ELSEVIER

Journal of Chromatography A, 830 (1999) 365–376

JOURNAL OF CHROMATOGRAPHY A

Experimental study on solvent-less sample preparation methods Membrane extraction with a sorbent interface, thermal membrane desorption application and purge-and-trap

G. Matz*, G. Kibelka, J. Dahl, F. Lennemann

Department of Environmental Measurement Technology, Technical University of Hamburg–Harburg, D-21071 Hamburg, Germany

Received 16 June 1998; received in revised form 1 September 1998; accepted 13 October 1998

Abstract

Different solvent-free sample preparation techniques for the enrichment of volatile and semivolatile organic compounds from aqueous samples for subsequent gas chromatographic separation and detection are compared. The methods under study are purge-and-trap, membrane extraction with a sorbent interface in two different configurations, and thermal membrane desorption application. The study has been performed with polar as well as with non-polar compounds in respect to sampling yield, enrichment, repeatability and analysis cycle rate. All experiments have been performed with a mobile GC–MS system.

Keywords: Sample preparation; Membrane extraction with a sorbent interface; Thermal membrane desorption application; Purge-and-trap methods; Volatile organic compounds

1. Introduction

A lot of work has been done in recent years on speeding up and simplifying sample preparation techniques. As a result new solvent free techniques have been developed and found their way to field and laboratory analysis. The aim of this work is to compare membrane based sample preparation techniques for environmental and process monitoring of aqueous samples. Additionally the significance of the applied membranes is described by performing comparative experiments with the membrane free purge-and-trap method.

Methods using an extraction by membrane for the enrichment of volatile organic compounds (VOCs) from different sample streams have been used for analytical purposes since the 1970s [1]. Membrane transport theory was reviewed by Mason and Lonsdale [2]. Technical applications of membrane extraction for waste water treatment are described in [3]. Membrane extraction with a sorbent interface (MESI) combines the process of membrane extraction with a sorbent interface. Solutes from aqueous matrices or from a gas phase are first extracted by a polymer membrane and subsequently trapped either on a thick film capillary column, on a trap with a

*Corresponding author. Tel.: +49-40-7718-3113; fax: +49-40-7718-2382; e-mail: matz@tu-harburg.de

0021-9673/99/$ – see front matter
PII: S0021-9673(98)00853-X

porous sorbent or a cryotrap. The extraction membrane acts as separation and first enrichment step, the sorbent interface as a second enrichment step. MESI has been extensively studied in different configurations [4], the impacts of membrane and sampling parameters have been determined [5,6]. Recently more theoretical work has been done to develop an insight into mass transfer phenomena on the membrane surfaces [7,8]. Typical applications for MESI are the detection of VOCs in waste water, in soil samples or air [4].

Other membrane based MESI-like techniques have been described. Burger et al. applied a 1.1 m long spiral wound capillary membrane for the extraction of VOCs from water coupled to a cryo trap and to GC–flame ionization detection (FID) [9]. Mitra et al. developed and characterised a sample preparation method using an extraction module with up to 20 parallelly arranged capillary membranes, which has been linked to a micro sorbent trap and GC–FID [10,11]. This sampling technique has been well characterised [12] and is applicable to gas and aqueous samples.

The MESI set-up and procedure of this work differs from that of the cited references in higher carrier gas flow rates and a higher sorption capacity of the trap.

Thermal membrane desorption application (TMDA) utilises the storage capacity of a polymer membrane for the enrichment of organic compounds from aqueous matrices. It has been applied for monitoring of VOCs and semivolatile organic compounds (SOCs) in waste water [13] and fermentation broth [14] in analysis cycles of 5–15 min. In comparison to the cited TMDA set-ups the apparatus for the current work has changed markedly. The internal heating wire has been substituted by an external coaxial heater. Whereas permeating and desorbed solutes have been trapped on thick film capillary columns in the former work, now a sorbent trap has been introduced.

Purge-and-trap is an extensively used technique in combination with cryo- and sorbent traps for the enrichment of purgeable solutes from liquid matrices. It is applied as well for sampling polar compounds in beverages stressing the reproducibility [15] as well as for trace [16] and ultratrace enrichment [17] of non-polar compounds.

2. Experimental

2.1. Detector

All analyses have been performed with the mobile GC–MS system MEM (Bruker–Franzen, Bremen, Germany) [18]. The MEM is equipped with a heated membrane inlet (50 μm poly(dimethylsiloxane) (PDMS) at 220°C). The quadrupole scans the mass range from 15–210 u with a rate of one scan per second.

The secondary electron multiplier was set to 1815 V, ionisation energy to 70 eV.

2.2. Chromatographic conditions

A 5 m DB-5 capillary column with 0.25 μm stationary phase and an I.D. of 320 μm is applied for fast but low resolving chromatographic separation. Charcoal cleaned ambient air, which serves as carrier gas, is sucked from the membrane inlet through the capillary column. The outlet pressure at the membrane inlet is 700 mbar absolute, at the column head prevails ambient pressure. The resulting gas flow rate is 2–5 ml/min depending on the GC temperature.

Thermo desorption injection with 30 s stop flow of carrier gas and 30 s injection at a flow rate of 400 μl/min is applied. Desorption temperature is set to 230°C. The GC program starts at 30°C with a slope of 1°C/s up to 200°C. A complete description of the GC–MS system including thermo desorption injection can be found in [18].

2.3. Chemicals

Chemicals were supplied by Merck–Schuchardt (Hohenbrunn, Germany).

The selection of the solutes was mainly guided by the application of TMDA to fermentation processes [14]. Benzaldehyde, toluene and naphthalene (commonly used as internal standard) have been included to cover together with the biologically interesting compounds a relevant range of polarity and volatility.

