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# Headspace Solid Phase Microextraction 방법에 의한 HAAs 분석에 관한 연구

# Analysis of Haloacetic Acids in Drinking Water by Direct Derivatization and Headspace-SPME Technique with GC-MS

조 덕 희*

Cho Deok-Hee*

성남시 상하수도사업소 정수과

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**Abstract**

In many drinking water treatment plants, chlorination process is one of the main techniques used for the disinfection of water. This disinfecting treatment leads to the formation of haloacetic acid (HAAs). In this study, headspace solid-phase microextraction (HS-SPME) was studied as a possible alternative to liquid-liquid extraction for the analysis of HAAs in drinking water. The method involves direct derivatization of the acids to their methyl esters without methyl tert-butyl ether (MTBE) extraction, followed by HS-SPME with a 2cm-50/30$\mu$m divinylbenzene/carboxen/polydimethylsiloxane fiber. The effects of experimental parameters such as selection of SPME fiber, the volume of sulphuric acid and methanol, derivatization temperature and time, the addition of salts, extraction temperature and time, and desorption time on the analysis were investigated. Analytical parameters such as linearity, repeatability and limit of detection were also evaluated.

The 2cm-50/30$\mu$m-divinylbenzene/carboxen/polydimethylsiloxane fiber, sulphuric acid of 1ml, methanol of 3ml, derivatization temperature of 50°C derivatization time of 2hrs, sodium chloride salt of 10g, extraction time of 30 minutes, extraction temperature of 20°C and desorption time of 1 minute at 260°C were selected as the optimal experimental conditions for the analysis of HAAs. The linearities ($r^2$), relative standard deviations (%RSD) and limits of detection (LOD) for HAAs were 0.9978~0.9991, 1.1~9.8% and 0.05~0.2$\mu g/l$, respectively.

**Key words:** HAAs, Derivatization, HS-SPME, Drinking water analysis
**주제어**: HAAs, 유도체화방법, HS-SPME, 먹는물 분석방법

*Corresponding author Tel: +82-31-729-5861, FAX : +82-31-751-0838, E-mail: deck@cans21.net (Cho, D.H.)

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## 1. Introduction

Chlorine is applied to drinking water in order to deactivate microorganism and to ensure the residual concentration in drinking water distribution systems, thus protecting water from microorganism regrowth. However, water chlorination for disinfection leads to the formation of a wide range of halogenated compounds from natural organic matter. The most common disinfection by-products (DBPs) are trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitrils (HANs) (Bull & Kopfler, 1991).

The United States Environmental Protection Agency (US EPA) has established, in the first stage of the D/DBP Rule, a maximum contaminant level (MCL) of 60$\mu g/l$ for the sum of five haloacetic acids : monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) (US EPA, 1998). Korea also has established drinking water quality standard of 100$\mu g/l$ for the sum of DCAA and TCAA. Because of the very high toxic and carcinogenic risks of some HAAs (World Health Organization, 1996), fast and accurate analytical methods for these substances are needed to monitor their concentrations, behaviours and distributions in drinking water. For HAAs analysis, currently, there are three US EPA approved methods, including the EPA Method 552.1, EPA Method 552.2 and Standard Method 6251 (US EPA, 1992; 1995; Clesceri et al., 1998). In all three methods, HAAs are extracted from water samples using methyl tert-butyl ether (MTBE) or anion exchange resins, converted into methyl esters using diazomethane or acidic methanol, and analyzed using gas chromatography-electron capture detection (GC-ECD).

Solid-phase microextraction (SPME) is of the newest approach in the analysis of environmental analytes. This technique has been successfully applied to the analysis of THMs (Stack et al., 2000; Cho & Oh, 2001; Cho et al., 2003), aldehydes (Cancho et al., 2001), geosmin and MIB (Watson et al., 2000), BTEX (Liompart et al., 1999), organochlorine pesticides (Doong & Liao, 2001), PAHs (Popp et al., 2000) and HAAs (Sarrion et al., 1999; Cho & Oh, 2003). It is fast, sensitive, inexpensive, portable and solvent-free.

In this paper, a new method for the analysis for HAAs in water using headspace SPME is proposed. Instead of methyl ester conversion using acidic methanol after MTBE extraction, direct derivatization without MTBE extraction was chosen.

The aim of this study was to develop the rapid and simple method for HAAs analysis in drinking water by headspace SPME and then apply this technique for an investigation program concerning the HAAs concentration in Seongnam drinking water.

