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Combining membrane extraction with mobile gas chromatography for the field analysis of volatile organic compounds in contaminated waters

Barbara Hauser*, Peter Popp

UFZ Centre for Environmental Research Leipzig–Halle, Department of Analytical Chemistry, Permoserstrasse 15, D-04318 Leipzig, Germany

Abstract

A mobile gas chromatographic device (Airmobtx HC 1000 monitor manufactured by Airmotec, Germany), originally designed for the analysis of benzene, toluene, ethylbenzene and xylenes (BTEX) in air, was connected to a flow cell for dynamic membrane extraction. Volatile organic compounds (VOCs) diffuse out of a water stream through a hollow fibre, are enriched onto sorption tubes integrated in the mobile device, and are then thermally desorbed and analysed by gas chromatography–flame ionisation detection. Battery operation of the device enables continuous on-site analysis of VOCs. Influences of the water flow-rate on system response and memory effects were investigated. The linear range of the method depends on the flow-rate of the water sample and did not exceed two orders of magnitude. The detection limits for trichloroethene, chlorobenzene and the BTEX compounds were found to be between 0.1 and 1.0 μg/l using a water flow-rate of 30 ml/min. Dynamic membrane extraction combined with the mobile gas chromatographic device was used for the on-site analysis of contaminated waters in the area of Leipzig.

Keywords: Membrane extraction; Extraction methods; Water analysis; Environmental analysis; Volatile organic compounds

1. Introduction

Contamination of water by volatile organic compounds (VOCs) is a common environmental problem. In order to analyse these contaminants by chromatographic techniques, the analytes first need to be enriched. The established methods for sample preparation are liquid–liquid extraction, solid-phase extraction, headspace, and purge-and-trap [1–4]. Other developments include solvent-free methods such as solid-phase microextraction (SPME) [5–8], stir bar sorptive extraction (SPSE) [9], and membrane extraction techniques [10–12].

Membrane extraction is a promising technology for fast, simple and inexpensive sample preparation. It allows on-site extraction and can be adapted to on-line monitoring. VOCs diffuse out of water through a hydrophobic polymer membrane into a flowing extractant normally followed by pre-concentration of the analytes on an appropriate trap. Continuous monitoring of VOCs was achieved by Blanchard and Hardy [13], who used a flat membrane to isolate the compounds from an aqueous solution and a sampling loop connected to a six-port valve for collection. In a different set-up, a nitrogen stream transferred the compounds to a bed of activated charcoal. After desorption with carbon disulfide, the substances were analysed by gas chromatography (GC). Melcher and Morabito [14] developed an automated introduction system for the

*Corresponding author.

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extraction and analysis of semivolatile compounds in a water stream using a tubular silicone rubber membrane and hexane as the extractant. Pawliszyn and co-workers [15–18] described 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. For enrichment, condensation with liquid nitrogen [19–21], short thick-film capillary columns [15,18,22,23] and adsorbent filled traps have been used [24–26].

Membrane extraction can also be directly coupled to mass spectrometry (MS). In this technique known as membrane introduction mass spectrometry (MIMS), the membrane probe can either be located outside the mass spectrometer in the water sample or directly in the ion source [27–30]. Bauer and Cooks have reviewed various inlet configurations and applications of MIMS [31]. Matz and co-authors [32–34] used a combination of pervaporation and direct thermodesorption of silicone hollow fibres and developed several membrane probes directly coupled to a mobile GC–MS device for the on-site analysis of contaminated water [32] and application to fermentation processes [33,34].

Hauser et al. [35] used a mobile gas chromatograph optimised for the continuous monitoring of benzene, toluene, ethylbenzene and xylenes (BTEX) in air to analyse VOCs in water by coupling this device to a membrane extraction module. The specially constructed cell enabled the usage of both flat membranes and hollow fibres.

The aim of the investigations described in the following was to develop and test a dynamic membrane extraction cell in combination with this mobile gas chromatograph for the continuous extraction of VOCs, and to use this combination for the field analysis of VOCs in contaminated waters.

2. Experimental

2.1. Reagents and material

Analytical-grade methanol was purchased from Merck (Darmstadt, Germany); spiking standards of individual compounds were obtained from Supelco (Bellefonte, PA, USA). Several composite working standard solutions at 1 to 200 ng/μl were prepared in methanol. Aqueous standards for membrane extraction were prepared by diluting suitable aliquots (10–500 μl) of composite working standards with 100 to 1000 ml of bidistilled water. Aqueous standards were placed in glass bottles and transferred to the extraction cell by a peristaltic pump. The size of the glass bottle was chosen depending on the sample volume needed in order to minimise the volume of the headspace above the water sample.