Two different solutions have been prepared by spiking tap water with aliquots of ethanolic solutions of the target compounds. The target compounds are:

Compound	Quantifying ion	Solution 1	Solution 2
Acetic acid	60	1 g/l	0.5 g/l
Propanoic acid	74	1 g/l	0.5 g/l
Phenol	94	20 ppm	10 ppm
m-Cresol	108	20 ppm	10 ppm
Indole	117	10 ppm	5 ppm
Benzaldehyde	105	2 ppm	800 ppb
Toluene	92	50 ppb	50 ppb
[$^2H_8$]Naphthalene	136	50 ppb	50 ppb

No chlorinated compounds have been selected, as these compounds exhibit a very similar sampling behaviour with TMDA as non-chlorinated VOCs or SOCs. Kesners showed that the sensitivity of chlorobenzene and naphthalene is the same applying TMDA [19].

Quantification of water has been performed on ion track $m/z=18$.

2.4. Sorbent trap

A simple self-made sorbent trap is used for the experiments. The sorbent trap is made of a glass tube (11 cm×1.5 mm O.D.×1.2 mm I.D., with 7 cm of sorbent packing) filled with 18 mg of Tenax TA (20–35 mesh), the adsorbent is fixed with spun glass wads at both sides. The tube is coupled to the different sampling devices. The sampling gas stream is specified in Sections 2.5–2.7 for each preparation technique. After sampling the sorbent tube is taken to the thermo desorber injector of the GC–MS and is thermally desorbed. One thermal desorption procedure taking 1 min is sufficient to completely remove the analytes. Sampling time and carrier gas flow rate have been chosen to avoid breakthrough of the analytes on the Tenax tube. Breakthrough volumina have been taken from [20]. The issue of breakthrough volumina has been checked by running two sorbent tubes in series. These tests confirmed the sufficient capacity of the applied trap.

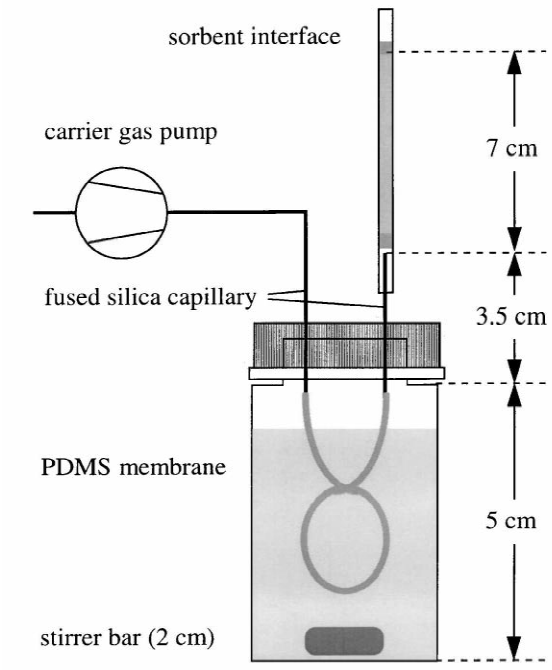

Fig. 1. MESI device, sample volume 15 ml.

2.5. MESI

Fig. 1 outlines the set-up used for the MESI experiments. The sample of 15 ml is agitated with a magnetic stirrer at 1000 rpm and 25°C. The analytes are extracted with a silicone (PDMS) capillary membrane (Reichelt Chemietechnik, Heidelberg, Germany, 11 cm length×1.1 mm O.D., 200 μm wall thickness). Two sets of experiments have been carried out: the first set to check the impact of the gas flow rate through the capillary membrane. For these first experiments the gas flow rate was adjusted to 2.0 ml/min as done in [4] and alternatively to 20 ml/min for comparison with TMDA. The second set compares headspace sampling with sampling with a submersed membrane, which has been the standard sampling mode.

In order to find an appropriate sampling time for MESI, preliminary experiments have been carried out. These experiments showed a significant rise in signal intensity by raising the sampling time from 5 to 10 min, but no comparable effect by raising the sampling time by another 5 min. This observation reflects the time characteristics of membrane sampling [14,21]. The first minutes of the sampling process are absorbed by establishing a steady state across the sampling membrane with little resulting trans-membrane flux. When the membrane is saturated or steady state is established the permeation rate of solutes reaches a constant maximum. For all experiments sampling time has been set to 10 min.

Between two sampling cycles the membrane is flushed for 10 min with purge-gas (inside) and tap water (outside) in order to reduce memory effects. The results of the different experiments are given in Table 1.

Additional MESI experiments with an alternative flow-over configuration have been carried out with the membrane probe described in Section 2.6. Results are presented together with TMDA experiments.

2.6. TMDA

The membrane probe used for TMDA is made of a 8 cm long stainless steel tube with an inner diameter of 2 mm. This tube carries a 11 cm long PDMS capillary membrane with the same dimensions as given in Section 2.5. A coaxial heater (Philips, Hamburg, Germany) is mounted on the tube with silver solder (Fig. 2).

In the first sampling step (sorption phase) the sample liquid is sucked by a peristaltic pump through the small gap between the outer surface of the membrane and the inner surface of the stainless steel tube. The liquid flow rate is set to 2.5 ml/min at 25°C, the sample volume is 25 ml. Solutes migrate according to their hydrophobicity from the sample liquid into the membrane material. VOCs partially permeate the membrane, SOCs mainly dissolve in the membrane material. Particles and ions do not pass the polymer [22]. Permeating compounds are carried by a continuous gas flow to the Tenax tube at the head of the membrane probe and are trapped on the adsorbent. After 10 min the sorption phase is finished and the aqueous sample is removed from the

