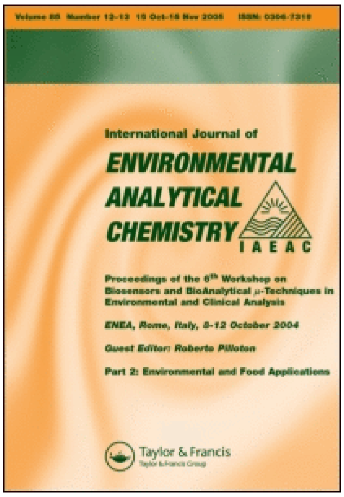

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# Comparison of membrane assisted liquid-liquid microextraction devices applied to a series of volatile organic compounds in aqueous environmental matrices

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# Comparison of membrane assisted liquid–liquid microextraction devices applied to a series of volatile organic compounds in aqueous environmental matrices

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An extraction device has been investigated for the separation and preconcentration of a series of volatile organic compounds ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) in aqueous matrices. The device consisted of a microporous membrane system utilising a hollow fibre tube filled with organic solvent directly immersed into the sample solution. The hollow fibre containing 160 µL organic solvent was immersed in a glass vial with 10 mL capacity, and the extraction took place through diffusive transport between the aqueous sample and the small amount of solvent. For validation of the method, some operational conditions, such as extraction solvent, temperature, stirring rate and separation time, were optimised. Limit of detection was at low ppb levels, with GC-MS analysis under selected ion monitoring (SIM), whereas enrichment factors between 22 and 35 were obtained. Good reproducibility with RSDs between 7.2% and 9.8% and large linear dynamic ranges with $R^2$ between 0.996 and 0.998 were also achieved. In addition, the performance of the membrane assisted solvent extraction (MASE) system was compared with two existing configurations: a non-porous membrane separation device, as well as with a comparable microporous configuration. The comparison considered the extraction mechanism and the underlying transport processes. The application to real samples showed a good concordance with classical analytical methods.

**Keywords:** microextraction; preconcentration; volatile organic compounds; aqueous matrices; hollow fibre membrane

## 1. Introduction

Liquid-liquid extraction is a well-accepted and widely used sample preparation technique for subsequent analyte determination by chromatographic techniques [1]. However, the common format with extraction funnels, despite the advantage of simplicity, is unfavourable in several respects. Considerable amounts of expensive and sometimes hazardous solvents are consumed, many manual operations with the risk of contamination and analyte losses are involved and in several instances the formation of emulsions can create severe practical problems. Miniaturisation and automation of liquid-liquid

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extraction has been a subject of considerable concern in recent years and several different approaches have been proposed [2–8].

In this respect extraction into a single drop of solvent is one of the simplest means that is well compatible with gas chromatographic (GC) analysis [3,9,10]. Though high preconcentration factors can be achieved for compounds with high partition coefficients [11] practical problems remain such as shearing the drop off during the extraction process and emulsification of a substantial amount of the solvent.

An alternative concept for miniaturised liquid-liquid extraction introduced by Pedersen-Bjergaard and Rasmussen [12] is based on the stabilization of the liquid-liquid interface by a membrane support. Hydrophobic microporous hollow fibre membranes are generally used. Microextraction with non-porous (homogeneous) membranes is an alternative concept that is widely employed for very similar purposes. In these systems the membrane itself constitutes an own phase which can alter the selectivity of the extraction process [13,14]. The organic solvent contained within the lumen of the hollow fibre and within the membrane pores (microporous membranes) is thus immobilised and the entire system gets mechanically robust. In addition the low-cost membranes are disposable so that problems with cross-contamination can be totally eliminated. Since 1999 when the first paper appeared on hollow fibre-based liquid-liquid microextraction (HFLLME), applications of the concept to various compounds [12,15], instrumental modifications [15] and the partial automation of the extraction process particularly in hyphenation with GC [16] have been presented in many additional publications.

Our own initial attempts to apply this technique for the preconcentration of trihalomethanes and pesticide residues have drawn attention to a series of principle and practical problems that are of general interest. Hence it was decided to re-investigate the influence of chemical and physical parameters on the extraction process and on the basis of these findings to make a critical assessment of the utility and limitation of the techniques for particular applications. Moreover, a comparison with the performance of two existing configurations: a comparable microporous configuration and a non-porous membrane separation device was accomplished.

## 2. Experimental

### 2.1 *Chemicals and standards*

The primary standard used in all experiments was a trihalomethanes calibration mix 2000 $\mu g\,mL^{-1}$, Supelco, Bellefonte, USA. A stock solution in methanol was prepared at a concentration of 400 $\mu g\,L^{-1}$ and aliquotes were spiked in the respective aqueous matrices, to obtain the final concentration in the range 1-10 $\mu g\,L^{-1}$. The solvents used for dilution were analytical grade heptane, isooctane and cyclopentane, purchased from Sigma Aldrich, Germany.

