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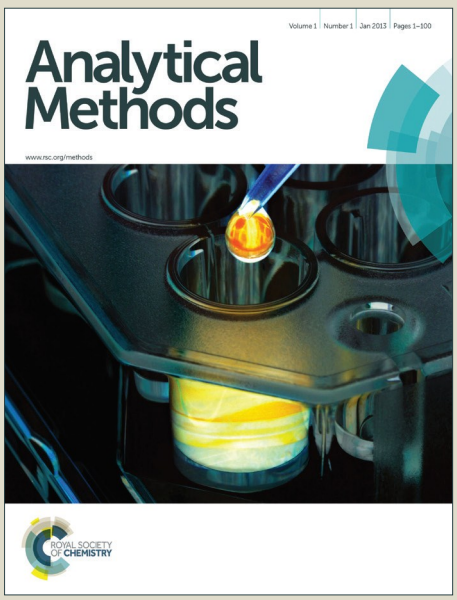

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Cold on-Column Injection Coupled with Gas Chromatography/Mass Spectrometry for Determining Halonitromethanes in Drinking Water

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Abstract

Halonitromethanes (HNMs) are a class of halogenated nitrogenous disinfection by-products (N-DBPs) in drinking water which possess health concerns due to their potentially higher toxicity than regulated disinfection by-products (DBPs). A cold on-column (COC) injection in track-oven mode coupled with gas chromatography-mass spectrometry (GC-MS) system for the analysis of HNMs has been developed. Comparative experiments showed COC had an advantage over the conventional split/splitless injection in minimizing thermal degradation of HNMs, especially dibromochloro- and tribromo-nitromethanes in water. Both debromo- and denitro-products of HNMs were observed in the splitless injection mode at 117 °C and 170 °C. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) procedures were compared for sample pretreatment. LLE showed good recoveries of 73-91% for all nine HNMs. In comparison, SPE provided similar recovery range for four commonly detected HNMs in drinking water: dichloronitromethane, trichloronitromethane, bromochloronitromethane and dibromonitromethane in drinking water, while the recoveries of the other HNMs were below 50%. This indicated that SPE-COC-GC-MS method can be a good alternative to LLE-COC-GC-MS for the identification and quantification of the four HNMs commonly present in tap water due to simplicity of SPE pretreatment technique.

Keywords

Halonitromethanes; Cold on-column injection; Gas chromatography – mass spectrometry; Solid phase extraction; Drinking water

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1. Introduction

Chlorine is an effective disinfection agent in removing harmful microorganisms in drinking water, but at the same time chlorine also oxidizes organic matter to produce disinfection by-products.[1, 2] Among the DBPs, halonitromethanes (HNMs) have received special attention due to their higher cytotoxicity, genotoxicity and developmental toxicity than those regulated DBPs.[3, 4] Generally, HNMs consist of nine chlorine- and bromine- substituted nitromethanes, namely monochloro-(CNM), dichloro-(DCNM), trichloro-(TCNM), monobromo-(BNM), dibromo-(DBNM), tribromo-(TBNM), bromochloro-(BCNM), bromodichloro-(BDCNM) and dibromochloro-(DBCNM). Development of analytical methods for the determination of HNMs in drinking water is important to generate knowledge on drinking water quality. It has been reported that the average concentrations of the two most commonly detected HNMs, TCNM and DBNM, ranged from undetectable to 3.4 μg/L in drinking water treated with chlorine or monochloramine.[5] TCNM levels in waste water processing effluents ranged from 0.9 to 1.5 μg/L.[6]

For the detection of HNMs, most analytical methods are based on USEPA 551.1 method. In these methods, a liquid-liquid extraction procedure is used for the sample pretreatment, followed by analysis using gas chromatography with an electron-capture detection (GC-ECD) [7, 8] or gas chromatography with a mass spectrometer detector (GC-MS).[6, 9-11] Besides LLE, other analytical methods for determining volatile organic compounds including trichloronitromethane in water are solid phase microextraction (SPME) GC-MS, headspace (HS)-SPME-GC-ECD and Purge & Trap-GC-MS, have also been reported for the determination of TCNM and other volatile organic compounds in water.

Recently, three specialized sample pretreatment methods for the determination of the nine HNMs in water have been reported. They are single drop microextraction (SDME) in headspace mode,[9] micro liquid-liquid extraction (MLLE) in combination with a programmed temperature vaporizer (PTV) for the large sample volumes

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injection[10] and static HS-GC-MS,[11] providing a detection limit range of 0.06-1.2, 0.03-1.3 and 0.03-0.6 μg/L for the nine HNMs, respectively.

Analysis using GC-MS operated in traditional split/splitless injection mode could lead to thermal degradation of some HNMs that are thermally unstable.[12] Even at the low injection temperature of 170 °C, which is used in most reported studies, decomposition of some HNMs can be observed.[9, 11, 13] Cold on-column technique has been already used to minimize degradation of thermally labile compounds during GC analysis.[12, 14-16] The COC injection greatly reduces the risk of thermal degradation by directly injecting the sample onto the GC column at reduced temperature. Instead of using low injection temperatures as most methods have done, COC injection offers a better solution since frequent use of GC injection with too low temperatures may increase the retention of less thermally labile substances (other than HNMs) in the injection port, leading to more frequent maintenance. For example, COC injection has been shown to be more sensitive than both programmable temperature vaporizer (PTV) injection and pulsed splitless injection for the analysis of thermally labile fungicides, pesticides and explosive residues.[14-16]

The aim of this study is to develop an analytical method which applies COC injection technique to measure the nine HNMs in drinking water. Both LLE and SPE sample pretreatment procedures have been evaluated for their performance in extracting HNMs from drinking water.