## 2. Experimental

### 2.1. Gas chromatography-mass spectrometric system and conditions

Separations were carried out on a Platform mass spectrometer (Micromass, Britain UK) equipped with Agilent 6890 gas chromatography. The analytical column was HP-5MS (60m × 0.25mmID, 0.25$\mu m$ film thickness, J&W Scientific). The detailed operating conditions for GC-MS are shown in **Table 1**. For quantification, two characteristic ions of the spectrum obtained for methyl haloacetate were selected: 77/59m/z for methyl monochloroacetate, 93/59m/z for methyl monobromoacetate, 83/59m/z for methyl dichloroacetate, 117/59m/z for methyl trichloroacetate, 129/59m/z for methyl bromochloroacetate and 173/59m/z for methyl dibromoacetate. The first ion was used for determination and second ion for confirmation.

### 2.2. Reagents

2.2.1. Reagent water

Standards and blanks were prepared from double distilled water (using a Milli-Q plus system from millipore, France) which was boiled for 1 hour in a large beaker.

**Table 1.** Operation conditions for GC-MS

| Class | Conditions | |
|---|---|---|
| Carrier gas | helium, 1.2ml/min | |
| Split ratio | 1 : 1 | |
| Inlet liner | 0.75mm ID (SPME injection sleeve) | |
| Injector temp. | 260°C | |
| Oven | 40°C for 1 min, 20°C /min to 80°C, 5°C /min to 130°C, 10°C/min to 200°C, 25°C/min to 250°C and held 2 min (total time 24 min) | |
| Solvent delay | 5 min | |
| Interface temp. | 250°C | |
| Mass(Source) | Mode | EI positive, SIR mode |
| | Electron energy | 70 eV |
| | Emission | 200μV |
| | Temperature | 200°C |
| | Multiplier | 500V |
| | Reference gas | heptacosa |
| | Tune ion | 69, 131, 219, 414 |

2.2.2. Standard solutions

After opening vials or tubes containing standards or samples, they must be sealed as quickly as possible to avoid evaporation or contamination. A stock solution of a HAA mixture (MCAA, MBAA, DCAA, TCAA, BCAA and DBAA) containing each compound at 2mg/ml MTBE was purchased from Supelco. Intermediate standard solutions at 0.04, 0.4, 4mg/l MTBE were obtained by the dilution of stock standard solution with MTBE (EM science, USA). The working standard solution in the range of 0.5~40μg/l aqueous (n = 6) were diluted from 0.04, 0.4, 4mg/l MTBE directly in 50ml vials. The appropriate reagent water volume was 40ml in each vial. The each standard solution and sample were added into the internal standard (i.s., spiked at a level of 1μg/l of 1.2.3-trichloropropane, 1.2.3-TCP, Supelco) and 10g of sodium chloride (baked for 4 hrs at 450°C) was also added into the solution.

### 2.3. Sample collection

Water samples were collected in the test tubes. The dechlorination agent (L-ascorbic acid, Junsei), as neat material, was first added into test tubes, 10mg for 10ml sample (Norin & Renberg, 1980). Before sampling, the tap was allowed to run for 1 minute after the test tubes were carefully and completely filled. The sample were analyzed directly or stored up to a maximum of 3 day at 4°C.

### 2.4. Derivatization and headspace SPME procedure

Optimal derivatization procedure were established in order to obtain maximal reaction yields for HAAs. This optimization was developed by consecutively changing volume of sulphuric acid and methanol, derivatization temperatures and derivatization times, while the headspace SPME extraction temperature and time were maintained at 20°C and 30min, respectively. In order to optimize the volume of sulphuric acid and methanol, the volume of sulphuric acid was increased from 0.25 to 2.5ml when the methanol volume was fixed at 3ml and methanol was increased from 1 to 6ml when the sulphuric acid volume was fixed at 1ml. For this purpose, the derivatizing temperature and time were fixed at 50°C and 2 hours, respectively. In order to optimize the derivatization temperature and time, the temperature was increased from 40 to 70°C when the time was fixed at 2 hours and derivatization time was increased from 0.5 to 3 hours when temperature was fixed at 50°C. During the derivatization optimization, the volume of sulphuric acid and methanol volume were fixed at 1ml and 3ml, respectively. After optimal conditions for an efficient derivatization of HAAs had been established, parameters that affect the sensitivity of headspace SPME, such as effect of the addition of salts (sodium chloride and anhydrous sodium sulfate), extraction temperature, extraction time (increased from 10 to 80 minutes at 20°C) and desorption time (increased from 0.5 to 2 minutes at 260°C) were optimized.

Water samples were analyzed in duplicate with each fiber. Samples (40ml) were transferred into vial (50ml) which contained 1ml sulphuric acid, 3ml methanol and 10 g sodium chloride salt. The sample was vortex mixed and incubated for 2 hrs at 50°C in order to derivate the HAAs. The extraction time was 30 minutes at 20°C and desorption time was 1 minute at 260°C for all fibers.