#### 2.1.1 *Methods and experimental arrangements*

In configurations A and B samples were placed in glass vials of 10 mL capacity ($d = 19$ mm, liquid height $h = 35$ mm) which were stirred by a small bar ($d = 3$ mm, length $= 7$ mm) to achieve proper sample agitation. Microporous polypropylene hollow fibres (see Table 1) were used to entrap the organic solvent. The membrane length was 30 mm and the lower end (see Figure 1a) was closed by heat-fusion.

Table 1. Types and characteristics of polymeric membranes.

| Material | Properties | Manufacturer |
|---|---|---|
| Polypropylene | 0.6 mm i.d., 0.2 mm thickness, 0.2 µm pore size, 65% porosity, Q3/2 | Accurel, Membrana, Wuppertal, Germany |
| Polypropylene | 1.8 mm i.d., 0.4 mm thickness, 0.2 µm pore size, 73% porosity, S6/2 | Accurel, Membrana, Wuppertal, Germany |
| LDPE bag | 0.03 mm thickness, 600 µL volume, 750 $\mathrm{mm}^2$ surface area | Gerstel, Mülheim an der Ruhr, Germany |

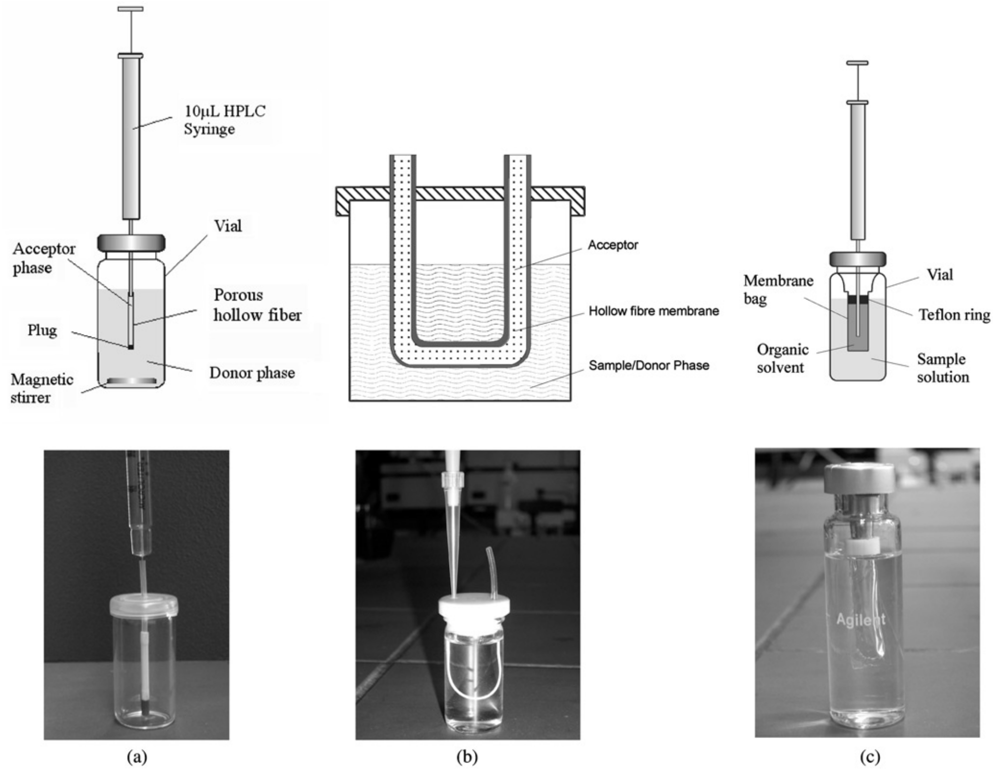

Figure 1. Configurations A, B, C illustrate the experimental configurations for porous hollow-fibre (A, B) and non-porous membrane (C) liquid-liquid microextraction.

Short pieces (55 mm effective length) of the membrane were cut and the two ends were fixed to metal capillaries penetrating the PTFE cover that is eventually used to close the sample vial (see Figure 1b). Though the surface to volume ratio of the thin tube is favourable, the larger diameter membrane type of configuration A has the great advantage of much easier handling.

In configuration C a commercial available LDPE (low density polyethylene) membrane bag (see Table 1) was immersed into the sample solution (15 mL). After appropriate time for extraction the total volume of organic solvent was removed from the bag and transferred into another headspace vial for GC analysis.

The capillary configurations (A and B) were prepared following the procedure: 160/50 µL extraction solvent (*n*-octanol) were filled in the lumen of the membrane dipped in a vessel filled with distilled water, and ultrasonicated for 10 seconds to remove the excess of solvent from the outer surface and from the lumen of the membrane. After preparation, the membrane with the filled pores (volume 61/18 µL) was transferred in the analyte solution where volumes of 100/30 µL were added in the lumen, thus resulting in a total extracting solvent volume of 160/50 µL, that ensures a constant phase to volume ratio of 60/200.

