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Membrane-assisted solvent extraction of triazines and other semi-volatile contaminants directly coupled to large-volume injection–gas chromatography–mass spectrometric detection

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Abstract

A simple device was developed for in-vial liquid–liquid extraction using a polymer membrane (nonporous polypropylene) to separate an aqueous sample from an organic extractant. The membrane consisted of tubing with an internal diameter of 6 mm and a wall thickness of 0.05 mm, which was heat-sealed at the lower end and filled with 500 μl hexane. This membrane bag was incorporated into a conventional 20 ml headspace vial suitable for a multi-purpose sampler (MPS 2, Gerstel, Mülheim, Germany) directly interfaced to a gas chromatograph with a mass-selective detector. The sampler enabled the extraction vial to be mixed at a defined temperature with subsequent large-volume injection of the organic extract taken from the membrane bag. The method was evaluated using several triazines, 2,4-dichloroaniline, α-hexachlorocyclohexane and phenanthrene as model compounds. Extraction parameters such as temperature, agitation speed, and extraction time were optimised. Recoveries of 60–90% were achieved after 30 min extraction. By increasing the injection volume to 100 μl, detection limits of 1–10 ng/l were determined.

Keywords: Membrane-assisted solvent extraction; Extraction methods; Large-volume injection; Instrumentation; Triazines

1. Introduction

Liquid–liquid extraction (LLE) is still a widespread and versatile sample preparation technique for chromatographic analysis. The selectivity of enrichment can be chemically ''tuned'' to the analyte of interest by incorporating various specific reagents in the extraction media. In many standard methods, LLE is the prescribed extraction technique. LLE usually involves several steps that are difficult to automate. After extraction with relatively large volumes of toxic organic solvents, the extract often needs to undergo further clean-up. Subsequently, it has to be dried and evaporated to improve detection limits. The automation of liquid–liquid extraction has been achieved using continuous-flow systems, where the aqueous and organic phases are mixed as a segmented flow stream [1]. Extraction is usually carried out in a coil, followed by phase separation using a semipermeable membrane and the collection of the extract, which is then transferred to the gas chromatograph. Another way of partly automating LLE is ''in-vial'' extraction. This miniaturised liquid–liquid extraction is carried out in an autosampler vial, followed by centrifugation for phase separation and subsequent large-volume injection (LVI). As almost all the organic extract is submitted to GC

