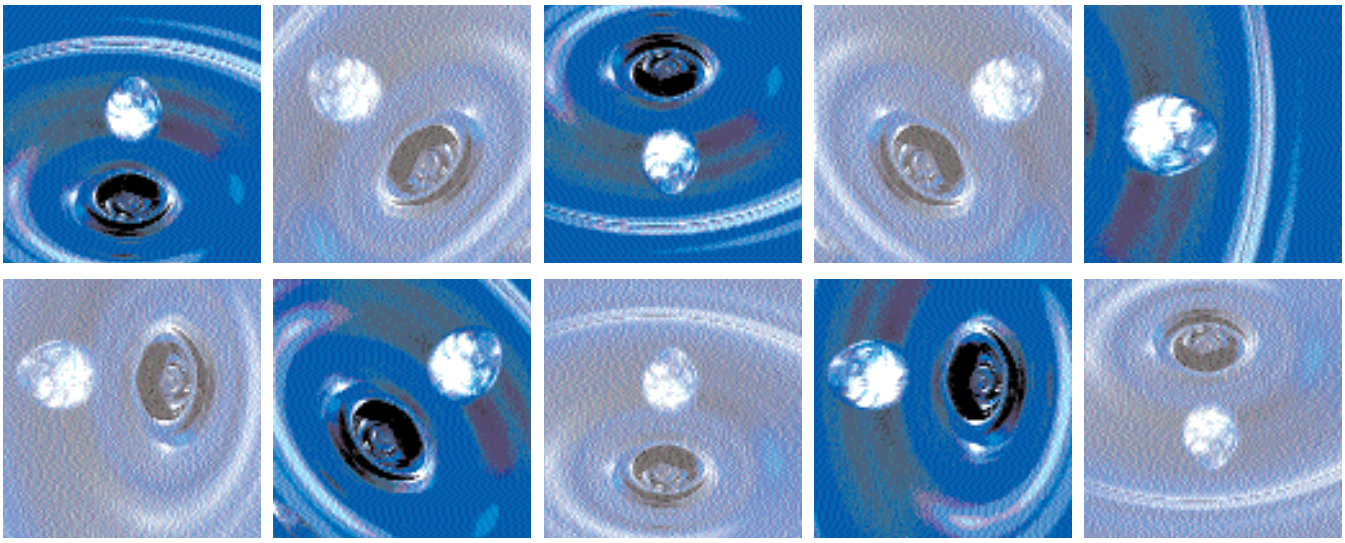

Single-Drop Extraction versus Solid-Phase Microextraction for the Analysis of VOCs in Water

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Single-drop extraction (SDE) and solid-phase microextraction were compared for the isolation of trace organic pollutants from aqueous samples. Both techniques were found to be rapid and reliable. Adequate repeatability for both extraction techniques was obtained, with RSD values ranging from 2.5–5.2%. SDE in combination with gas chromatography–electron capture detection shows potential for the analysis of chlorocompounds in water.

Introduction

An important part of any analytical process is sample preparation, which involves isolation and preconcentration of various analytes of interest.[1] Liquid–liquid extraction (LLE) is one of the oldest pretreatment procedures and because of its simplicity and low cost is commonly used. However, conventional LLE requires large volumes of high-purity solvents, which are often expensive and/or hazardous. The desire to reduce both time and the volumes of organic solvent required has led to the development of newer techniques, such as solid-phase extraction (SPE)[2,3] or solid-phase microextraction (SPME).[4–6] SPME, as a universal tool for isolation and preconcentration of pollutants from different matrices, was introduced and developed by Pawliszyn and co-workers.[7] It uses a fused-silica fibre coated with a sorbent to extract samples and pass analytes directly into a heated injector for gas chromatography (GC) or with a solvent into a high performance liquid chromatography interface. Coupling with GC is frequently used for the determination of various organic micropollutants in water, allowing extraction without solvents.[8]

Cantwell and Jeannot[9] introduced a micro-LLE method in which a single drop of organic solvent was contained at the end of a PTFE rod. This system required two discrete parts: the first for extraction and the second for injection. Liu and Dasgupta[10] described a microdrop liquid extraction system for trace amounts of analytes, which were subsequently identified in situ by UV/vis detection. In 1997 Jeannot and Cantwell[11], and He and Lee[12] independently introduced a simpler kind of microextraction in which an organic drop hangs from the tip of a GC syringe needle. The latter system has since been applied to speciation investigations.[13]

In LLE, the distribution of analyte (AN) between the aqueous and the organic phases is described by the distribution coefficient (K_d).[14] Equilibrium can be reached faster by shaking or stirring the aqueous phase containing the analyte, with the organic phase:

$$AN_{(aq)} \rightleftharpoons AN_{(org)} \qquad [1]$$

where (aq) and (org) are the aqueous and organic phases, respectively.

