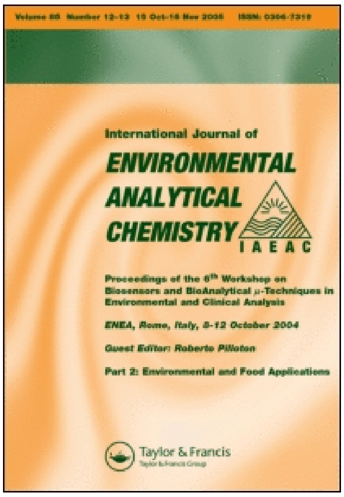

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GC Trace Analysis of Haloethers in Water — Comparison of Different Extraction Techniques

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GC TRACE ANALYSIS OF HALOETHERS IN WATER – COMPARISON OF DIFFERENT EXTRACTION TECHNIQUES

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The capabilities of three extraction techniques (solid-phase microextraction, solid-phase extraction, and liquid-liquid extraction) for the GC trace analysis of di- and tetrachlorinated haloethers in natural water samples were studied. The extraction procedures are described and evaluated with respect to recoveries, precision and detection limits using FID and MS detection. The results are compared. Investigations of the matrix influence show that efficiency and precision of the extraction procedures tested are not significantly influenced by dissolved organic matter in the relevant concentration range. Combined with GC-MS in SIM mode all three extraction techniques are generally suitable for the haloether analysis at ng/L level. However, the precision of solid-phase microextraction (SPME) is poor in this concentration range. Nevertheless, because of several advantages (low time consuming for sample preparation, no employment of solvents) the SPME is favorable for the determination of haloethers at µg/L level, like in Elbe river water samples.

Keywords: Haloether; gas chromatography; solid-phase microextraction; solid-phase extraction; liquid-liquid extraction; matrix influence

INTRODUCTION

GC-MS screening analysis of Elbe river water in the beginning of the nineties revealed the relatively high concentration of di-, tri-, and tetrachlorinated ethers (haloethers) [1,2]. The three isomeric tetrachlorinated bis(propyl) ethers belong to the most prominent organic contaminants of this river. In 1997, concentrations in the range of 2 to 10 µg/L for the sum of these isomers were determined depending on the sampling site [3]. There are only a few papers describing the behavior of haloethers. Evidently, the determination of these compounds in environmental samples is of great concern because of their toxicity and cancerogenity [4-6]. Five

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haloethers with one or two halogen atoms in the molecule were classified as priority pollutants by the US Environmental Protection Agency (EPA) in 1979. The occurrence of halogenated bis(propyl) ethers in the Elbe river water between the border to the Czech Republic and the estuary of the Elbe river illustrates their persistence in the aquatic environment.

Normally, the application of capillary GC in water analysis requires sample extraction steps to concentrate the analytes and to remove the matrix. The first studies resulting in the detection of haloethers in Elbe river water [1,2] were based on the liquid-liquid extraction (LLE) with n-hexane.

As known, LLE procedures require large amounts of organic solvents, are time-consuming, and involve the risk of analyte loss in the extraction and concentration processes. Using the solid-phase extraction (SPE) the solvent and time consumption can be reduced significantly. Solid-phase microextraction, developed by Pawliszyn and coworkers [7-11], is a solvent-free and inexpensive procedure for the extraction of organic compounds from water. Nowadays, the SPME is a practical alternative to other commonly used extraction techniques like LLE and SPE (see review [12]).

In a previous paper [3], some capabilities of SPME for the determination of selected di-and tetrachlorinated haloethers, which are relevant for the river Elbe, are shown. The goal of this paper is the comparison of the efficiency of different extraction techniques (SPME, SPE, LLE) for the determination of the haloethers mentioned above. The influence of dissolved organic carbon (DOC) on the extraction efficiency is studied.