Quantification of the five analytes was performed using

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**Table 2.** Commercially available fiber coatings (Supelco, Bellefonte, PA)

| Stationary Phase | Film Thickness | Description |
|---|---|---|
| Polydimethylsiloxane | 100$\mu$m | Non-bonded |
| Divinylbenzene/carboxen/polydimethylsiloxane | 50/30$\mu$m | Highly crosslinked |
| | 2cm-50/30$\mu$m | |
| Polydimethylsiloxane/divinylbenzene | 65$\mu$m | Partially crosslinked |
| Polyacrylate | 85$\mu$m | Partially crosslinked |

the peak area ratios of the analyte relative to the internal standard based on multi-level calibration from 0.5 to 40$\mu g/l$ (n = 6). The concentrations of analytes were automatically calculated by relating to created calibration curves, where the peak area relationships (sample/i.s.) were plotted as a function of concentration (sample/i.s.).

## 3. Results and discussion

### 3.1. Selection of SPME fibers

The choice of an appropriate coating is essential for the establishment of a headspace SPME method and it is dependent on the chemical nature of the target analytes.

In this study five types of fibers, 100$\mu$m polydimethylsiloxane (100-PDMS), 50/30$\mu$m divinyl benzene/carboxen/polydimethylsiloxane (50/30-DVB/CAR/PDMS), 2cm-50/30$\mu$m divinylbenzene/carboxen/polydimethylsiloxane (2-50/30-DVB/CAR/PDMS), 65$\mu$m polydimethylsiloxane/divinylbenzene (65-PDMS/DVB) and 85$\mu$m polyacrylate (85-PA) were used to select the appropriate fiber for the analysis. New fibers were conditioned, following the manufacturer's recommendations. **Table 2** presents a summary of commercially available fiber coatings (Supelco, Bellefonte, PA) and their suggested applications.

In order to evaluate the extraction efficiency, the peak areas obtained for each HAAs with the different fibers are shown in **Fig. 1**. Extraction efficiencies for the HAAs were increased according to the following order; 100-PDMS < 85-PA < 65-PDMS/DVB < 50/30-DVB/CAR/PDMS < 2-50/30-DVB/CAR/PDMS. The polydimethylsiloxane (PDMS) fiber (a non-polar phase) is not the best coating due to its low capacity to extract these compounds. Property of the mixed divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was different from that of PDMS due to the porous carbon adsorbent (Carboxen). This modifies the selectivity toward polar compounds and thus improves the extraction efficiency. The 2cm-50/30$\mu$m-divinylbenzene/carboxen/polydimethylsiloxane fiber is suitable for the extraction of HAAs with a relatively high efficiency due to the increase in the surface area of fiber and the suitable polarity.

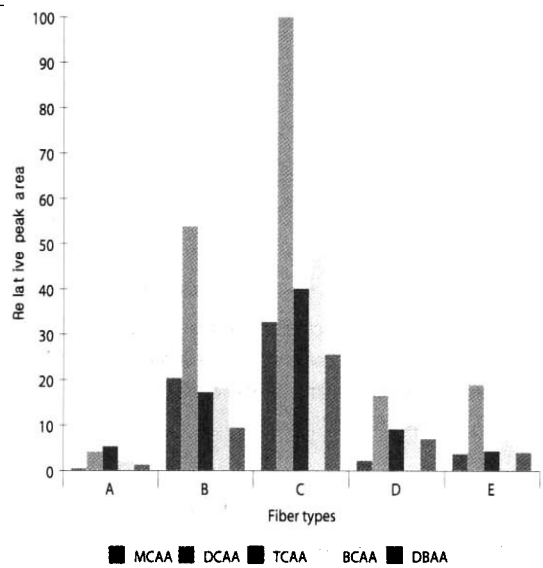


**Fig. 1.** Extraction efficiencies of various fibers: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time: 2 hrs at 50°C, extraction time: 30min at 20°C, desorption time: 1min at 260°C, n = 2.
(A) 100-PDMS (B) 50/30-DVB/CAR/PDMS (C) 2-50/30-DVB/CAR/PDMS (D) 65-PDMS/DVB (E) 85-PA

### 3.2. Derivatization conditions

3.2.1. The volume of sulphuric acid and methanol

In order to optimize the volume of sulphuric acid and methanol, the volume of sulphuric acid was increased

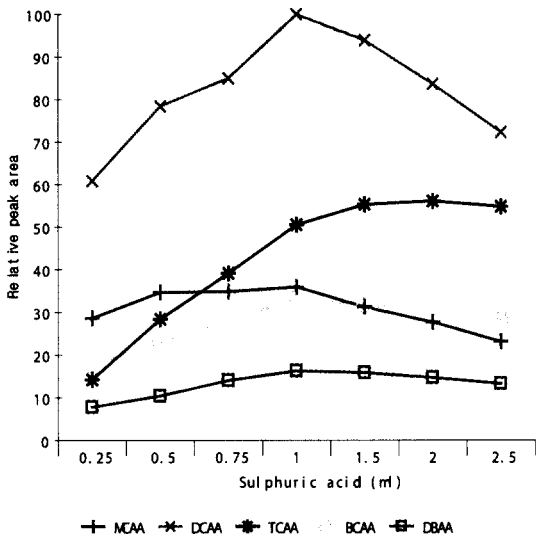


**Fig. 2.** Effect of volume of sulphuric acid on the reaction yield of HAAs: dosage of methanol: 3ml, derivatization time: 2 hrs at 50°C, extraction time: 30 min at 20°C, desorption time : 1min at 260°C, n = 2.