The activity ratio of AN in the solvents is expressed by the constant:

$$K_d = [AN]_{org}/[AN]_{aq} \quad [2]$$

In LLE, the equilibrium concentration of analyte in the organic phase is given by:[11]

$$C_{o,eq} = Kc_{aq,eq} = \frac{Kc_{aq,init}}{1 + KV_o / V_{aq}} \quad [3]$$

where K is the distribution coefficient, $c_{aq,init}$ is the initial concentration of analyte in the aqueous phase, $c_{aq,eq}$ and $c_{o,eq}$ are the equilibrium concentrations in aqueous (aq) and organic (o) phases, and V_o and V_{aq} are the organic and aqueous phase volumes, respectively.

Thus, K and $c_{aq,eq}$ must be sufficiently large, and the phase ratio must be reasonably small to avoid detection problems. Moreover, the applicability of the method in routine analysis may be limited to the time of equilibration. Also, the organic phase concentration may be somewhat lower than $c_{o,eq}$. Jeannot and Cantwell[9] described solvent microextraction in a si ngle drop, such that the rate equation for LLE can be defined by:

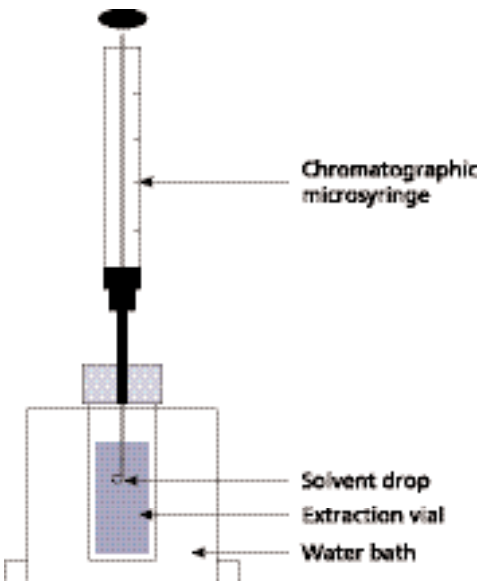
$$\frac{dc_o}{dt} = \frac{A_i}{V_o} \bar{\beta}_o (Kc_{aq} - c_o) \quad [4]$$

where c_o is the concentration of analyte in the organic phase at time 't', $\bar{\beta}_o$ is the overall mass transfer coefficient with respect to the organic phase (cm/s), A_i is the interfacial area, and c_{aq} is the analyte concentration in the aqueous phase at time 't'.

If transfer across the liquid–liquid interface is rapid, the overall mass transfer can be described as follows:

$$\frac{1}{\bar{\beta}_o} = \frac{1}{\beta_o} + \frac{K}{\beta_{aq}} \quad [5]$$

Figure 1: Schematic of single-drop extraction apparatus.



where β_o and β_{aq} are the individual mass transfer coefficients for both phases.

Flux at the interface is defined by:

$$\frac{1}{A_i}\frac{dn}{dt} = \beta_{aq}(C_{aq} - C_{aq,I}) = \beta_o(C_{o,I} - c_o) \quad [6]$$

Equation 5 reveals the influence of experimental variables on analysis time. In addition, for fast applications V_{aq} must be minimized and A_i, β_o and β_{aq} must be maximized.

In this study, a modified micro-solvent technique is compared with SPME. Both the organic drop and the polymeric coating of the SPME fibre are exposed to an aqueous solution of halogenated compounds. The analytes are transferred from aqueous solution to organic layer by diffusion only (extraction without stirring). The same conditions (sample volume, temperature and sampling time) are applied for both techniques. In micro-solvent experiments different conditions, such as a sampling time and temperature, are compared.

Coupling with GC is frequently used for the determination of various organic micropollutants in water, allowing extraction without solvents.

