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Determination of haloacetic acids in hospital effluent after chlorination by ion chromatography

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Abstract

The ion chromatography combined solid phase extraction (SPE) method was developed for the analysis of low concentration haloacetic acids (HAAs), a class of disinfection by-products formed from chlorination of hospital wastewater. The monitored HAAs included monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid. The method employed a sodium hydroxide eluent at a flow rate of 0.8 ml/min, electrolytically generated gradients, and suppressed conductivity detection. To analyze the HAAs in real hospital wastewater samples, C18 pretreatment cartridge was utilized to reduce samples' turbidity. Preconcentration with SPE and matrix elimination with treatment cartridges were investigated and found to be able to obtain acceptable detection limits. Linearity, repeatability and detection limits of the above method were evaluated. The detection limits of monobromoacetic acid and dibromoacetic acid were 2.61 μg/L and 1.30 μg/L, respectively, and the other three acids are ranging from 0.48 to 0.82 μg/L under 25-fold preconcentration. When the above optimization procedure was applied to three hospital wastewater samples with different treatment processes in Tianjin, it was found that the dichloroacetic acid was the major compound, and the growth ratios of the HAAs after disinfection by sodium hypochlorite were 91.28%, 63.61% and 79.50%, respectively.

Key words: hospital wastewater analysis; ion chromatography (IC); sample pretreatment; solid phase extraction (SPE); chlorination; haloacetic acids (HAAs)

Introduction

Chlorination as a disinfection process is often used for disinfecting hospital wastewater to prevent the spread of pathogenic microorganisms and causal agents of nosocomial infectious diseases. In China, chlorination has been the main strategy for disinfecting hospital wastewater due to its very broad-spectrum of biocide activity against bacteria, virus and fungi, and its low cost. However, when water or wastewater is chlorinated, chlorine reacts readily with a wide variety of organics to form disinfection by-products (DBPs), such as haloacetic acids (HAAs), which are degradation products of halogenated compounds of both natural and anthropogenic origin, and are considered potentially carcinogenic (Cantor *et al*., 1998; Sirivedhin and Gray, 2005). More recently, HAAs have been associated with adverse reproductive outcomes following exposure during pregnancy (Bove *et al*., 1995; Rodriguez *et al*., 2004; Pavelic, 2005). Naturally occurring organohalogens have been identified as the main precursors for brominated and chlorinated acetic acids in the marine and terrestrial environment (Hanson and Solomon, 2004a, 2004b). At present, lots of studies are focusing on the HAAs in drinking water. However, the global distribution and high stability of some HAAs have prompted concern that they will tend to accumulate in surface waters and pose threats to humans and the ecosystem (Monarca *et al*., 2000; Kanokkantapong *et al*., 2006). As an incontestable release source of many toxic substances in the aquatic environment, hospital effluents reveal the presence of organochlorine compounds in high concentrations (Emmanuel *et al*., 2004, 2005; Jolibois and Guerbet, 2005). Additionally, dichloroacetic acid is a pharmacon in common clinical use for the cardiovascular and metabolic disease, and some residuals not being absorbed by patients would have been discharged into the hospital sewage with their excrement (Ternes, 1998). It is necessary to analyze and monitor the HAAs in hospital effluent after chlorination, and control their release to aquatic environment.

Presently, the analytical methods proposed by the USEPA (U.S. Environmental Protection Agency) for analyzing for HAAs in water have either used gas chromatography with electron capture detection (GC-ECD) or gas chromatography mass spectrometry (GC-MS). These methods employ off-line preconcentration using liquid-liquid extraction (EPA method 552.3 along with the other methods) (Hodgeson *et al*., 1990; Munch *et al*., 1995; Domino *et al*., 2003). HAAs are extracted, then derivatizated from water samples. However, some of