2. Material and methods

2.1. Standards and chemicals

CNM (93.1%), DCNM (98.2%), BCNM (91.2%), BDCNM (92.9%), DBNM (96.3%), DBCNM (97.6%) and TBNM (99.9%) were supplied by Cansyn Chem. Corp. (Canada). TCNM (99.9%) and BNM (90.0%) were obtained from Supelco (USA). The internal standard, 1-Chloro-2-fluorobenzene (99.0%), was purchased from Sigma-Aldrich (USA). A stock solution of a trihalomethanes (THMs) mixture (chloroform, bromodichloromethane, dibromochloromethane and bromoform)

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containing each compound at 0.2 mg/ml MeOH was purchased from Supelco (USA). The solvents, ethyl acetate, acetone and methyl tert-butyl ether (MTBE) were supplied by Tedia (USA). Sulfuric acid, sodium hydroxide and anhydrous sodium sulfate were purchased from Nanjing Chemical Reagent Corporation (China). Solvents and salts were of analytical grade or better. Stock standard solutions containing 2 g/L of individual halonitromethane and mixture solution (0.1 g/L) were prepared in MTBE and stored in amber glass vials at -20 ºC. Working solutions were prepared daily by diluting the mixture solution with MTBE. Pure water (free of DBPs) was supplied by Hangzhou Wahaha Group Co., Ltd. (China) and the ultrapure water was produced using a Millipore S.A.S. SMART water purification system (France) in the laboratory.

2.2. Sample Pretreatment.

2.2.1. Sampling

Tap water samples were collected in 1-L amber glass bottles and immediately adjusted to pH 2-3 with diluted H_2SO_4 solution (4.5 M). The water samples were then transferred to the laboratory and pre-concentrated immediately.

2.2.2. Liquid–liquid extraction procedure

Liquid-liquid extraction (LLE) was conducted according to EPA method 551.1 method with some modifications. Briefly, 200 mL of water sample was adjusted to pH range of 4.5-5.5 with sodium hydroxide (0.1 M) and saturated by addition of 20 g Na_2SO_4, after which it was poured into a 1000-mL separation funnel. Then, the sample was extracted with 20 mL of MTBE through shaking the separation funnel for 5 min. After shaking, the separation funnel was left to stand for 2 min. Then, the upper MTBE layer was transferred to a 50-mL amber pear type glass bottle and dried over 5 g of anhydrous sodium sulfate for 2 hrs.

2.2.3. Solid phase extraction procedure

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Based on the characteristics of HNMs, three types of solid phase extraction (SPE) cartridges, Oasis HLB (6cc, 500 mg ,Waters, USA), Water Sep-pak Vac (6cc, 500 mg, Waters, USA) and Supelclean TM ENVI-18 (6cc, 500 mg, Supelco, USA), were selected to extract and concentrate the nine HNMs from drinking water samples. Prior to sample loading, each cartridge was conditioned with 5 mL of MTBE and 5 mL of methanol in sequence, followed by washing with 10 mL of ultrapure water, at a flow rate of 5 mL/min. The SPE bed was not allowed to dry before sample loading. A water sample (1 L) passed through the SPE cartridge at a flow rate of 5-8 mL/min (2-3 drop/s). After sample loading, the cartridge was washed with 5 mL of ultrapure water and then dried for 10 min under vacuum. The SPE column was immediately eluted with 15 mL of MTBE. The organic eluent was dried over 5 g of anhydrous sodium sulfate for 2 hrs.

The dry organic solution containing HNMs from both LLE and SPE extractions was filtered and concentrated to 1 mL at 20 ℃ using a pressured nitrogen gas blowing concentrator (N-EVAP111 Organomation Associates. Inc, China) and stored in a refrigerator at 4 °C prior to GC-MS analysis.

2.3. Instrumentation

An Agilent 7890A GC equipped with a cold on-column injector and a 5975C MS (Agilent) was used for COC-GC-MS. Another Agilent 7890A GC equipped with a split/splitless (S/SL) injector and a 5975C MS (Agilent) was used for Splitless injection GC-MS. The separation of HNMs was achieved using a capillary column (30 m × 0.25 mm × 0.25 μm film thickness) coated with a stationary phase of 5%-phenyl-95%-methylpolysiloxane (DB-5MS, Supelco, USA). The cold on-column injector was operated in track-oven mode and liquid N_2 acted as coolant, while the conventional S/SL injector temperature was set at 170 °C. The temperature of the GC oven was initially set at 35 °C (6 min) and then raised at 35 °C /min to 130 °C (2 min), and ramped at 20 °C /min to 180 °C (2 min). Helium (6.0 grade purity) was used as carrier gas at a flow rate of 1 mL/min and a solvent delay of 4.8 min was set. The

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transfer line temperature was set at 200 °C. The ion source had a temperature of 200 °C and the quadrupole was kept at 200 °C. The MS was operated in the electron impact ionization mode using electron energy of 70 eV. Optimisation experiments were conducted in a full scan mode (m/z 40 to m/z 300) at 3.5 scans per second. The selected ions monitoring (SIM mode) was used for the quantification of HNMs, the ions monitored are listed in Table 1; m/z 95, m/z 130 (base peak) and m/z 132 were monitored for 1-chloro-2-fluorobenzene acting as internal standard.

GC/ECD analysis was conducted using an Agilent 7890A gas chromatograph equipped with a DB-1 capillary column (30 m×0.25 mm×0.25 μm film thickness) and an electron capture detector, according to EPA 551.1 method. The initial GC oven temperature was at 35 °C (3 min), the temperature was increased at 35 °C /min to 120 °C (1 min) and then 10 °C /min to 180 °C (2 min). The sample (1μL) was injected in splitless mode. The carrier and make-up gases were ultra-high purity (UHP) helium at 1.2 mL/min and UHP nitrogen at 60 mL/min, respectively. The injector temperature was set at 117 °C or 170 °C, and the detector was kept at 280 °C.