Experimental

Materials and reagents: Trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane purris were bought from Promochem (Wessel, Germany); methanol and hexane (pesticide grade) were purchased from J.T. Baker (Deventer, The Netherlands), helium (99.9999% purity) was purchased from Praxair (Gliwice, Poland), and nitrogen (99.999% purity) from Messer Griesheim (Gliwice, Poland). A non-polar 100% methylsilicone SB 1 (WGA, Düsseldorf, Germany) column (60 m × 0.25 mm × 0.25 µm) was used. The SPME fibre, with holder for manual sampling, (Supelco, Bellefonte Pennsylvania, USA) was coated with PDMS (film thickness 100 µm). A refrigerated circulator (Julabo Labortechnik, Seelbach, Germany) was used for temperature control of the extraction vial. Extraction and injection in the micro-solvent extraction experiments were performed using a GC syringe (HP part no. 9301–0511). Deionized water was prepared using a Milli-Q water-purification system (Millipore, El Paso, Texas, USA).

Chromatographic investigations: Chromatographic analyses were performed using an Autosystem XL (PerkinElmer Instruments, Norwalk, Connecticut, USA) with an electron capture detector (ECD). The carrier gas was helium with a linear velocity of 30 cm/s. Data acquisition was performed using a Nelson 1020 personal integrator (PerkinElmer Instruments).

The temperature of the split-splitless injector was 250 °C. The splitless time was 0.5 min, and the split ratio 1:25. The ECD detector temperature was 280 °C, and the make-up gas was nitrogen at 50 mL/min. The oven temperature programme was as follows: 30 °C for 1.5 min, to 60 °C at 5 °C/min (hold for 0 min), to 180 °C at 10 °C/min (hold for 3 min).

Sample preparation: Standard mixtures for calibration extractions were prepared by spiking deionized water with methanolic solutions of trichloro-, bromodichloro-, dibromochloro- and tribromomethane at the required concentrations.

Quantification was performed by injecting four solutions containing different amounts of halocarbons. The calibration curves were based on the peak area calculation. Figure 1 shows a schematic of the SDE set-up.

The micro-solvent extraction procedure was as follows:
(1) 2 µL of hexane was drawn into a microsyringe.
(2) The needle of the syringe was passed through the sample vial valve and immersed in the aqueous sample.
(3) The syringe plunger was depressed to expose a 2 µL drop of solvent to the sample.
(4) The drop was drawn back into the syringe and the needle was removed from the sample vial.
(5) The needle was inserted into the hot injector and injection was performed.

Results and Discussion

SPME analysis: Of all the commercially available SPME fibre coatings probably the most thoroughly investigated are poly(dimethylsiloxane) (PDMS) and polyacrylate (PA) ones.[15] PDMS fibres are recommended for non-polar constituents, whereas PA fibres are more suitable for the analysis of more polar compounds.[16] This study used a PDMS fibre.

Optimzation of desorption time: The desorption temperature should be high enough to completely release all volatiles adsorbed onto a fibre, as an analyte's carryover influences quantification and requires additional desorption before subsequent sampling. The limiting factors are compound character and fibre temperature resistance.[15] Analytes were desorbed from the PDMS fibre at 220 °C for 0.8 min. After desorption, the fibre was kept in a second injector (temperature: 250 °C, time 10 min) for complete desorption of the analysed compounds.

Exposure time and temperature: SPME analysis was performed at 25 °C with an extraction period of 15 min, similar to the micro-solvent extraction procedure.

SDE as a micro-solvent extraction: The earlier work on micro-solvent extraction studied factors such as drop volume, exposure time and temperature.[17] Based on these results a 2 µL drop volume was used in this study. However, temperature and exposure time are key parameters for this method. With longer exposure times higher concentrations of halocarbons are observed in the organic solvent drop (Figure 2). The analytical signal rapidly increases up to 15 min, after which the rate of increase slows down. Precision of the immersion time is fundamental for high reproducibility, because an equilibrium is not reached after 45 min.

In addition, when the organic drop was exposed to aqueous sample, a small amount of solvent started to dissolve reducing the drop volume. In fact, during the extraction process 10–15% loss of solvent was observed. An extraction time of 15 min was selected for these investigations. The reproducibility of peak area was investigated in 10 replicate experiments. The RSDs ranged from 2.5–5.2% depending on the exposure time.

Temperature also exerts an influence on extraction (Figure 3). The analytical signal rapidly increased for all compounds with increasing immersion temperature. However, temperatures higher than 40 °C caused a fast dissolution of the hexane drop.