In order to start the extraction, stirring was initiated and after extraction the entire solvent remaining within the lumen was transferred either into a headspace vial for separation and detection of the trihalomethanes by HS-GC-ECD or into a micro-vial of an autosampler for direct injection into GC-MS for the determination of organic contaminants.

### 2.1.2 *Membrane material and extracting agent*

Regarding the interaction between the extracting agent and membrane material, the appropriate selection of both is essential for an optimised separation.

*Membrane material*: the membrane materials and their main features are summarised in Table 1. The polypropylene membranes represent hydrophobic microporous membranes with different geometries for configurations A and B into which organic solvents can penetrate. The pore size was 0.2 µm for both configurations and the porosity was 73/65% for configurations A and B, respectively. The pore volume of these membranes is in the same order of magnitude as the lumen and has a strong influence on the extraction process, especially when equilibrium is not attained. Therefore, the amount of extraction agent applied within the system was measured exactly for the accurate calculation of the extraction efficiency and the enrichment factor. In contrast in configuration C a nonporous solution diffusion membrane (low density polyethylene) with a smaller mass transfer rate was selected, which does not put so many limitations regarding the retention of the solvent in the membrane.

*Selection of extracting agent*: The basic requirements for a solvent to be applicable in a liquid-liquid extraction process in general are selectivity, a high distribution coefficient, as well as an appropriate viscosity and volatility.

A very important issue for membrane extraction is the immobilisation of the extracting agent within the membrane pores in order to prevent leakage. There are four factors that determine the strength of immobilisation, i.e. the interaction between solvent and polymeric membrane material, the pore size, the viscosity of the extracting agent and the pressure difference. Therefore, a few solvents (*n*-octanol, hexane, heptane, isooctane) are applicable/suitable for membrane-assisted liquid-liquid microextraction.

In all subsequent experiments described, *n*-octanol was exclusively used as extracting agent for the microporous membranes. However, in the experiments performed with the nonporous LDPE membrane, heptane was used, as the extraction efficiency of *n*-octanol was too small. Experimental validation approved that the high viscosity of *n*-octanol is the reason for the limited molecular dynamic within the non-porous membrane.

## **2.2** ***GC analysis of extracts***

The instrumental configurations for the analysis of the four selected trihalomethanes in solvent matrices are listed in Table 2.

Table 2. Instrumental configurations.

| Instrumentation | GC-ECD | GC-MS |
|---|---|---|
| Autosampler | 7120 Hewlett Packard | CTC Analytics |
| GC | Gas Chromatograph HP 6890 Series with ECD and FID, Hewlett Packard (Agilent) | Agilent 6890/MSD 5973 |
| Carrier gas | Nitrogen, 60 kPa | He at 37 cm $\text{sec}^{-1}$, flow 1,5 ml $\text{min}^{-1}$, constant flow |
| HS | 1 h at 80°C vial pressurisation | – |
| Transfer line | 1 ml gas phase transferred at 100°C | – |
| Injector | Split 1/10, 250°C | 1 : 20, 250°C |
| Capillary column | HP 5, 30 m, 0.25 mm i.d., 1.45 μm Film, Agilent | DB-5 MS; 30 m, 0,25 mm i.d., 0,25 μm film, Agilent |
| Temperature program oven | 1 min. 40°C, 10°C $\text{min}^{-1}$ to 80°C, 30°C $\text{min}^{-1}$ to 180°C | 40°C for 2 min<br>40–150 at 10°C $\text{min}^{-1}$<br>150–220 at 30°C $\text{min}^{-1}$<br>220°C for 2 min |
| Detector | ECD, 300°C | 230°C, Full scan, 35–300 amu 3,25 scans $\text{sec}^{-1}$ |

For easier handling, determination of trihalomethanes in *n*-octanol was realised relying on the support of headspace technique. To this end, the entire solvent (generally *n*-octanol) recovered from the lumen of the hollow-fibre (typically 160 μL, conf. A and 50 μL conf. B) was dispensed into the headspace vial and the vial was closed immediately. Then the automated headspace system (Perkin Elmer, HS-PE 40) was initiated and analytes quantified by ECD detection. In order to correct for the solvent influence observed in headspace analysis the same solvent and also the same volume of solvent were used for calibration and sample analysis.

Heptane, the other solvent used, has a higher vapour pressure than *n*-octanol and the analyte detection by headspace was overlapped by the solvent signals. Therefore, GC-MS was applied for the non-porous membrane extracts.

For quality assurance additional analyses of the organohalogen compounds without performing the extraction and within the estimated range were executed. To this end definite volumes of the standard solutions containing the analytes in *n*-octanol were directly pipetted into the headspace sampler to obtain the reference signal values, whereas the respective concentrations of standard solutions prepared in heptane were used for GC-MS calibration.