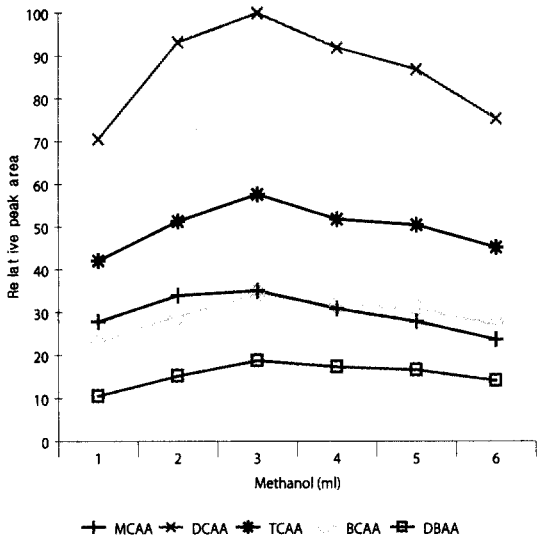


**Fig. 3.** Effect of volume of methanol on the reaction yield of HAAs: dosage of sulphuric acid: 1ml, derivatization time: 2 hrs at 50°C, extraction time: 30min at 20°C, desorption time: 1 min at 260°C, n = 2.

from 0.25 to 2.5ml when the methanol volume was fixed at 3ml and methanol was increased from 1 to 6ml when the sulphuric acid volume was fixed at 1ml. For this purpose, the derivatizing temperature and time were fixed at 50°C and 2 hours, respectively.

The volume of sulphuric acid significantly affected the responses obtained for the HAAs (**Fig. 2**). Generally, the area of the HAAs increased, reached a maximum, then decreased. For four HAAs (MCAA, DCAA, BCAA and DBAA), the highest peak areas were obtained for 1ml of sulphuric acid. However, the TCAA was obtained highest peak areas at 2ml, although other HAAs were decreased. At a volume of sulphuric acid higher than 1ml, a decrease for HAAs was observed that could be due to lower esterification efficiency or decomposition of the esters. In addition, the presence of large amounts of sulphuric acid in the headspace can oxidize the fiber coating giving dimethyl sulfate, which appeared as an important component in the chromatogram (Sarrion et al., 1999). So, in order to good responses for HAAs, 1ml of sulphuric acid was chosen. The effect of methanol volume when the sulphuric acid volume was fixed at 1ml is shown in **Fig. 3**. Maximum sensitivity for all HAAs was achieved at 3ml of methanol. In increased of methanol volume over 3ml, the response was decreased. This decrease could be due to lower derivatization efficiency or to a decrease in the fiber absorption capacity at high percentages of methanol. So, in order to obtain good responses for HAAs, 3ml of methanol was chosen for the reminder experiments of this study.

3.2.2. Effect of derivatization temperature and time

In order to optimize the derivatization temperature and time, the temperature was increased from 40 to 70°C when the time was fixed at 2 hours and derivatization time was increased from 0.5 to 3 hours when temperature was fixed at 50°C. For this purpose, the volume of sulphuric acid and methanol volume were fixed at 1ml and 3ml, respectively.

The effect of derivatizing temperature on the reaction yield of the HAAs was studied. The highest response was obtained at 50°C and increasing of derivatizing temperature over 50°C was decreased (**Fig. 4**). The derivatizing time significantly affected the responses obtained for the HAAs. For MCAA, the highest peak

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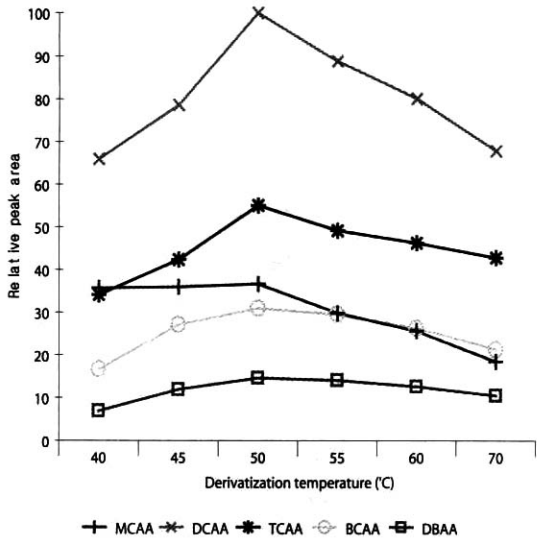


**Fig. 4.** Effect of derivatization temperature on the reaction yield of HAAs: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time: 2hrs, extraction time : 30min at 20°C, desorption time: 1min at 260°C, n = 2.