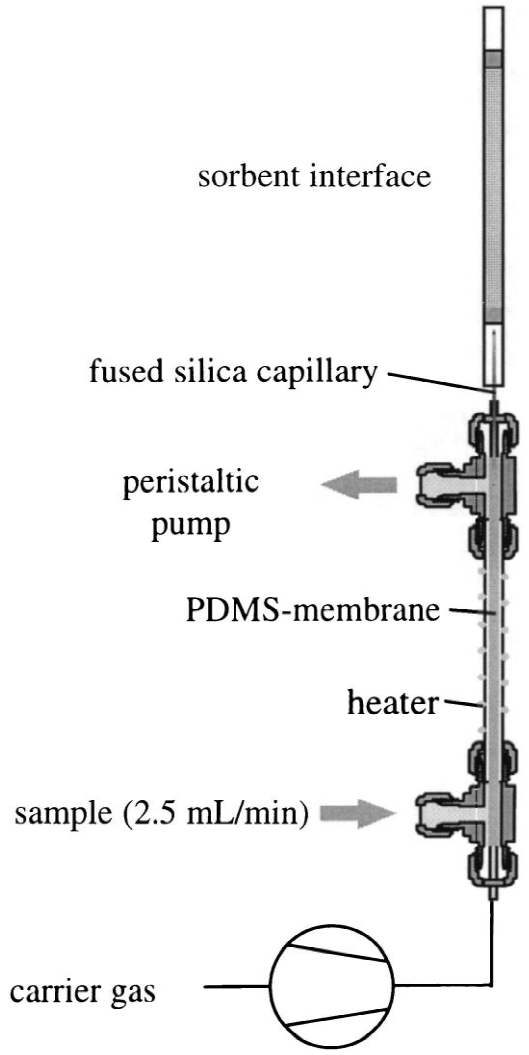

Fig. 2. TMDA membrane probe with sorbent interface.

Table 1
Results of sample preparation with MESI: signal intensity in counts$\times 10^6$; in parentheses: R.S.D. in percent; organic acids have not been detected; mode 1 and 2 with solution 1, mode 3 and 4 with solution 2

Mode	Gas flow rate (ml/min)	Toluene	Benzaldehyde	Phenol	*m*-Cresol	[$^2H_8$]Naphthalene	Indole	Water
1	20	1.1 (8)	0.62 (8)	0.19 (7)	0.12 (21)	0.67 (25)	0.18 (27)	94 (12)
2	2	0.18 (15)	0.031 (30)	0	0	0.057 (11)	0	270 (6)
3	20	1.3 (5)	0.25 (8)	0.11 (15)	0.067 (16)	0.6 (19)	0.14 (18)	140 (20)
4	20[a]	1.2 (2)	0.11 (5)	0.024 (32)	0.006 (41)	0.33 (52)	0.011 (6)	99 (6)

[a]Headspace.

membrane probe. The desorption phase starts and the membrane temperature is raised by the coaxial heater within 30 s from ambient temperature to 195°C. The analytes are thermally desorbed from the sampling membrane and trapped on the Tenax tube (see Section 2.4) at the head of the probe. The tee-union between membrane and sorbent tube is continuously heated to 120°C to reduce compound adsorption. The carrier gas flow rate during sorption and desorption phase is 20 ml/min.

Usually the sampling time for TMDA is 2–5 min. In order to provide comparable experimental conditions with MESI, the sampling time has been set to 10 min.

The membrane probe has been used for three different sampling modes:

1. TMDA as described above.
2. Flow-over MESI (no thermal desorption of the PDMS membrane). This variation allows to determine the impact of thermally assisted membrane desorption.
3. TMDA as described, but trapping only the analytes set free by thermal desorption of the capillary membrane. This experiment allows to study the analyte storage-capacity of the membrane itself.

Fig. 3a–c shows GC–MS runs after applying the respective preparation modes. The results of this experiments are listed in Table 2.

2.7. Purge-and-trap

Purge-and-trap experiments allow to study the impact of the sampling membrane applied for the above described sample preparation techniques. Fig. 4 shows the set-up with a sample volume of 10 ml. Preliminary experiments showed no significant signal alteration when using a volume of 25 ml. This observation suggests that the applied set-up does not use the complete analyte content of the 10 ml sample. The sorbent interface is described in Section 2.4. The purge gas rate has been varied between 10 and 20 ml/min of ambient air, sampling time between 5 and 10 min. Additionally experiments have been performed at 80°C. The results of these experiments are given in Table 3.

3. Results and discussion

3.1. Theoretical aspects of membrane sampling

Sampling solutes from aqueous solutions with purge-and-trap or with a membrane based method implicates the transfer from liquid to gas phase. The mass transfer processes of both methods show some parallels, for instance the occurrence of boundary layers at the phase boundaries. The main difference between both mass transfer processes is that a third phase (i.e. the membrane material) is introduced. As a result the interphase mass transfer does not solely depend on a distribution coefficient (like the Henry constant for purge-and-trap) but additionally on the mobility (or diffusion coefficient) of the solutes inside the membrane material.

Commonly the overall mass transfer for membrane processes is described by the resistances-in-series model [23], considering the impact of three main transport steps. These steps are: transfer from the sample liquid to the membrane, transfer through the membrane and transfer from the membrane into the carrier gas flow. The transfer to and from the membrane depends mainly on the prevailing flow regime [8]. It is enhanced by a turbulent flow regime, provided by stirring or high flow rates. The transfer through the membrane is expressed by the membrane permeability. As the applied membranes in this work are of a solution–diffusion type, the permeability depends on solute diffusion and solute solubility in the membrane [24]. Solute diffusion described by Fick's laws determines the time necessary to reach saturation inside the membrane [25]. The amount of solute that can be absorbed by the membrane is linked to the solubility. This parameter can be derived from interaction parameters [26] or from the LSER equation [27].