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the derivatization reagents such as methyl tertiary-butyl ether (MTBE) are harmful compounds and the extraction procedure is time-consuming. These methods require a great deal of sample preparation prior to analysis and the analytical costs are significant, even though, which somewhat compensates for those with good selectivity and low detection limits (0.0074–0.085 μg/L). Several alternative separation methods have recently been investigated for the determination of HAAs. These include capillary electrophoresis (CE) (Martinez *et al*., 1999), electrospray ionization mass spectrometry (ESI-MS) (Hashimoto and Otsuki, 1998; Ells *et al*., 2000), and ion chromatography (IC) (Brett and Barron, 2004). For CE method, the extraction is also needed. Currently, this method is not rugged or reliable enough to meet the demands of trace-level quantitation of HAAs. The ESI-MS based technique is a sensitive and selective method. However, for some samples liquid-liquid extraction may be necessary, yet this is time consuming and adds cost to the analysis (Urbansky, 2000). Given that the pK_a of all the HAAs of interest is lower than 2.86, they existing as anions in water. Therefore, a direct analysis of haloacetates is possible by IC, eliminating complex derivatization procedures. In recent years, various modes of IC have been applied to the separation of HAAs and their subsequent determination in drinking waters (Loos and Barcelo, 2001; Liu and Mou, 2003, 2004; Barron and Brett, 2004a, 2004b, 2006; Barron *et al*., 2005). For analyse of HAAs in wastewater samples, it is more complicated to pretreat sample than that in drinking water by the above methods. However, few have studied the HAAs concentrations in hospital effluent after chlorination, which will accumulate in the aquatic environment and impact the source of water.

In this study, HAAs in hospital effluent before and after chlorination were analyzed by applying IC combined with solid phase extraction (SPE). The HAAs selected for investigation were HAA_5 legislated species in drinking water by USEPA (1998), because the effluent would reach the receiving body of water and might impact directly or indirectly the drinking water quality, which include monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and trichloroacetic acid (TCAA). A full evaluation of sample pretreatment and extraction conditions was carried out and optimal conditions were identified with real hospital wastewater samples containing HAAs. The combination of the optimized pretreatment and separation conditions was then applied to determination of HAAs concentrations in hospital wastewater samples.

1 Materials and methods

1.1 Instruments

A Dionex DX-600 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with a GP50 gradient pump, a Dionex IonPac AS16 analytical column (250 mm × 4 mm) with IonPac AG16 guard column (50 mm × 4 mm) was used for chromatographic separations. A Dionex ED50 electrochemical detector in the conductivity mode performed the detection. Conductivity suppression of the eluent was by a Dionex ASRS-Ultra (4 mm) suppressor operated in the autosuppression external water mode. All tubing in the chromatography path (from the outlet of the pump to the exit of the suppressor) was polyether ether ketone (PEEK) (I.D., 0.125 mm). A Gilson Minipuls 3 peristaltic pump (Gilson, Middleton, WI, USA) was employed and fitted with Anachem 0.63 mm poly (vinyl chloride) (PVC) peristaltic tubing (Anachem, Luton, UK) for the pretreatment and preconcentration procedure. Pretreatment was proceeded using C18 cartridges (250 mg, Xiboshi, Tianjin, China) at a flow rate of 4 ml/min. Preconcentration was carried out using Merck LiChrolut EN solid-phase extraction (SPE) cartridges (Merck, Darmstadt, Germany) at a load rate of 2 ml/min. For chloride and sulfate removal, Dionex OnGuard IC-Ba, IC-Ag and IC-H cleanup cartridges (each of 2.5 ml) were used. The sample loop volume was 500 μl. Both instrument control and data collection were performed with a personal computer and ChromeleonTM chromatography workstation.

1.2 Chemicals

All reagents used were of analytical reagent grade purity: MCAA (99.5%), MBAA (99.0%), DCAA (98.3%), DBAA (98.0%) and TCAA (99.0%) were all ordered from Chem Service (USA). The sodium hydroxide eluent was purchased from Fluka (Germany) and the methanol from Fisher Chemicals (USA). The standard solutions (1000 mg/L) of fluoride, chloride, nitrite, nitrate and sulfate were purchased from the National Research Center of Standard Reference Material (Beijing, China). Stock HAAs solutions were prepared to a concentration of 10 mmol/L by methanol and stored in a refrigerator for a maximum of 2 weeks at 4°C in the dark. All working standards were freshly prepared daily using diluent water from a Milli-Q water purification system (Millipore, Bedford, MA, USA) with a specific resistance of 18.3 MΩ·cm. Sulfuric acid using for acidification of preconcentration sample and standard was of 99% purity. The working standards were initially prepared to a concentration of 10 mmol/L and were prepared along with the stock HAAs solutions. Hospital wastewater samples for HAAs determinations were collected from three hospitals with different wastewater treatment process in Tianjin, China.