2.2. Membrane extraction cell

The set-up of the extraction cell for dynamic extraction is shown in Fig. 1. Ambient air was first purified by activated charcoal and then passed through the hollow fibre. Previous experiments with various hollow fibre membranes [35] indicated that the highest extraction efficiency is achieved with a silicone hollow fibre with an internal diameter of 0.7 mm, a wall thickness of 100 μm, and a length of 30 cm. These dimensions were chosen for the silicone hollow fibre used here. The length of the flow cell was 30 cm. The water sample was sucked out of a glass bottle through the flow cell consisting of a glass tube with a 6 mm outer and 3 mm internal diameter by a peristaltic pump (GLV, 1-62-6, Meredos, Bovenden, Germany). The design of the adjustable membrane connection used in this study is shown in Fig. 2. The hollow fibre membrane (a) with an internal diameter of 0.7 mm is pressed onto the 0.8 mm stainless steel capillary (b). Initially this capillary is freely movable, allowing the hollow fibre to be tightened. The capillary and fibre are then fixed using the bolt (d) and the O-ring (g). A tube connector is soldered into the bolt, and a short piece of Nalgene tubing connects the extraction cell to the Airmobtx. The flow direction of the water sample (i) is opposite that of the air stream (h) through the hollow fibre membrane.

2.3. Airmobtx HC 1000 monitor

Fig. 3 contains a diagram of the Airmobtx HC 1000 monitor manufactured by Airmotec (Essen, Germany). The air sample is passed through an adsorption tube using an external sampling pump at a

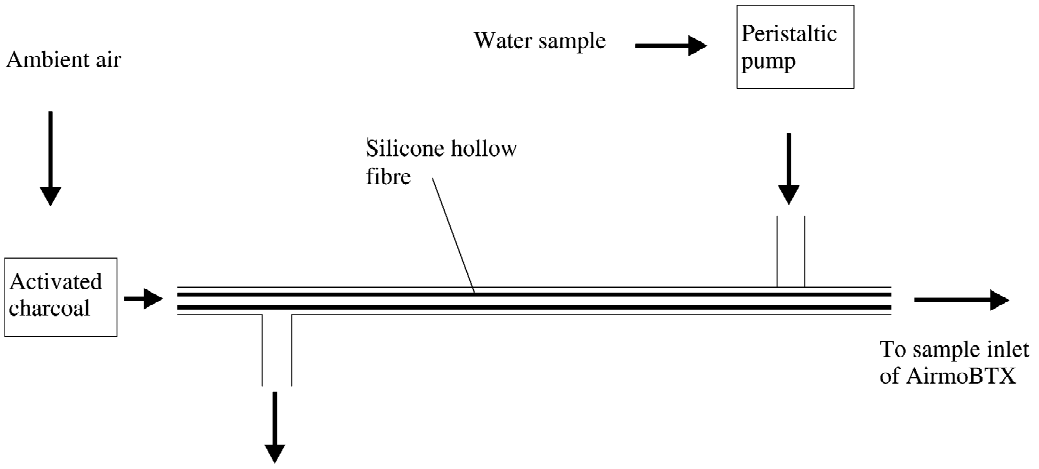

Fig. 1. Flow cell for dynamic extraction with hollow fibres.

flow-rate of 55–60 ml/min. Adsorption tubes are filled with 40 mm Carbotrap to enrich VOCs. Six such tubes are mounted on the revolving adsorption unit included in the Airmobtx monitor. The volume of the air sample is measured after the adsorption process via a critical orifice. The enrichment time was 560 s. The adsorbed samples are transferred to the chromatographic path by turning the revolver carrying the adsorption tubes and analytes are thermally desorbed by heating the tube to 350°C for 180 s. Desorbed analytes are trapped on a small cryofocusing column at 15°C, which is heated to 350°C at a rate of 350°C/s for 20 s to produce a sharp injection into the GC column. The column is a DB-624 10.3 m×0.2 mm with a film thickness of 1.12 μm (J & W Scientific, Folsom, CA, USA). The column temperature is maintained at 40°C for 50 s and then programmed to increase to 140°C at 20°C/min. Analytes are measured with a flame ionisation detection (FID) system, with one analytical cycle lasting 10 min. During the enrichment of one sample, another adsorption tube is desorbed and analysed, allowing continuous operation of the system. A chromatogram obtained after extraction of an aqueous BTEX standard (Fig. 4) demonstrates a sufficient resolution and symmetrical peak shapes for all analytes.