Which of the three above steps is the rate limiting step depends on the solute's nature. Stürken [28] showed that for 1,1-dichloroethane (DCE) extracted with a PDMS membrane, the rate limiting step is the transport to the membrane, whereas for phenol it is the transport through the membrane. This means that the sampling result with a PDMS membrane for DCE (or any other non-polar VOC) can be improved by establishing turbulent flow conditions in the liquid

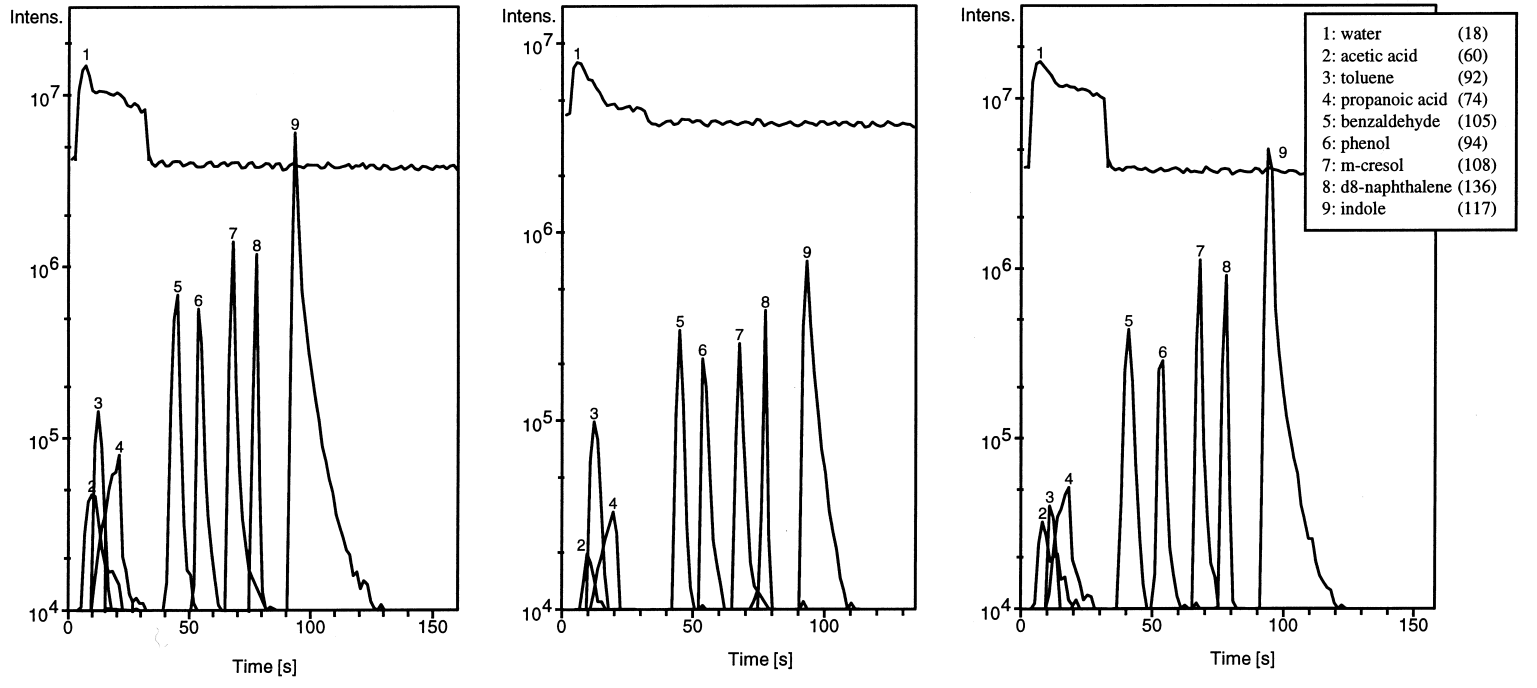

Fig. 3. GC–MS runs after applying: (a) TMDA, (b) flow-over MESI, (c) TMDA thermal desorption only; signal intensities in counts per second on logarithmic scale.

Table 2
Results of sample preparation with TMDA: signal intensity in counts×10^6; in parentheses: R.S.D. in percent. Mode 1, 2 and 3 have been performed with solution 1, sampling time 10 min, carrier gas flow rate 20 ml/min.

Mode		Acetic acid	Propanoic acid	Toluene	Benzaldehyde	Phenol	*m*-Cresol	[$^2H_8$]-Naphthalene	Indole	Water
1	TMDA	0.23 (4)	0.48 (7)	0.51 (12)	2.1 (9)	1.6 (6)	2.5 (5)	2.0 (15)	16.0 (7)	180 (8)
2	Flow-over MESI	0.11 (23)	0.21 (19)	0.35 (5)	0.7 (4)	0.6 (4)	0.6 (7)	0.5 (7)	2.7 (13)	40.0 (4)
3	TMDA[a]	0.16 (6)	0.32 (4)	0.14 (6)	1.4 (4)	0.9 (1)	0.2 (5)	1.7 (3)	17.0 (5)	190 (11)

[a]Only thermally desorbed compounds have been trapped on the TENAX tube.

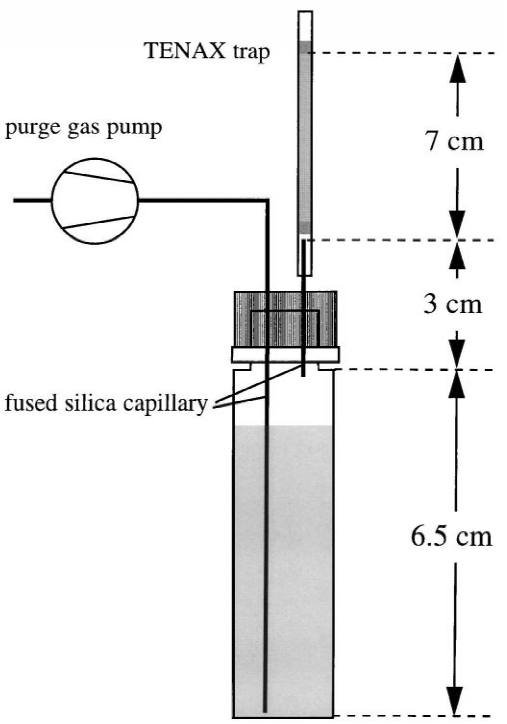

Fig. 4. Purge-and-trap device, sample volume 10 ml.

sample. On the other side the result for phenol (or any other polar compound) can not be improved the same way.