Comparison of SPME and SDE: For a comparison of methods, repeatability and linearity were determined. For SDE and SPME standard solutions of target compounds with the same concentrations were used. The extraction of halocarbons was performed with a 2 µL hexane drop (SDE) and a PDMS fibre (SPME) for 15 min. The temperature was kept at 25 ± 0.03 °C. The measured detector response was plotted against the aqueous concentration of halocarbons and the linearity of both methods was investigated over a concentration range for individual compounds. Results of this comparison are

Figure 2: Extraction-time profile for $CHCl_3$ (15.8 µg/L), $CHBrCl_2$ (8.2 µg/L), $CHBr_2Cl$ (2.1 µg/L) and $CHBr_3$ (1.3 µg/L), drop volume 2 µL, temperature 25 °C.

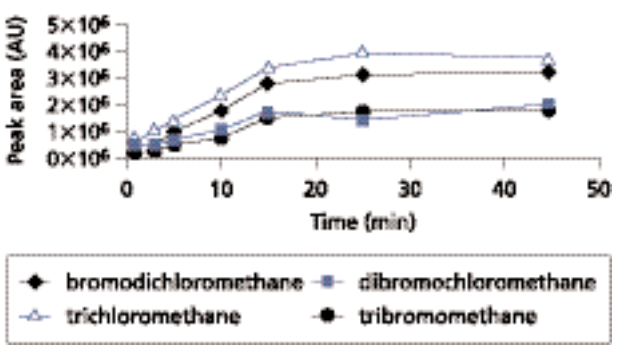


Figure 3: Extraction-temperature profile for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ (concentrations and drop volume same as in Figure 1), exposure time: 15 min.

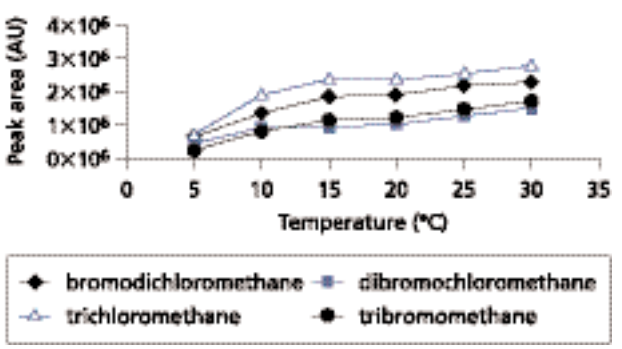


Table 1: Comparison of repeatability and linearity of SDE and SPME.

Compound	Calibration curve range (µg/L)	SDE		SPME	
		r	RSD	r	RSD
$CHCl_3$	1.9–26.2	0.982	4.4	0.992	3.4
$CHBrCl_2$	2.1–12.0	0.979	5.1	0.996	2.8
$CHBr_2Cl$	1.6–10.8	0.989	3.1	0.994	2.8
$CHBr_3$	0.5–9.2	0.997	2.5	0.996	2.1

* r = regression coefficient of the standard curve, RSD = relative standard deviation (estimated for peak areas, n = 10), calculated by: (standard deviation/mean) × 100%).

summarized in Table 1. The four-point calibration curves were prepared to cover the concentrations of the compounds usually found in chlorinated tap water. The correlation coefficients (r) were similar for both extraction techniques: 0.979–0.997 for SDE and 0.992–0.996 for SPME. This shows that the methods have high linearity in the examined concentration range. Repeatability of the SPME method determined by peak area comparison was somewhat better than for the SDE method. The RSD for SPME was <3.4%, while the RSD values for SDE did not exceed 5.1%. Limits of detection for both methods were determined by extrapolation of the lowest concentration points of the standard curves. For trichloromethane, bromodichloromethane and dibromochloromethane the limit of detection determined for SDE was higher than that found with SPME, usually 8–10 times higher. The SDE method can be a relatively cheap alternative to SPME instrumentation (holder and fibre kit), with appropriate choice of method parameters (solvent or solvents mixtures).

Precision of the SDE method is comparable to other methods such as purge and trap, direct aqueous injection and conventional liquid–liquid microextraction (at phase ratio 10:1), which are recommended for drinking water analysis. In general, the RSD calculated for trichloromethane using SDE is better than that found with conventional micro-LLE (Figure 4).

Figure 4: Comparison of purge and trap (PTI), direct aqueous injection (DAI), liquid–liquid extraction (LLE) and SDE. For all methods standard solutions of trichloromethane (15 µg/L) have been used — see reference 18.