3. Results and discussion

3.1. Comparison of injection methods

HNMs, especially the trihalonitromethanes, are thermally unstable under temperatures commonly used in the GC-MS analysis.[9, 13] Relatively low temperatures (170°C) for the injection port and for both the transfer line and the ion source of the mass spectrometer (200 °C) were reported by others to minimize degradation of HNMs.[9] In the present study, nine HNMs were individually analyzed using a GC-ECD equipped with a S/SL injector. The degradation products of two trihalonitromethane (TBNM and DBCNM) were observed at injection temperature of 117 °C and 170 °C (Fig. 1) in the GC-ECD analysis; the degree of the degradation however was greater at 170 °C (Fig. 1B and 1D) than at 117 °C (Fig. 1A and 1C). Degradation of another trihalonitromethane, TCNM, however was not observed at both injector temperatures. Moreover, neither mono- nor dihalonitromethanes

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degraded at these two temperatures.

Debromination and denitration were the major degradation routes of DBCNM and TBNM through loss of a bromine atom or a nitro group to form BCNM and dibromochloromethane (DBCM) (Fig. 1A and 1B), and DBNM and bromoform (TBM) (Fig. 1C and 1D), respectively. Debromination products (BCNM and DBNM) could be verified by comparing their retention times with those of the HNM standards. Both debromination and denitration products of DBCNM and TBNM were further confirmed by using GC-MS with S/SL injection at 170 °C (Fig. 2C, 2D). This result agreed with a previous study in which trihalonitromethanes degraded to haloforms by losing the nitro-group in the molecule when GC injection port temperature was at or greater than 170 °C.[9]

The degradation of two trihalonitromethanes at 170 °C and 117 °C indicated that S/SL injection might not be the best injection technique for these thermally liable compounds. A cold on-column (COC) injection technique was therefore employed to minimize the thermal degradation. In the COC injection, HNMs solution was introduced directly onto the column. During the injection, the inlet was maintained cold at the initial temperature（35°C）to minimize the degradation of the HNMs. The results showed that the cold on-column injection employed in this study was sufficiently gentle to prevent HNMs from degradation in the injection port (Fig. 2A). Total ion chromatograms of the nine HNMs obtained under splitless injection condition at 170 °C showed reduced peak intensity of DBCNM (peak number 8) and TBNM (peak number 9) (Fig. 2B) compared to the peaks in Fig. 2A.

3. 2. Analytical performance of LLE-COC-GC-MS method

LLE is a common sample pre-treatment procedure used in EPA 551.1 method to determine TCNM and other halogenated VOCs in water. In EPA551.1 method, the enrichment ratio [ratio of aqueous volume (50 mL)/organic volume (3 mL)] is 17, which is not high enough for the determination of some trace substances, including HNMs. In this study a larger volume of water sample (200 mL) and a smaller final

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extraction volume (1 mL) was used, resulting in an enrichment ratio of 200. The linearity was assessed in the range of 1.0-1000 μg/L for LLE-COC-GC-MS. The nine- to eleven-point calibration curve for each HNMs showed good linear response of the signal in both methods ($r^2 \geq 0.99$) (Table 1). The limits of detection (LODs) and limits of quantification (LOQs) were calculated based on three times and ten times the standard deviation of the response, respectively. To estimate the LODs, seven purified water samples spiked with 0.1 μg/L of the four HNM (DCNM, TCNM, BCNM and DBNM) and 1 μg/L of the other HNMs (CNM, BNM, BDCNM, DBCNM and TBNM) were analyzed. As shown in Table 1, the LODs of the LLE-COC-GC-MS method were in the range of 0.06 to 0.09 μg/L DCNM, TCNM, BCNM and DBNM, which was in agreement with the previously reported values using modified EPA 551.1 method.[9-12] LODs for the rest of the HNMs were about 10 time higher at 0.7 to 0.9 μg/L. Reproducibility and recovery of the nine HNMs in LLE-COC-GC-MS method were evaluated by analyzing 7 individual standard mixtures at two spiking levels (low level: 0.1 μg/L for DCNM, TCNM, BCNM and DBNM, and 1.0 μg/L for the rest of the HNMs; high level: 5.0 μg/L) in purified water. Low relative standard deviation (RSD) values (~12%), which represent good reproducibility, was achieved for all nine HNMs. The recoveries at high spiking level were in the range of 80 – 91 %. Even at low spiking level, the lowest recovery was 73% (Table 1).

3. 3. SPE as an alternative pretreatment method

Generally, SPE has greater selectivity, good reproducibility and low solvent volumes compared with LLE. There is no report to date on using SPE method for the pre-treatment of HNMs in water for GC/MS analysis. Selecting proper SPE absorbent and eluting solvent for the concentration of analyte of interest is essential in developing a SPE method.[10] Three types of commercial SPE cartridges, Oasis HLB, Supelclean Envi-18 and Water Sep-pak Vac, were tested in this study to compare their extraction efficiencies for the nine HNMs in the purified water spiked with 5 μg/L for each HNMs. Among the three types of cartridges, Oasis HLB showed best

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performance in terms of recoveries (Fig. 3). The average recoveries using Oasis HLB were in the range of 75 – 88% for DCNM, TCNM, BCNM and DBNM. However, recoveries of the other five HNMs (CNM, BNM, BDCNM, DBCNM and TBNM) were < 50%, which might result from their high volatility and instability in the SPE pre-treatment. For example, the very low recovery of CNM (<20%) might attribute to lower boiling point (122 ºC/760 mmHg) and manipulations by SPE extraction which leads to more loss of CNM.

To date, few investigations have been conducted to study the effects of different eluting solvents for the recoveries of HNMs in SPE sample pretreatment. The choice of eluting solvents depends on the chemical and physical properties of the target compounds such as solubility in water and boiling point.[10] Based on the existing knowledge on the commonly used solvents in SPE, several eluting solvents including ethyl acetate, MTBE and acetone, were tested. As shown in Fig.4, MTBE provided best recoveries among the three tested solvents. MTBE, due to its low boiling point (55 °C), usually can accommodate a low temperature in the injection port for the splitless injection to minimize the degradation of trihalonitromethanes among other compounds.[9]