Before starting membrane extraction of standards

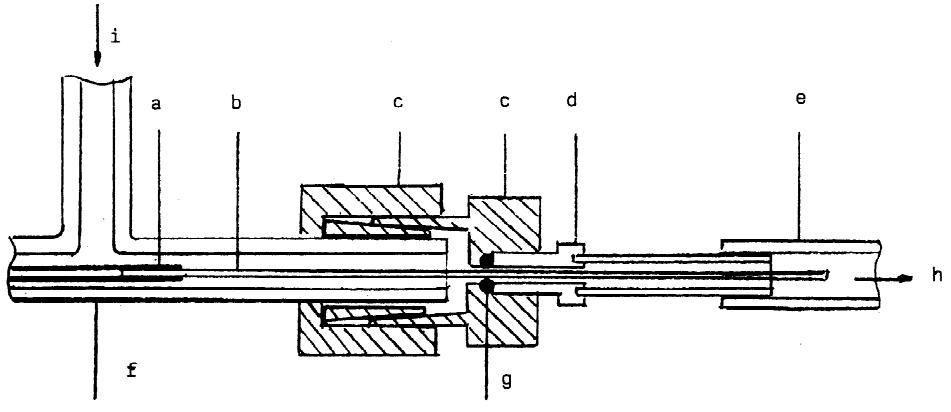

Fig. 2. Adjustable membrane end connector. (a) Silicone hollow fibre 0.7×0.9 mm, (b) 0.8 mm stainless steel capillary, (c) Swagelok 1/4-in. (1 in.=2.54 cm), (d) bolt and connector to Airmobtx, (e) Nalgene 280 tube, (f) glass tube 3.0×6.0 mm, (g) O-ring, (h) air flow to Armobtx, (i) sample flow.

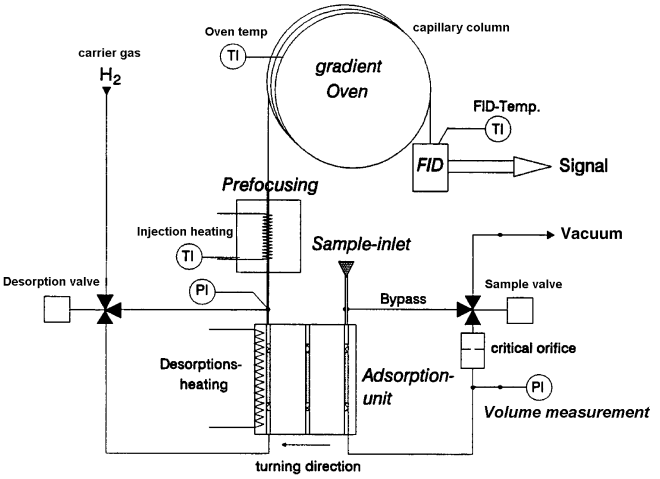

Fig. 3. Diagram of the Airmobtx HC 1000.

