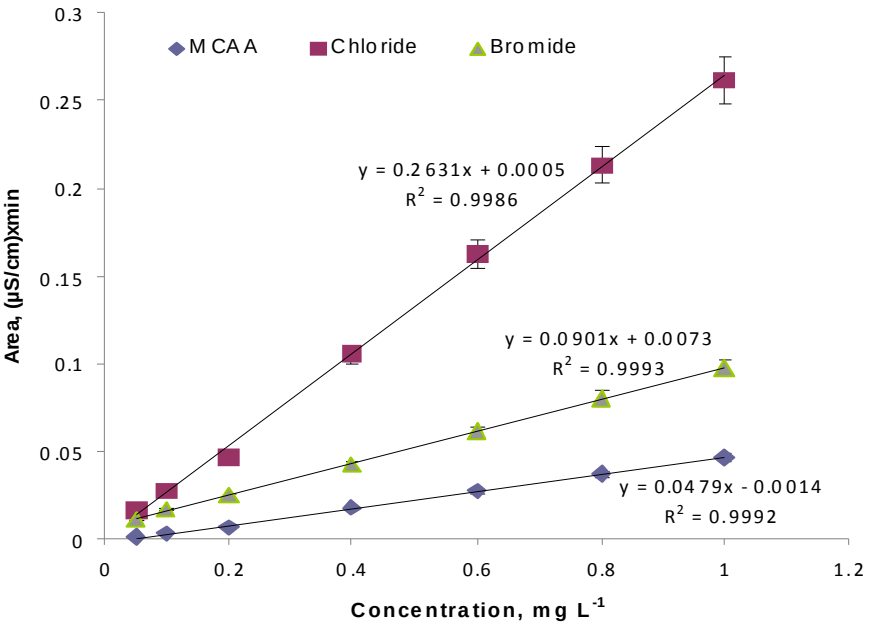

Figure 2. Calibration plots of 0.05 to 1 mg L^{-1} monochloroacetic acid (MCAA), chloride and bromide solutions (n=3 for each concentration).

Table 1. Analytical performance of the optimized ion chromatographic method

Analyte	Retention time, min (SD), n=3	Linear range, mg L^{-1}	Correlation coefficient, R^2	Repeatability[a] of peak area, (µS/cm) x min (% RSD) n=10	IDL[b] mg L^{-1}
Monochloroacetic acid	6.3 (0.03)	0.05-1.0	0.9992	0.052 (15)	0.02
Chloride	7.1 (0.05)	0.05-1.0	0.9986	0.27 (8)	0.01
Bromide	10.5 (0.1)	0.05-1.0	0.9993	0.11 (8)	0.05

[a] Interday analyses of a 1 mg L^{-1} standard solution for 6 days

[b] Measured using a 0.05 mg L^{-1} standard solution; IDL= SD x 3.143 (n=7; student's t-value at 99% confidence level)

and optimized by Rodriguez and Espino (2010). Using GC-ECD, monochloroacetic acid that was derivatized with acidified methanol had a quantitation limit of 0.0169 mg L^{-1}. However, this method had low recoveries mainly due to the sample preparation steps involved, including microextraction, derivatization and preconcentration. Table 2 summarizes the recoveries of monochloroacetic acid spiked in two brands of commercial bottled water, tap water and swimming pool water and analysed by ion chromatography-conductivity detection. At spike levels of 0.1 to 0.6 mg L^{-1}, the recoveries were between 43 and 122%. In the GC-ECD method, the recovery of monochloroacetic acid spiked in ultrapure water was only 16.4%.

The detection limit for monochloroacetic acid in this present study is also comparable to the detection limits of other methods reported in literature. Sun and Gu (2007) studied haloacetic acids in hospital effluents using ion chromatography and reported a monochloroacetic acid detection limit of 0.01235 mg L^{-1}. HPLC with electrochemical detection was also used for monochloroacetic acid determination with a relatively high detection limit of 10 mg L^{-1} (Carrero and Rusling 1999). Various electrophoresis methods were also reported in which the detection limits were 2.1-2.7 mg L^{-1} (Ding and Rogers 2010), 0.044 mg L^{-1} (Kuban and others 2012), and 0.005 mg L^{-1} (Martinez and Calull 1998). Matthew and others (2009) studied haloacetic acids in drinking water using ion chromatography-mass spectrometry with a superior detection limit of 2.158×10^{-5} mg L^{-1} for monochloroacetic acid. It should be noted that the recoveries of these methods varied widely as the sample preparation involved different extraction and pre-treatment techniques using a variety of sorbent materials.