EXPERIMENTAL

Apparatus

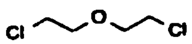
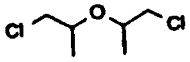
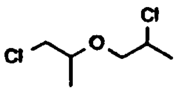
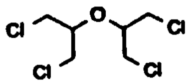
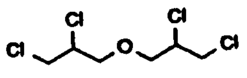
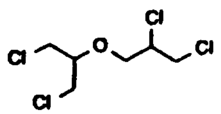
GC analyses were done using a Hewlett-Packard gas chromatograph (HP 5890 series II) with split/splitless injector and FID. A PTE-5 capillary column (30 m, 0.25 mm i. d., 0.25 µm film thickness) from Supelco was employed with the following temperature program: 30°C, 1 min isothermal, 5°C/min to 85°C, then 10°C/min to 195°C. The carrier gas was hydrogen with an inlet pressure of 70 kPa. The split/splitless injector was used in the splitless mode with a splitless time (desorption time in case of SPME) of 1 min. The temperature of both injector and detector was 250°C.

GC-MS analyses were performed using a Shimadzu GC-17A gas chromatograph combined with a QP-5000 mass spectrometer and equipped with a split/splitless injector. The capillary column and the chromatographic conditions were the same as described for the GC-FID measurements. The carrier gas was helium. The mass spectrometer was used in the single-ion monitoring (SIM) mode. The following ions were selected for the quantification: 63, 93 for 2,2'-BEE; 77, 79 for 1,1'-BPE and 1,2'-BPE ; 63, 93, 123 for 2,2'-BEOM; 75, 77 for 1,3,1',3'-BPE, 2,3,2',3'-BPE, and 1,3,2',3'-BPE (abbreviations see Table I).

Reagents

Bis(2-chloroethyl) ether, bis(2-chloroethoxy)methane, and a mixture of bis(1-chloro-2-propyl) ether and 1-chloro-2-propyl 2-chloro-1-propyl ether were purchased from Supelco. The isomeric mixture of the tetrachlorinated bis(propyl) ethers [bis(1,3-dichloro-2-propyl) ether, bis(2,3-dichloro-1-propyl) ether, and 1,3-dichloro-2-propyl 2,3-dichloro-1-propyl ether] was synthesized by the reaction of 1-chloro-2-propene, epichlorohydrin, and chlorine according to (13). The formulas of these substances and the abbreviations used are given in Table I.

TABLE I Investigated haloethers

compound	abbreviation	formula
bis(2-chloroethyl) ether	2,2'-BEE	
bis(1-chloro-2-propyl) ether	1,1'-BPE	
1-chloro-2-propyl-2-chloro-1-propyl ether	1,2'-BPE	
bis(2-chloroethoxy)methane	2,2'-BEOM	
bis(1. 3-dichloro-2-propyl) ether	1,3,1',3'-BPE	
bis(2.3-dichloro-1-propyl) ether	2,3,2',3'-BPE	
1.3-dichloro-2-propyl-2.3-dichloro-1-propyl ether	1,3,2',3'-BPE	

A stock solution in acetone (Merck) was prepared which contained the haloethers mentioned in concentrations between 0.38 and 1.5 μg/μL. Spiked water samples were prepared by diluting this stock solution with distilled water. The influence of salt was studied by addition of sodium chloride (Merck).

Water samples

For the investigation of the matrix influence three kinds of water samples were used: distilled water (DOC: <0.01 mg/L), Elbe river water (DOC: 4.9 mg/L), and an aqueous extract of wetland soil (DOC: 30.7 mg/L).

The Elbe river water was sampled at site 173 km (Dommitzsch) in September 1997. The aqueous extract of wetland soil was prepared from a river Elbe wetland soil (sampling: near estuary of the river Mulde in July 1997).

Briefly, 150 g of sieved wetland soil and 1 L of distilled water were given in a 2 L-flask and shaken for 24 h. Then the undissolved soil residue was separated by subsequent centrifugation (10 min at 3500 upm) and pressure filtration using cellulose acetate filters (0.45 μm pore size).

SPME procedure

The SPME experiments were done using a manual SPME device from Supelco. For haloether extraction 100μm-polydimethylsiloxane (PDMS) fibers were chosen. The optimization of the SPME procedure is described in [3]:

Briefly, 3 mL of the NaCl-saturated water sample are filled in a 5mL-sample vial. Applying a stirring rate of 1000 rpm the PDMS fiber is exposed for 30 min. (Without salt addition an exposure time of 10 min is sufficient.) The extracted haloethers are desorbed inside the GC injector at a temperature of 250°C for 1 min. The GC analysis of the desorbed analytes is carried out under the conditions mentioned above.