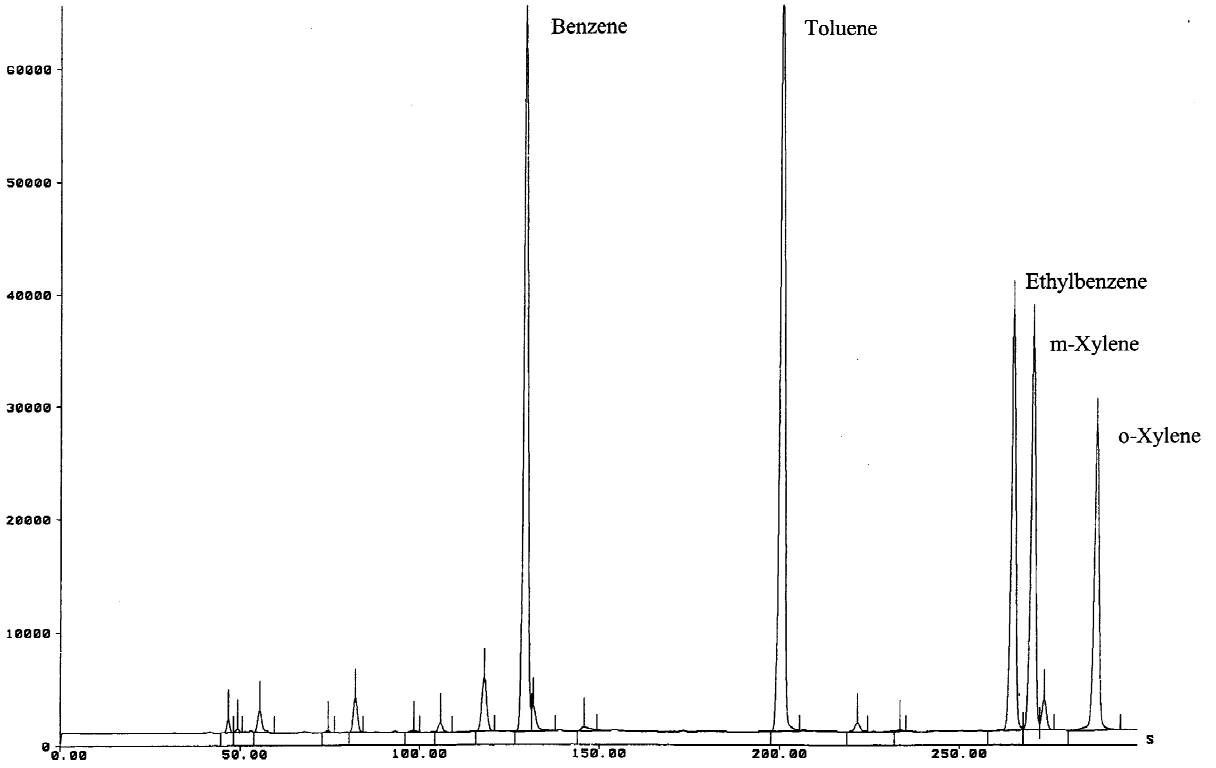

Fig. 4. Chromatogram obtained after extraction of 5 μg/l BTEX in 250 ml water with 0.3 m silicone hollow fibre 0.7×0.9 mm (temperature: 20°C, extraction time: 10 min).

or samples the blank of the whole system was checked each day by passing pure distilled water through the extraction cell connected to the Airmobtx. The blank response ranged from 200 area counts for benzene and trichloroethene to 3000 for *o*-xylene and was the basis for calculation of detection limits.

3. Results and discussion

3.1. Influence of the water flow-rate

Fig. 5 shows a distinct increase in the amount of extracted analyte as the rate of water flow increases. At higher water flow-rates, a larger amount of the water sample comes into contact with the membrane surface during one analytical cycle. Consequently, more analyte can be extracted, and so peak areas increase with rising water flow-rate. Furthermore, a rapid water stream allows better mixing, thus decreasing the interfacial resistance in the water phase. At low water flow-rates the formation of boundary layers impedes the diffusion of analytes to the outer membrane surface [28,36]. Xu and Mitra [37] investigated the influence of the water flow-rate on dynamic membrane extraction using a silicone hollow fibre with a similar arrangement. In their set-up, the water sample containing several volatile compounds passed through the hollow fibre while a stream of nitrogen flowed countercurrently above the hollow fibre towards an adsorption tube which was directly connected to a gas chromatograph. Therefore the gas stream had to be compatible with the capillary column of the gas chromatograph and could not exceed 4 ml/min. Using this system, the authors observed an increasing response up to a water flow-rate of 3 ml/min before a constant value was reached. Shoemaker et al. [26] also found no further increase in the extracted amount of volatile analytes out of a flowing water sample when the flow-rate of water reached the same value as the flow-rate of gas on the other side of the membrane. Consequently, although the extraction rate increases with increasing water flow-rate up to a certain value, the extraction efficiency decreases. Higher flow-rates result in a shorter contact time between the water sample and membrane, and so the percentage of analytes extracted from the water is reduced [38]. This effect was mathematically modelled by Pratt and Pawliszyn

