Flow-assisted automated solid-phase microextraction for the determination of chloroethers in aqueous matrices

Amayreh Mousa\textsuperscript{a}, Chanbasha Basheer\textsuperscript{a,b,*}, Alsharaa Abdulnaser\textsuperscript{a}, Khaled Alhooshani\textsuperscript{a,b} and Abdulrahman Al-Arfaj\textsuperscript{a}

\textsuperscript{a}Department of Chemistry, King Fahd University of Petroleum and minerals, Dhahran 31261, Saudi Arabia; \textsuperscript{b}Center for Excellence in Nanotechnology, KFUPM, Dhahran 31261, Saudi Arabia

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In this study a method of flow-assisted automated solid-phase microextraction (FA-SPME) was developed for the determination of organic pollutants in aqueous samples. A CTC Combi-PAL autosampler coupled with gas chromatography–mass spectrometry (GC–MS) was used to automate the entire extraction process. In this method, the SPME fibre was exposed to 100 mL of sample in a direct immersion mode for 10 min. After exposure, the fibre was desorbed at the injection port of GC–MS. To demonstrate the applicability of FA-SPME, chloroethers were selected as model compounds. Good linear correlation was found over a concentration range of 0.5–100 µg/L. The detection limits of the method were determined between 0.02 and 0.05 µg/L with the coefficients of determination ($R^2$) from 0.9980 to 0.9996. The relative standard deviations (RSDs) of the FA-SPME for three sequential FA-SPME analyses were determined to be in the range between 1.2% and 6.2% ($n = 3$). The applicability of the method was assessed by means of recovery studies and satisfactory values for all compounds were obtained. This optimised method was used in the analysis of water and human urine samples to show the matrix effect on FA-SPME. This FA-SPME/GC–MS is substantially faster and suitable for the routine continuous flow-mode environmental monitoring applications.

**Keywords:** chloroethers; atomisation; on-site applications; flow-assisted solid phase microextraction; GC–MS

1. Introduction

Chloroethers (CEs) are compounds which contain an ether moiety ($R$–O–$R$) and halogen atoms attached to the aryl or alkyl groups. CEs are produced in large quantities – more than 50 million pounds per year – and commonly used as solvents in various industrial applications \cite{1–3}. CEs are stable and non-biodegradable in aqueous samples \cite{1}.

CEs have been used in a wide range of applications, which includes as solvents in textile industry, and as alkylating agents and chemical intermediates in the manufacture of dyes and other chemicals \cite{4}.

Bis(2-chloroethyl)ether (BCEE), bis(2-chloroisopropyl)ether (BCIE) and bis(2-chloroethoxy) methane (BCEM) are the class of CEs frequently found in drinking waters and urine \cite{5–8}. Thus, the release of CEs into the environment is of great concern because of their toxicity and carcinogenicity \cite{5,9,10}. In 1979, the United States Environmental Protection Agency (USEPA) classified five haloethers (HEs) as priority pollutants \cite{9} and proposed a maximum permitted contaminant level (MCL) of 500 µg/L \cite{10}. The USEPA and the International Agency for Research

*Corresponding author. Email: cbasheer@kfupm.edu.sa

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on Cancer have classified CEs as carcinogenic compound category D. (http://dnr.wi.gov/topic/drinkingwater/documents/haltable.pdf, Accessed on 12/7/2013).

CEs are classified as disinfection by-products inadvertently produced by the reactions of disinfectants with organic matter naturally present in water [1]. They are harmful to humans and are suspected carcinogens at low parts per billion concentrations. In industry, CEs are widely employed as solvents in fibre processing and in the production of polymers, pesticides and medicines [1,3,11]. CEs are persistent and therefore of great concern due to their carcinogenicity and toxicity [5,9,10].

No data that address the toxicity of BCEM to humans were found. However, its volatility and water solubility could result in human exposure by inhalation, ingestion or dermal contact in the course of occupational exposures. The minimum half-life of BCEM in water has been reported to be 2 years [12,13] and is persistent to environmental exposure.

