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Determination of Trihalomethanes in Drinking Water from Beijing, People's Republic of China

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In many drinking water treatment plants, chlorination process is still one of the main techniques used for the disinfection of natural water (Cho et al., 2003). Chlorine has traditionally been a preferred disinfection agent because of its proven effectiveness and its being relatively inexpensive (Rodriguez, et al., 2001). The research undertaken in the middle of the 1970s (Rook,1974; Bellar et al.1974), however, indicated this chemical treatment resulted in the formation of trihalomethanes (THMs). The formation of THMs in drinking water results from the reaction of chlorine with naturally occurring organic matters, principally humic acid and fulvic acid (Cho et al., 2003). The THMs formed are mainly composed of chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform ($CHBr_3$). These compounds have drawn significant scientific attention during the last decades, due to the adverse health effects they may have on human beings (Table 1) (Nikolaou et al., 2002). Basing on the potential carinogenicity effects of these compounds, many countries have set limits for THMs in drinking water. In 1979, the United States EPA initiated a regulatory standard of 100 μg l^{-1} for THMs, under the " Safe Drinking Water Act". Currently, this standard has been reduced to 80 μg l^{-1}. Reduction of this level to 40 μg l^{-1} is being considered (Nikolaou et al., 2002). In China, the standard of drinking water for chloroform is 60 μg l^{-1}. The World Health Organization (WHO) has also set quality target levels for the concentrations of THMs (Table 1) (Nikolaou et al., 2002). As drinking water is directly linked with people's health, it is important to investigate the levels of THMs and TTHMs in it.

In terms of the analysis of THMs in water, the conventional pretreatment method often needs large amount of toxic solvent and time-consuming procedures. Recently, liquid-phase microextraction (LPME) or solvent microextraction (SME) was developed as a solvent-minimized pretreatment technique (Jeannot et al., 1996), which is fast, simple and inexpensive. This novel technique eliminates the disadvantages of conventional extraction methods, such as time-consuming operation and using specialized apparatus. Since very little solvent is used, there is minimal exposure to toxic organic solvent for the operator. To our knowledge, in routine analysis there is seldom report on the monitoring of THMs in water

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Table 1. Cancer group classification and quality target levels set by the WHO for THMs

Compound	Cancer group (EPA)[a]	WHO guideline ($\mu g\,l^{-1}$)
$CHCl_3$	B2	200
$CHCl_2Br$	B2	60
$CHClBr_2$	C	100
$CHBr_3$	B2	100

[a]Group B2, probable human carcinogen (sufficient data from animal studies); Group C, possible human carcinogen.

samples using this new method. In this work, drinking water samples from Beijing City were analyzed by headspace-liquid-phase microextraction （HS-LPME） combined with a capillary gas chromatography-electron capture detector (GC-ECD).

MATERIALS AND METHODS

Standard solutions of $100mg\,l^{-1}$ THMs in methanol were purchased from ChemService, Inc. (West Chester. PA, USA), including $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, respectively. HPLC-grade methanol was purchased from Tianjin Siyou Technical Company. 1-octanol and sodium chloride were of analytical grade. 1-octanol were further purified by vacuum distillation for 45min to remove residual volatile contaminants, and stored at 4℃. A fixed concentration of 1,1,1-trichloroethane internal standard ($4mgl^{-1}$) was prepared in 1-octanol. Working solutions of THMs were diluted using double distilled water, which had been boiled for 1h in a large beaker to remove THMs. All solutions were stored at 4℃in dark.

Water samples were collected in glass jars (250ml) with screw caps and Teflon inserts. Glass jars were carefully and completely filled. Samples were stablized by the addition of 25mg ascorbic acid per 20ml water samples. The samples were analyzed directly or stored at 4℃within 48h.

A Varian 3740 gas chromatograph equipped with ^{63}Ni electron-capture detection system was used for all analyses. The GC was fitted with a SE-54 capillary column (40m×0.25mm I.D. J& W Scientific Inc.USA). The gas chromatography conditions were as follows: injector temperature 280℃; detector temperature 300 ℃; initial oven temperature 50℃ for 5min, increased to 275℃ at a rate of 25℃ min^{-1}, then maintained at 275℃ for 3min. The total time for one GC run was 17min. The inlet was operated in split mode with a split ratio 10 : 1 and nitrogen of high purity was used as carrier gas. A WDL-95 workstation (Dalian Inst. Chem. Phys, CAS, China) was utilized to control the system and for acquisition of analytical data.

