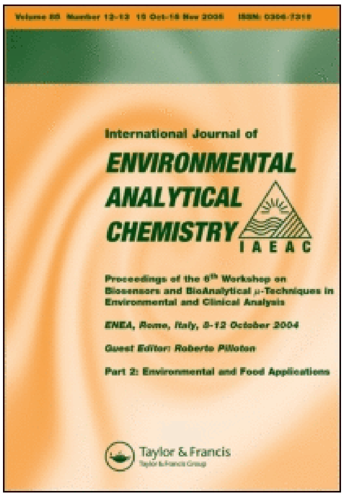

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Hauser, Barbara , Popp, Peter and Paschke, Albrecht(1999) 'Membrane Extraction of Volatile Organic Compounds in Combination with Mobile Gas Chromatographic Analysis', International Journal of Environmental Analytical Chemistry, 74: 1, 107 — 121

To link to this Article: DOI: 10.1080/03067319908031419

URL: http://dx.doi.org/10.1080/03067319908031419

Intern. J. Environ. Anal. Chem., Vol. 74(1-4), pp. 107-121
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MEMBRANE EXTRACTION OF VOLATILE ORGANIC COMPOUNDS IN COMBINATION WITH MOBILE GAS CHROMATOGRAPHIC ANALYSIS

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(Received 30 April 1998; In final form 20 January 1999)

The field of application of a mobile gas chromatographic device (Airmobtx monitor HC 1000 manufactured by Airmotec GmbH) originally conceived for the analysis of BTEX in air was extended to water analysis by using it in conjunction with membrane extraction. Volatile organic compounds diffuse out of water through a hollow fibre or flat membrane, are enriched onto sorption tubes integrated in the device, and then thermally desorbed and analysed by the gas chromatograph/flame ionisation detector. The suitability of various flat membranes and hollow fibres was investigated. Maximum extraction efficiency was obtained with a silicone hollow fibre measuring 0.3 m long, and with an inner diameter of 0.7 mm and a wall thickness of 100 µm. The extraction parameters were optimised. The linear dynamic range of the optimised method spans two orders of magnitude and the detection limits were found to be 0.1 µg/L for all BTEX compounds. By way of environmental applications, highly contaminated groundwater samples were analysed. The results correspond well to those achieved using conventional headspace/gas chromatography/flame ionisation detection.

Keywords: Membrane extraction; mobile gas chromatography; silicone hollow fibre; flat membrane; volatile organic compounds (VOCs)

INTRODUCTION

The presence of volatile organic compounds (VOCs) in water is a public health hazard as many VOCs are toxic and/or carcinogenic. VOC contamination occurs in groundwater, surface water, industrial wastewater and drinking water. The current methods of VOC analysis such as purge and trap, headspace analysis and liquid-liquid extraction are time-consuming, tedious and often incur the loss of analytes. Moreover, errors may be introduced during the various steps such as concrete sampling, sample transport, storage, extraction and analysis. A sample

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preparation technique should ideally be simple, rapid, solvent-free and selective. It should also allow on-site extraction and be adaptable to on-line monitoring.

Membrane extraction represents a promising technology for solvent-free sample preparation which meets some of these requirements. VOCs selectively diffuse out of air or water through a hydrophobic polymer membrane into a flowing gas stream or vacuum. Recent developments often use hollow fibres, which afford greater mechanical stability and a higher surface-to-volume ratio for the stripping gas than flat membranes, which allow more efficient extraction. Membrane extraction can be directly coupled to gas chromatography or mass spectrometry [1–5] to perform continuous monitoring. The theoretical effects of various membrane extraction parameters can be studied by the mathematical modelling of the extraction kinetics [6–9]. Pawliszyn et al. [10,11] describe the combination of membrane extraction with a sorbent interface (MESI) consisting of a hollow fibre membrane module and a cryofocusing and thermal desorption sorbent interface directly connected to a gas chromatographic device. In our case the sorbent interface is part of a mobile gas chromatograph equipped with a flame ionisation detector (Airmobtx, manufactured by Airmotec GmbH) optimised for continuous monitoring of BTEX in air. This device automatically analyses VOCs at certain time intervals after enrichment on Carbotrap and thermal desorption. The objective of our study was to broaden the field of application of the Airmobtx to the analysis of VOCs in water by using it in conjunction with membrane extraction. Our specially constructed extraction cell enabled the usage of both flat membranes and hollow fibres. The suitability of flat membranes of different polymers and of several silicone hollow fibres was investigated. The influence of length, diameter and wall thickness of the hollow fibres was studied. The effect of stirring speed and temperature was determined in order to optimise the extraction process. The reproducibility of the method is demonstrated, and both the linear dynamic range and the detection limits are given.

Extraction efficiency can be increased by saturating samples with NaCl. Other matrix effects such as the effect of pH, humic acids, organic solvents and detergents were demonstrated. The performance of the method was checked by analysing contaminated groundwater and comparing the results with those of conventional headspace/gas chromatography/flame ionisation detection.