SPE procedure

The SPE experiments were done using a spe-12 G vacuum manifold from Baker. Preliminary investigation using the adsorbent RP18 “Polar Plus” (Baker) and LiChrolut EN (Merck) without and with salt addition had shown that LiChrolut EN is the more suitable adsorbent, especially for the enrichment of the dichlorinated ethers. The optimized SPE procedure is described in the following:

0.5g LiChrolut EN is filled in a 8mL-SPE column. For conditioning the adsorbent bed is subsequently rinsed with acetone (6 mL), methanol (6 mL), and distilled water (12 mL). 0.5 L of the water sample is sucked through the SPE column with a flow of about 10 mL/min. Then the adsorbent bed is purged with distilled water (6 mL). For drying, filtered air is sucked over the adsorbent for 80 min using a protection column filled with 0.25 g LiChrolut EN. The analyte elution is done with acetone into a test tube to a volume of 2 mL. The acetone eluate is concentrated carefully to a volume of 0.5 mL using a slow nitrogen flow.

LLE procedure

Following the procedure of Franke et al. [2] 0.5 L of the water sample is filled in a 1L-Erlenmeyer flask and extracted twice with 25 mL n-hexane for 30 min under intensive stirring. After phase separation the organic phases are combined, dried by filtration over 1 g of anhydrous sodium sulfate (Merck) and then concentrated to a volume of 0.5 mL using a rotary evaporator and later a slow nitrogen flow.

RESULTS AND DISCUSSION

SPME

The optimized SPME procedure combined with GC-FID and GC-MS in SIM mode was evaluated with respect to precision, limits of detection, and linearity of calibration [3]. The results are summarized in Table II.

TABLE II SPME of haloethers using FID and MS(SIM) detection, precision (% RSD) and detection limits (ng/L)

compound	*precision*		*detection limits*		
	GC-FID		*GC-FID*	*GC-MS*	
	A	*B*	*B*	*A*	*B*
2,2′-BEE	2.5	2.2	1200	220	50
1,1′-BPE	1.6	9.0	500	200	25
1,2′-BPE	1.8	7.3	500	210	20
2,2′-BEOM	0.7	2.0	700	180	20
1,3,1′,3′-BPE	0.7	5.4	300	45	10
2,3,2′,3′-BPE	1.4	6.5	400	50	12
1,3,2′,3′-BPE	1.1	5.1	300	40	8

A variant A: without salt addition, exposure time 10 min.
B variant B: saturated sodium chloride solution, exposure time 30 min.

Investigations to the influence of salt addition on the extraction efficiency of the haloethers had shown, that a distinct improvement of SPME sensitivity could be reached working with NaCl-saturated salt solution. The factor of peak area increase obtained was in the range of 5 to 12. This improvement is accompanied by significant decreased precision. The precision of the procedures results from 5 subsequent SPME experiments using spiked water samples at 100 µg/L level.

For all haloethers investigated the relative standard deviations (RSD) of the peak areas were 2.5% or better. The addition of salt resulted in RSD values up to 9.0%. However, these values could only be reached by a subsequent cleaning procedure of the SPME fiber after each sampling (removal of the deposited sodium chloride crystals by purging the fiber in intensively stirred distilled water for 5 min).

Detection limits (LOD) were calculated by comparing the signal-to-noise ratio (S/N) of the lowest detectable concentration to a S/N of 3. Working with salt addition and FID, detection limits of the compounds investigated were in the range of 300 to 1200 ng/L. The mass spectrometric detection in SIM mode allows a distinct improvement of the sensitivity of the method. Working without salt the detection limits are between 40 and 220 ng/L. With salt addition for all haloethers LOD values lower than 100 ng/L could be reached.

External calibrations in the range from 1 to 100 µg/L (FID) and 0.1 to 10 µg/L (MS) show linearity between haloether concentrations and detector signal (correlation coefficients >0.996).

SPE

The optimized SPE procedure using the adsorbent LiChrolut EN was characterized by recoveries, precision, and detection limits. The recovery experiments were carried out using spiked water samples at 10 and 1 µg/L levels. The results are given in Table III.