THMs in drinking water samples were monitored by capillary gas chromatography with electron capture detector using headspace liquid-phase microextraction (HS-LPME) technique. Briefly, a vial with a stir bar was placed on a magnetic stirrer and maintained at a desirable temperature in a water bath. HS-LPME was performed with a commercially available 10ul GC microsyringe (Shanghai, China). Before each extraction, the syringe was rinsed for at least 20 times with 1-octanol. During the extraction, the microsyringe was fixed above the extraction vials with a septum. After passing through the septum, the needle tip must be kept about 1 cm above the surface of sample solution. Then 1 μl of the extraction solvent containing I.S. was extruded out of the needle and kept suspending at the needle tip. When the extraction was finished, the drop was retracted into the needle and injected directly into the GC inlet.

RESULTS AND DISCUSSION

Several factors have been found to affect the sensitivity of the LPME technique for GC-ECD analysis. Among the organic solvents, xylene, ethylene glycol and 1-octanol, 1-octanol was the most suitable solvent for the analytes. Extraction conditions such as headspace volume, extraction time, stirring rate, extraction temperature and salting-out effect were optimized. The optimized conditions were as follows: 15ml headspace volume in a 40ml vial, 10min extraction time, 800 rpm stirring rate at 20℃ and 0.3 $g\,ml^{-1}$ NaCl added. These conditions must be kept constant during the procedure of analysis.

Extended standard method was used for quantitative determination of the THMs. Five point calibration curves with concentrations of 1, 10, 30, 50, 100 $\mu g\ l^{-1}$ for four THMs, were used, which give high correlation coefficients (R) than 0.995. The recoveries for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ were from 101 to 112% in tap water and well water. The repeatability of the method was determined by performing six times using aqueous standard solutions with 10 $\mu g\ l^{-1}$ THMs. The RSD% was found to be below 10% except that the repeatability of $CHCl_3$ was 11.3%.The limits of detection (LODs), based on a signal-to-noise ratio (S/N) of 3, ranged from 0.15 ($CHCl_2Br$ and $CHClBr_2$) to 0.4 $\mu g\ l^{-1}$ ($CHCl_3$), which were sensitive enough to determine THMs at the required levels in the present study.

The sampling sites cover 4 main tap water factories in Beijing City. They are located in the west (S1), south (S2), east (S3) and north (S4) of the city, respectively, and are providing 80% drinking water of the whole city (2,400,000t per day). Raw water of S4 comes from Miyun Reservoir while that of S1 and S3 is groundwater, and raw water of S2 constitutes 50% each of water from Miyun Reservoir and groundwater. Fig.1a shows the concentrations of THMs in raw water of four tap water factories. In view of THMs, raw water of four tap water factories has only small differences. It is obvious that raw waters of S3 and S4 are less contaminated by THMs. Although chloroform level (3.12 $\mu g\ l^{-1}$) in S2 is extremely high when compared with that in the other three raw waters, it is close to the data reported (3.0 $\mu g\ l^{-1}$) by huang et al in 1987 (Huang et al., 1987) and much lower than the maximum value previously reported (12 $\mu g\ l^{-1}$) by (Zhao