3.2. MESI

Experiments in two different modes have been carried out to study the impact of the carrier gas flow rate (2 ml/min and 20 ml/min). The positive effect of a higher carrier gas flow rate is obvious from Table 1. The strength of the impact depends on polarity and volatility. As a low carrier gas velocity implicates a low mass transfer coefficient at the inside of the extraction membrane, the transfer of analytes from the extraction membrane into the carrier gas stream is hindered. The results of the above experiments coincide in principle with experiments described in [7]. The difference lies in the higher sorption capacity of the trap used in this work, which allows significantly higher carrier gas flow rates. A second set of experiments has been carried out to check the impact of the phase contacting the sampling membrane. A comparison between mode 3 and 4 of Table 1 suggests, that for toluene as a typical non-polar VOC it does not make any

Table 3
Results of sample preparation with purge and trap: signal intensity in counts×10^6; in parentheses: R.S.D. in percent. Mode 1, 2, 3, 4 and 5 have been performed with solution 1, sampling temperature 25°C

Mode	Purge gas (ml/min)	Time (min)	Acetic acid	Propanoic acid	Toluene	Benzaldehyde	Phenol	*m*-Cresol	[$^2H_8$]-Naphthalene	Indole	Water
1	20	10	0.51 (11)	0.33 (21)	2.1 (9)	1.3 (11)	0.3 (9)	0.27 (7)	4.6 (5)	0.81 (15)	1700 (13)
2	20	5	0.23 (24)	0.1 (44)	2.6 (4)	0.8 (4)	0.18 (9)	0.14 (15)	4.2 (4)	0.54 (11)	1200 (13)
3	10	10	0.31 (14)	0.21 (17)	1.8 (4)	0.6 (5)	0.14 (19)	0.09 (10)	2.6 (5)	0.35 (6)	1200 (15)
4	10	5	0.25 (18)	0.16 (6)	1.5 (3)	0.3 (2)	0.07 (6)	0.05 (32)	0.9 (1)	0.1 (3)	1000 (11)
5	10[a]	5	0.05 (14)	0	1.5 (4)	3.3 (8)	0.2 (3)	0.29 (6)	9.1 (8)	0.91 (3)	2900 (2)

[a]Sampling temperature 80°C.

difference whether the sampling membrane is contacted by the liquid or by the gas-phase. This observation is in good agreement with [4]. Analogous to the effect of the carrier gas flow rate, the impact of the contacting phase is stronger, the less volatile and the more polar an analyte is. Especially compounds like indole and cresol interact with the membrane material, but the transfer from the liquid phase into the gas phase seems to be unfavourable.

Obviously MESI – as applied for this work – is not suited for the extraction of carboxylic acids. It was assumed that the organic acids are adsorbed on the 3.5 cm long deactivated fused silica capillary transfer line between sampling membrane and sorbent trap. But additional experiments with a heated transfer line showed no signal alteration for the acids.

3.3. TMDA

Table 2 lists the results of the three different experimental modes. It can be stated that an important feature for the detection of organic acids and the less volatile compounds is the thermal desorption of the sampling membrane. The signal area count is improved by a factor of 2–5 depending on the compounds volatility and polarity. On the other side detecting very volatile compounds does not necessarily require the thermal membrane desorption. The signal intensity for toluene is only improved by a factor of 1.5.

Flow-over MESI in contrast to standard MESI allows to detect acetic and propanoic acid.

3.4. Purge-and-trap

Varying purge gas flow rate and sampling time showed that 10 min sampling time at 20 ml/min flow rate provides acceptable results in respect to sampling yield, repeatability and chromatographic separation. These variations have been carried out in order to check for analyte depletion in the sample resulting in lower signal intensities. One drawback of purge-and-trap is the high amount of sampled water which results in a deteriorated chromatographic resolution. Though the breakthrough volume for water on TENAX is very low, water condensation inside the trap is the reason for this observation. Increasing the sample temperature to 80°C enlarges this effect, what requires more sophisticated injection techniques. The positive impact of sample temperature on signal intensity for the less volatile compounds is counteracted.

3.5. Comparison of preparation techniques

A comparison between the different sample preparation techniques is done in terms of sampling yield, enrichment, repeatability and the memory effect or carry over.

The sampling yield of a sample preparation technique affects the signal intensity that can be obtained with a specific sensor system. The enrichment describes the quality of the analyte separation from its sample matrix. Sampling yield and enrichment combined determine the efficiency of a sampling method. The repeatability of a sampling technique is a measure for the reliability for obtained result. The memory effect reflects the success of removing any residues of analyte from the sampling system. If only negligible amounts of or no analyte remains in the sampling set-up, the next sample can be processed without any delay. This enables high sample throughput and high analysis cycle rates.