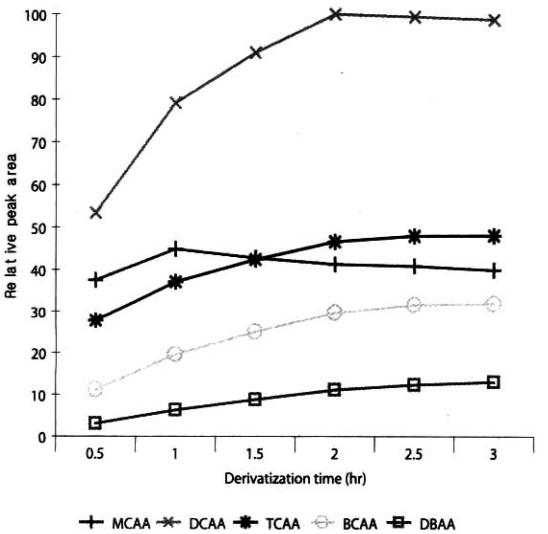


**Fig. 5.** Effect of derivatization time on the reaction yield of HAAs: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time: 2 hrs, extraction time: 30min at 20°C, desorption time: 1min at 260°C, n = 2.

areas was obtained at 1 hr of derivatization time. However, the TCAA, BCAA and DBAA were obtained highest peak areas at 2.5 hrs and DCAA was obtained at 2

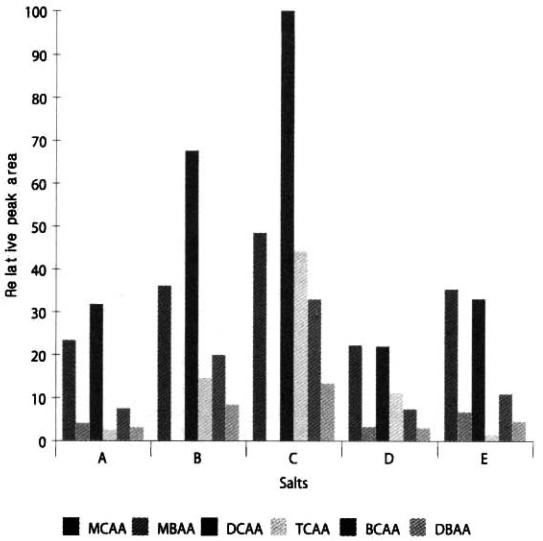


**Fig. 6.** Effect of the addition of salts on the extraction: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time: 2hrs at 50°C, extraction time: 30min at 20°C, desorption time : 1min at 260°C, n = 2.
(A) without salt (B) NaCl 5g (C) NaCl 10g (D) $Na_2SO_4$ 5g (E) $Na_2SO_4$ 10g

hrs (**Fig. 5**). So, in order to obtain adequate responses for HAAs, 50°C and 2 hrs of derivatization temperature and time were chosen, respectively.

### 3.3. Headspace SPME conditions

3.3.1. Effect of the addition of salts

Addition of salts may result in the change of the vapor and partial pressure, solubility, thermal conductivity, density, surface tension, etc. of an analytes. These changes, if they occur, will result in the variation of the vapor/liquid equilibrium system (Banal et al., 1999). Two types of salts were used to improve performance (analyte recovery) in HS-SPME such as sodium chloride and anhydrous sodium sulfate. The highest recoveries of HAAs were achieved with 10g sodium chloride salts (**Fig. 6**). Compared to unsalted samples, relative recovery of 10 g sodium chloride salted sample was 2.1, 3.1, 17.6, 4.4 and 4.3 times greater for MCAA, DCAA, TCAA, BCAA and DBAA, respectively, but MBAA was not detected. When 10 g sodium chloride salted sample, recoveries of MCAA, DCAA, TCAA, BCAA and DBAA were 1.4, 3.0, 30, 3.0

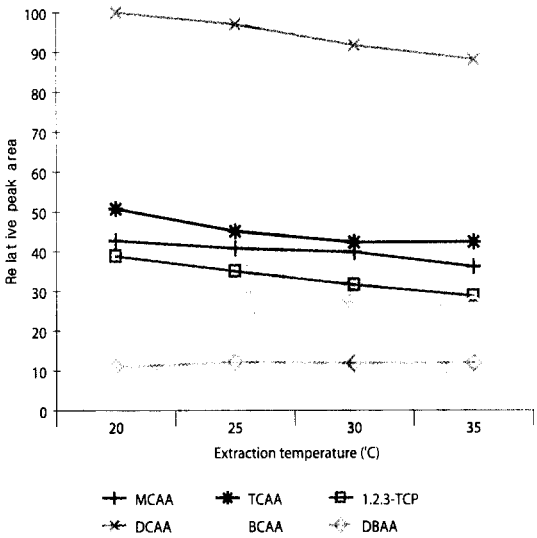


**Fig. 7.** Effect of extraction temperature for HAAs: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time : 2hrs at 50°C, extraction time: 30min, desorption time: 1min at 260°C, n = 2.