EXPERIMENTAL

Reagents and materials

Analytical-grade methanol was supplied by Merck (Darmstadt, Germany). Spiking standards of single components were obtained from Supelco (Bellefonte, PA, USA). Composite working standard solutions at 1 ng/μL and 100 ng/μL were prepared in methanol. Aqueous standards for membrane extraction were prepared by diluting suitable aliquots of composite working standards with bidistilled water. For internal standardisation, a working standard of 1.73 ng/μL 1-bromo-2-chloroethane was prepared in methanol. 25 μL of this standard was added to aqueous samples before extraction. The additives for the study of matrix influences such as NaCl and SDS (sodium dodecylcsulphate) were purchased from Merck. The humic acids were produced by Roth (Karlsruhe, Germany).

Membranes

Silicone sheeting was purchased from AMT (Düsseldorf, Germany). Porous polypropylene and porous polyethersulphone membranes were supplied by Akzo Nobel (Wuppertal, Germany). All silicone hollow fibres and flat membranes of polyethylene, polypropylene, PTFE, polyimide and polyetherether ketone were obtained from Reichelt (Heidelberg, Germany). The dodecanol-collodion-membranes were prepared according to the following procedure: 2 g dodecanol was dissolved in 48 g of a diethylether-ethanol mixture (mass ratio 8.5: 1.5) and 50 g collodion (4% solution) was added. This mixture was spread onto a glass plate to create a thin film. After 3–4 hours the solvents had evaporated and the membrane was removed from the glass plate. The membrane sheet was dried for 24 h between filter paper, and circular membranes pieces were cut out and stored in a dessicator until use.

Airmobtx-monitor HC 1000

Figure 1 contains a diagram of the Airmobtx monitor HC 1000 manufactured by Airmotec GmbH (Essen, Germany). The air sample was passed through one adsorption tube using an external sampling pump at a flow rate of 55–60 mL/min. Adsorption tubes were filled with 40 mm Carbotrap™ to enrich volatile aromatic compounds. Six such tubes were mounted on the revolving adsorption unit included in the Airmobtx monitor. The volume of the air sample was measured after the adsorption process with a critical orifice. The enrichment time was 560 sec. In our case the ambient air stream was first purified with activated charcoal and then passed through the hollow fibre membrane placed in the water sample. Details of the membrane extraction device are given in Figures 2 and 3. The adsorbed sample was transferred to the chromatographic path by turning the revolver carrying the adsorption tubes and analytes were thermally desorbed by heating the tube to 350°C for 180 sec. Desorbed analytes were trapped onto a small cryofocusing column at 15°C, which was heated to 350°C at a rate of

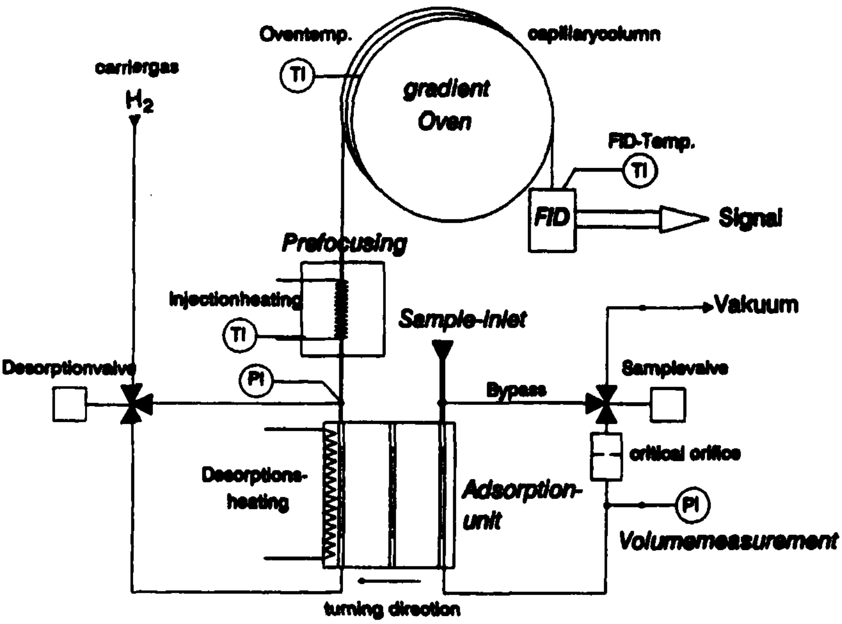

FIGURE 1 Airmobtx HC 1000

350°C/sec for 20 sec to produce a sharp injection onto the GC column. The column was a DB-624 10.3 m × 0.2 mm with a film thickness of 1.12 μm. The column temperature was maintained at 40°C for 50 sec and then programmed to increase to 140°C at 20°C/min. Analytes were measured with a flame ionisation detector. One analytical cycle took 10 minutes. During the enrichment of one sample, another adsorption tube was desorbed and analysed, allowing continuous operation of the system.