3.5.1. Sampling yield

Fig. 5 displays the sampling yield obtained with the respective sample preparation technique as method A versus method B. Intensities of method A taken from Tables 1–3 are normalised to method B. Values greater than 1 express that the sampling yield of the respective solute is higher with method A than it is with method B. Comparing purge-and-trap with TMDA, the less astonishing observation is that the flow of water is ten times higher with purge-and-trap than it is with TMDA, because the sampling membrane acts as a barrier for water. More astonishing is the observation that the yield of polar solutes (phenol, cresol and indole) is much higher with TMDA. It has been expected that more polar compounds could be favourably sampled by purge-and-trap, because they do not have to pass the PDMS membrane, which discriminates in favour of non-polar compounds. Comparing purge-and-trap with MESI shows that the sampling yield of VOCs and the polar compounds is roughly halved and the flow

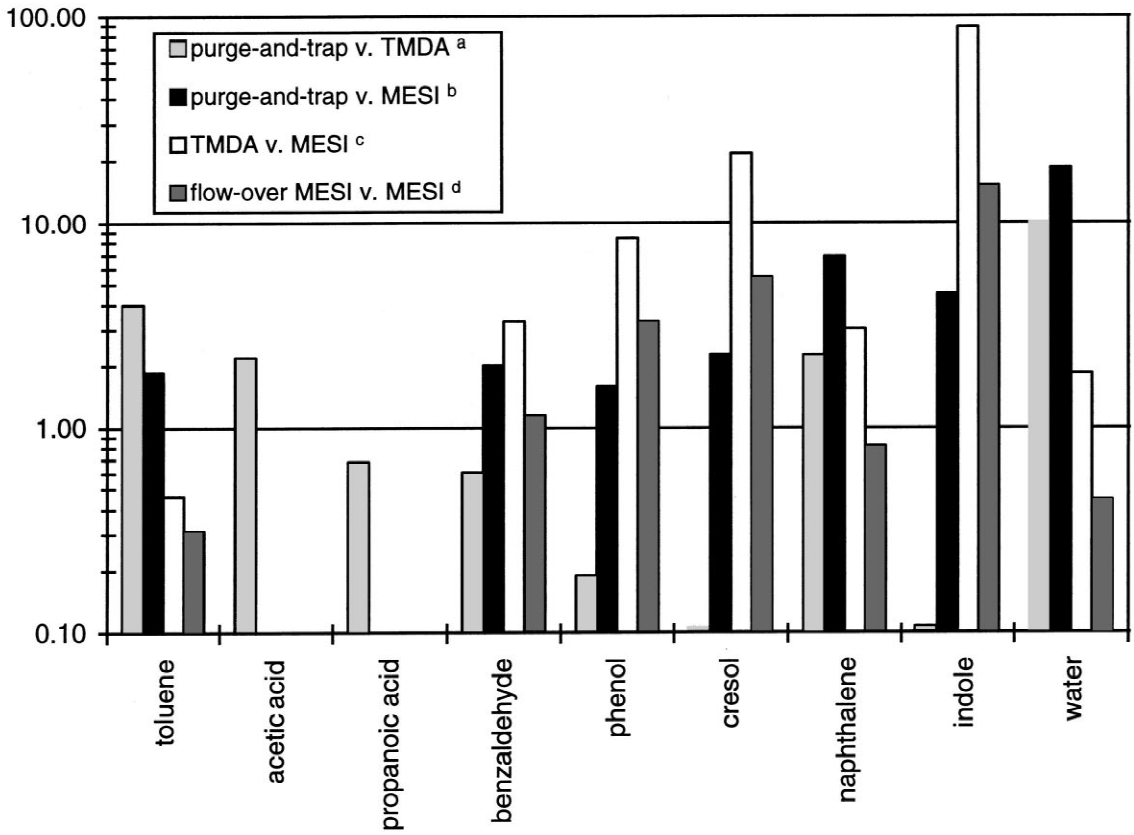

Fig. 5. Comparison of sampling yield expressed by the ratios of signal intensities attained with the respective sampling methods: (a) mode 1 Table 3 versus mode 1 Table 2, (b) mode 1 Table 3 versus mode 1 Table 1, (c) mode 1 Table 2 versus mode 1 Table 1, (d) mode 1 Table 1 versus mode 2 Table 2.

of the less volatile compounds is cut to 20% by introducing a PDMS membrane. These observations correspond to the expected barrier function of the membrane. Fig. 5 obviously demonstrates that TMDA in comparison to MESI allows to sample less volatile organic and polar compounds more effectively, which demonstrates the impact of thermal membrane desorption. This impact is particularly marked for phenol, cresol and indole. The amount of sampled water is roughly doubled, which is a consequence of water evaporation due to thermal desorption.

As discussed above, turbulent flow conditions are favourable for the membrane extraction of non-polar VOCs, as for these compounds the transfer to the membrane determines the overall permeation rate. This explains the better sampling yield for toluene with standard MESI in comparison to TMDA or flow-over MESI and coincides with the results for toluene in Fig. 5 and results from [4].

Higher signal intensities are obtained for phenol, cresol and indole applying flow-over MESI in comparison to standard MESI because the membrane is continuously contacted with fresh sample liquid. This in contrast to a batch extraction (i.e. standard MESI) maintains a higher concentration gradient, which results, according to Fick's first law, in a higher trans-membrane mass flow of solutes.

3.5.2. Enrichment

The quality of enrichment of compound *i* from an aqueous solution can be characterised with the separation factor α, which is defined as:

$$\alpha_{i,\text{water}} = \frac{y_i x_{\text{water}}}{x_i y_{\text{water}}}$$

where x_i is the mole fraction of compound i in sample; x_{water} the mole fraction of water in sample; y_i mole fraction of compound i in gas phase and y_{water} the mole fraction of water in gas phase.

The separation factor is commonly used for classifying separation unit operations in chemical engineering, for instance membrane processes [29].

Table 4 displays data for enrichment in terms of the modified separation factor $\tilde{\alpha}_{i,\text{water}}$, which is defined as follows:

$$\tilde{\alpha}_{i,\text{water}} = \frac{\frac{S_i}{\Sigma S_j}}{c_i \cdot \frac{S_{\text{water}}}{\Sigma S_j}} = \frac{S_i}{S_{\text{water}} c_i}$$

where S_i is the GC–MS signal intensity for compound i, S_{water} the GC–MS signal intensity for water; ΣS_j the sum of signal counts of one GC–MS run and c_i the concentration of compound i in sample. The mole fraction of compound i in the sample has been replaced by its concentration, the mole fraction of water in the sample is one (diluted samples) and the mole fractions in the gas phase have been substituted by the ratio of signal intensities.