In this regard, different preconcentration methods were reported for the analysis of CEs in water samples, including USEPA methods 611 and 625, which are based on liquid–liquid extraction (LLE) [2]. However, LLE procedures have a number of drawbacks: they require larger volumes of hazardous organic solvents and multi-step extractions, are time-consuming, involve the risk of analyte loss in the extraction and concentration processes, and are not suitable for trace-level determination [10,14]. Solid-phase extraction (SPE) is the solvent-minimised alternative to the LLE approach [10], where SPE-C$_8$ is used as a CE. The main problem associated with SPE-C$_8$ is the low selectivity of the retention mechanism of CEs, which yields low recoveries [5,15].

In recent years, continuous progress in microextraction techniques for CEs has produced an important development in trace-level analysis from various environmental samples. Liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) are alternative microextraction methods reported for CEs in the literature [5,16,17]. LPME is a solvent-minimised extraction technique in which CEs were extracted using immiscible organic solvents. The selection of suitable organic solvents for polar analytes and full automation of LPME are challenging tasks [16].

SPME is widely used as a solvent-free extraction microextraction technique which combines sampling, sample clean-up and preconcentration into a single step [18]. On the other hand, SPME requires careful calibration and optimisation for the quantification of trace-level analytes. This requires more time and once the procedures are optimised, SPME can be conveniently used for routine analysis [19,20]. Manual SPME optimisation methods are sometimes prone to human error and the possibility of contamination associated with manual processing [21]. Automated sample preparation eliminates human intervention in order to improve overall sample analysis efficiency and reliable robustness of the method [22].

The objective of this study is to demonstrate flow-assisted automated solid-phase microextraction (FA-SPME) combined with GC–MS for water analysis. The method is suitable for larger volume samples and applicable for on-site continuous monitoring of organic pollutants without human intervention. SPME automation has been widely used in various modes such as headspace-SPME, direct immersion-SPME and different formats which include thin film-SPME, in-tip-SPME and 96 vial plate-SPME [22–25]. In general, SPME automation has been reported only for small volume samples at static mode; to our knowledge, this is the first time that FA-SPME has been developed for continuous-flow mode.

2. Experimental

2.1. Chemicals and materials

A mixture of CE standards was purchased from Supelco (Bellefonte, PA, USA). The mixture contained BCEE, BCIE and BCEM at a concentration of 2000 µg/mL. A working standard solution was prepared daily by appropriate dilution of stock solution of CEs in the same solvent
(acetone). Physical and chemical properties of target analytes are shown in Table S1 (Supplemental data). Analytical-grade solvents were purchased from Supelco (Bellefonte, PA, USA). Double deionised water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Sodium hydroxide, hydrochloric acid and sodium chloride were obtained from Merck (Darmstadt, Germany). To avoid any carryover of CEs, all laboratory glassware was washed with concentrated hydrochloric acid and rinsed with deionised water followed by acetone and dried out in the laboratory oven at 100°C for 1 h. A peristaltic pump was purchased from J.P. Selecta (Abrera-Barcelona, Spain), which provided flow rates ranging from 20 to 200 mL/min. The speed can be automatically controlled through an external controller. GC–MS retention time and fragment ions of CEs are shown in Table S2 (Supplemental data).

2.2. GC–MS instrumentation

Analysis was performed using a gas chromatograph (Agilent technologies, 7890A GC) coupled with a quadrupole mass selective spectrometer (Agilent technologies, 5975C) equipped with an inert ion source and provided with a split-splitless injection port and a HP-5 GC fused silica capillary column (Agilent 19091J-413; 30 m × 320 µm ID × 0.25 µm thickness). A CTC Combi-PAL autosampler (GC sampler 80, Zwingen, Switzerland) was used for the FA-SPME. Ultra-high-purity helium (99.999%) was used as the carrier gas at a constant flow rate of 1.3 mL/min. The samples were injected in the splitless mode. The temperature programme used for the analysis was as follows: the initial temperature was 40°C held for 1 min which was then increased to 118°C at 10°C/min and held for 3 min, then to 190°C at 15°C/min and held for 4 min. The total run time was 18.6 min. The injection port, ion source and interface temperatures were 280°C, 230°C and 250°C, respectively. For qualitative determinations, the mass spectrometric detector was operated under the electron impact ionisation mode with full-scan range from m/z 50 to 550 and selective ion monitoring mode was used for the quantification of the analytes.

2.3. Samples

CEs are commonly present in the water samples after disinfection process; in Saudi Arabia, most of the drinking water samples were undergoing different types of pretreatment processes. Thus, we decided to select bottled drinking water (purchased from a local supermarket) and tap water (collected from the main campus of King Fahd University, Saudi Arabia). To understand the exposure level to humans, urine samples (from a volunteer working at the water desalination facility) were analysed. All samples were stored at 4°C prior to analysis.