Membrane extraction

The set-up of the membrane extraction cells for hollow fibres and flat membranes is given in Figures 2 and 3. Aqueous standards for membrane extraction were prepared by diluting composite working standards in methanol with 250 ml bidistilled water. The quantification of VOCs in real samples was mainly performed by external calibration. In some experiments 1-bromo-2-chloroethane with a concentration of 17.3 μg/L was used as the internal standard. The extraction cells were surrounded by a glass coating through which temperated water was passed in order to adjust the temperature of the water samples. The stirring

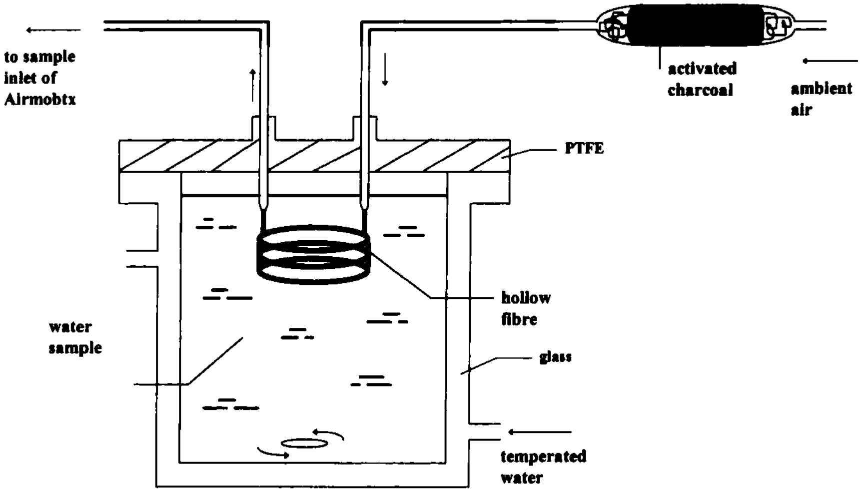

FIGURE 2 Membrane extraction device for hollow fibres

speed was varied between 250 and 1,250 rpm. Ambient air was first sucked through activated charcoal or a molecular sieve and then passed through the hollow fibre or above the flat membrane immersed in the water sample. Each aqueous sample was extracted during at least three analytical cycles. For most interpretations the second analytical cycle was chosen.