Together with the sampling yield the separation factor is a useful tool to judge the sampling success. The values for $\tilde{\alpha}_{i,\text{water}}$ demonstrate the problems for enriching polar compounds: they are either hardly enriched or even depleted ($\tilde{\alpha}_{i,\text{water}} \leq 1$), whereas non-polar compounds are enriched with a separation factor $\tilde{\alpha}_{i,\text{water}} > 1000$. The separation factors for the membrane based preparation techniques in comparison to those for purge-and-trap demonstrate the ability of the sampling membrane to exclude water. TMDA exhibits smaller $\tilde{\alpha}$ than flow-over MESI as the thermal desorption sets free relatively more water from inside the membrane probe than are analytes desorbed from the membrane itself.

3.5.3. Repeatability

The average values' relative standard deviations listed in Tables 1–3 are mainly in the range of 5–15%. Higher R.S.D.s up to 50% are noticed in the wake of low signal intensities. The R.S.D. for a single measurement obtained with an automated TMDA–GC–MS system is reported to be about 10% [21]. For different in-line MESI–GC–FID configurations R.S.D.s of less than 5% have been published [4,5]. Typical R.S.D. values for purge-and-trap vary between 5 and 25% [15,30]. As a consequence the tested sample preparation techniques are equivalent in respect to repeatability.

3.5.4. Memory effects

The analysis cycle rate determines the number of analyses which can be carried out per day (for laboratory use) or per hour (for process monitoring). One important factor influencing the analysis cycle rate is the time required for sampling and additionally the time to reduce the memory effect to an acceptable level.

Fig. 6 outlines the extent of the memory effects for each sample preparation technique in terms of the

Table 4
Enrichment of solutes by the sample preparation methods in terms of the modified separation factor $\tilde{\alpha}_{i,\text{water}}$

	Acetic acid	Propanoic acid	Toluene	Benzaldehyde	Phenol	*m*-Cresol	[$^2H_8$]-Naphthalene	Indole
MESI[a]	0	0	$2.4 \cdot 10^5$	3323	101	63	$1.4 \cdot 10^5$	193
TMDA[b]	1.4	2.8	$0.6 \cdot 10^5$	6003	465	741	$2.4 \cdot 10^5$	9317
Flow-over MESI[c]	2.8	5.1	$1.7 \cdot 10^5$	8599	753	771	$2.6 \cdot 10^5$	6626
Purge-and-trap[d]	0.3	0.2	$0.2 \cdot 10^5$	364	9	8	$0.5 \cdot 10^5$	47

[a]Mode 1 Table 1.
[b]Mode 1 Table 4.
[c]Mode 2 Table 4.
[d]Mode 1 Table 5.

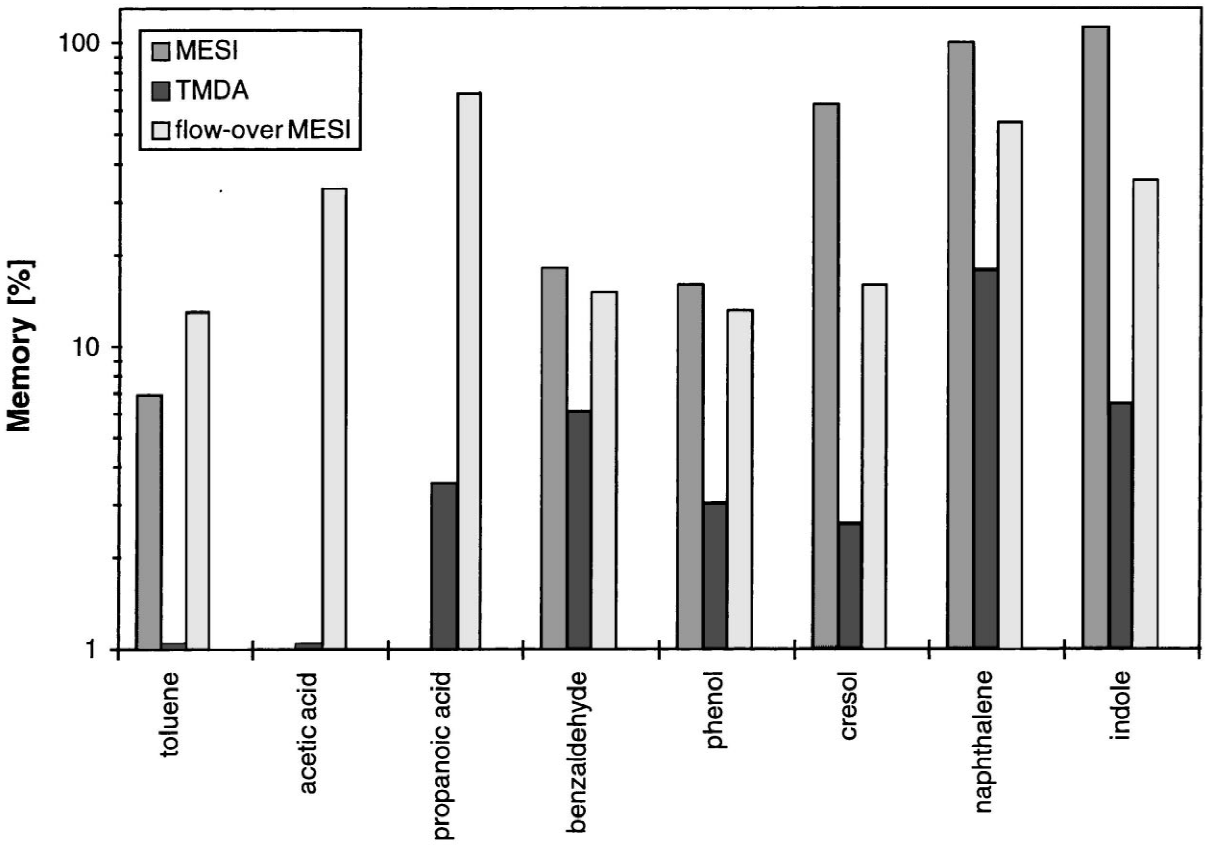

Fig. 6. Memory effect of sample preparation techniques: no memory is displayed for purge-and-trap, as none has been observed.

ratio of signal intensities of sampling cycles with tap water (blank) and with test solutions.