1.3 Procedures

The hospital wastewater in China is generally treated by sedimentation followed by disinfection, and occasionally by biological process combined with disinfection. Therefore the hospital wastewater before or after chlorination still contains some suspended solids (SS) and soluble organic substances. The hospital effluent first required removal of interferences by pretreatment with 2 C18 cartridges at a flow rate of 4 ml/min for each 50 ml sample in this experiment.

The Merck LiChrolut EN (3 ml, 200 mg) cartridge was used for SPE of standards and samples. The conditioning of SPE cartridge applied the method mentioned by Barron

and Brett (2004a): LiChrolut EN SPE cartridges were conditioned prior to use using two rinse steps of 3 ml methanol, followed by 3 ml of 200 mmol/L sulphuric acid; each sample was acidified to a pH below 0.3 by adding 4.5 ml of concentrated sulphuric acid to 50 ml of sample; the acidified sample was then pumped through the preconditioned LiChrolut EN cartridges using a Gilson Minipuls 3 peristaltic pump at a load rate of 2 ml/min. But, here the cartridge was washed with 1 ml of Milli-Q water first, and then the HAAs were eluted finally with 2 ml of 10 mmol/L NaOH at a flow rate of 1 ml/min. This solution was then passed through a series of Dionex OnGuard IC-Ba, IC-Ag and IC-H cartridges at a flow rate of 1 mL/min, which was preconditioned with 10 ml Milli-Q water prior to the cleaning step. The first 0.5 ml of the eluate was discarded and the remaining solution was passed through a 0.22-μm filter prior to injection onto the IC using the optimum chromatographic conditions.

2 Results and discussion

2.1 Separation of HAAs

To separate the HAAs in the hospital wastewater before or after chlorination, the IonPac AS16, a extremely hydrophilic, high-capacity and hydroxide-selective anion-exchange column, was employed in this experiment. The strongly retained anions such as TCAA have intensive affinity on the column, which must be eluted by eluent with stronger affinity. In order to separate the weakly retained anions such as fluoride, chloride and MCAA, a weak eluent should be used. Therefore, a gradient of NaOH and Milli-Q water is preferred. Among the analyzed compounds, chloride and MBAA, nitrate and DCAA almost have the same affinity on the column. It is difficult to effectively separate the two groups of compounds with only the gradient of NaOH and the Milli-Q water. As the choice of eluting species is governed by the compatibility of IC eluent of choice, a water-methanol mixture had been used in some studies (Liu and Mou, 2003). However, the use of methanol as the eluting species in this experiment results in subsequent substantial baseline disturbances, and shows no significant improvements in recovery data compared with the NaOH eluent.

Here, a concentration gradient of NaOH was used to elute HAAs in a minimum timeframe without compromising resolution between matrix inorganic anions. Optimum separation conditions with the AS16 column was a NaOH gradient of 3.5 mmol/L for 7 min, 3.5–4.0 mmol/L for 2 min and held at 4.0 mmol/L for a further 4 min, 4.0–4.5 mmol/L for 5 min, then ramped linearly to 20 mmol/L for 12 min and kept at 20 mmol/L for another 15 min (eluent flow rate = 0.8 ml/min). Post-run equilibration time was 10 min between successive runs. From Fig.1, it can be seen that five HAAs, fluoride, chloride, nitrite, nitrate, and sulphate can be separated and quantitated with the selected eluent in gradient. MCAA and MBAA are very hydrophilic and are eluted first at 11.98 min and 13.75 min. The later eluting DCAA and DBAA are eluted with the ramp of 4.5–20 mmol/L NaOH, and TCAA requires 20 mmol/L NaOH for elution. All the five HAAs can be eluted in a 45-min runtime using the gradient program.