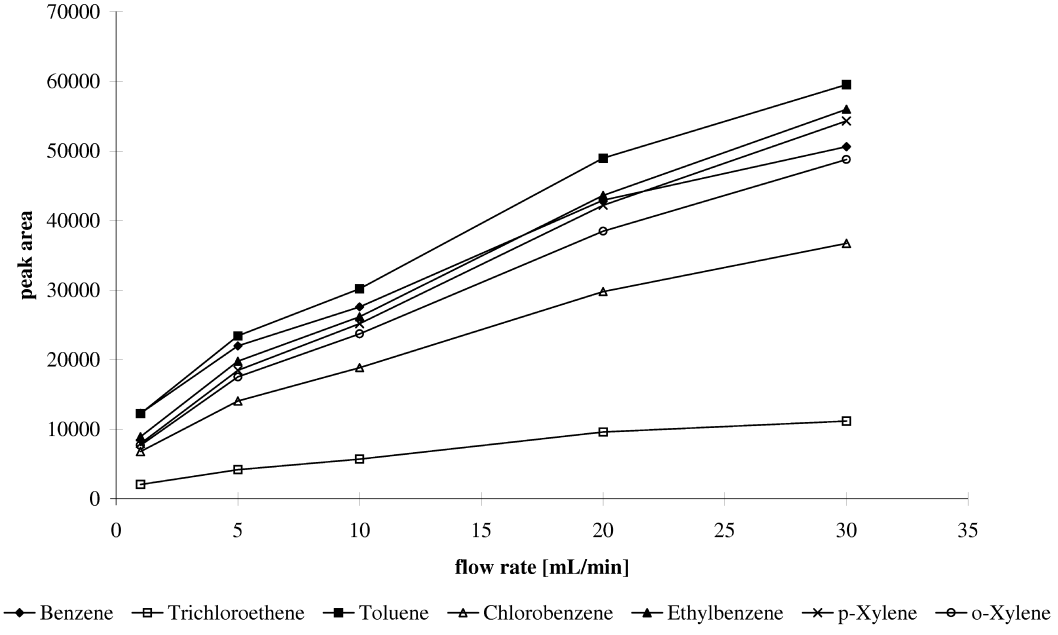

Fig. 5. Influence of the water flow-rate. Concentration: 20 μg/l of each compound.

[39]. In our investigation, peak areas continued to increase with the water flow-rate, and a plateau was not reached because the peristaltic pump used could not generate flow-rates exceeding 35 ml/min. As the air stream generated by the sampling pump was 60 ml/min, the plateau of the curve would probably have been reached at a water flow-rate of about 60 ml/min as well. As working with such high flow-rates would require sample volumes of more than 1 l, water flow-rates between 1 and 30 ml/min were chosen for the investigations described here. Another possibility of reaching the plateau with smaller sample volumes would be reducing the air flow through the membrane. This could not be tested here because the flow-rate of the sampling pump conceived for the Airmobtx cannot be adjusted.

3.2. Response of the system to a step change in concentration

The Airmobtx mobile gas chromatograph can be used for the continuous monitoring of VOCs in a water stream by connecting it to the dynamic membrane extraction cell. In order to evaluate the system's response to a rapid change of analyte concentration in the water stream, a 10-min pulse introduction of an aqueous VOC mixture was simulated (Fig. 6, shown for benzene, chlorobenzene and *o*-xylene as examples). First of all, pure distilled water was passed through the extraction cell during four analytical cycles. A VOC mixture of 20 μg/l per compound was then conducted through the cell for 10 min (one analytical cycle), before being subsequently replaced by pure distilled water again. The water flow-rate was 10 ml/min during the whole experiment. As Fig. 6 shows, peak areas of the more volatile compounds like benzene increased immediately after the start of the concentration pulse (after 50 min) and decreased rapidly in the following analytical cycles when the VOC mixture had been replaced by distilled water again. For these compounds (benzene, trichlororethene and toluene), it took just 10 min to reach the chromatographic baseline again after the end of the step change. By contrast, peak areas of the less volatile compounds ethylbenzene and xylene continued to increase after