At the 10 µg/L level the recoveries are between 90 and 100% with relative standard deviations <3%. At the lower level of 1 µ/L the recoveries are in the range of 73 and 91% with RSD values up to 7%. Because of the high recoveries using LiChrolut EN the addition of salt to the water samples was not necessary. Using the described SPE procedure and FID detection limits are between 100 and 200 ng/L. The mass spectrometric detection in SIM mode allows detection limits in the range of 1 to 3 ng/L.

TABLE III SPE of haloethers on LiChrolut EN, recoveries (n=3) and relative standard deviations (RSD) at 10 µg/L and 1 µg/L level

compound	*10 µg/L*		*1 µg/L*	
	recovery (%)	*RSD (%)*	*recovery (%)*	*RSD (%)*
2,2'-BEE	96.7	2.0	73.4	0.9
1,1'-BPE	99.7	1.4	82.2	3.6
1,2'-BPE	90.8	2.8	74.0	3.6
2,2'-BEOM	98.1	2.6	80.9	6.5
1,3,1',3'-BPE	89.7	3.1	86.7	3.0
2,3,2',3'-BPE	98.2	0.8	91.0	7.1
1,3,2',3'-BPE	92.6	1.0	85.6	2.6

LLE

The LLE procedure using n-hexane as solvent according to [2] was evaluated. The recovery experiments were also done using spiked water samples at 10 and 1 µg/L levels. The results are given in Table IV.

At both concentration levels the LLE procedure gives only for the di- and tetra-chlorinated bis(propyl) ethers satisfied recoveries with values between 60 and 91%. The extraction efficiency for the more hydrophilic dichlorinated ethers bis(2-chloroethyl) ether and bis(2-chloroethoxy)methane is insufficient with recoveries lower than 50%. The precision is <4% RSD at 10 µg/L level and <7% RSD at 1 µg/L level. The detection limits are in the range of 100 to 300 ng/L using FID and in the range of 2 to 5 ng/L using MS detection in SIM mode.

TABLE IV LLE of haloethers with n-hexane, recoveries (n=3) and relative standard deviations (RSD) at 10 µg/L and 1 µg/L level

compound	*10 µg/L*		*1 µg/L*	
	recovery (%)	*RSD (%)*	*recovery (%)*	*RSD (%)*
2,2'-BEE	28.4	2.7	34.4	4.9
1,1'-BPE	62.0	1.0	66.4	3.7
1,2'-BPE	60.2	1.4	68.1	2.9
2,2'-BEOM	45.5	1.2	48.5	0.3
1,3,1',3'-BPE	87.6	3.7	76.1	3.9
1,3,2',3'-BPE	91.1	2.0	73.9	6.5

Matrix influence

The influence of natural dissolved organic matter (DOC) in relevant matrices on the efficiency of the extraction procedures was investigated. Therefore, samples of distilled water (DOC: <0.01 mg/L), Elbe river water (DOC: 4.9 mg/L), and an aqueous extract of wetland soil (DOC: 30.7 mg/L) were spiked with haloethers (10 µg/L). The GC analyses were done using FID. Applying the different extraction procedures recoveries or peak areas (in case of SPME) and their relative standard deviations (n=3) were determined and compared. The results are given in Figure 1 and Table V and VI.

TABLE V SPE of haloethers from different matrices, recoveries (in %, n=3) and relative standard deviations (RSD in %) at 10 µg/L-level

compound	*distilled water*		*Elbe river water*		*aqueous extract of soil*	
	recovery	*RSD*	*recovery*	*RSD*	*recovery*	*RSD*
2,2'-BEE	96.7	2.0	90.0	2.6	95.6	1.7
1,1'-BPE	99.7	1.4	105.1	4.8	96.1	1.6
1,2'-BPE	90.8	2.8	92.4	4.5	98.6	2.4
2,2'-BEOM	98.1	2.6	87.5	0.9	95.8	2.7
1,3,1',3'-BPE	89.7	3.1	84.5	3.4	98.6	3.6
2,3,2',3'-BPE	98.2	0.8	100.0	6.1	103.2	5.7
1,3,2',3'-BPE	92.6	1.0	90.7	3.4	95.6	4.2