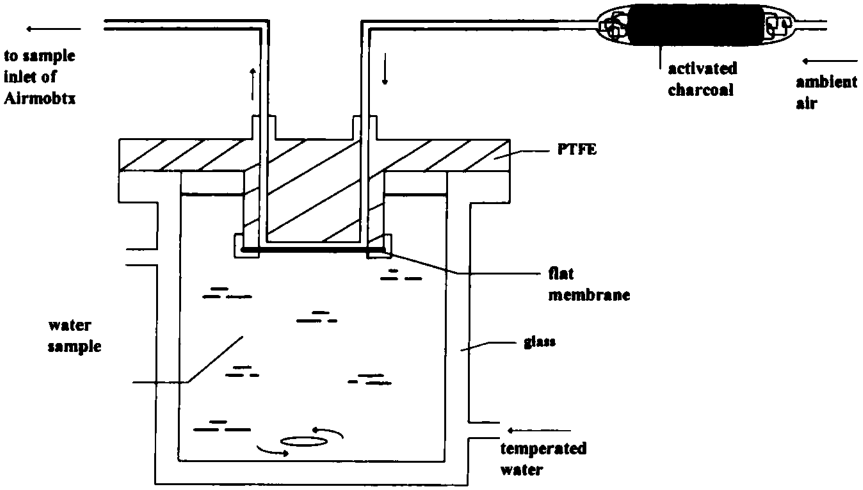

FIGURE 3 Membrane extraction device for flat membranes

RESULTS AND DISCUSSION

Comparison of different membrane materials

In order to compare the permeability of different polymers for BTEX, chlorobenzene and trichloroethylene, several flat membranes 4 cm in diameter and with an active area of 12.6 cm^2 were tested. The results are shown in Figure 4 for ethylbenzene as an example. For all compounds except benzene, the silicone membrane (125 μm thickness) exhibited the highest permeability followed by our own collodium membrane (ca. 20 μm) and the porous polypropylene membrane (92.5 μm thickness, 0.1 μm pore size). In the case of benzene the porous polypropylene membrane resulted in the highest extraction rate, followed by the collodium membrane and the silicone membrane. Expressed simply, the pervaporation process proceeds via the solution of the analytes in the membrane, permeation through the membrane, and evaporation from the downstream surface of the membrane. With regard to benzene, the most volatile of the test compounds, diffusion through the pores of the polypropylene membrane seems to be the dominating part in the extraction process. However, as the permeability of porous polyethersulphone (110 μm thickness, 0.1 μm pores) was much lower, the nature of the polymer also plays an important role. Membranes of polyethylene (50 μm), nonporous polypropylene (4 μm) and PTFE (10 μm) resulted in very low extraction rates for all test compounds, while polyimide with a thickness of 8 μm as well as polyetherether ketone with a thickness of 25 μm showed no permeability at all. The higher suitability of silicone for the membrane extraction of volatile compounds compared to other polymeric materials is confirmed by several authors [12–14]. As can be seen in Figure 4 the highest extraction rate of ethylbenzene was reached in the third analysis cycle, the amount of analyte extracted decreasing in the following cycles owing to depletion. The extraction kinetics of benzene, trichloroethylene and toluene varied due to their higher volatility and faster diffusion. For benzene and trichloroethylene the highest amount was extracted during the first or second analysis cycle depending on the membrane material. In the case of toluene the highest extraction rate was reached in the second analysis cycle.

Comparison of different silicone hollow fibres

Recent developments in membrane extraction techniques have focused on the use of hollow fibres, which offer greater mechanical stability and a higher surface-to-volume ratio than flat membranes. For this reason three silicone hollow fibres of different diameters were tested in connection with the Airmobtx. The

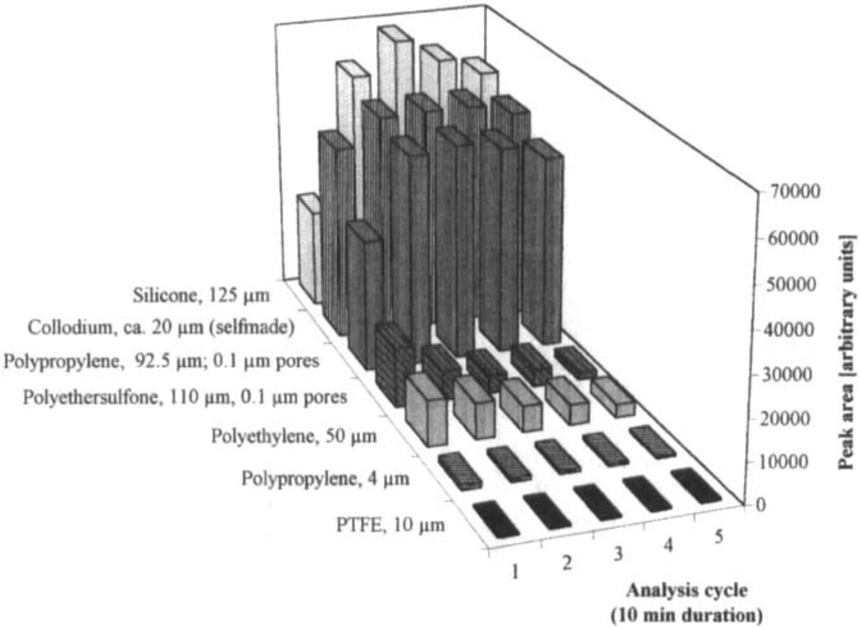

FIGURE 4 Comparison of the extraction efficiency of different flat membranes for 10 μg/L ethylbenzene (12.6 cm^2 active surface, 4 cm diameter; 1000 rpm, 20 °C)

highest extraction efficiency was obtained with a silicone hollow fibre with an inner diameter of 0.7 mm and a wall thickness of 100 μm (Figure 5). This diameter was evidently the most suitable for the flow rate generated by the sampling pump. The lower extraction rate of the hollow fibre with an inner and outer diameter of 2.0 mm and 2.4 mm respectively can be explained by the thicker wall of this fibre, which impedes diffusion and therefore results in slower extraction kinetics (Figure 5). As the amount of analyte extracted by the silicone hollow fibre measuring 0.7 × 0.9 mm also exceeded that of the flat silicone membrane, this fibre was used in all further experiments.

Dependence of the extraction rate on the length of the hollow fibre

The length of the silicone hollow fibre of 0.7 × 0.9 mm was varied between 0.1 and 4 m. As demonstrated by Figure 6 the highest extraction rate for all BTEX compounds was obtained with a hollow fibre 0.3 m long. The increase in extracted analyte from 0.1 m hollow fibre to 0.3 m can be explained by the larger surface area of the 0.3 m fibre. Longer hollow fibres resulted in a considerable