For chloride and bromide determination in this study, the detection limits were a little higher than those of the sequential chemical and CO_2-suppressed ion chromatographic method reported by De Vera and Espino in 2011. With chemical and CO_2 suppression, the background conductivity was reduced, which resulted in lower detection limits for chloride and bromide at 0.001 and 0.007 mg L^{-1}, respectively. This tandem suppression technique was used solely for the analysis of inorganic anions namely fluoride, chloride, bromide, nitrate, phosphate and sulphate. The recoveries of these anions in ultrapure water ranged from 94 to 154%. In this present study wherein the ion chromatographic method involved only chemical suppression for detection, the recoveries of chloride and bromide in bottled, tap and swimming pool waters ranged between 28 and 121%. This wider range of recoveries may be attributed to the different water matrices that were used.

Overall, the optimized ion chromatography with conductivity detection method developed in this study has low detection limits, relatively low linear concentration range for trace analysis, good reproducibility, and acceptable recoveries.

Table 2 Percent recoveries in different water matrices

Spiked Water	% Recoveries (SD), n=3		
	Monochloroacetic acid	Chloride	Bromide
Bottled water:			
A			
low (0.1 mg L^{-1})	100 (17)	73(4)	43 (10)
high (0.4 mg L^{-1})	117 (15)	82(4)	67 (7)
B			
low (0.2 mg L^{-1})	70 (17)	71 (2)	51 (10)
high (0.4 mg L^{-1})	65 (16)	90 (8)	72 (14)
Tap water			
low (0.2 mg L^{-1})	82 (14)	121 (14)	72 (6)
high (0.6 mg L^{-1})	76 (2)	79 (1)	86 (2)
Swimming pool water*			
low (0.2 mg L^{-1})	122 (36)	102 (15)	28 (4)
high (0.6 mg L^{-1})	43 (0)	95 (1)	65 (2)

A= Summit®; B= Evian®; *Swimming pool water sample that does not contain monochloroacetic acid was used

Analysis of Monochloroacetic Acid in Swimming Pool Water

The applicability of the ion chromatography-conductivity detection method was tested in the analysis of monochloroacetic acid in swimming pool water samples. In water containing high concentrations of chloride, the detection of monochloroacetic acid was found to be affected by the large chloride ion signal. Thus, the analysis of monochloroacetic acid and chloride in highly chlorinated water samples requires special sample preparation. Dilution was necessary particularly for chloride determination because the concentration was anticipated to be above the highest concentration in the established linear range of the optimized method. Monochloroacetic acid was separately analysed after chloride was removed from the sample or after its concentration was minimized.

An Ag/H cartridge was used for the sample preparation in the analysis of monochloroacetic acid in chlorinated swimming pool water. This cartridge consists of layers of Ag and H resins that retain chloride, bromide, iodide and carbonate ions. Figure 3 compares the ion chromatograms of a swimming pool water sample that was not passed through an Ag/H cartridge and the same water sample that was passed though an Ag/H cartridge. The use of an Ag/H cartridge minimized the signal due to chloride allowing the detection and quantitation of monochloroacetic acid.