In previous studies, the acidity of water sample was related to the extraction efficiency and the hydrolysis of HNMs.[9, 13, 17] For this reason, the influence of pH in water sample on the stability of HNMs was evaluated in the pH range of 2 to 7.5. As shown in Fig. 5, the similar recoveries of the nine HNMs were observed in water samples between pH 2 and 7.5, although there was a slightly declining trend in recoveries for some HNMs with the increase of the pH. The influence of pH values in water samples for the simultaneous extraction of the nine HNMs by headspace-single drop microextraction (HS-SDME) with 1-hexanol as the solvent was also reported by Montesinos et al..[9] They have shown that recoveries of TCNM were not influenced by the sample pH in 2.0-7.5 and recoveries of DCNM, BCNM, BNM BDCNM, DBCNM, CNM and DBNM were only marginally affected. However, TBNM was influenced by the sample pH, especially when pH value 5.5 exceeded, the extraction efficiency of TBNM decreased more than 50% when compared with pH=3. In EPA 551.1 method,

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water sample was maintained at pH 4.5-5.5 in sample preservation and preparation for analysis of DBPs, chlorinated solvents and halogenated pesticides/herbicides in drinking water. The pH 2-3 of water sample was selected in this study for SPE method development and application of HNMs analysis.

Compared to the performance of LLE-COC-GC-MS method, the SPE-COC-GC-MS method had similar performance in terms of LODs, and reproducibilities (Table 1). SPE, however, showed poorer recoveries for a number of HNMs. The good agreement in performance between the two methods demonstrated that SPE-COC-GC-MS method can be a good alternative for the analysis of four common HNMs, namely DCNM, TCNM, BCNM and DBNM.

3.4. Analysis of water samples

Between December 2014 and January 2015, eleven treated drinking water samples were collected from water treatment plants in several cities and towns along the Yangtze River in Jiangsu Province, China. All surface water treatment plants utilize conventional treatment and use chlorine as disinfection agent.[19-20] Various dechlorinating agents have been recommended for tap water sampling, including sodium sulphite, sodium thiosulfate，ammonium sulfate，ammonium chloride and ascorbic acid.[8-10, 18, 21] However, none of the dechlorinating agents was added in this study. This is because previous studies have demonstrated that dechlorinating agents could interact with certain DBPs and thus change their concentrations.[10, 18] HNMs are known to undergo rapid degradation when exposed to certain dechlorinating agents such as sodium sulphite and ascorbic acid, which suggested some controversy over the most suitable dechlorinating agent. [10]

Both methods, LLE-COC-GC-MS and SPE-COC-GC-MS, were applied to the determination of HNMs in these water samples. Analysis was carried out in triplicate. Table 2 showed the concentrations of the four HNM (DCNM, TCNM, BCNM and DBNM) found in tap waters. They ranged from <0.2 (LOQ) to 0.29 μg/L for DCNM and 0.41 to 0.64 μg/L for TCNM. The results were in agreement with previous studies

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which reported that TCNM concentrations ranged from 0.3 to 0.9 μg/L in drinking waters in Shanghai,[19] and from below detection to 2.08 μg/L in Beijing, China.[20] BCNM and DBNM levels in tap water samples were detected in all waters samples, except for one sample, but the levels were all below LOQ (Table 2). The other five HNMs (CNM, BNM, BDCNM, DBCNM and TBNM) were below the LOD. The two methods provided similar results in terms of the measured levels for the four detected HNMs and non-detection for the rest of the HNMs. This indicated that the SPE-COC-GC-MS method described in this study can be a good alternative to LLE-COC-GC/MS method to meet the objectives in analyzing HNMs in drinking water.

4. Conclusions

It is the first time a COC injection technique was applied to analysing HNMs in drinking water. The use of COC technique minimizes the possible thermal degradation of HNMs, especially the brominated HNMs that are thermally liable. This study also demonstrated that even at low injection temperature of 117 °C some degree of degradation of HNMs could occur, and at the conventional injection temperature of 170 °C, such degradation was significant. It is also reported for the first time that not only the bromine atom, but also the nitro group could be lost at injection temperature of 170 °C.

The COC-GC-MS method combined with LLE sample pretreatment provides a sensitive and reliable quantification method for the simultaneous analysis of nine HNMs in drinking water. The study also demonstrated that SPE sample pretreatment could serve as an alternative when measurement of the four commonly detected HNMs (DCNM, TCNM, BCNM and DBNM) in drinking water is concerned in the daily determination of HNMs in drinking water. Further research is needed to find out more suitable SPE pretreatment methods for the determination of all nine HNMs in water samples.

Conflict of interest

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The authors have declared that no conflict of interest exists.

Acknowledgements

This work has been supported by Jiangsu province Natural Science Foundation of China (BK20131271) and National High-tech R&D Program of China (Grant no. 2013AA06A309). The authors wish to thank Dr. Jiping Zhu of Health Canada for his review and editing of the manuscript.

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Figure Captions

Fig. 1. GC-ECD Chromatgrams of DBCNM (A，B); TBNM (C，D) in two splitless injection temperatures: 117 °C (A, C) and 170 °C (B, D), respectively. The HNM standard was prepared in MTBE at 100 pg/μL. Degradation products of DBCM and TBM were identified by comparing their retention time with that of the standard compounds.

Fig. 2. GC–MS total ion chromatograms of the 9 HNMs standard solution in MTBE when using cold on-column at 1 mg/L(A) and splitless technique at 10 mg/L (B). Peak identification: CNM (1); DCNM (2); TCNM (3); BNM (4); BCNM (5); BDCNM (6); DBNM (7); DBCNM (8); TBNM (9). GC–MS total ion chromatograms of DBCNM (C); TBNM (D) at 10 mg/L in MTBE in injection temperature 170 ºC, respectively.

Fig. 3. Recoveries of nine HNMs using different SPE cartridges at pH=2~3. Error bars are the standard deviation of triplicate analyses.

Fig. 4. Effect of eluting solvents on the extraction of the 9 HNMs using HLB from aqueous samples at pH=2~3. Error bars are the standard deviation of triplicate analyses.

Fig. 5. Influence of pH on the extraction of HNMs from aqueous samples with MTBE. Error bars are the standard deviation of triplicate analyses.