2.4. Analytical procedure

The experimental set-up of FA-SPME shown in Figure 1 clearly shows the modified SPME set-up in which the autosampler vial was fabricated to be suitable for flow mode. A flat-top, flat-bottom, long-neck stainless steel screw cap vial of 20 mL capacity with the specification of 22.5 × 75.5 mm was fabricated at the university mechanical lathe facility as shown in Figure 1. To improve sample mixing in the vial, the sample is introduced at the bottom of the vial and it leaves from the top. A 100 mL sample solution spiked with CEs, sample pH 10 and salt concentration of 10% (w/v), was placed in a 125 mL flask and connected to a 20 mL modified autosampler vial with a flexible polyetheretherketone tubing. The samples were circulated with different flow rates using a peristaltic pump. Extractions were performed by SPME fibre in direct immersion mode at modified autosampler vial for 10 min in a continuous flow mode. After the extraction, the fibre was thermally desorbed in the GC–MS injection port for 3 min at 280°C.
3. Result and discussion

3.1. Selection of SPME fibre

To optimise the SPME conditions, three commercially available fibres were tested to extract CEs. Fibres coated with polydimethylsiloxane (PDMS, 30 µm), carbowax/divinylbenzene (CW/DVB, 65 µm) and polyacrylate (PA, 85 µm) were purchased from Supelco (Supelco, Bellefonte, PA, USA) and used without any modifications. The fibres were conditioned prior to use according to the instructions provided by the suppliers. Figure 2 shows the extraction performance, and CW/DVB gave the highest peak areas for all studied CEs. This could be due to the thinner coating and higher surface area of CW/DVB compared with that of PA fibres [19], and aligns with the fact that more polar compounds are best extracted by polar fibres like CW/DVB.

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Figure 1. Schematic of FA-SPME/GC–MS.

Figure 2. Selection of SPME fibre (extraction conditions – 100 mL of sample spiked with 100 µg/L of CEs, absorption time 10 min, desorption time 3 min and sample flow rate of 40 mL/min).
From the result, CW/DVB fibre was finally selected for use in further optimisation studies.

3.2. Effect of pump flow rate

FA-SPME has advantages for on-site applications and the aim of this part was to investigate the effect of sample flow rates on the extraction efficiency of CEs. The flow rate of the pump is an important parameter that permits continuous exposure of the SPME fibre to fresh aqueous samples. The flow rate of samples was examined to be in the range 30–80 mL/min. Figure 3 shows that extraction efficiency increased with an increasing flow rate from 30 to 50 mL/min. A decrease in extraction efficiency at higher flow rates (>50 mL/min) was observed. It is likely that either the SPME fibre had reached maximum extraction, or at high flow rates analytes had desorbed from the SPME fibre, resulting in loss of analytes. The influence of flow rate was compared with static mode (0 flow rate) and normal DI-SPME (with regular 20 mL SPME autosample vial with sample agitation speed of 250 rpm for 10 min.). Results clearly indicated that the use of flow instead of conventional agitation provided high sensitivity (Figure 3). Thus, FA-SPME has advantages for on-site applications real samples can be directly analysed without sub-sampling (batch application) by continuously pumping the sample in to the extraction vial.

3.3. Effect of absorption time of SPME

The effect of the absorption time profile using CW/DVB fibre was examined in the range between 5 and 30 min. Peak areas were plotted against absorption time and shown in Figure 4. The equilibrium was achieved at 10 min, and no further increase in extraction was observed. A decrease in extraction efficiency beyond 10 min is most likely due to desorption of analytes. This kind of phenomenon is common in equilibrium-based SPME extraction [19]. Thus, an absorption time of 10 min was selected for further optimisation.

3.4. Effect of ionic strength

The effect of the ionic strength on the extraction efficiency of FA-SPME was investigated by adding NaCl concentrations ranging from 0 (no salt addition) to 30% (w/v) (Figure S1, Supplemental data).