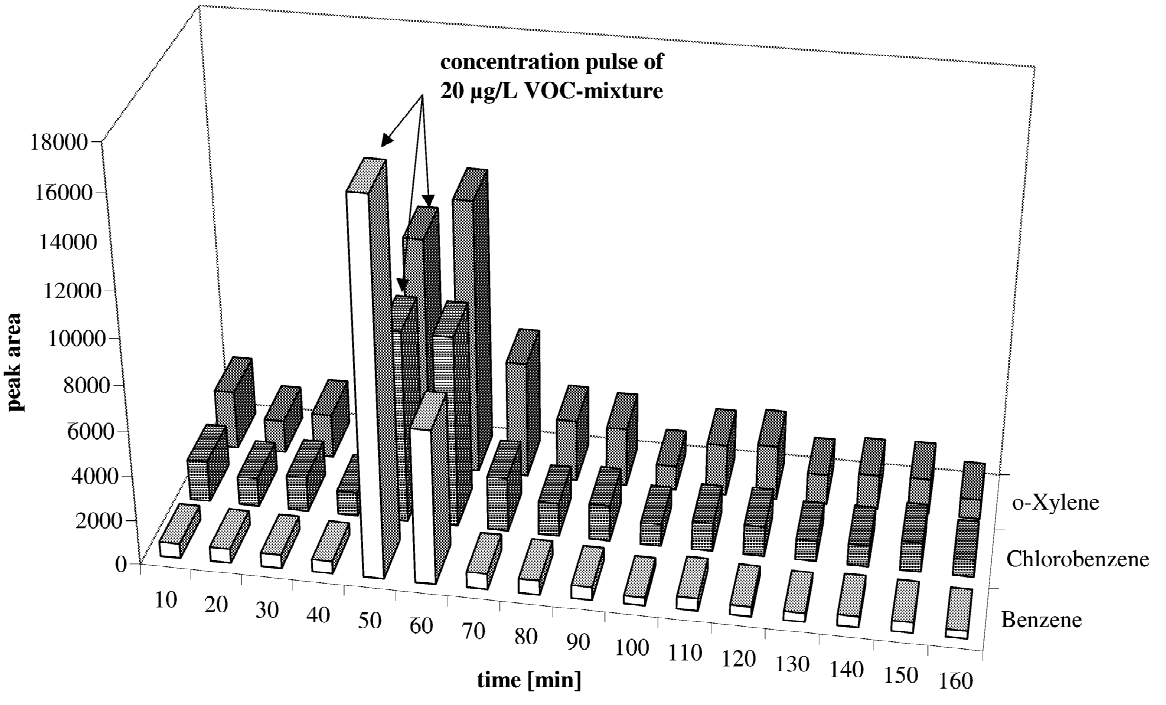

Fig. 6. Response of dynamic hollow fibre extraction to a concentration pulse of 20 μg/l. Water flow-rate: 10 ml/min, pulse width: 10 min.

the end of the step change, and the baseline was not reached until 20 min after the VOC mixture had been replaced by distilled water. Thus, the permeation of these substances is slower, so that compound rests present in the membrane and the tube leading to the sample inlet of the GC result in the delayed response of the system. Memory effects are even more important for lower water flow-rates and larger step changes in concentration. Guo and Mitra [40] observed a time delay of 40 min until a step change of 45 μg/l benzene to a concentration of 4.5 μg/l in a water flow of 1 ml/min led to a constant signal using dynamic membrane extraction–GC–FID. Yang et al. [17] also found a memory effect for trichloroethene using a similar flow-cell, which required a purge-time of 5 min before the next measurement could be carried out. Consequently, memory-effects must always be taken into account when dynamic membrane extraction is used. This means, with the experimental set-up presented here rapid and large concentration changes in the water flow will be noticed but cannot be quantified exactly. For more accurate measurements the water stream could be diluted using a bypass in order to work just about the detection limit. An improvement of dynamic membrane extraction would be to integrate a backflushing step of the cell while heating the membrane.

3.3. Effects of temperature and matrix

The effects of temperature and matrix were investigated in connection with the membrane extraction cells described in Ref. [35]. An increase in the extraction temperature accelerates molecular movement in both water and the membrane, thus increasing the diffusion coefficient of the analytes. The investigations show that although the extraction yields increase in a temperature range between 10 and 50°C, a higher amount of water also penetrates the membrane. The field measurements with the dynamic extraction cell were performed in the summer and the temperature of the waters investigated was about 20°C. The calibration was accordingly carried out at a water temperature of 20°C. In the case of the groundwater investigated, the temperature after sampling was about 15°C, and so the temperature difference between calibration and field analysis was low.

The impact of matrix components such as different pH (pH 2 and pH 9), varying levels of humic acids (17 mg/l and 130 mg/l), detergent (20 mg/l sodium dodecylsulfate) or a larger amount of organic solvent (1% methanol) on the extraction rates of the BTEX compounds was found to be relatively small [35]. This was why calibration was performed with spiked pure water.