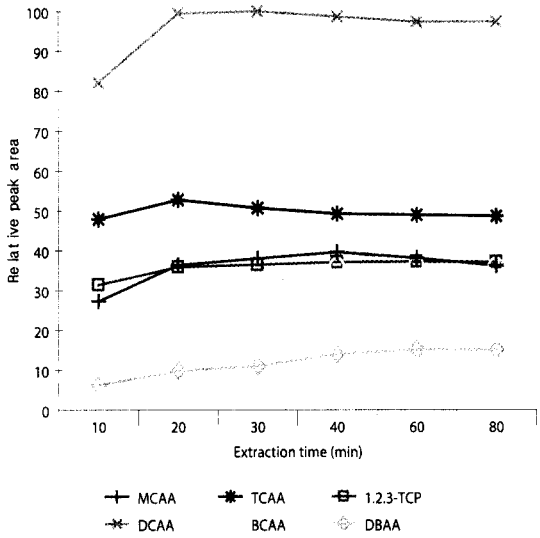


**Fig. 8.** Effect of extraction time for HAAs: dosage of sulphuric acid: 1ml, dosage of methanol: 3ml, derivatization time: 2hrs at 50°C, extraction temperature 20°C, desorption time : 1min at 260°C, n = 2.

and 2.9 times better than those at 10g anhydrous sodium sulfate salted sample.

With HS-SPME, the addition of salts into the aqueous sample prior to the extraction process, an increase of the ionic strength of the solution was obtained. As a consequence, the diffusion of the analytes into the headspace is favored and extraction time for each analyte is reduced.

3.3.2. Effect of extraction temperature

In order to evaluate the extraction efficiency, the experiment was performed using 2-50/30-DVB/CAR/PDMS fiber and extraction temperature was increased from 20 to 35°C.

As can be seen in **Fig. 7** that MCAA, DCAA, TCAA, BCAA and 1.2.3-TCP were yielded the higher extraction efficiencies at 20°C, whereas DBAA was yielded the higher extraction efficiencies at 25°C.

With HS-SPME, higher temperature may result in the increased vapor pressure of volatile analytes in the headspace owing on the temperature dependence of the Henry's constant. However, higher temperature may also have the negative effect of less favorable coating-headspace (air) partition coefficients (Zhang & Pawliszyn, 1995; Nilsson et al., 1995; Jia et al., 1998).

3.3.3. Effect of extraction and desorption time

In order to evaluate extraction efficiency, the experiment was performed using 2-50/30-DVB/CAR/PDMS fiber and extraction time was increased from 10 to 80 minutes at 20°C. The peak areas obtained for each HAAs with different extraction times are shown in **Fig. 8**. Acceptable equilibrium states (30 min) were achieved for MCAA, DCAA, TCAA, BCAA, DBAA and 1.2.3-TCP. However, the equilibrium state was reached until 60 minutes for each compound, indicating that the diffusion of the analytes from the liquid phase into the headspace was important in the equilibration process. With extraction process, there is no need to achieve complete equilibrium concentrations if only the exposure time of the fiber is kept exactly constant.

In order to determine desorption time, the time was increased from 0.5 to 2 minutes at 260°C (not printed). The desorption was completed for each compound after 0.5 minute at 260°C.

Previous studies (Nilsson et al., 1995) on the effect of

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**Table 3.** Correlation coefficients ($r^2$) of linearity, repeatability and limits of detection at standard concentration range from 0.5 to 40$\mu g/l$.

| Compound | R.T. (min) | Linear ($r^2$) | %RSD | | LOD($\mu g/l$) |
|---|---|---|---|---|---|
| | | 0.5~40 (n = 6) | 5 (n = 5) | 20 (n = 5) | |
| MCAA | 5.62 | 0.9978 | 5.13 (9.8) | 20.08 (5.6) | 0.2 |
| DCAA | 6.76 | 0.9991 | 5.05 (4.8) | 19.66 (2.3) | 0.05 |
| TCAA | 8.17 | 0.9987 | 4.94 (2.4) | 19.87 (1.1) | 0.1 |
| BCAA | 8.22 | 0.9988 | 4.91 (2.6) | 20.07 (1.3) | 0.1 |
| DBAA | 9.91 | 0.9989 | 5.11 (3.9) | 20.13 (2.4) | 0.2 |

temperature on absorption of analytes showed that at lower temperatures the range of diffusion was slower and equilibration time was longer. Increasing the temperature decreases the distribution constants as absorption is generally on exothermic process and the amount of analyte absorbed onto the fiber decreased. For this reason, the extraction time of 30 minutes at 20°C in the headspace mode and desorption time of 1 minute at 260°C were selected for the linearity, repeatability and limits of detection (LOD) studies.