Figure 3. Influence of flow rate and comparison of normal DI-SPME with FA-SPME/GC–MS (extraction conditions for FA-SPME is as Figure 2 except flow rate). For normal DI-SPME, 20 mL of sample was spiked with 100 µg/L CEs, absorption time 10 min, desorption time 3 min and agitation speed of 250 rpm in the CTC-Combi-Pal agitator).
The highest extraction efficiency of CEs was at 10% (w/v) concentration of NaCl. The extraction efficiency decreased for solutions that contain higher than 10% (w/v). The anomalous effect of NaCl on the extraction of CEs is probably due to two factors. The first is the salting-out effect, which decreases the solubility of the analytes, and thus increases the absorption \[2,5\]. Second, salt dissolved in the solution may change the physical properties of the static aqueous layer on the fibre, and thereby reduce the rate of diffusion of the analyte through the static aqueous layer into the fibre \[5\]. Therefore, 10% (w/v) NaCl was added in the subsequent studies.

3.5. Sample pH

CEs are neutral compounds; however, sample pH has some influence in the extraction efficiency by SPME \[20\]. To determine the effects of pH on the performance of FA-SPME, samples at different pH values between 2 and 12 were investigated (sample pH was adjusted using NaOH and HCl solutions). The extraction performance slightly increased with increasing sample pH (Figure 5). At sample pH 10, all three analytes reached a maximum partitioning into the CW-DVB-SPME fibre. At acidic conditions, 20–50%
(BCIE 55%, BCEE, 77% and BCEM, 80%) lesser extraction was observed when compared to alkaline conditions. CEs are relatively less stable at acidic conditions.

3.6. **Analytical performance of FA-SPME method**

To evaluate the quantitative performance of the FA-SPME, the linear range, repeatability and the limits of detection were investigated under the optimised conditions (10 min absorption time, 50 mL/min pump flow rate, 10% (w/v) NaCl and sample pH 10). The results are summarised in Table 1. Linearity of the calibration was good over the concentration range of 0.5–100 µg/L with favourable coefficient of determination ($R^2$) ranging from 0.9980 to 0.9996. The repeatability study was carried out by extracting spiked water samples at different concentration levels (0.5, 1, 5, 10, 20, 40, 70, 100 µg/L), and the average percentage relative standard deviations (%RSDs) were between 1.2% and 6.2% ($n = 3$). The LODs, based on an S/N ratio of 3, ranging from 0.02 to 0.05 µg/L were obtained. These results confirmed that the proposed method is suitable for trace-level analysis of CEs in aqueous samples. A comparison of the main characteristics of the proposed method with previously reported works is summarised in Table 2. The developed method showed promising results compared with other previously reported microextraction methods. An important advantage of the present work over other microextraction techniques [5,10] is that it is a simple, solvent-free preconcentration system with high precision and accuracy.

### Table 1. Features of the FA-SPME method. Linear range (L.R), coefficient of determination ($R^2$), linear equations, %RSDs and LODs.

| Compound | L.R (µg/L) | $R^2$   | Equation                  | %RSDs ($n = 3$) | LODs (µg/L) |
|----------|------------|---------|---------------------------|----------------|--------------|
| BCIE     | 0.5–100    | 0.9996  | $Y = 0.0001X - 5.210$     | 6.2            | 0.04         |
| BCEE     | 0.5–100    | 0.9980  | $Y = 0.0001X - 19.26$     | 1.2            | 0.05         |
| BCEM     | 0.5–100    | 0.9994  | $Y = 0.0001X - 4.316$     | 2.3            | 0.02         |

Note: $Y$: concentration (µg/L), $X$: peak area.

### Table 2. Comparison of the proposed method with other previously reported.

| Analytical technique | Sample       | %Salt (µg/L) | Extraction time (min) | %RSDs | LODs (µg/L) | % Recovery | Ref.     |
|----------------------|--------------|--------------|-----------------------|-------|-------------|------------|----------|
| HF-LPME/GC-FID       | Water        | 0            | 30                    | 10.8–11.5 | 4.28–4.30 | 93.0–95.0 | [2]      |
| HF-LPME/GC-ECD       | Water        | 0            | 30                    | 8.4–9.7  | 0.25–0.33  | 93.0–95.0 | [5]      |
| SPME/GC-FID          | Water        | -e           | 10                    | 10–13   | 0.82–480   | -e         | [5]      |
| SPE/GC-FID           | Water        | 0            | 80                    | 0.9–6.5  | 0.001–0.003 | 73.4–80.9 | [10]     |
| LPE/GC-FID           | Water        | 0            | 30                    | 0.3–4.9  | 0.10–0.30  | 34.4–48.5 | [10]     |
| SPME/GC–MS           | Water        | 0            | 10                    | -e      | 0.18–0.22  | -e         | [10]     |
| SPME/GC-FID          | Water        | 35           | 30                    | 2–2.20   | 0.70–1.20  | -e         | [10]     |
| HS-SPEME GC–MS       | Grapes       | -e           | 20                    | 0.3–41.1 | 0.02–0.29  | -e         | [25]     |
| FA-SPME/ GC–MS       | Water/ urine | 10           | 10                    | 1.2–6.2  | 0.02–0.05  | 92.6–107.7 | Present  |