### 2.3 *Collection and analysis of real samples*

Four water samples collected from the Teufelspfuhl lake near Berlin were extracted with two of the miniaturised techniques and were compared with liquid-liquid extraction. The lake is situated in an area where for a long period a dry cleaning company was located. Therefore the groundwater within an extended area is contaminated with chlorinated hydrocarbons. Dominant are trichlorethene, tetrachlorethene and dichloroethene, the latter as a microbiological anaerobic degradation product of the other two. Additionally, considerable amounts of trihalomethanes and vinylchloride have been quantified. The results of the trihalomethanes analysis are presented in Table 3.

The samples were diluted 1 : 100 with distilled water, extracted with *n*-octanol in the straight hollow fibre membrane configuration (Figure 1a) and analysed with headspace GC-ECD. Parallel aliquotes were extracted with heptane in the membrane bag configuration (Figure 1c) and in the classical liquid-liquid extraction ($\theta = 20$) followed by analysis with GC-MS.

The extracts in octanol were analysed after transfer into the gas phase by heating the samples to 80°C and subsequent transfer of 1.0 mL gas phase into the inlet of GC-ECD.

## 3. Results and discussion

To seek a simple preparation and a robust device for the separation and preconcentration of trihalomethanes, which in addition permits simplified solvent handling due to the larger diameter, the straight configuration shown in Figure 1a was designed. The performance of the system was compared with a similar configuration, proposed by Rasmussen's group [12,17,18] and also in the work of King *et al.* [19] (see Figure 1b) as well as with a non-porous membrane separation method [3,9] (see Figure 1c).

From the theoretical point of view the amount of analyte extracted ($n_{org}$), the resulting concentration of analyte in the organic phase ($c_{org}$) and the mass fraction extracted (extraction efficiency E) are related to the distribution coefficient of the analyte K and the phase volume ratio $\theta$ of sample to solvent ($c_S$ = initial sample concentration, $V_S$ = initial sample volume) [20]. Beside extraction efficiency, the enrichment factor (EF) is a decisive parameter.

Taking the typical experimental conditions of membrane mediated liquid-liquid extraction with $\theta$ between 50 and 200, complete extraction (>95%) can be expected for analytes with distribution coefficients of about 10 [4] or higher. This holds, however, only for equilibrium conditions which are readily attained in conventional liquid-liquid extraction due to the small phase to volume ratio and the vigorous mass transfer within the extraction funnel. In membrane-assisted microextraction the transport of analytes is a

Table 3. Concentration of trihalomethanes in Teufelspfuhl lake, Berlin.

| | [μg $l^{-1}$] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sample T1 | | | Sample T2 | | | Sample T3 | | | Sample T4 | | |
| Compound | Straight | Bag | LLE | Straight | Bag | LLE | Straight | Bag | LLE | Straight | Bag | LLE |
| $CHCl_3$ | 490 | 560 | 520 | 1850 | 1930 | 1870 | 190 | 255 | 220 | 145 | 190 | 170 |
| Median | | 523 | | | 1883 | | | 222 | | | 168 | |
| E rel (%) | −5.8 | +7.7 | | −1.1 | +3.1 | | −13.6 | +16 | | −14.7 | +12 | |
| $CHCl_2Br$ | 395 | 450 | 425 | 1490 | 1640 | 1560 | 125 | 165 | 140 | 120 | 155 | 135 |
| Median | | 423 | | | 1547 | | | 143 | | | 137 | |
| E rel (%) | −7 | +5.8 | | −4.5 | +5.1 | | −10.7 | +18 | | −11 | +15 | |
| $CHClBr_2$ | 300 | 375 | 330 | 1280 | 1380 | 1320 | 105 | 130 | 115 | 135 | 170 | 150 |
| Median | | 335 | | | 1327 | | | 117 | | | 1512 | |
| E rel (%) | −9 | +14 | | −3 | +4.5 | | −8.7 | +13 | | −10 | +13 | |
| $CHBr_3$ | 190 | 255 | 220 | 850 | 970 | 890 | 105 | 130 | 115 | 175 | 215 | 190 |
| Median | | 222 | | | 903 | | | 117 | | | 193 | |
| E rel (%) | −13.6 | +16 | | −4.5 | +8.9 | | −8.7 | +13 | | −7.9 | +13 | |

diffusion controlled process. Considering the distribution coefficients of the solvent-analyte systems investigated of about 10 [2] in combination with the diffusion controlled mass transfer it is expected that the extraction efficiency of the membrane assisted liquid-liquid microextraction in the parallel configurations investigated is smaller than in the classic LLE attaining equilibrium. Therefore, the influence of extraction time and the stirring rate were investigated for the straight hollow fibre configuration.

An initial concentration of 5μg $L^{-1}$ was used for all substances and configurations tested.

## 3.1 *Optimisation of the straight hollow fibre microextraction method*

### 3.1.1 *Influence of the temperature*

As analyte transfer within the membrane and the lumen is a diffusion controlled process, an increase of the sample temperature will improve analyte transfer. This was investigated for the polypropylene hollow fibre material. Figure 2 shows an increase of the specific extraction rate of analytes with higher temperature. The mass transfer improves and the thermal strain of the membrane material increases with higher temperatures, which lead to rates 2.5 to 6 times higher at 80°C compared to the rates at 20°C.