3.4. Efficiency of the combination of dynamic membrane extraction and mobile GC–FID

3.4.1. Linear dynamic range for different water flow-rates

The linear range of dynamic membrane extraction connected with GC–FID depends on the flow-rate of the water through the extraction cell. The slope of the calibration line increases with the flow-rate as demonstrated by Fig. 7. Table 1 shows that the calibration range of the dynamic membrane extraction rises with decreasing flow-rate of the water. The linear dynamic range was limited by the capacity of the flame ionization detector integrated in the Airmobtx. Using a flow-rate of 1 ml/min, the linear dynamic range can be extended to 250 μg/l. This can be explained by the fact that with flow-rates of 1 ml/min during the 10-min extraction cycle, only 10 ml of spiked water comes into contact with the membrane, whereas with a flow-rate of 30 ml/min the mass of spiked water which passes the cell during one analytical cycle is 300 ml. The correlation coefficients of all compounds for the three water flow-rates chosen were satisfactory.

3.4.2. Reproducibility and detection limits

The reproducibility of the dynamic membrane extraction was determined by sevenfold extraction at two different water flow-rates (see Table 2). The aqueous standards were produced by diluting methanolic standard with water and sucked for 70 min (seven cycles) with the peristaltic pump through a Fluran tube from a glass bottle to the extraction cell. Apart from trichloroethene, the relative standard deviations were $<10\%$, and reproducibility was not found to depend on the flow-rate of the spiked water. The poorer reproducibility of the trichloroethene extraction may be due to the use of Carbotrap as adsorbent. Carbotrap was recommended for the

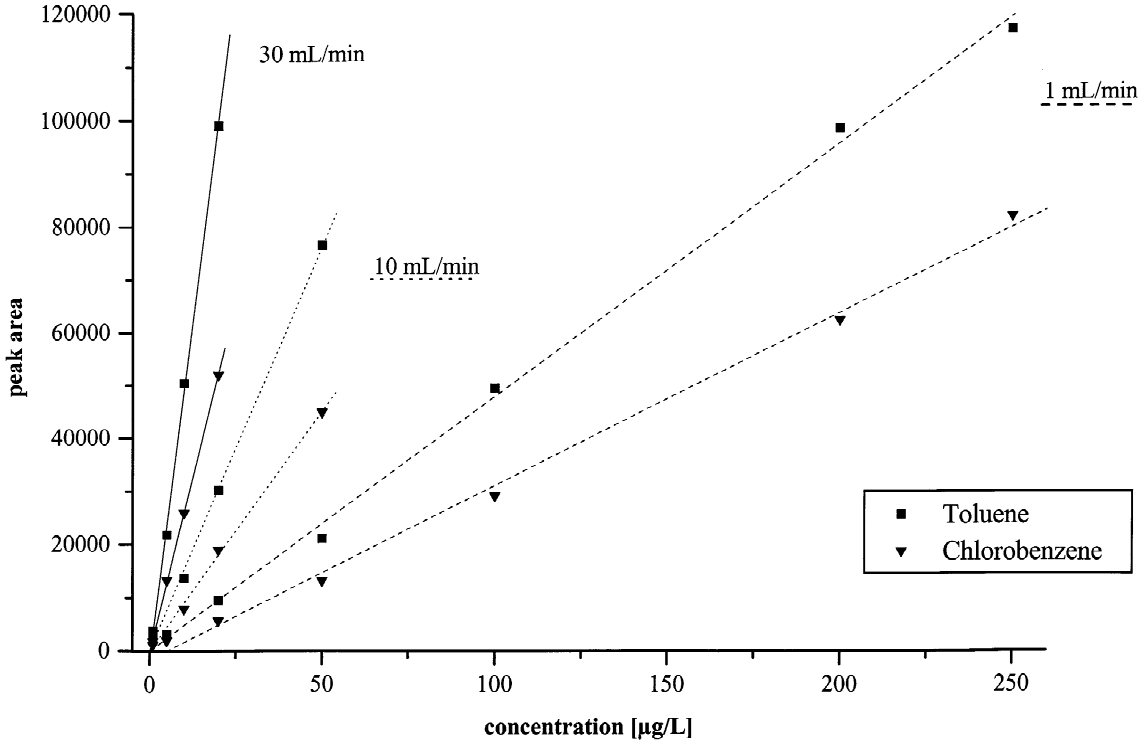

Fig. 7. Calibration of the dynamic membrane extraction for various water flow-rates. Temperature: 20°C, extraction time: 10 min.

determination of BTEX by the manufacturer of the Airmobtx, but is less suitable for trichloroethene. The detection limits (also given in Table 2) improved with increasing water flow-rate. Using a flow-rate of 1 ml/min, the detection limits of the compounds investigated were between 2 and 5 μg/l. Using a flow-rate of 30 ml/min, the detection limits improved to 0.1–1.0 μg/l.