### 3.4. Linearity, repeatability and limits of detection

The linearity range of the HS-SPME method was evaluated by plotting the calibration curves of the area relative to the internal standard 1.2.3-trichloropropane versus the concentration of each analyte. Standard calibration curves were plotted for concentrations ranging from 0.5 to 40$\mu g/l$ (n = 6). The correlation coefficients ($r^2$) of linearity obtained for each compound are shown in **Table 3**.

The correlation coefficients ($r^2$) for MCAA, DCAA, TCAA, BCAA and DBAA were 0.9978, 0.9991, 0.9987, 0.9988 and 0.9989, when analyte concentration ranges from 0.5 to 40$\mu g/l$, respectively.

The sensitivity of the HS-SPME method was considered in terms of limits of detection (LOD) which depend on the basis of the signal-to-noise ratio (s/n > 3). The average s/n of triplication at low concentration was used the LOD, under the experimental conditions, the detection limits (**Table 3**) were 0.05$\mu g/l$ for DCAA, 0.1$\mu g/l$ for TCAA and BCAA and 0.2$\mu g/l$ for MCAA and DBAA. The repeatability of HS-SPME was investigated by analyzing the fortified reagent water. The relative standard deviations (%RSD) for repeatability ranges 2.4~9.8% and 1.1~5.6% at standard concentration of 5 and 20$\mu g/l$, respectively, indicating that HS-SPME was properly performed.

Previous studies (Sarrion et al., 1999) showed that the correlation coefficients ($r^2$) and LOD using the 100$\mu$m-PDMS fiber were 0.998~0.999 and 0.01~0.2$\mu g/l$ at HAAs concentration range from 0.5 to 135$\mu g/l$, respectively. In Sarrion's study, 30ml of sample was concentrated at 50°C to 400$\mu$l for 15 min using a rotary evaporator, and the residue was transferred to 5ml vial. After evaporation to dryness, 0.1 g of sodium sulfate, 30$\mu$l of concentrated sulphuric acid and 40$\mu$l of ethanol were added to vial. The solution was vortex mixed and the HAAs were derivertized at 50°C for 10 min. An extraction time of 10 min, an extraction temperature 25°C and desorption time of 2 min at 250°C were used. In direct derivatization of the acids to their methyl esters without methyl tert-butyl ether (MTBE) extraction (Cho & Oh, 2003), the linearity ($r^2$), %RSD and LOD for DCAA and TCAA using the 2cm-50/30$\mu$m-divinylbenzene/carboxen/polydimethylsiloxane fiber were 0.9981~0.9997, 3.5~2.1% and 0.05~0.1$\mu g/l$, respectively. In liquid-liquid extraction (US EPA 552) (Dalvi et al., 2000), LOD was 0.1~10$\mu g/l$ at HAAs concentration range of 0.1~100$\mu g/l$ and liquid-liquid extraction (US EPA 552) (Benanou et al., 1998), LOD and %RSD were 0.06~2$\mu g/l$ and 0.3~10% at HAAs concentration range of 0.1~20$\mu g/l$.

### 3.5. HAAs concentrations in Seongnam drinking water

The method described has been used for HAAs investigations of Seongnam (Kyonggi province, Korea)