### 3.1.2 *Influence of the stirring rate*

The transport of the analytes from the water sample to the surface of the membrane can be stimulated through a mixing of the sample. During intensive stirring, or in a turbulent flow of the water sample, the mass transfer resistance in the fluid phase is smaller, and more analyte per time comes in contact with the membrane. It is also noticed that the time required for attaining equilibrium is shortened.

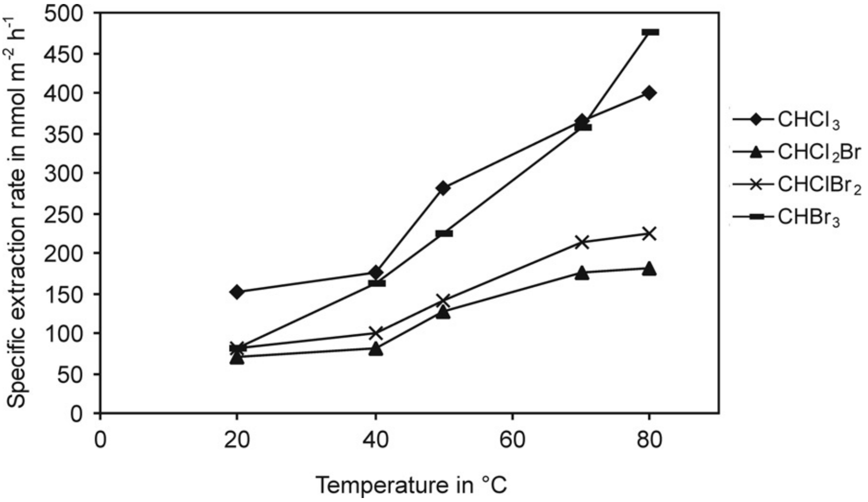

Figure 2. Influence of temperature on the specific extraction rate of the hollow fibre membrane extraction (config. A) for THM's, polypropylene membrane, o.d. = 2.7 mm, stirring rate 200 rpm, 60 min.

As shown in Figure 3 the efficiency of the membrane extraction of trihalomethanes increased with the stirring rate from 200 to 800 rpm.

The results are in concordance with the stirring rates applied by Schellin and Popp [21] for the analysis of VOCs in groundwater samples and demonstrate clearly the strong influence of the mixing intensity on the mass transfer. The results of the experiments performed above 800 rpm were unreproducible due to the enhanced evaporation of the volatile compounds.

### 3.1.3 *Performance parameters*

*Linear range and limit of detection*: In order to test the method and to calculate the extraction efficiency a calibration curve was obtained for the solvent used for extraction. *n*-octanol was selected as the extracting agent for the porous membranes (hollow fibre) while heptane was chosen for the non-porous membrane (bag configuration). Considering the enrichment factors and the phase volume ratios the efficiency of extraction as well as theoretical values for limit of detection (LOD) were calculated; the LOD was 0.03–0.05 $\mu g\,L^{-1}$ for all investigated components (see Table 4). The validation data are in the same range with those obtained with the purge and trap method presented by

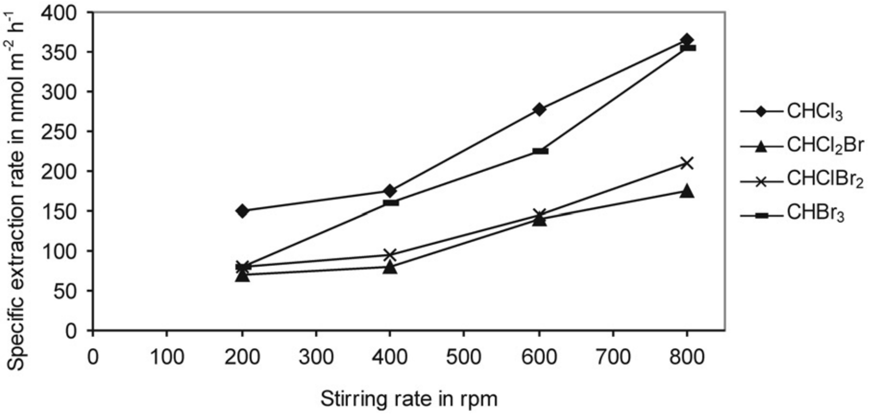

Figure 3. Influence of the stirring rate on the specific extraction rate of the hollow fibre membrane extraction (config. A), polypropylene membrane, o.d. = 2.7 mm, 60 min., 20°C.