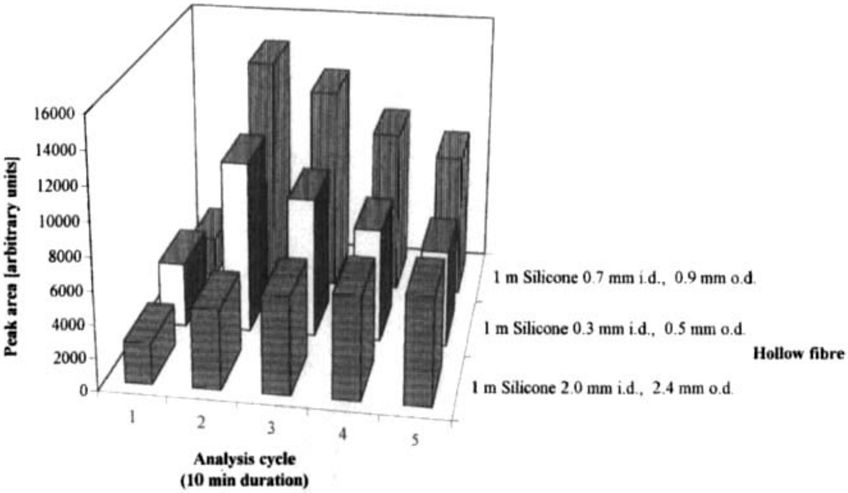

FIGURE 5 Comparison of the extraction efficiency of different silicone hollow fibres (1 μg/L ethylbenzene, 500 rpm, 20 °C)

decrease in the extraction rate. This might be due to the back-diffusion of extracted analyte into the water sample. Apparently the removal of extracted analyte from the inner surface of longer membranes by the sampling pump is not as quick as diffusion through the membrane back into the solution. Therefore all further extractions were performed using 0.3 m of the hollow fibre with an inner diameter of 0.7 mm and a wall thickness of 100 μm.

Comparison of headspace extraction with direct extraction

In Figure 7 the efficiency of two different extraction modes is compared. For direct extraction, 0.3 m silicone hollow fibre (0.7 × 0.9 mm) was immersed in the water sample, while the second extraction was performed with the fibre placed in the headspace above the aqueous sample. Due to their higher volatility, the extraction yield for benzene and trichloroethene was higher in headspace extraction. In the case of chlorobenzene, ethylbenzene and o-xylene, however, direct extraction led to higher extraction rates than headspace extraction.

Effect of stirring speed

The transport of analytes out of the aqueous sample to the membrane surface can be enhanced by stirring. The influence of the stirring speed on the extraction rate

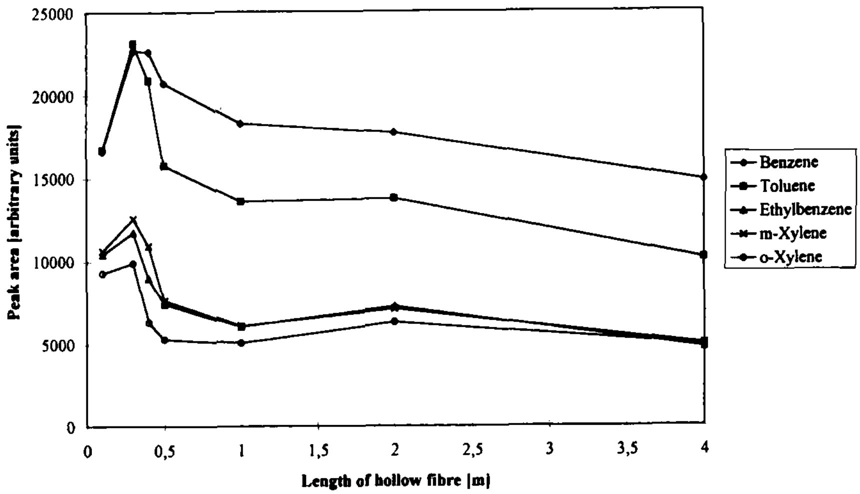

FIGURE 6 Dependence of the extraction rate on the length of the silicone hollow fibre 0.7 x 0.9 mm (1 μg/L each compound, 20 °C, 1000 rpm)

of BTEX is shown in Figure 8. From 0 to 750 rpm there was a sharp increase in the extraction efficiency for all compounds, especially benzene and toluene, which then weakened from 750 rpm to 1,000 rpm. A further rise in stirring speed to 1,250 rpm failed to further improve extraction rates. Consequently a stirring speed of 1,000 rpm was chosen for the following experiments.

Effect of temperature

An increase in extraction temperature accelerates molecular movement in both water and the membrane, thus increasing the diffusion coefficient of the analyte. As can be seen in Figure 9, the extracted amount of all compounds rose at elevated temperatures. Nevertheless 20°C was chosen as a general extraction temperature, because at higher temperatures – especially at 40°C and 50°C – not only more analyte but also a higher amount of water was found to penetrate the membrane, as was revealed by the condensation of water vapour in the tubing leading to the sample inlet as well as enhanced peak tailing in the chromatograms. Water vapour should obviously be excluded as far as possible in order not to reduce the lifetime of the GC column. In order to benefit from the higher extraction rates at elevated temperatures a drying device should be included in the experimental set-up.