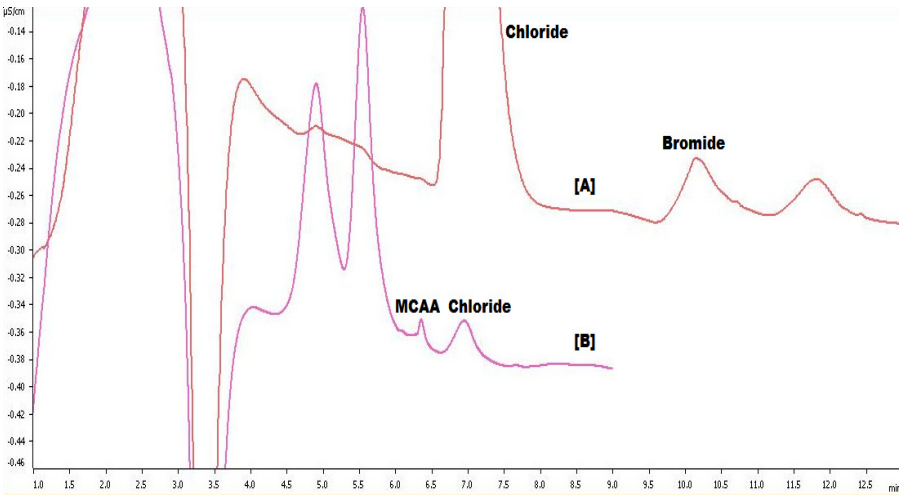

Figure 3. Ion chromatograms of [A] a swimming pool water sample and [B] the same swimming pool water sample after passing through an OnGuard Ag/H cartridge. Conditions: 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$ mobile phase, 0.5 mL min^{-1} flow rate, 20 uL injection volume.

In a spiking experiment of 0.6 mg L^{-1} monochloroacetic acid and chloride in distilled water using Ag/H cartridges, the retention time of monochloroacetic acid on the anion column was invariable at 6.3 min and the recovery was good at 122% (n=6, SD 13).

Monochloroacetic acid, chloride and bromide concentrations in six swimming pool water samples were determined using the optimized ion chromatography-conductivity detection method. Because the Ag/H cartridge removes the inorganic anions, chloride and bromide were determined separately without pre-treatment using Ag/H cartridges. Monochloroacetic acid was detected in the swimming pool water samples with an average pH of 7.1 and high chloride concentrations. Monochloroacetic acid was found in three of the six samples with concentrations ranging from 0.020 to 0.093 mg L^{-1} (Table 3). The chloride and bromide concentrations in all samples were 24-104 mg L^{-1} and 0.16-7.52 mg L^{-1}, respectively. These water samples registered UV absorbances at 254 nm ranging from 0.002 to 0.060 a.u., suggesting the presence of dissolved organic compounds which may serve as precursors of monochloroacetic acid. Bromide found in the water samples also indicate the possible occurrence of brominated haloacetic acids such as monobromo- and dibromoacetic acids belonging to the five regulated haloacetic acids. And because monochloroacetic acid was detected in the swimming pool

Table 3. Concentrations of monochloroacetic acid, chloride and bromide in swimming pool water samples

Water Sample Code	Sampling Date	pH	Absorbance at 254 nm	Mean Concentration in mg L^{-1} (%RSD)[a]		
				Monochloroacetic Acid	Chloride[b]	Bromide[b]
A	8/19/12	6.8	0.002	0.020 (0)	104 (0)	5.98 (0)
B	8/22/12	6.9	0.010	*not detected*	66 (0.69)	2.04 (0.97)
C	8/22/12	6.5	0.002	*not detected*	24 (0.34)	1.86 (0.58)
D	8/22/12	7.1	0.012	0.083(0)	67 (0.96)	7.52 (1.89)
E	8/28/12	7.8	0.014	0.093(0)	53 (0.50)	0.80 (0.47)
F	8/28/12	7.6	0.060	*not detected*	24 (0.13)	0.16 (0)

[a] n=3

[b] Measured using water samples diluted 20, 50, 80, 100 or 150x depending on the response which should be within the range of the calibration solutions

water samples, it could be expected that other disinfection by-products may also be present. The concentrations of monochloroacetic acid found in these swimming pool samples are within the 0.011-0.117 mg L^{-1} range of monochloroacetic acid concentrations in Swiss swimming pools reported by Berg and others (2000). However, the concentrations are relatively high compared to the 0.0006-0.0132 mg L^{-1} monocloroacetic acid concentrations in swimming pools in Portugal (Sa and others 2012). To the best of our knowledge, this is the first study on the occurrence of the disinfection by-product monochloroacetic acid in the swimming pools in the Philippines. Although disinfection by-products such as trihalomethanes and haloacetic acids have been studied in the local drinking water supplies (Rodriguez and others 2006, Rodriguez and others 2010), these compounds have not been studied yet in the local swimming pool waters.