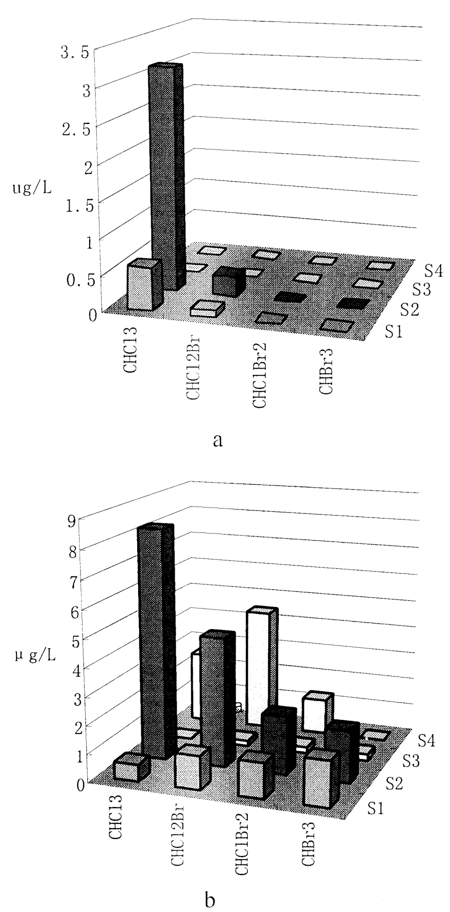

Figure 1. Concentrations of THMs in water samples
a. Raw water samples b. Tap water samples

et al., 1986). It was reported that in raw water of Jialingjiang tap water factory of Chongqing chloroform level ranged from 3.0 to 4.2 μg l^{-1}(Huang et al., 1987).

Fig.1b shows the concentrations of THMs in tap water of four tap water factories. For all samples, concentrations ,varied, between 0 and 8.26 μgl^{-1} (chloroform), 0.185 and 4.63 μ g l^{-1} (dichlorobromomethane), 0.218 and 2.09 μ g l^{-1} (chlorodibromomethane), 0 and 1.83 μ g l^{-1} (bromoform), with the mean concentrations of 2.86, 2.61, 1.21, and 0.91 μg l^{-1}, respectively. THMs levels in S2 and S4, whose raw waters are surface water of Miyun Reservoir, are higher than those of S1 and S3, whose raw waters are groundwater. It is clear that the concentrations of THMs in tap water have close relationship with the raw water. Previous investigations also drawn the same conclusion (Zhao et al., 1986). It means that surface water of Miyun Reservoir contains much more organic matrices, which can react with available chlorine in the disinfection, than groundwater.

Table 2. Comparison of THMs and TTHMs levels (μg l^{-1}) in tap water from other areas and Beijing

Locality	Survey year	CHCl3	CHCl2Br	CHClBr2	CHBr3	TTHMs	Reference
Zhabei District of Shanghai	1997	14.65	22.66	20.08	8.43	65.82	Yan JC (2002)
Tanggu District of Tianjin		33.66	20.63	8.05	0.61	62.95	
Chengguan District of Lanzhou		10.65	3.62	0.91		15.18	
Chaoyang District of Beijing		9.95	4.31	1.18		15.44	
Haidian District of Beijing		0.49				0.49	
Fengtai District of Beijing		0.67		1.63	11.83	14.13	
Xicheng District of Beijing		8.98	3.58	1.80	1.72	16.08	
Xuanwu District of Beijing		2.39	0.78	1.67	2.92	7.76	
Alacant of Spain	2001 or earlier	13.6	24.73	25.67	21.93	85.93	Villanueva CM, et al. (2003)
Barcelona of Spain		20.00	22.68	10.81	10.19	63.64	
Asturias of Spain		14.57	4.96	2.23	0.56	22.25	
Tenerife of Spain		0.39	0.85	1.18	5.55	8.00	
Beijing City	2003	2.86	2.61	1.21	0.91	7.59	Present work

To understand the status of THMs contamination in the tap water of the city, the levels of THMs and TTHMs determined in the present study were compared with the results in tap water obtained from different places and Beijing in 1997 (Table 2) (Yan, 2002). Among the data the concentration levels of THMs and TTHMs in Beijing in 1997 were close to or higher than those of the recent data, while our data were lower than those of Zhabei District of Shanghai, Tanggu District of Tianjin, and close to those of Chengguan District of Lanzhou. Then we can conclude that the present contamination levels of THMs in Beijing City are lower than those in other areas of China. At the same time, total and specific THM levels in the present work are close to or lower than results reported in four provinces of Spain (Villanueva et al, 2003). Our preliminary survey showed that the concentrations of THMs and TTHMs in tap water of Beijing City were much lower than the recommended maximum residue levels in drinking water established by the guideline of the World Health Organization (WHO) (Table 1).

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