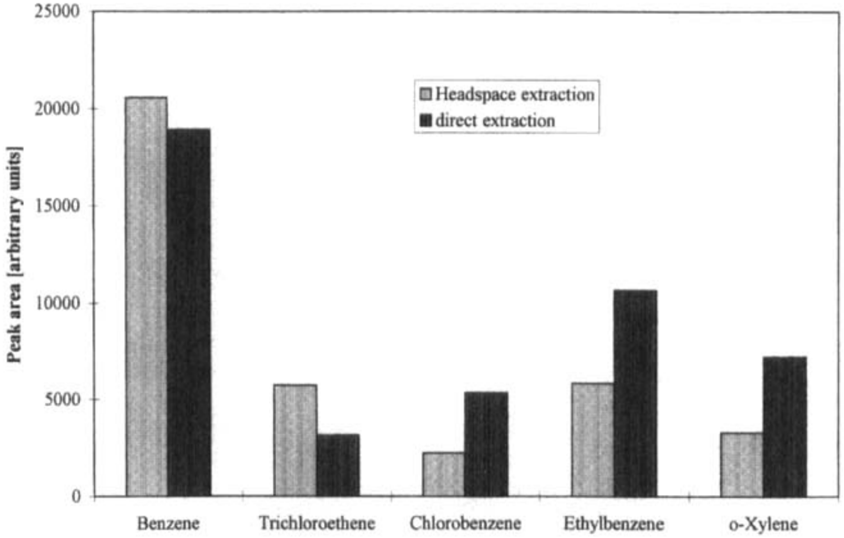

FIGURE 7 Comparison headspace – direct extraction (1 µg/L each compound, 0.3 m silicone hollow fibre 0.7 × 0.9 mm, 1000 rpm, 20 °C)

Linear dynamic range and detection limits

The linear dynamic range of the optimised extraction method (20°C, 1,000 rpm, 0.3 m silicone hollow fibre 0.7 × 0.9 mm) spanned two orders of magnitude and ranged from 0.1–10 µg/L (Figure 10). The detection limits were limited by blanks probably caused by the adsorption of analytes on the inner wall of the tubing connecting the membrane extraction cell with the Airmobtx. Therefore in our investigations the detection limit was equal to the quantification limit, namely 0.05 µg/L for benzene and 0.1 µg/L for all other BTEX compounds.

Reproducibility

Table I shows the relative standard deviation of six consecutive hollow fibre extractions under optimised conditions. Six separately spiked aqueous standards were extracted and analysed during three analytical cycles in order to determine the reproducibility of the whole method including errors occurring during the preparation of calibration standards. The relative standard deviation was calculated on the basis of peak areas. The reproducibility of the method varied between 3% and 15% and was improved in most cases by adding 1-bromo-2-chloroethane as an internal standard. With the internal standard, the

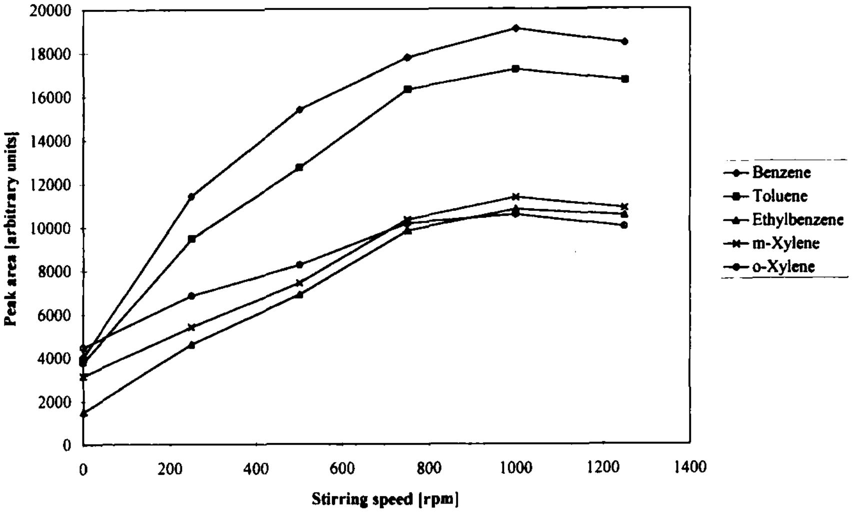

FIGURE 8 Influence of stirring speed on the extraction of 1 µg/L BTEX with 1 m silicone hollow fibre 0.7 × 0.9 mm (20 °C)

relative standard deviation did not exceed 10.5% except for o-xylene, which appeared at the far end of the chromatogram. The reproducibility of o-xylene-extraction could probably be increased by raising the temperature of the GC column at the end of the chromatographic analysis. The reproducibility of extraction improved from the first to the third analysis cycle. However, for most interpretations the second analysis cycle was chosen, because in the third cycle the depletion of the more volatile compounds in the aqueous solution resulted in lower sensitivity for these compounds.