**Table 4.** HAAs concentrations ($\mu g/l$) in Seongnam drinking water (October 2003).

| Sample sites | MCAA | DCAA | TCAA | BCAA | DBAA | $HAA_2$* | $HAA_5$ |
|---|---|---|---|---|---|---|---|
| Water works | ND | 3.68 | 5.16 | Tr | ND | 8.84 | 8.84 |
| Tap water-1 | ND | 3.47 | 5.17 | Tr | ND | 8.64 | 8.64 |
| Tap water-2 | ND | 3.37 | 4.92 | Tr | ND | 8.29 | 8.29 |
| Tap water-3 | ND | 3.76 | 5.85 | Tr | ND | 9.61 | 9.61 |
| Tap water-4 | ND | 2.99 | 11.66 | ND | ND | 14.65 | 14.65 |
| Tap water-5 | ND | 2.52 | 6.51 | ND | ND | 9.03 | 9.03 |
| Tap water-6 | ND | 2.87 | 4.82 | ND | ND | 7.69 | 7.69 |
| Tap water-7 | ND | 4.12 | 7.90 | Tr | ND | 12.02 | 12.02 |
| Tap water-8 | ND | 4.11 | 8.88 | ND | ND | 12.99 | 12.99 |
| Tap water-9 | ND | 3.19 | 5.81 | ND | ND | 9.00 | 9.00 |
| Tap water-10 | ND | 4.24 | 6.89 | Tr | ND | 11.13 | 11.13 |
| Tap water-11 | ND | 2.73 | 6.56 | Tr | ND | 9.29 | 9.29 |
| Tap water-12 | ND | 4.03 | 6.68 | Tr | ND | 10.71 | 10.71 |
| Tap water-13 | ND | 3.82 | 6.91 | ND | ND | 10.73 | 10.73 |
| Tap water-14 | ND | 2.65 | 7.12 | 0.54 | ND | 9.77 | 10.31 |
| Tap water-15 | ND | 3.08 | 4.83 | 0.38 | ND | 7.91 | 8.29 |
| Tap water-16 | ND | 3.02 | 3.69 | 0.87 | ND | 6.71 | 7.58 |
| Tap water-17 | ND | 4.16 | 5.96 | 0.88 | ND | 10.12 | 11.00 |
| Tap water-18 | ND | 4.11 | 6.21 | 0.91 | ND | 10.32 | 11.23 |
| Tap water-19 | ND | 3.22 | 4.29 | 0.52 | ND | 7.51 | 7.76 |
| Average | ND | 3.46 | 6.29 | 0.21 | ND | 9.75 | 9.96 |

*) $HAA_2$: DCAA + TCAA

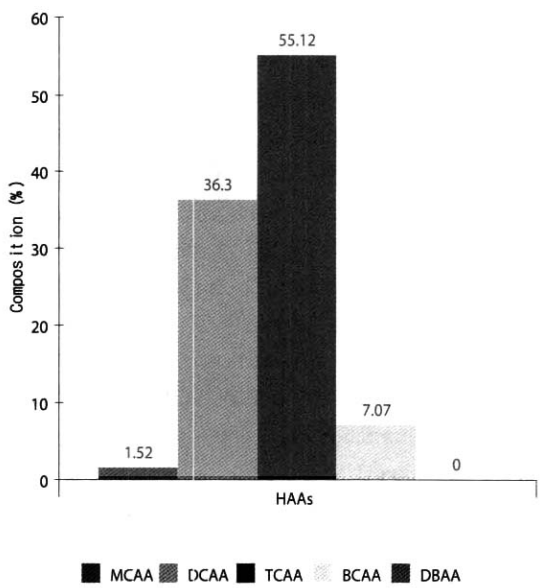


**Fig. 9.** Composition of HAAs in Seongnam drinking water (October 2003)

drinking water. Bok-Jeong (Seongnam) water treatment plants supply drinking water, to nearly 600 thousand peoples, treating 280,000$m^3$/day, and chlorination process is the only technique used for disinfection of drinking water. The sampling was performed at the terminal point for the distribution system in October 2003.

The range of $HAA_5$ and $HAA_2$ concentrations were 7.58~14.65$\mu g/l$ and 6.71~14.65$\mu g/l$, respectively (**Table 4**). **Fig. 9** shows the composition of HAAs in Seongnam drinking water. The TCAA was the largest class of HAAs measured. The next significant HAAs fraction was DCAA. The highest $HAA_5$ and $HAA_2$ concentrations were recorded at tap-water 4, with a level of 14.65$\mu g/l$. This is within the proposed US EPA MCL of 60$\mu g/l$ and Korea drinking water standard of 100$\mu g/l$.

## 4. Conclusions

Direct derivatization of the acids to their methyl esters without methy tert-butyl ether (MTBE) extraction,

followed by HS-SPME technique was applied to determine haloacetic acids (HAAs) in drinking water. Experimental parameters such as 2cm-50/30$\mu$m divinylbenzene/carboxen/polydimethylsiloxane fiber, sulphuric acid of 1ml, methanol of 3ml, derivatization temperature of 50°C, derivatization time of 2 hrs, sodium chloride salt of 10g, extraction time of 30 minutes, extraction temperature of 20°C and desorption time of 1 minute at 260°C were selected as the optimal experimental conditions for the analysis of haloacetic acids. The linearities ($r^2$) for HAAs were 0.9978~0.9991 when analyte concentration ranges from 0.5 to 40$\mu g/l$. The relative standard deviations (%RSD) for HAAs were 2.4~9.8% and 1.1~5.6% for concentration of 5 and 20$\mu g/l$ (n = 5), respectively. The limits of detection (LOD) were between 0.05 and 0.2$\mu g/l$. It can be concluded that HS-SPME technique with direct derivatization has a great potential for the analysis of drinking water.

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