2.2 Extraction and elution of HAAs using LiChrolut EN SPE cartridges

It is difficult to quantify the HAAs concentrations directly using IC for the excessive matrix in real hospital wastewater samples. The use of anion exchange cartidges would adversely preconcentrate the common anions prior to analysis; therefore, the use of a polymeric reversed-phase material is regarded as the most promising approach. Merck LiChrolut EN cartridge was employed in this study, which appeared to provide the most acceptable recovery percentage values for the HAAs, in some cases up to 10 times the capacity of other available sorbents in previous research (Barron and Brett, 2004a; Loos and Barcelo, 2001; Sarzanini *et al*., 1999; Martinez *et al*., 1998).

The pK_a values for the common HAA_5 are all in the range 0.65–2.86. This means the acids only exist in protonated form under strongly acidic conditions. It has important implications for extraction and preconcentration techniques. For the successful preconcentration of HAAs it is necessary to acidify sample/standard solutions to pH < 0.3 (Brett and Barron, 2004). After conditioning the SPE cartridge (as described in Section 1.3), lower load rates of 2 ml/min (Barron and Brett, 2004a) were adopted in this experiment. The SPE cartridge was washed with 1.0 ml of Milli-Q water to elute off excess sulphate and other inorganic anions present, and there was very little elution of the preconcentrated acids. It was shown that when HAAs were eluted using either a methanol-water solution (Martinez *et al*., 1998) or a 10-mmol/L NaOH solution (Barron and Brett, 2004a) that the best results came from using the 10 mmol/L NaOH (2 ml at load rate 1 ml/min).

With the optimizing method mentioned above and 25-folds preconcentration, the recoveries of DCAA, TCAA and DBAA reached to 85.95%–93.70%, the MCAA and MBAA were at 76.09% and 63.50%, respectively (Table 1). In addition, the results showed that Merck LiChrolut

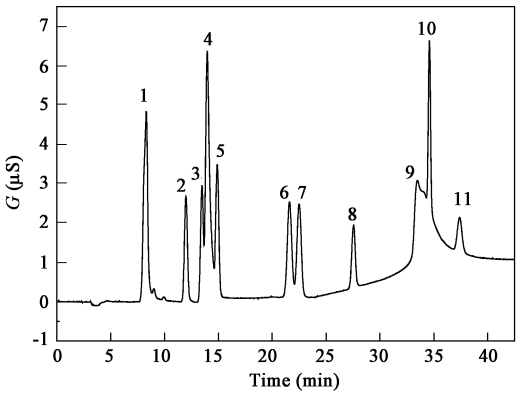

Fig. 1 Chromatogram of mixed standard solution of HAAs and five standard anions. (1) F^- (0.05 mg/L); (2) MCAA (0.51 mg/L); (3) Cl^- (0.03 mg/L); (4) MBAA (1.50 mg/L); (5) NO_2^- (0.25 mg/L); (6) NO_3^- (0.20 mg/L); (7) DCAA (0.73 mg/L); (8) DBAA (0.79 mg/L); (9) system peak; (10) SO_4^{2-}(0.05 mg/L); (11) TCAA (0.605 mg/L).

EN cartridge retained the nitrate weakly, which eliminated its interference and also reduced the interferences from the other matrix anions.

2.3 Detection limits and linear ranges

We employed the above significant improvements and utilized a 500-μl injector loop in the experiment. To assess of the limits of detection, a standard for the five HAAs was prepared in Milli-Q water to a concentration of 10 μmol/L and serial dilutions were carried out until a signal-to-noise ratio was just of above 3:1 for each HAAs. All the detection limits and linear ranges for the chromatographic method are listed in Table 2. It can be seen that the detection limits for the three of the five HAAs are between 0.48 and 0.82 μg/L, for the MBAA and DBAA are 2.61 μg/L and 1.30 μg/L, respectively. All correlation coefficients are above 0.99 and demonstrate excellent linearity.