TABLE I Reproducibility of membrane extraction (20°C, 1,000 rpm, 0.3 m silicone hollow fibre 0.7 × 0.9 mm – six separately spiked aqueous standards were extracted and analysed during three analytical cycles-% RSD was calculated on the basis of peak areas); ISTD = internal standardisation, ESTD = external standardisation)

Compound	*[% RSD] ESTD*	*Cycle 1 ISTD*	*[% RSD] ESTD*	*Cycle 2 ISTD*	*[% RSD] ESTD*	*Cycle 3 ISTD*
Benzene	9.4	5.1	12.6	4.8	13.2	3.3
Toluene	8.4	7.7	7.7	6.9	10.6	5.1
Ethylbenzene	13.4	7.4	7.6	10.2	11.9	5.7
m-Xylene	12.1	6.8	6.2	10.5	10.8	5.1
o-Xylene	21.1	12.7	14.5	15.4	13.1	5.3

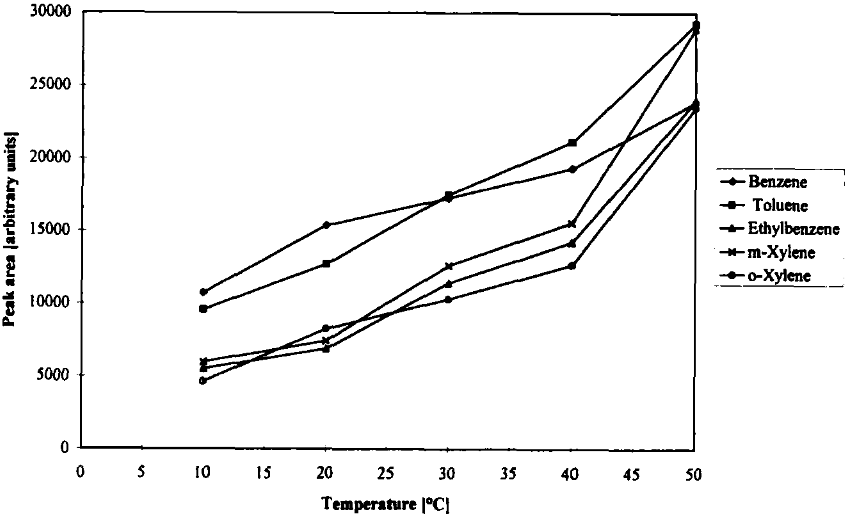

FIGURE 9 Influence of temperature on the extraction of 1 μg/L BTEX with 1 m silicone hollow fibre 0.7 × 0.9 mm (500 rpm)

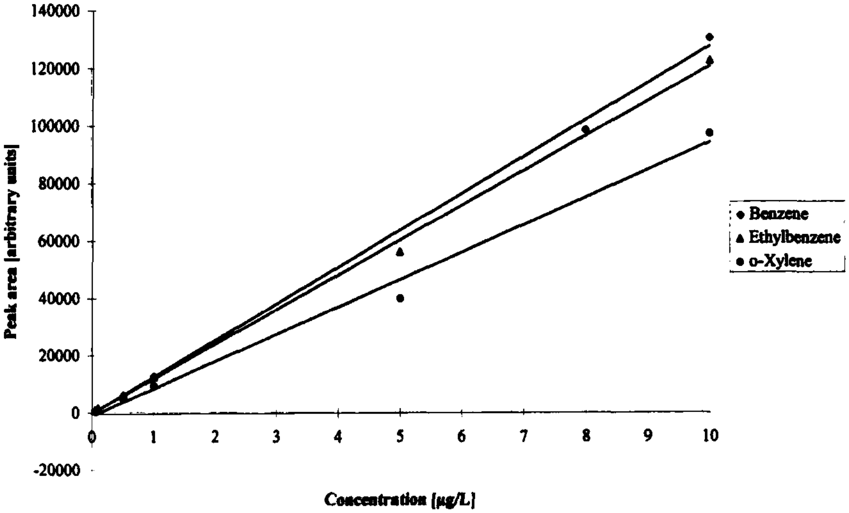

FIGURE 10 Calibration of membrane extraction with 0.3 m silicone hollow fibre 0.7 × 0.9 mm (20 °C, 1000 rpm)

Matrix effects

The effect of different matrix components on the extraction of BTEX is shown in Figure 11. Two different humic acid concentrations (17 mg/L and 130 mg/L) were examined. The lower concentration represents the order of humic acid levels in river and surface water in central eastern Germany. The higher concentration is supposed to simulate wastewater high in organic matter. Sodium chloride, the anionic detergent SDS (sodiumdodecylsulphate) and methanol were added as other examples of possible matrix components. The increase in ionic strength by adding NaCl led to increased extraction rates of all BTEX compounds. Saturation with NaCl enhances the polarity of the aqueous phase, so that the distribution equilibrium of the analyte is shifted towards the membrane. In contrast to this effect, the impact of different pH, varying levels of humic acids, detergent or a larger amount of organic solvent were relatively small on the extraction rates of benzene and toluene, although in the case of ethylbenzene, m- and o-xylene, the total amount extracted rose by 10–30%. Matrix components evidently have a greater effect on the distribution of the higher boiling compounds in the membrane. In the case of high matrix levels in environmental samples, these effects must be taken into account by internal standardisation or the standard addition procedure.