The memory effect for both MESI configurations has been evaluated by flushing the membrane 10 min with tap water (outside) and air (inside) after a standard sampling cycle. The flushing cycle has been followed by a sampling cycle with tap water instead of sample liquid. The signal intensities obtained with this sampling cycle have been normalised to the intensities of the first sampling cycle. The obtained results are comparable to those published in [31]. The memory effect for TMDA and purge-and-trap have been evaluated without an intermediate flushing cycle.

As can be seen from Fig. 6 TMDA exhibits an acceptable memory effect, whereas purge-and-trap did not show any memory. As these two techniques do not require a flushing cycle, they enable higher analysis cycle rates than the two MESI techniques.

4. Conclusion

The advantages of purge-and-trap in the presented work are the simple set-up, the high analysis cycle rate and the good sensitivity. The main drawback is the high amount of trapped water and the chromatographic problems linked to it. This technique is suited for non polar VOCs and SOCs. Polar compounds are either weakly enriched or even depleted.

MESI is particularly suited for the detection of nonpolar VOCs. The main advantage is its simple set-up and the exclusion of water by the sampling membrane. Due to its pronounced memory effect, MESI provides a low analysis cycle rate for less volatile organic compounds.

TMDA combines the advantages of water exclusion and high separation factors with low memory effects and high analysis cycle rates. The thermal membrane desorption improves sensitivity and en-

ables the detection of very polar compounds. Depending on the required sensitivity TMDA is suited for a broad spectrum of solutes.

Acknowledgements

This work is funded by the Deutsche Forschungsgemeinschaft and is part of the Sonderforschungsbereich 238 at the Technical University of Hamburg–Harburg.

References

[1] L.B. Westover, J.C. Tou, J.H. Mark, Anal. Chem. 46 (1974) 568.
[2] E.A. Mason, H.K. Lonsdale, J. Mem. Sci. 51 (1990) 1.
[3] H. Nijhuis, Ph.D. Thesis, University of Twente, Enschede, 1990.
[4] M.J. Yang, S. Harms, Y.Z. Luo, J. Pawliszyn, Anal. Chem. 66 (1994) 1339.
[5] M.J. Yang, J. Pawliszyn, Anal. Chem. 65 (1993) 1758.
[6] K.F. Pratt, J. Pawliszyn, Anal. Chem. 64 (1992) 2101.
[7] Y.Z. Luo, M. Adams, J. Pawliszyn, Anal. Chem. 70 (1998) 248.
[8] Y.Z. Luo, M. Adams, J. Pawliszyn, Analyst 122 (1997) 1461.
[9] B.V. Burger, W.J.G. Burger, I. Burger, J. High Resolut. Chromatogr. 19 (1996) 571.
[10] S. Mitra, N. Zhu, X. Zhang, B. Kebbekus, J. Chromatogr. A 736 (1996) 165.
[11] S. Mitra, X. Guo, Anal. Lett. 31 (1998) 367.
[12] S. Mitra, L. Zhang, N. Zhu, X. Guo, J. Microcol. Sep. 8 (1996) 21.
[13] G. Matz, P. Kesners, Analysis Mag. 23 (1995) M12.
[14] G. Matz, F. Lennemann, J. Chromatogr. A 750 (1996) 141.
[15] A. Kaufmann, J. High Resolut. Chromatogr. 20 (1997) 10.
[16] M.D.F. Askari, M.P. Maskarinec, S.M. Smith, P.M. Beam, C.C. Travis, Anal. Chem. 68 (1996) 3431.
[17] R. Borelli, T. Fiorani, P. Golfetto, J. High Resolut. Chromatogr. 19 (1996) 457.
[18] G. Matz, W. Schröder, Field Anal. Chem. Techn. 1 (1996) 77.
[19] P. Kesners, Ph.D. Thesis, Technical University of Hamburg–Harburg, 1993, p. 116, Fig. 43.
[20] http://www.sisweb.com/index/referenc/tenaxta.htm.
[21] G. Matz, M. Loogk, F. Lennemann, J. Chromatogr. A 819 (1998) 51.
[22] T. Meyer–Jens, Ph.D. Thesis, Technical University of Hamburg–Harburg, 1994, p. 97.
[23] Q.T. Nguyen, J.L. Ninow, I. Marc, J. Mem. Sci. 59 (1991) 249.
[24] D.W. Van Krevelen, Properties of Polymers, Elsevier, Amsterdam, 3rd ed., 1990, p. 536.
[25] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 2nd ed., 1992.
[26] A.F.M. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, FL, 2nd ed., 1991.
[27] M.H. Abraham, J. Phys. Org. Chem. 6 (1993) 660.
[28] K. Stürken, Ph. D. Thesis, Technical University of Hamburg–Harburg, 1993, p. 94.
[29] M. Bennet, B.J. Brisdon, R. England, R.W. Field, J. Mem. Sci. 137 (1997) 63.
[30] I. Silgoner, E. Rosenberg, M. Grasserbauer, J. Chromatogr. A 768 (1997) 259.
[31] K.F. Pratt, J. Pawliszyn, Anal. Chem. 64 (1992) 2107.