2.4 Analysis of hospital wastewater samples

2.4.1 Sample collection and pretreatment

Samples of hospital wastewater were collected from three hospitals with different treatment method in Tianjin, China during late summer 2005. These three hospitals are named A, B and C in this article. Hospital A adopts a membrane bioreactor (MBR) for wastewater treatment coupled with disinfection. In the B hospital wastewater is disinfected without any pretreatment. C applies the coagulation/sedimentation combined with disinfection. All their disinfecting processes utilize sodium hypochlorite (NaClO) as the disinfectant. The sample bottles (1000 ml) were rinsed three times with the hospital wastewater before sampling and both the hospital wastewater before and after chlorination were collected. The sample bottles were stored in an insulated container containing an ice pack during transportation and then immediately chilled in a refrigerator at 4°C and kept in the dark to minimize degradation of HAAs in the laboratory for analysis.

(1) Sample pretreatment with C18 cartridges: The hospital wastewater contains lots of SS (solid sludges) and soluble organic substances, which the conventional treatment process can only remove some of them at different degrees. These complex components in the wastewater have negative effects to the subsequence handling and even jam the later SPE cartridge, so the sample pretreatment to reduce its turbidity is essential before SPE. Each sample was filtrated with 0.45 μm glass-fiber filter prior to being loaded into the C18 pretreatment cartridge in the experiment. Subsequently filtrated 50 ml samples with 2 C18 cartridges in series at 4 ml/min using the calibrated peristaltic pump. The results show that the average turbidity is less than 15 NTU (n=15, RSD=4.62). The sample obtained from the effluent of the MBR (A) did not require this step, since the turbidity was much lower. When the recovery of 5 μmol/L HAAs standard concentration was investigated by this method, we found that the C18 pretreatment cartridge did not retain the HAAs with significant level (Table 3). So it is feasible to use the C18 cartridge to reduce SS in wastewater samples and does not influence the determination results of HAAs.

(2) Sample clean-up: After the pretreatment and preconcentration procedure, many matrix anions had been eliminated, but some generated from the sample pretreatment step such as sample acidification. It is expected from our optimization procedure that excess chloride present

Table 1 Recovery and precision of HAAs after treatment with LiChrolut EN and Dionex OnGuard cartridge series

HAAs	Standard concentration (μmol/L)	Preconcentrated volume[a] (ml)	Eluent volume (10 mmol/L NaOH)[b] (ml)	LiChrolut EN cartridge (n=9)[c]		Dionex OnGuard cartridge series (n=9)[d]	
				Recovery (%)	R.S.D (%)	Recovery (%)	R.S.D (%)
MCAA	0.5	50	2	76.09	5.29	98.8	1.29
MBAA	0.5	50	2	63.5	5.31	86.5	1.13
DCAA	0.5	50	2	93.7	6.33	101.2	2.86
DBAA	0.5	50	2	85.95	10.49	100.0	1.88
TCAA	0.5	50	2	89.61	1.68	97.2	2.90

[a] Adjusted using sulfuric acid and loaded at 2.0 ml/min; [b] following 1.0 ml wash using Milli-Q water; [c] each repeat preconcentration carried out using fresh LiChrolut EN cartridges; [d] carried out on IC-Ba, IC-Ag and IC-H in turn preconditioned with 10 ml Milli-Q water prior to use.

Table 2 Analytical performance data for NaOH gradient IC methods for HAAs and the detection limits

	MCAA	MBAA	DCAA	DBAA	TCAA
Average retention time (min)	11.982	13.750	22.342	28.557	38.405
Average peak height (μS)	2.420	3.156	2.025	2.078	1.172
Reproducibility (RSD) (%)[a]					
Retention time	0.2	0.5	0.1	0.3	0.1
Peak height	2.1	3.0	1.6	1.9	2.2
Concentration range[b] (μg/L)	4.72–94.5	6.95–139	6.40–128	10.9–218	8.18–163
Linearity (r^2)	0.994	0.999	0.997	0.999	0.996
Slope	0.0864	0.0556	0.0589	0.0492	0.0644
Intercept	0.0129	0.1126	0.013	-0.0211	0.0072
Detection limits[c] (μg/L)					
Without SPE	12.35	60.70	20.89	26.78	19.91
With SPE	0.55	2.61	0.48	1.30	0.82

[a] Data based upon 30 repeat injections of a 5.0-μmol/L HAAs standard without SPE; [b] based upon 25-folds preconcentration. Process as described in Section 2.3. Each standard injected in triplicate. Linearity based on peak height; [c] based upon 3 times baseline noise, 500 μl injection volume.