Table 4. Linear range and limit of detection for the compounds determined with hollow fibre membrane extraction (config. A) and *n*-octanol as extracting agent at 20°C, 60 min and 800 rpm.

| Compound | LOD [$\mu g^{-1}$] | Linear range [$\mu g^{-1}$] | Correlation coefficient for linear range | Reproducibility RSD* [%] |
|---|---|---|---|---|
| Chloroform | 0.05 = 7 pg absolute | 1–100 | 0.996 | 7.2 |
| Dichlorobromomethane | 0.03 = 5 pg absolute | 1–100 | 0.998 | 8.3 |
| Chlorodibromomethane | 0.03 = 5 pg absolute | 1–100 | 0.998 | 8.9 |
| Bromoform | 0.04 = 6 pg absolute | 1–100 | 0.997 | 9.8 |

*RSD: Relative Standard Deviation = standard deviation related to the median value.

Zoccolillo *et al.* [22] and Campillo *et al.* [23] Comparison with the calibration curves obtained in the linear range showed good concordance with the calculated values. For all components the correlation coefficients were higher than 0.996.

*Reproducibility*: The reproducibility of the method was investigated by extracting five water samples spiked with $5\,\mu g\,L^{-1}$ individual components. A representative chromatogram is presented in Figure 4. The relative standard deviations of the batch membrane extraction for the organochlorine compounds investigated are summarised in Table 4. The area of the component peaks in the extract shows a standard deviation in the range of 7.2 to 9.8%. On this basis the technique is considered to be reliable in conditions of smaller quantities of sample and solvent.

## 3.2 *Comparison of the methods*

### 3.2.1 *Influence of extraction time*

The influence of extraction time at the optimised stirring rate (diminishing the thickness of the outer diffusion layer in the vicinity of the hollow-fibre membrane) was investigated. A typical result obtained is shown in Figure 5. Clearly stirring has a considerable influence but even with intense stirring it takes 2 hours to approach the distribution equilibrium. As expected, equilibrium was attained faster for the U shaped configuration in comparison to the straight hollow fibre configuration. This fact clearly demonstrates the diffusion controlled mass transfer within the membrane and the lumen, as the membrane thickness and the diameter of the U shaped membrane is 2 respectively 3 times smaller. For practical reasons extraction was interrupted for all further investigations after 60 minutes, and calibration was obtained in the same practical conditions.

An important observation was the effect of the gas volume above the liquid phase on the recovery of volatile trihalomethanes. This is obviously due to the fact that in the three phase system water-solvent-air, analyte distribution also occurs between the sample and the headspace. Therefore the headspace should be as small as possible and at least it must be warranted that it is unchanged during calibration and sample analysis.

Investigations with a U-shaped system ($CHCl_3$, *n*-octanol) resulted in a similar dependence of the extraction efficiency on the time [24]. The reduced efficiency of 15% achieved after 60 minutes is due to the diffusion controlled mass transfer without agitation.

### 3.2.2 *Influence of the phase-volume ratio*

The enrichment factor is the important measure for the sensitivity of the overall process for moderate partition coefficients and non-equilibrium systems. Therefore, the phase to volume ratio of the different systems was investigated ranging from $\theta = 20$ to 200.

In Table 5 the results are given for the three different extraction systems (20°C, stirring rate 800 rpm, $t = 60$ min) and the conventional LLE under optimised conditions. Clearly, the U-shaped hollow fibre configuration showed the highest enrichment factor of up to 124 for all compounds investigated. This is in concordance with the results obtained by Rasmussen *et al.* [25] in a similar experimental set-up for the preconcentration of drugs (up to 125). Further improvement is principally possible by using larger sample volumes and reduced amount of solvent. However, trials to realise this were met with burdens due to considerably prolonged extraction time and practical difficulties to recover the organic solvent. Although the performance of the U-shaped hollow fibre system in