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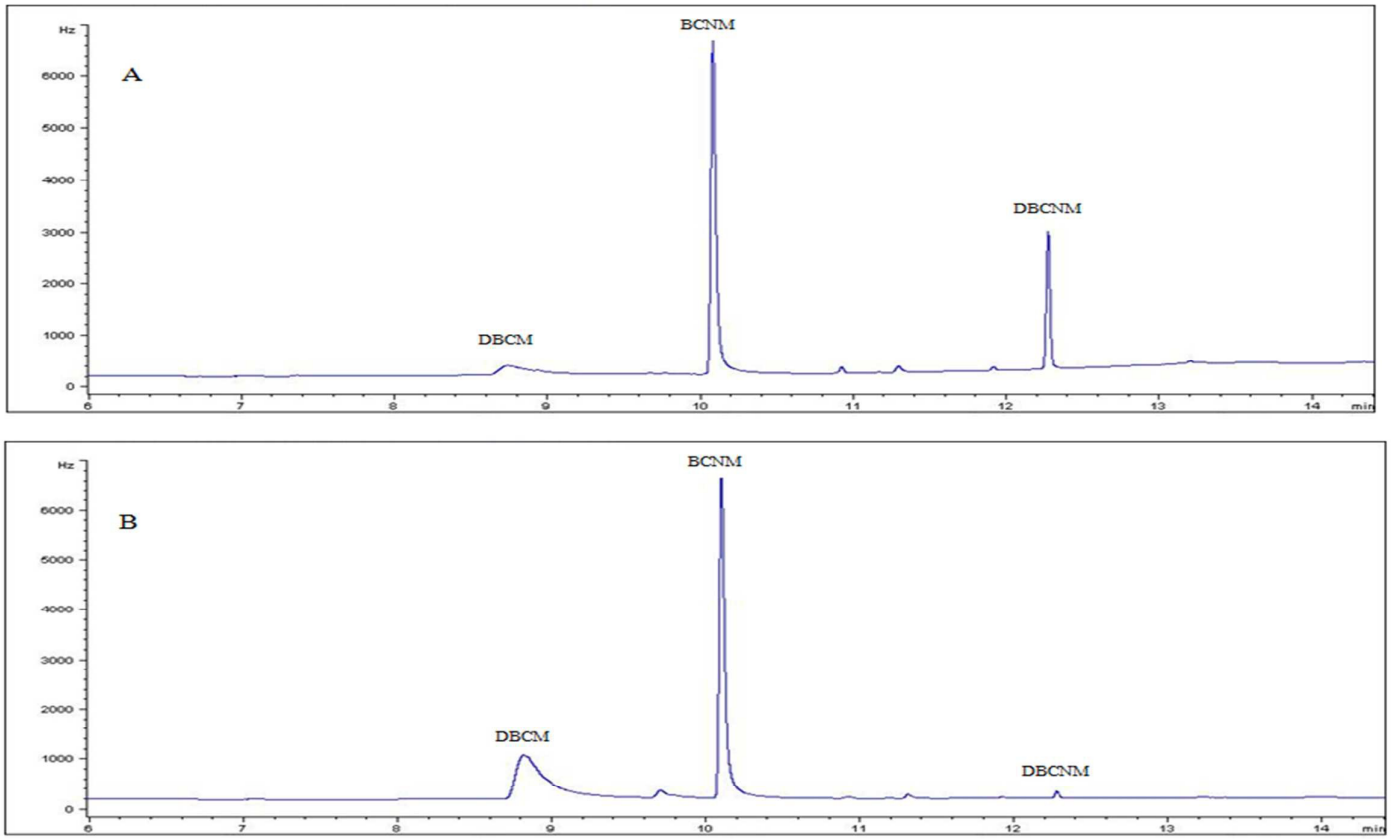

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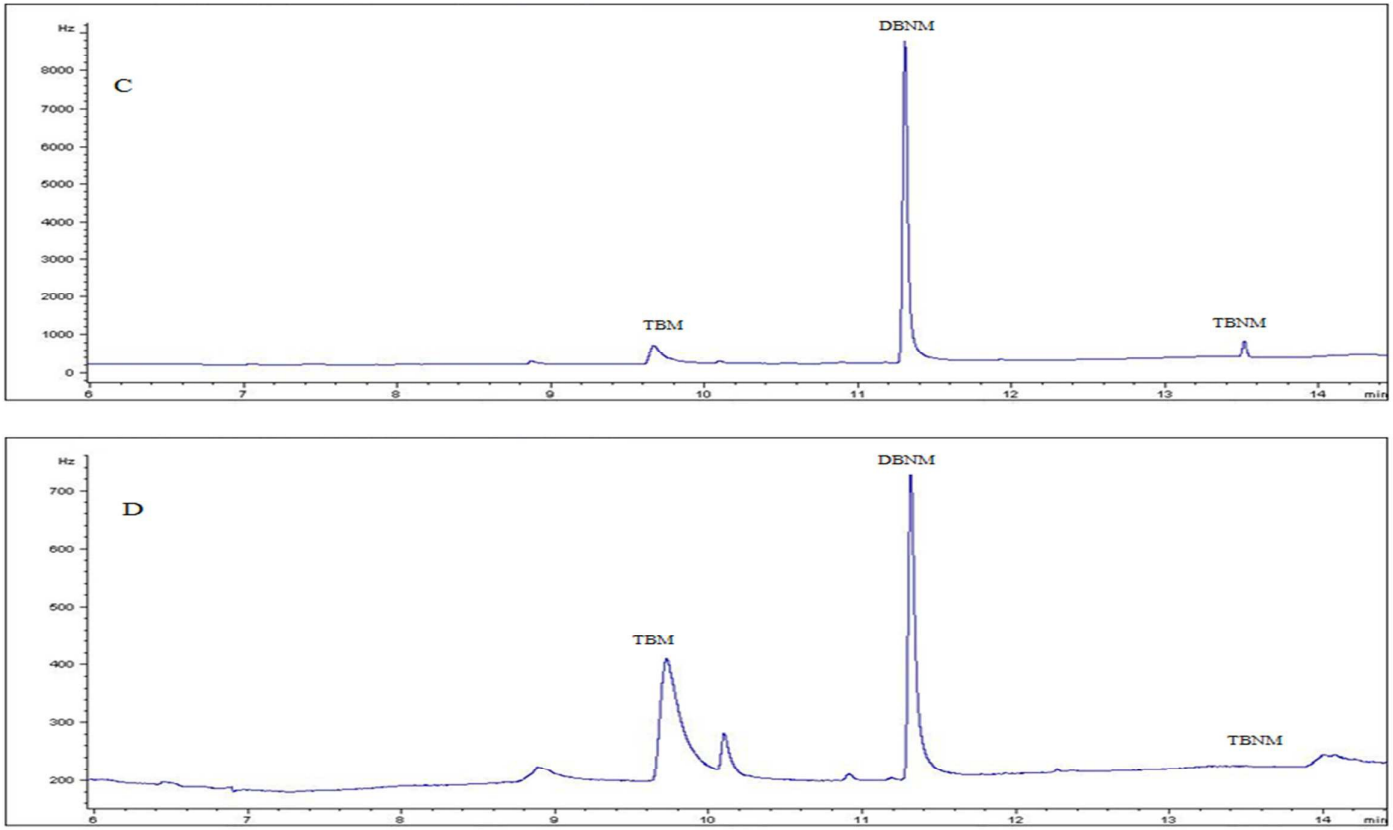