Table 3 Recovery and precision of HAAs after treatment with C18 pretreatment cartridges[a] (n=9)

Analyte	MCAA	MBAA	DCAA	DBAA	TCAA
Recovery (%)	101.3	101.1	103.2	102.5	99.6
RSD (%)	0.59	1.47	2.01	1.80	1.90

[a]50 ml filtrated volume loaded at 4 ml/min.

in the sample would interfere significantly with weakly retained MCAA and MBAA; furthermore, sulfate is also expected to interfere with trace DBAA and TCAA. Therefore, sample extracts from the LiChrolut EN cartridge were immediately passed through an OnGuard IC-Ba cartridge, followed by an OnGuard IC-Ag and an IC-H, all in sequence at a flow rate of 1 ml/min. Prior to the cleanup step, these cartridges were preconditioned with approximately 10 ml of Milli-Q water. The process by which these inorganic anions are removed with the above cartridges is described elsewhere (Slingsby and Kiser, 2001). This would reduce sulphate and chloride levels, with the OnGuard IC-H cartridge used to remove any Ag ions originating from the OnGuard IC-Ag cartridges, which could otherwise foul the analytical IC column (Dionex, Sunnyvale, CA, 2000). The recovery percentages of LiChrolut EN and Dionex OnGuard cartridge series are listed in Table 1, with four out of the five HAAs, percentage for the Dionex OnGuard cartridges ranging between 97.20% and 101.20%.

2.4.2 Application of the developed methods to real hospital wastewater samples

The methods developed were applied to the determination of the five HAAs in hospital wastewater samples, which were treated immediately (as described in Section 2.3). Fig.2 shows the chromatogram of standard addition of HAAs in the effluent of MBR with the chlorination in hospital A. We can see that it could not be detected the sub-μg/L HAAs in samples without SPE (see from Fig.2b). The actual samples of the A were spiked with 0.1, 0.25, 0.5 μmol/L of MCAA, MBAA, DCAA, DBAA and TCAA and the whole pretreatment, extraction, and cleanup procedures were carried out once more. The results from these standard additions are also shown in Fig.2. As can be seen from the chromatograms, MCAA is now well resolved from traces of chloride and TCAA can be clearly seen to elute after residual sulphate. The results obtained clearly validated the sample pretreatment, extraction and cleanup procedures, with excellent linearity for almost all spiked HAAs. Also, the chromatograms of HAAs in

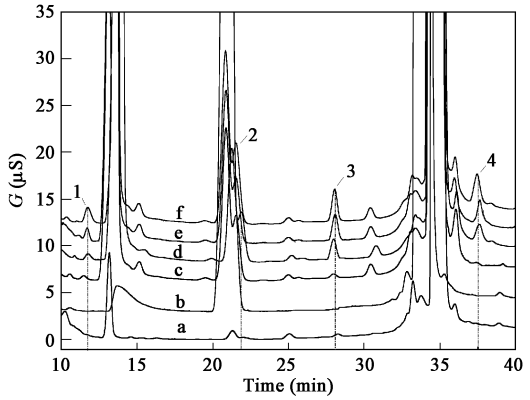

Fig. 2 Chromatogram of standard addition of HAAs in sample A. (a) before chlorination with preconcentrated 25-folds using SPE; (b) after chlorination without SPE; (c) after chlorination with preconcentrated 25-fold using SPE; (d)–(f): spiked "c" samples (0.1, 0.25 and 0.5 μmol/L HAAs) with preconcentrated 25-folds using SPE. Peak identifications: (1) MCAA; (2) DCAA; (3) DBAA; (4) TCAA.

other hospital wastewater samples are shown in Fig.3. The concentrations of the analytes in the samples of the three-hospital wastewater are listed in Table 4. Unfortunately, MBAA in all of the three hospital wastewater samples was not detected for the interferences of excess chloride and other anions.