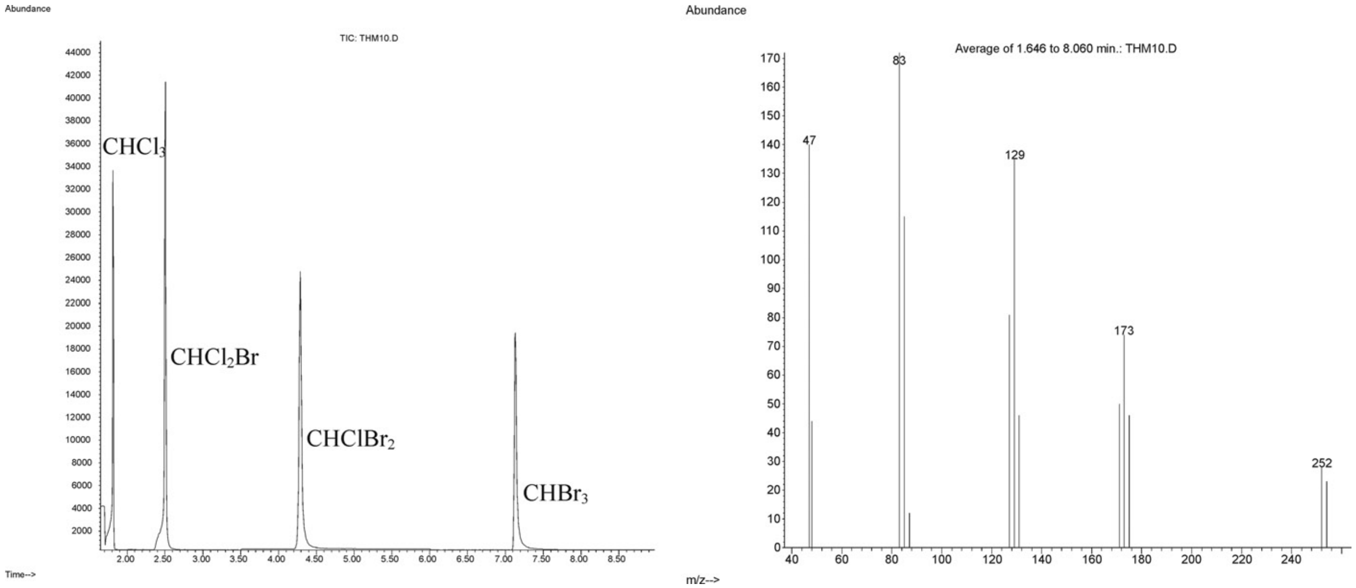

Figure 4. (left) GC-MS chromatogram of a water sample spiked with trihalomethane mixture containing 5 µg L$^{-1}$ individual components pre-concentrated with membrane assisted solvent extraction device. Hollow fibre material: polypropylene (config. A), phase to volume ratio: 1 : 60. (right) Selected ions in SIM mode for quantification: CHCl$_3$ 47, 83, 85; CHCl$_2$Br 83, 129; CHClBr$_2$ 129, 131; CHBr$_3$ 173, 252.

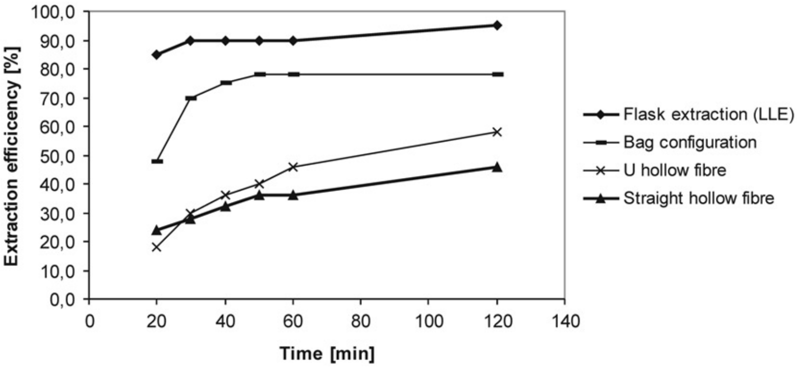

Figure 5. Dependence of extraction efficiency on extraction time for different experimental conditions at 20°C and 800 rpm for $CHCl_3$ as example.

Table 5. Extraction efficiencies (E) and enrichment factors (EF) for selected trihalomethanes using different extraction configurations.

| | U-shaped hollow fibre $\theta = 200$ | | Straight hollow fibre $\theta = 60$ | | Conventional flask extraction $\theta = 20$ | | Bag configuration $\theta = 25$ | |
|---|---|---|---|---|---|---|---|---|
| Compound | *E* (%) | *EF* | *E* (%) | *EF* | *E* (%) | *EF* | *E* (%) | *EF* |
| $CHCl_3$ | 46 | 92 | 36 | 21.6 | 90 | 18 | 78 | 23,4 |
| $CHCl_2Br$ | 62 | 124 | 58 | 34.8 | 95 | 19 | 85 | 25,5 |
| $CHClBr_2$ | 55 | 110 | 50 | 30 | 92 | 18.4 | 88 | 26,4 |
| $CHBr_3$ | 48 | 96 | 39 | 23.4 | 91 | 18.2 | 84 | 25,2 |

terms of enrichment is 3.5 to 4.2 times higher compared with the straight hollow fibre assembly, it is hardly applicable due to handling difficulties.

Significantly enhanced enrichment factors up to 3.3 were obtained in the present study in comparison to results recently presented by Vora-Adisak *et al.* [24] for the U-shaped configuration investigated under similar conditions. The predominant reason for the increased performance is the better mass transfer resulting from the optimised stirring (see Figure 3) and the extended extraction time (60/30 min). The influence of the temperature difference can be neglected as presented in Figure 2 (20/35°C).

The enrichment factor in the bag configuration was in the same order of magnitude as in the straight configuration. The extraction efficiency was higher but with the undesirable aspect of a 2.5 times higher specific solvent consumption. As expected, the conventional LLE achieved a medium performance with a high extraction efficiency and a small enrichment factor. Nevertheless, the required volume of solvent for the similar volume of sample was up to 10 times higher than in the miniaturised systems.