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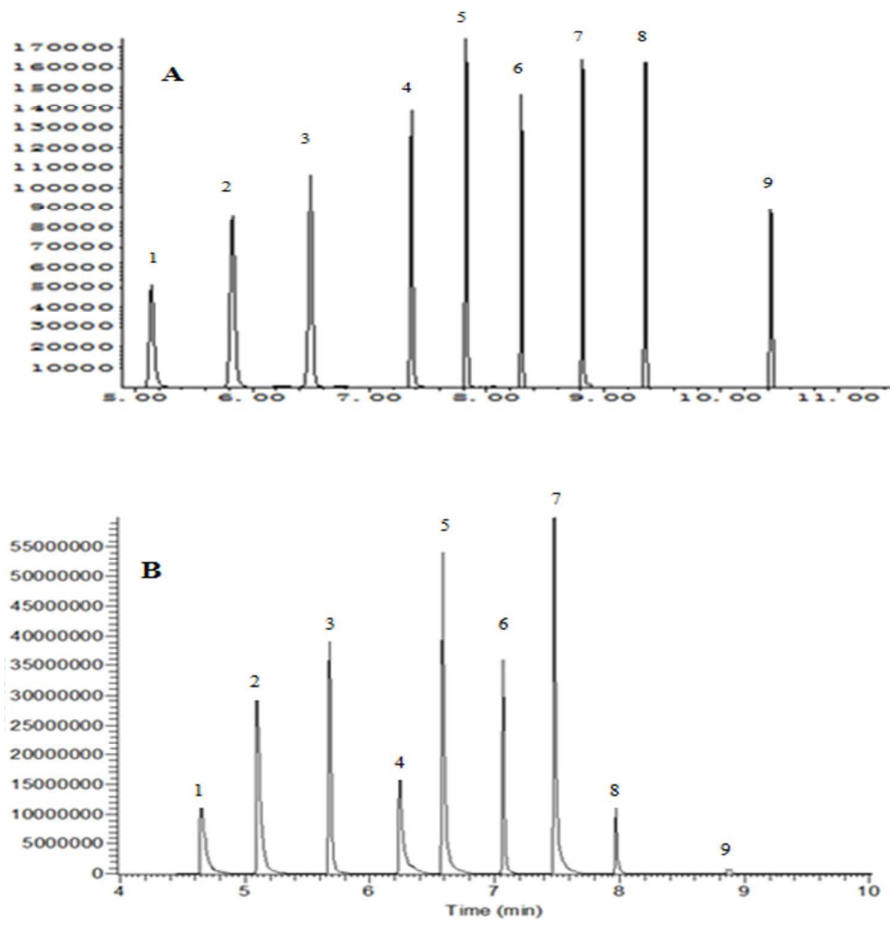

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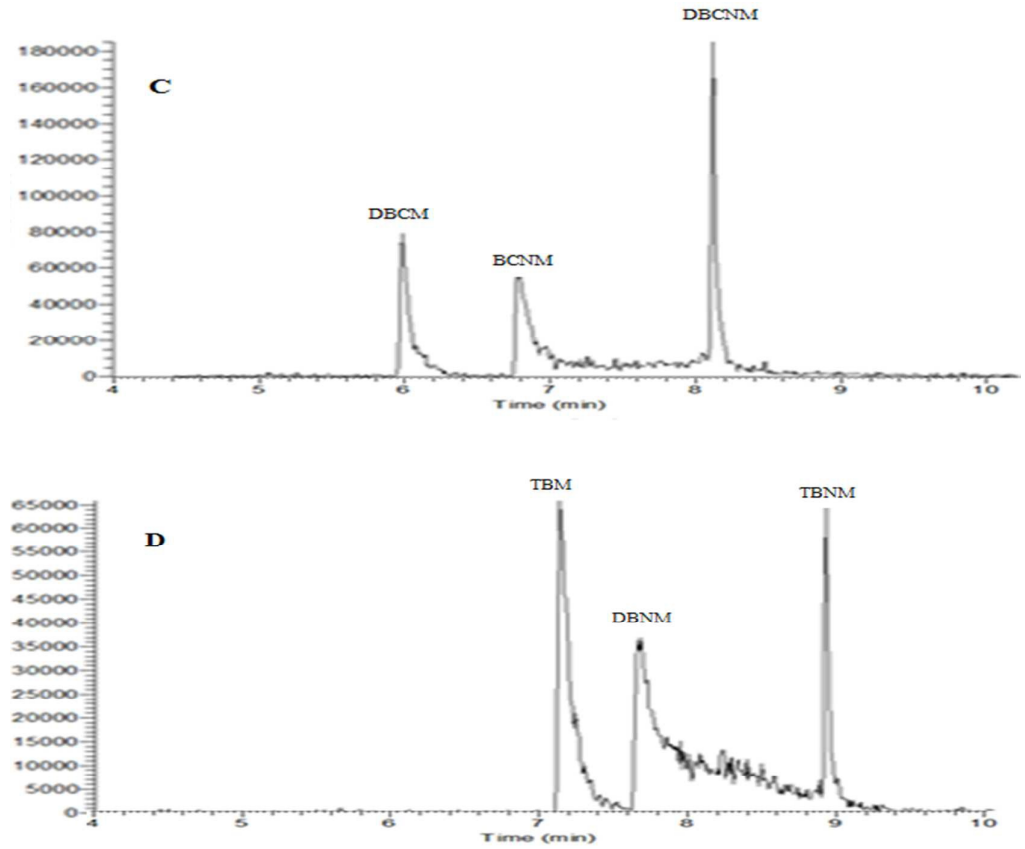