It is desirable to note the dominance of DCAA as opposed to the others after disinfection by sodium hypochlorite (Table 4), as it is the species that give most cause for concern in terms of suspected toxicity. Addition-

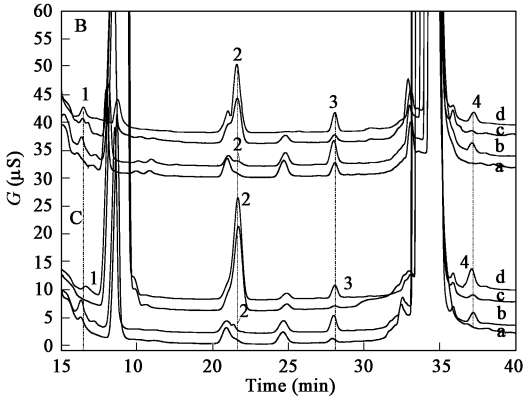

Fig. 3 Chromatogram of HAAs in samples B and C preconcentrated 25-folds using SPE. (a) before disinfection; (b) spiked sample "a" with 0.25 μmol/L standard HAAs; (c) after disinfection; d: spiked sample "c" with 0.25 μmol/L standard HAAs. Peak identifications: (1) MCAA; (2) DCAA; (3) DBAA; (4) TCAA.

Table 4 Concentration of HAAs in different sampling spot of hospitals

Sampling spot		MCAA (μg/L)	MBAA (μg/L)	DCAA (μg/L)	DBAA (μg/L)	TCAA (μg/L)	Total HAAs (μg/L)
A	Before chlorination	<LOD	N/A	5.19	5.42	3.48	10.61
	After chlorination	10.60	N/A	82.21	19.66	9.29	121.76
B	Before chlorination	4.90	N/A	8.62	58.29	<LOD	71.81
	After chlorination	22.14	N/A	138.15	25.54	11.48	197.31
C	Before chlorination	7.98	N/A	36.41	14.18	<LOD	58.57
	After chlorination	<LOD	N/A	257.84	8.67	19.14	285.65

N/A: not calculated due to residual chloride interference; <LOD: peaks observed less than detection limits value (calculated as signal-to-noise ratio of 3:1).

ally, it is worth noting that when the samples were treated after disinfection by sodium hypochlorite, the growth ratio of HAAs of the A, B and C hospital wastewater were 91.28%, 63.61% and 79.50% respectively. The content of HAAs in the effluent of MBR is the lowest (which is 10.61 μg/L), but the growth ratio of HAAs is the highest. The quantity of organic substances with small-molecule weight in the effluent of MBR is more than that in the raw wasetwater, and this part of organics is easier to react with chlorine to form HAAs. So for the disinfection of effluent of MBR, it is better to adopt other disinfection methods substituted chlorination. However, in the chlorine disinfected wastewater without any treatment or primary treatment as the sample B and C, the total HAAs is higher than that in the effluent of MBR both before and after chlorination.

3 Conclusions

This study investigated the sample pretreatment and IC separation methods for determination of HAAs in hospital wastewater. The pretreatment method using C18 cartridges reduces the turbidity in samples and leads to insignificant retention for the HAAs. The preconcentration method provides good recoveries for all HAAs species, also gives a reduction in residual nitrate for identification and quantification of DCAA. The detection limits for the HAAs are between 12.35 and 60.7 μg/L without SPE. However, combined with the preconcentration factor of 25, the detection limits for MBAA and DBAA are 2.61 μg/L and 1.30 μg/L respectively, and the detection limits for the other three of the five HAAs are ranging from 0.48 to 0.82 μg/L. The method developed is simple, practical and a viable alternative to conventional gas chromatographic techniques. When the developed method was applied to the determination of the compounds in the effluent before and after chlorination from three different hospital wastewater treatment processes, the results indicate that the DCAA is the major compounds, and the growth ratios of the HAAs in the three-hospital wastewater samples range from 63.61% to 91.28%.

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