### 3.2.3 *Application to real samples – comparison liquid-liquid extraction-MS with headspace GC-ECD*

The miniaturised and the classic liquid-liquid extraction methods were applied for the analysis of four water samples of the Teufelspfuhl lake. Considering the optimised parameters, an extraction time of 60 minutes, a temperature of 20°C and a stirring rate equivalent to 800 rpm were applied for the membrane configurations.

The concentrations of trihalomethanes obtained from all three methods were in the same order of magnitude. The quantification was performed on the basis of the calibration curve in the range of 0.02 to $100\,\mu g\,L^{-1}$ for each component. The correlation coefficients varied between 0.9990 and 0.9999.

Generally, the concentrations determined with the liquid-liquid extraction compared to the membrane bag configuration (Figure 1c) were lower which is in concordance with the results obtained by Hauser and Popp [26] who analysed organochlorine compounds in groundwater samples. The explanation relies on the three steps necessary for liquid-liquid extraction (extraction, phase separation, drying) that increase the possibility of analyte losses. Additionally, the influences of the matrix interfere in the chromatogram of the final extract resulting in lower concentrations compared to the single step membrane bag configuration which rejects particles and most of the matrix influences. The extraction in the porous membrane configuration (Figure 1a) showed the lowest concentrations detected which can be explained by the sensitivity of the extraction time (see Figure 5). The mass transfer reduced by matrix effects resulted in lower extraction efficiencies for the same extraction time.

Generally, the deviation increased with decreasing concentration of the target components. For concentrations higher than $1000\,\mu g\,L^{-1}$ (see sample T2) the deviation from the median was below 9%, whereas 18% were achieved for concentrations lower than $300\,\mu g\,L^{-1}$ (see sample T3). Under the latter conditions the extraction was critical for all methods but the lowest concentrations resulted from the straight hollow fibre configuration which is due to incomplete extraction. The mass transfer limitations were resulting from the small membrane surface area, the thickness of the membrane, and the diffusion within the lumen. Although the extraction efficiency was almost complete in the classical LLE, the high consumption of extracting agent, the risk of emulsion formation, and a high background due to the matrix components are the main limitations of the method. This becomes obvious when considering that the highest concentrations among membrane devices were predominantly obtained with the bag membrane configuration. The disadvantage of the relatively high consumption of extracting agent was reduced with the introduction of the hollow fibre configuration which offers high enrichment factors up to 5.200 [27]. However, optimisation of the hollow fibre extraction method is required for mass transfer limited conditions in the lower concentration range.

## 4. Conclusions

Hollow fibre liquid-liquid microextraction (HFLLME) in its current format is certainly an interesting alternative to conventional liquid-liquid extraction with separatory funnels and also to single drop or thin film microextraction methods. Considerable reduction of solvent, no risk of formation of emulsions, improved enrichment factors (at least for analytes with high partition coefficients), and the increased robustness are striking attributes.

The optimisation of the straight hollow fibre configuration considered the temperature, stirring rate and the performance parameters. So, the increase of temperature from 20°C to 80°C leads to 2.5 to 6 times higher extraction rates. Better mass transfer conditions were achieved by enhancing the stirring rate from 200 to 800 rpm which resulted in 2 to 4 times higher specific extraction rates (e.g. up to 360 n mol m$^{-2}$ h$^{-1}$). Nevertheless, care has to be taken when volatile compounds are extracted, because of losses due to evaporation.

The linear range encompassed two orders of magnitude, between 1–100 μg l$^{-1}$, whereas the limit of detection was below 10 pg absolute amount. Reproducibility of the batch method lied between 7.2 and 9.8%.

The optimised method was compared with other microextraction methods (U-shaped hollow fibre, bag membrane) and the classical liquid-liquid extraction. The dynamic investigations revealed that the time necessary to achieve steady-state is longer for the hollow fibre configurations due to the reduced mass transfer. For practical reasons 60 minutes were chosen for all configurations.

The conventional LLE achieved a medium performance with a high extraction efficiency and comparatively a small enrichment factor. Nevertheless, the required solvent volume was up to 10 times higher than in the miniaturised systems which reached enrichment factors between 18 and 124. The enrichment factor in the bag configuration was in the same order of magnitude as in the straight configuration. The extraction efficiency was higher but with the undesirable aspect of a 2.5 times higher specific solvent consumption. Although the newly developed batch configuration showed a 3.5 to 4 times smaller enrichment factors than the U-shaped it unifies the advantages of the U-shaped geometry (pore diffusion, reduced length, small diameter for short diffusion pathways within the solvent) with the advantages of the bag configuration (easy handling and automation potential).

Applications to real samples showed a good concordance between the straight hollow fibre configuration and the two methods compared with a relative error below 9% for higher and until 18% for lower concentrations.

As the batch method supposes an extraction time in the order of many minutes to few hours, it is the automation of the extraction method in flow systems that offers the alternative for further development of miniaturised liquid-liquid extraction.

Future investigations should optimise the technique by applying thinner and better adapted membrane materials. As the mass transfer is essential for a high performance, the flow regimes at the inner and outer membrane surface have to be improved.

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