Fig. 2. GC–MS total ion chromatograms of the 9 HNMs standard solution in MTBE when using cold on-column at 1 mg/L(A) and splitless technique at 10 mg/L **(B)**. Peak identification: CNM (1); DCNM (2); TCNM (3); BNM (4); BCNM (5); BDCNM (6); DBNM (7); DBCNM (8); TBNM (9). GC–MS total ion chromatograms of DBCNM (C); TBNM (D) at 10 mg/L in MTBE in injection temperature 170 ºC, respectively.

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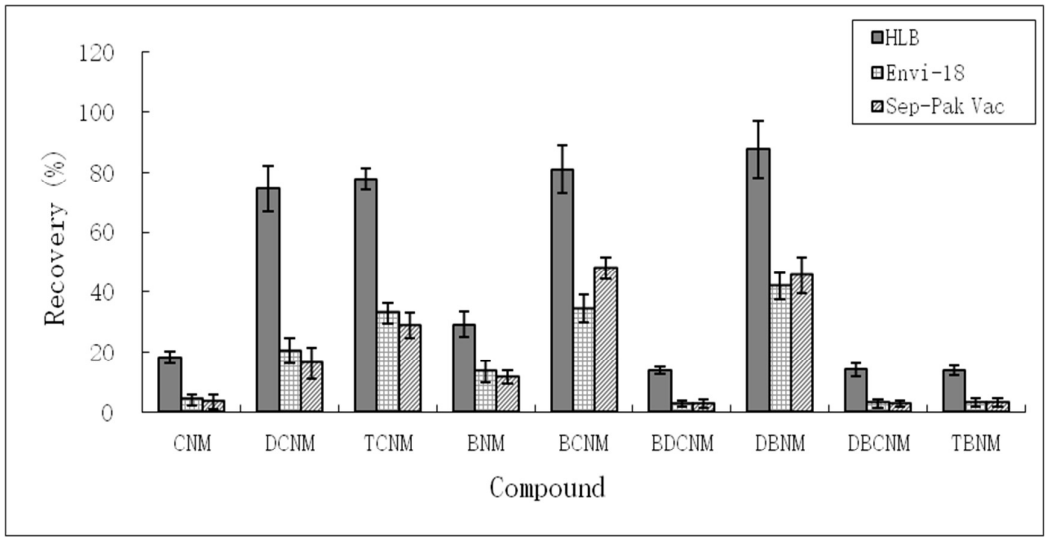

Fig. 3. Recoveries of nine HNMs using different SPE cartridges at pH=2~3. Error bars are the standard deviation of triplicate analyses.

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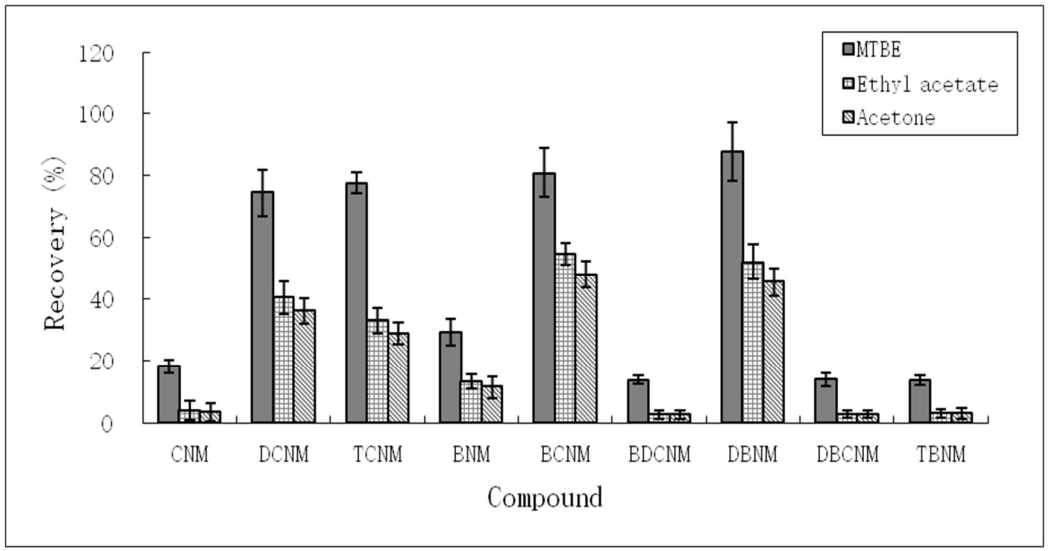

Fig.4. Effect of eluting solvent on the extraction of the 9 HNMs using HLB from aqueous samples at pH=2~3. Error bars are the standard deviation of triplicate analyses.