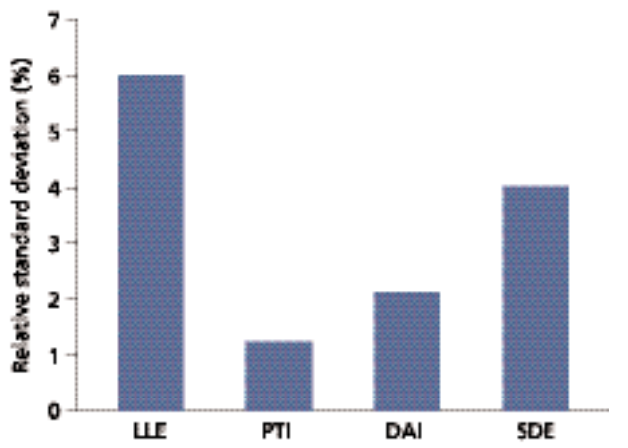


Table 2: Concentration of halocarbons in tap water using SDE and SPME.

Compound	SDE Mean concentration (µg/L)	SDE RSD	SPME Mean concentration (µg/L)	SPME RSD
$CHCl_3$	23.10	4.1	22.85	3.5
$CHBrCl_2$	4.30	5.0	4.11	3.2
$CHBr_2Cl$	0.60	8.2	0.50	4.8
$CHBr_3$	n.d.	—	0.06	8.9

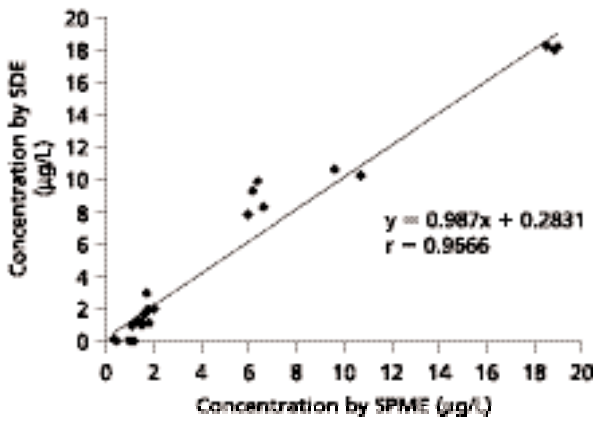
* n.d. = not detected, RSD = relative standard deviation (estimated for peak areas, n = 10).

Analyses of water samples by SDE and SPME: SDE and SPME were applied to water analysis. Suitable conditions for separation of the halocarbons were optimized. Samples of tap water from a municipal water treatment plant in Torun were analysed for haloforms using both methods. The concentration of the dominant halocarbon (trichloromethane) was in the range of 22–23 µg/L (Table 2). For quantification, the calibration curves method was chosen. Trihalomethane levels determined using the SDE method were somewhat higher than those obtained by SPME, but these differences were not statistically significant. For the SPME method RSD values were below 4.8%, except for tribromomethane which had an RSD value of 8.9%. Results obtained using these two methods were highly correlated (Figure 5) and the data indicated a good agreement between SDE and SPME determinations of chlorinated by-products in water. The results highlight the usefulness of SDE for the analysis of volatile halogenated compounds present in tap water at ppb levels.

Conclusions

Both techniques are comparable in terms of precision and analysis time. SDE is a simple method for reducing solvent consumption. However, the small amounts of solvent used in SDE is an advantage of this extraction. Pure solvents or mixtures can be used for the selective extraction of different organic species. SPME does not give a solvent peak in GC, but analyte desorption from the polymer in a hot injector is significantly slower than solvent evaporation, resulting in peaks with a tendency to tail. Therefore, this SDE method represents a cheap and attractive alternative to SPME requiring a standard GC syringe only. Alternatively, stirring the liquid sample increases extraction efficiency (extracted amount and extraction rate) by SPME. Stirring or sonification of samples in SDE experiments caused damage to the organic drop. Consequently, these two methods cannot be applied together with SDE methods. Adequate precision, linearity and repeatability indicate that this micro-solvent extraction is a reliable method for routine analysis of trihalomethanes in tap water.

Figure 5: Linear regression for halocarbons in tap water samples determined by SDE and SPME. Results shown are for four compounds measured in water from different source in triplicate (n = 36).



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