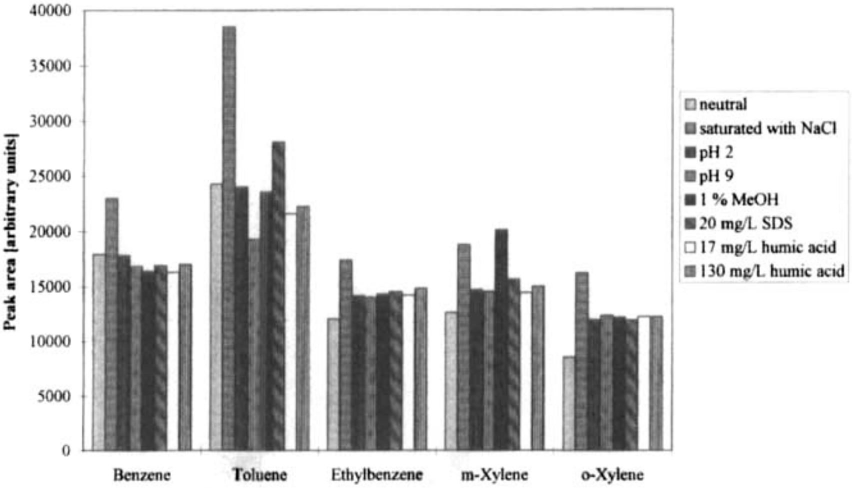

FIGURE 11 Influence of matrix components on the extraction of 1 µg/L BTEX with 0.3 m silicone hollow fibre 0.7 × 0.9 mm (20 °C, 1000 rpm)

Analysis of real samples

By way of environmental applications, highly contaminated groundwater samples were analysed by membrane extraction connected to the Airmobtx. Samples were taken from a previously heavily industrialised area where production waste from the chemical industry has been dumped. The results of optimised membrane extraction were compared with conventional headspace-GC-FID analysis. The concentrations of benzene, trichloroethene and chlorobenzene determined by both methods are listed in Table II. The results of both methods tally well. The analysis of samples 15 and 16 was performed with the addition of internal standard, which seems to result in a further reduction of discrepancy between the two analytical methods. Consequently the use of an internal standard ought to be included in the membrane extraction procedure for quantitative measurements.

TABLE II Analysis of groundwater samples – comparison of membrane extraction-GC-FID with headspace-GC-FID

Sample	*Analysis method*	*Benzene [mg/L]*	*Trichloroethene [mg/L]*	*Chlorobenzene [mg/L]*
Bitterfeld	Membrane extraction	0.009	-	-
Opencast mining	Headspace	0.008	-	-
Bitterfeld	Membrane extraction	0.15	0.39	31.53
Drilling 19/97	Headspace	0.26	0.67	32.43
Bitterfeld	Membrane extraction	1.32	-	28.70
Drilling 20/97	Headspace	1.91	-	30.49
Bitterfeld	Membrane extraction	0.20	0.38	25.22
Drilling 15/97	Headspace	0.21	0.39	26.40
Bitterfeld	Membrane extraction	1.02	10.50	0.55
Drilling 16/97	Headspace	1.20	11.80	0.24

CONCLUSIONS

The combination of membrane extraction with the mobile Airmobtx constitutes a suitable method for the determination of BTEX and other volatile compounds in water. Due to the simple, rugged design of our extraction cell, this method would also be appropriate for on-site analysis. Silicone rubber was revealed to be the most permeable polymer in our studies, while extraction efficiency was further improved by employing hollow fibres instead of flat membranes. The highest extraction efficiency was obtained with a silicone hollow fibre 0.3 m long, with an inner diameter of 0.7 mm and a wall thickness of 100 µm. For optimal extraction, the stirring speed should be maintained at 1,000 rpm with an extraction temperature of 20°C, as higher temperatures increase not only the extraction rate but also the amount of water permeating the membrane. The linear dynamic range of the optimised method spans two orders of magnitude (0.1–10 µg/l) and detection limits are 0.05 µg/L for benzene and 0.1 µg/L for all other BTEX compounds. The relative standard deviation of the method is 5–10% using internal standardisation. The study of matrix influences indicated a distinct increase in the extraction rates of all BTEX compounds following saturation with NaCl. Other matrix components such as humic acids, detergent, solvent or different pH only increased the extracted amount of ethylbenzene, m- and o-xylene.

The determination of benzene, trichloroethene and chlorobenzene in groundwater using our combined membrane extraction method corresponded well with the results of conventional headspace-GC-FID. For quantitative measurements the use of an internal standard is recommended.

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