3.4.3. Analysis of real samples

The dynamic membrane extraction connected with the mobile Airmobtx monitor was used for the field

Table 1
Linear dynamic range of dynamic membrane extraction in connection with Airmobtx at different water flow-rates (extraction time: 10 min)

Compound	Flow-rate 1 ml/min		Flow-rate 10 ml/min		Flow-rate 30 ml/min	
	Linear dynamic range (μg/l)	Correlation coefficient	Linear dynamic range (μg/l)	Correlation coefficient	Linear dynamic range (μg/l)	Correlation coefficient
Benzene	5–250	0.9932	1–50	0.9989	1–20	1.0000
Trichloroethene	5–250	0.9955	1–50	0.9976	1–30	0.9921
Toluene	5–250	0.9979	1–50	0.9986	1–20	0.9989
Chlorobenzene	5–250	0.9969	1–50	0.9981	1–20	0.9997
Ethylbenzene	5–250	0.9972	1–50	0.9984	1–20	1.0000
m/*p*-Xylene	5–250	0.9955	1–50	0.9983	1–20	0.9997
o-Xylene	5–250	0.9970	1–50	0.9995	1–20	0.9954

Table 2
Detection limits and reproducibility ($n=7$) of dynamic membrane extraction connected to Airmobtx with water flow-rates of 1 and 30 ml/min; temperature: 20°C, extraction time: 10 min

Compound	Detection limit (μg/l)		Reproducibility (RSD, %)	
	1 ml/min	30 ml/min	1 ml/min	30 ml/min
Benzene	2	0.1	2.5	3.1
Trichloroethene	5	1.0	12.4	12.8
Toluene	5	0.5	5.4	4.5
Chlorobenzene	2	0.5	5.8	4.6
Ethylbenzene	2	0.5	4.5	6.7
p-Xylene	5	1.0	5.0	6.7
o-Xylene	5	0.5	9.8	5.5

analysis of various ponds in the area of Leipzig and groundwater in Bitterfeld–Leipzig.

The device including the batteries and the gas bombs was transported by a small goods vehicle and was installed on-site within half an hour.

Field analysis was first carried out at the Bitterfeld research site of the UFZ Centre for Environmental Research Leipzig/Halle. Groundwater from a well downgradient the industrial plants was analysed on-site. The sample was sucked through the extraction cell at a flow-rate of 10 ml/min. A dilution of 1:1000 was necessary to meet the calibration range for chlorobenzene. An aliquot of this sample was analysed in the laboratory using headspace GC–FID as the reference method. The values of both methods are given in Table 3. Other samples measured on-site were surface water from the flooded open-cast mine at Goitsche (near Bitterfeld) and water from ponds within the city of Leipzig. The levels of BTEX, trichloroethene and chlorobenzene in these waters were below the detection limit. The groundwater sample from the disused hydrogenation plant in Zeitz (see Table 3) was analysed in the laboratory and also compared with headspace GC–FID. In these cases, the values tallied satisfactorily. In other cases – especially for very high BTEX concentrations – higher deviations between the field measurements and the headspace reference method were observed due to memory effects, especially for ethylbenzene and the xylenes.

4. Conclusions

Connecting the dynamic membrane extraction cell to the mobile GC–FID Airmobtx enables the continuous on-site monitoring of volatile organic compounds in groundwater and surface water. As the Airmobtx units are also available with an electron-capture detector and a sulfur-specific detector, the combination of membrane extraction and mobile GC can be extended to the sensitive determination of volatile sulfur and halogen compounds in water and other matrices (e.g., wine or beer). The method could

Table 3
Analysis of groundwater samples – comparison between dynamic membrane extraction/Airmobtx and headspace GC–FID

Sample	Method	Benzene (mg/l)	Toluene (mg/l)	Chlorobenzene (mg/l)	Ethylbenzene (mg/l)	*m*/*p*-Xylene (mg/l)	*o*-Xylene (mg/l)
Bitterfeld	Membrane extraction	0.20	<0.01	16.5	<0.01	<0.01	<0.01
	Headspace	0.10	<0.01	24.4	<0.01	<0.01	<0.01
Zeitz	Membrane extraction	203	0.43	<0.02	0.43	0.62	0.18
	Headspace	190	0.48	<0.01	0.53	0.80	0.17

be further improved by adjusting the temperature of the water sample. This would lower the detection limits and enhance the precision of measurements.

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