Note: *Hollow fibre, ‡liquid phase microextraction, §flame ionisation detector, †electron capture detector, ‡not determined in this work.
low detection limits. Lifetime of the SPME fibre was tested and the SPME fibre was found to be stable up to 80 analyses.

3.7. Application to the real aqueous samples

The applicability of the proposed FA-SPME technique for real water and urine sample matrices was evaluated. Dilution of the urine sample (1:1 ratio of dilution with ultrapure water) was carried out prior to the flow-assisted extraction. Mean concentrations of CEs in water and urine samples are shown in Table 3. To evaluate the matrix effects, one of the water and urine samples were spiked and recoveries were calculated based on the standard addition method and shown in Table 4. The data clearly show a high recovery, with %RSDs less than 10%. The excellent results demonstrated that the matrix effect had a negligible effect on FA-SPME for urine samples. Figure S2 (Supplemental data) shows the GC–MS chromatograms extracted from real water and urine samples and their respective spiked samples. Direct extraction from the urine sample could conceivably pose problems due to its complex sample matrix. The reason for diluting the urine samples in this work was to increase the sample volume, prevent the contamination of SPME fibre and increase the life of the fibres. The main focus of this work was on the FA-SPME procedure and its applicability to continuous flow mode, and this has clearly been demonstrated.

4. Conclusion

A novel continuous FA-SPME method was developed for the convenient analysis of CEs in water and urine samples. With the use of a CTC Combi-PAL autosampler, the automated SPME was enabled that allowed sample extraction, injection and SPME fibre conditioning to be carried out completely automatically. FA-SPME-GC/MS provides satisfactory analyte recovery, sensitivity and reproducibility when compared to normal DI-SPME. This FA-SPME approach

Table 3. The concentration of CEs in real samples determined by FA-SPME/GC–MS.

| Compound | Drinking water (n = 3) | Tap water (n = 3) | Human urine (n = 3) |
|----------|------------------------|------------------|------------------|
|          | µg/L   | %RSDs | µg/L   | %RSDs | µg/L   | %RSDs |
| BCEE     | 5.5    | 0.5   | 3.1    | 0.4   | 30.8   | 4.6   |
| BCIE     | 7.4    | 0.4   | 4.3    | 0.9   | 48.3   | 2.1   |
| BCEM     | 6.0    | 0.1   | 7.6    | 0.8   | 11.5   | 3.9   |

Table 4. Extraction recovery of CEs from water and human urine samples spiked by FA-SPME/ GC–MS.

| Compound | Drinking water | Tap water | Human urine |
|----------|----------------|-----------|-------------|
|          | 5 µg/L | 20 µg/L | 5 µg/L | 20 µg/L | 5 µg/L | 20 µg/L |
| BCEE     | 98.4 ± 1.3 | 95.1 ± 4.1 | 101.6 ± 6.9 | 92.7 ± 6.2 | 105.7 ± 8.1 | 98.8 ± 5.7 |
| BCIE     | 107.7 ± 3.6 | 91.6 ± 2.0 | 88.2 ± 4.2 | 94 ± 4.5 | 97.8 ± 1.0 | 92.6 ± 2.7 |
| BCEM     | 104.9 ± 10.0 | 90.7 ± 3.0 | 93.4 ± 2.5 | 98.5 ± 5.7 | 95 ± 4.0 | 106.2 ± 7.6 |
demonstrated the feasibility of a complete analytical system comprising sample preparation and GC–MS at the laboratory conditions. The entire set-up may be operated on-site, flow-assisted automatically without human intervention.

Disclosure statement
No potential conflict of interest was reported by the authors.

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