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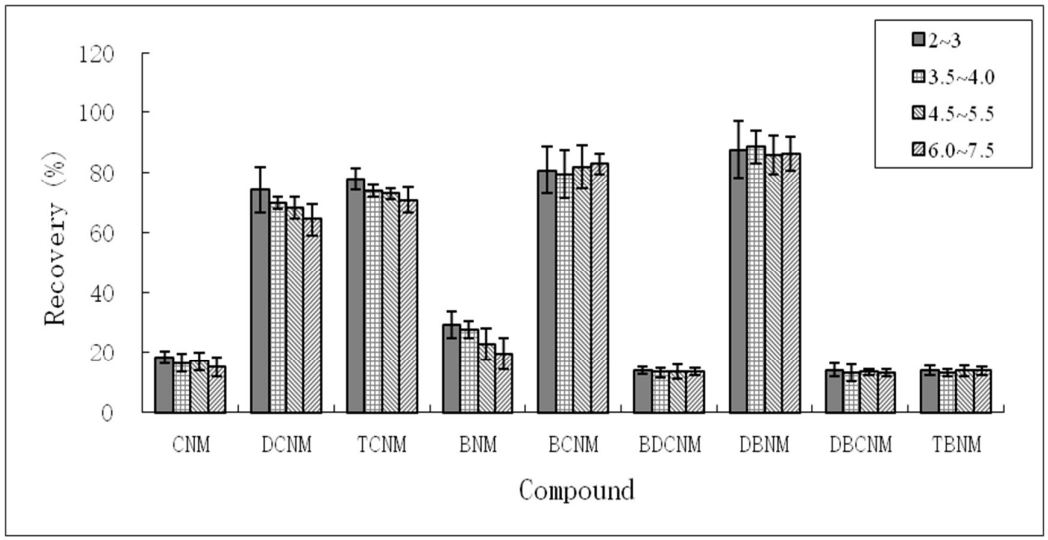

Fig.5. Influence of pH on the extraction of HNMs from aqueous samples with MTBE. Error bars are the standard deviation of triplicate analyses.

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Table 1 Analytical performance of LLE-COC-GC-MS and SPE-COC-GC-MS methods.

Compound	m/z[a]	LLE-COC-GC-MS						SPE-COC-GC-MS					
		LOD (μg/L)	LOQ (μg/L)	Linear range (μg/L)	r^2	Recovery[b] (%)	RSD[c]	LOD (μg/L)	LOQ (μg/L)	Linear range (μg/L)	r^2	Recovery (%)	RSD
CNM	**49**,51,46	0.7	2.23	5-1000	0.9963	80,85	10	0.6	1.91	5-5000	0.9945	18, 21	12
DCNM	**83**,85,48	0.08	0.25	1-1000	0.9981	83,89	6.3	0.06	0.19	1-5000	0.9964	68, 73	10
TCNM	**117**,119,82	0.06	0.19	1-1000	0.9984	90,91	4.2	0.05	0.16	1-5000	0.9923	72, 74	7.8
BNM	**93**,95,44	0.9	2.87	2-1000	0.9964	79,84	8.2	0.9	2.87	2-5000	0.9928	37, 45	11
BCNM	**129**,127,131	0.06	0.19	1-1000	0.9946	75,86	6.6	0.06	0.19	1-5000	0.9976	65, 76	11
BDCNM	**163**,161,47	0.8	2.55	5-1000	0.9928	84,88	9.9	0.7	2.23	5-5000	0.9901	16, 23	14
DBNM	**173**,171,175	0.06	0.19	1-1000	0.9930	88,90	3.4	0.05	0.16	1-5000	0.9932	71, 77	9. 5
DBCNM	**207,**209,47	0.8	2.55	5-1000	0.9911	79,83	8.5	0.8	2.55	5-5000	0.9903	12, 16	12
TBNM	**251**,253,46	0.9	2.87	10-1000	0.9902	73,80	12	1.0	3.18	10-5000	0.9900	15, 18	14

[a]Mass spectral ions selected for identification and quantification (bold) of halonitromethanes

[b] The first and second data corresponds to the average percent recoveries for the low amount level (0.1μg/L for DCNM, TCNM, BCNM and DBNM), (1μg/L for CNM, BNM, BDCNM, DBCNM and TBNM) and high amount level (5μg/L), respectively.

[c]The average relative standard deviation (RSD) of the two levels with DCNM, TCNM, BCNM(0.1 , 5μg/L) and DBNM and CNM, BNM, BDCNM, DBCNM and TBNM(1 , 5μg/L).

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Table 2 Analysis of treated water samples by LLE- and SPE-COC-GC-MS methods (n=3)

	Concentration of HNMs expressed in mean ± standard deviation (μg/L)							
	LLE-COC-GC-MS				SPE-COC-GC-MS			
	DCNM	TCNM	BCNM	DBNM	DCNM	TCNM	BCNM	DBNM
Tap1	n.d [a]	0.56±0.09	n.d	n.d	<0.2	0.42±0.06	<0.2	n.d
Tap2	<0.3 [b]	0.61±0.09	n.d	n.d	0.25±0.05	0.55±0.09	<0.2	<0.2
Tap3	0.31±0.11	0.67±0.11	n.d	n.d	0.27±0.06	0.64±0.11	<0.2	<0.2
Tap4	0.30±0.07	0.63±0.10	n.d	n.d	0.29±0.06	0.52±0.09	<0.2	<0.2
Tap5	<0.3	0.56±0.08	n.d	n.d	0.22±0.06	0.57±0.07	<0.2	<0.2
Tap6	n.d	0.59±0.08	n.d	n.d	<0.2	0.41±0.07	<0.2	<0.2
Tap7	<0.3	0.60±0.09	n.d	n.d	<0.2	0.50±0.07	<0.2	<0.2
Tap8	<0.3	0.56±0.08	n.d	n.d	0.21±0.06	0.47±0.08	<0.2	<0.2
Tap9	n.d	0.51±0.07	n.d	n.d	<0.2	0.60±0.11	<0.2	<0.2
Tap10	n.d	0.53±0.07	n.d	n.d	<0.2	0.62±0.13	<0.2	<0.2
Tap11	n.d	0.61±0.10	n.d	n.d	<0.2	0.56±0.10	<0.2	<0.2

[a] n.d., not detected, low than LOD; [b] values marked with < were above limit of detection (LOD) but below limit of quantification (LOQ).

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