Table 4. Comparison of analytical methods for monochloroacetic acid in swimming pool water

		Method performance			
Analytical technique	**Sample preparation**	**LOD**	**Linearity**	**% Recoveries**	**Reference**
Ion chromatography-conductivity detection	Ag/H cartridge	0.02 mg L^{-1}	0.05-1.0 mg L^{-1}	122 (0.2 mg L^{-1} spike level in swimming pool water and 0.6 mg L^{-1} in distilled water)	This study
GC-MS	MTBE extraction; diazomethane derivatization	2 ng L^{-1}	0-0.005 mg L^{-1}	96 (100-430 ng L^{-1} spike level in nanopure water)	Berg and others 2000
GC-ECD	MTBE extraction; 10% sulfuric acid in methanol derivatization	*not reported*	*not reported*	*not reported*	Lee and others 2010
GC-ECD	MTBE extraction; 10% sulfuric acid in methanol derivatization	0.1-1.6 µg L^{-1}	*not reported*	*not reported*	Catto and others 2012
GC-ECD	MTBE extraction; 10% sulfuric acid in methanol derivatization	1.3 µg L^{-1}	*not reported*	*not reported*	Simard and others 2013
Ultraperformance liquid chromatography-diode array detection	Membrane-protected micro-solid phase extraction	0.07 µg L^{-1}	1-150 µg L^{-1}	91.6-95.1 (10 µg L^{-1} spike level in swimming pool water)	Nsubuga and Basheer 2013

Table 4 lists analytical methods used in the determination of monochloroacetic acid in swimming pool water. The main advantage of the ion chromatographic method used in this present study is that it eliminates the use of harmful derivatization reagents such as diazomethane and extraction solvents such as MTBE. Solvent extraction and GC-ECD or MS are the common techniques in monochloroacetic acid analysis and when combined with sample preconcentration steps, very low detection limits can be achieved such as those reported by Catto and others (2012), and Berg and others (2000). Although the detection limit of monochloroacetic acid using the ion chromatographic method is relatively high, this method is less costly and easier to use than the GC-based methods.

The results of this initial study prompt the need to examine further the occurrence of disinfection by-products in swimming pool waters in order to protect the public from exposure to these compounds. Extensive data are required as basis for setting up measures in minimizing the levels of disinfection by-products in public swimming pools.

The analytical method involving ion chromatography with conductivity detection developed in this study provides a simple method for use in determining monochloroacetic acid in swimming pool water. In addition, this method has potential application in the determination of monochloroacetic acid in chlorinated drinking water. The method may be used by laboratories of water providers and regulatory agencies in the Philippines. If used in drinking water analysis, a pre-concentration step may be necessary because drinking water contains less organic matter than swimming pool water; thus, the monochloroacetic acid concentration may be lower. The 2007 Philippine National Standards for Drinking Water stipulates that monochloroacetic acid in our drinking water should not exceed 0.02 mg L^{-1}. The ion chromatographic method presented in this study has a detection limit of 0.02 mg L^{-1}. This is thus an available method for detecting monochloroacetic acid in concentrations above the guideline value for drinking water. This method can still be modified and improved if used in the determination of very low concentrations of monochloroacetic acid (<0.02 mg L^{-1}) especially in relatively clean water such as drinking water. The detection limit can be lowered with the use of SPE and preconcentration steps and more sensitive detection techniques such as mass spectrometry in ion chromatography. Nonetheless, this method in its present form can still be used in compliance monitoring of monochloroacetic acid in the local water supplies.

CONCLUSIONS

Ion chromatography with conductivity detection is applicable for the determination of monochloroacetic acid in swimming pool water. This method has low detection limit at 0.02 mg L^{-1}. It is reproducible and does not require harmful reagents such as diazomethane and MTBE extraction solvent. Low concentration chloride and bromide may be analyzed together with monochloroacetic acid in water using the optimized ion chromatographic method. In high chloride content water samples like swimming pool water, an Ag/H cartridge is necessary for monochloroacetic acid determination. The detection of monochloroacetic acid in the water of some swimming pools studied suggest the need to further investigate the occurrence of monochloroacetic acid as well as the other disinfection by-products in swimming pools in order to protect public health.

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