TABLE VI LLE of haloethers from different matrices, recoveries (in %, n=3) and relative standard deviations (RSD in %) at 10 µg/L-level

compound	*distilled water*		*Elbe river water*		*aqueous extract of soil*	
	recovery	*RSD*	*recovery*	*RSD*	*recovery*	*RSD*
2,2'-BEE	28.4	2.7	32.4	4.5	34.3	3.5
1,1'-BPE	62.0	1.0	76.0	3.9	75.4	2.4
1,2'-BPE	60.2	1.4	75.1	4.1	77.4	1.3
2,2'-BEOM	45.5	1.2	50.5	3.8	48.9	1.7
1,3,1',3'-BPE	87.6	3.7	94.9	3.1	91.4	1.7
1,3,2',3'-BPE	91.1	2.0	97.7	2.4	88.8	4.2

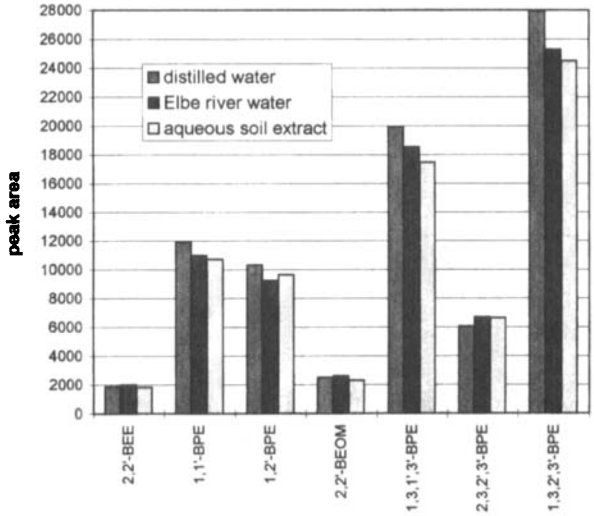


FIGURE 1 Influence of different matrices on SPME sensitivity of haloethers (concentration: 10 μg/L)

Considering RSD values up to 20% using SPME with salt addition the results given in Figure 1 illustrate, that the peak areas of the haloethers are not significantly influenced by the matrices with different DOC. Comparable results were also found for the two other extraction procedures (see Table V and VI). However, working with SPE and LLE, respectively, the relative standard deviations are lower (< 6%) than in SPME. That means, the efficiency of the different extraction procedures for the haloethers is not significantly influenced by the DOC content of the matrices tested.

Application of SPME procedure

The described SPME-GC-MS procedure without salt addition was used for the analysis of haloethers in Elbe river water (sampling: Aken, September 18, 1996) and in bank filtrate of Elbe river (sampling: groundwater observation well Meißen, infiltration pathway 1.5 m, November 7, 1996). Under the given experimental conditions only the three isomer tetrachlorinated bis(propyl) ethers could be detected in both samples. The quantification of the detected haloethers was done using external calibration. The results of the quantification are listed in Table VII. The total concentration of these pollutants in the Elbe river water was 6. 1 μg/L, whereas a value of 1.9 μg/L was found in the bank filtrate.

TABLE VII Tetrachlorinated bis(propyl) ethers in Elbe river water and bank filtrate of Elbe river (ng/L)

compound	*Elbe river water*	*bank filtrate*
1,3,1′,3′-BPE	920	810
2,3,2′,3′-BPE	1780	190
1,3,2′,3′-BPE	3400	920
Σ BPE	**6100**	**1920**

CONCLUSION

The results had shown that the three different extraction procedures especially combined with GC-MS in SIM mode are generally suitable for the trace analysis of haloethers at ng/L level in natural water samples.

SPME presents several important features such as negligible sample preparation and no employment of solvents. For the determination of haloethers the sample preparation is reducible to the exposition of the fiber in the aqueous sample for 10 or 30 min (without or with salt addition). However, the detection limits are increased about 10 times in comparison to SPE and LLE. Secondly, the SPME procedure, especially working with salt addition, still exhibits an unsatisfactory reproducibility (up to 10% at the 100 μg/L level). The precision can be improved (better than 3%) working without salt. However, this improvement is accompanied with a deterioration of the detection limits.

Because of the relatively high concentration of the tetrachlorinated haloethers in Elbe river water the salt addition in SPME procedure is not necessary for this task. As illustrated above the efficiency of the three extraction procedures investigated is not significantly influenced by the DOC content of the water matrix. That means, under these conditions the use of SPME is preferable.

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