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analysis, low detection limits can be achieved and only a minimum of organic solvent is required for extraction [2]. Phase separation is often the critical point when interfacing LLE directly to chromatographic systems. Hydrophobic polymer membranes can be used to overcome these problems. An automated system for the on-line dialysis of biological samples directly connected to HPLC was presented by Turnell and Cooper [3]. Jönsson and Mathiasson introduced supported liquid membrane extraction as an enrichment technique for polar and ionizable analytes [4,5]. This technique is based on a three-phase system, with the organic phase being immobilized in the pores of a porous hydrophobic membrane sandwiched between two aqueous phases. The pH of the acceptor ensures ionization of the analytes, thus preventing them from passing back through the membrane. Adding specific carrier molecules to the porous membrane enables the selectivity of the extraction to be influenced [6]. Modules for supported liquid membrane extraction are usually constructed as flow systems, where the acceptor flow is directly interfaced to HPLC [7]. One modification of this technique is ''microporous membrane liquid–liquid extraction'', which uses an organic solvent as acceptor phase that fills the pores of a microporous PTFE membrane. A flow module using hexane as acceptor was directly coupled to a gas chromatograph via a retention gap and a retaining precolumn for the on-line analysis of local anaesthetics in blood plasma [8]. Norberg and Thordarsson [9] presented another miniaturized membrane extraction unit directly mounted on top of a gas chromatograph. This ''extracting syringe (Esy)'' consists of a porous polypropylene hollow fibre filled with organic solvent, while the aqueous sample is pumped above the exterior of the fibre. After a certain enrichment time the device can be pneumatically lowered to inject 20 μl of organic extract. The on-line coupling of membrane extraction units to analytical instruments poses the problem of controlling memory effects. In order to avoid this problem, Pedersen-Bjergaard and Rasmussen established a liquid-phase microextraction technique (LPME) based on a disposable porous polypropylene hollow fibre [10]. The fibre is filled with a μl volume of acceptor solution and placed in a small volume of biological sample within a 4 ml vial. The device is agitated and the extract is finally transferred to an autosampler vial. No memory effects occur, as each hollow fibre is used only once. Extraction is carried out off-line, but, because of the simplicity of the extraction devices, high sample throughput can be achieved by performing many extractions in parallel. The method has been applied to drug analysis in blood plasma and urine in combination with GC [11], HPLC, CE [12] and flow injection analysis (FIA)–MS–MS [13]. The use of nonporous membranes enables very complex samples to be handled. In a comparison of microporous polypropylene with homogenous silicone, similar enrichment factors were obtained for the extraction of chlorophenols from water prior to HPLC analysis [14]. When applying flat silicone membranes to enrich phenols from raw oil into aqueous sodium hydroxide or methanol, extracts could be transferred to HPLC without additional clean-up [15]. The system proved to be suitable for the extraction of phenols from fuel and kerosene as well [16]. A similar flow cell containing a porous polypropylene hollow fibre was utilized for the enrichment of triazines from edible oil into a methanolic acceptor stream directed towards a solid-phase extraction (SPE)–HPLC system [17]. The technique of membrane-assisted solvent extraction was introduced recently [18]. It is based on a small-scale LLE with a flat low-density polyethylene (LDPE) membrane separating the aqueous sample and the organic solvent. Like LPME, membrane-assisted LLE is carried out within a vial and off-line with subsequent transfer of the organic extract into an autosampler vial followed by large-volume injection. In the present work, the extraction device for membrane-assisted LLE was modified so that it could be fitted into a conventional 20 ml headspace vial. For this purpose a membrane probe consisting of heat-sealed tubing 6 mm wide was prepared from a flat nonporous polypropylene membrane with a thickness of 0.05 mm. This membrane bag was attached to a stainless steel funnel and placed inside the 20 ml glass vial into 15 ml of aqueous sample. The device can be handled by a commercial multi-purpose sampler which is capable of filling the membrane bag with 500 μl of organic solvent, then agitating it at a defined temperature and finally performing large-volume injection with the extract taken directly out of the membrane bag.

2. Experimental

2.1. Chemicals

Analytical grade methanol and hexane were supplied by Merck (Darmstadt, Germany). Bidistilled water was obtained from a Seralpur Pro 90C water system (Seral, Ransbach, Germany); alternatively, deionized water prepared from an ion-exchange cartridge was used. Sodium chloride and sodium hydroxide were procured from Merck. Individual standards of neat triazines, α-hexachlorocyclohexane (α-HCH), 2,4-dichloroaniline and phenanthrene were obtained from Supelco (Bellefonte, PA, USA).

2.2. Preparation of standards

Neat standard substances were dissolved in methanol to 1 μg/μl. Composite working standards at 0.05, 0.5, 5 and 50 ng/μl were prepared in methanol. For internal standardization, methanolic standards of simetryne at 50 ng/μl and pentachlorobenzene at 20 ng/μl were used. Simetryne was chosen as I.S. for the optimization of extraction parameters and directly added to the extraction solvent hexane. Pentachlorobenzene was used as I.S. for the calibration of membrane-assisted LLE and added to the aqueous sample before starting the extraction. The direct calibration of LVI–GC–MS was performed using composite standards of 1–500 pg/μl in hexane for 10 μl injection and 0.01–100 pg/μl for 100 μl injection. Aqueous standards for subsequent membrane-assisted LLE were prepared by diluting suitable aliquots of methanolic composite standards in 15 ml water, the methanol content not exceeding 0.2% (v/v). Usually, 5 g sodium chloride was added to each water sample to promote the extraction of triazines.

2.3. Membrane-assisted solvent extraction

The setup of the device used for membrane-assisted solvent extraction is shown in Fig. 1. The extraction cell consisted of a conventional 20 ml headspace vial with a membrane insert. Membrane bags were prepared by heat-sealing a flat polypropylene film 0.05 mm thick (Goodfellow, Cambridge, UK). For this purpose a flat membrane 8 cm long and 2.5 cm wide was wrapped around a heat-resistant film 1 mm thick, 8 mm wide and 8 cm long. The first heat-sealing generated a longitudinal weld, resulting in a tubing of 8 cm length. Then two membrane bags were obtained by generating two vertical welds and cutting the tubing between them.

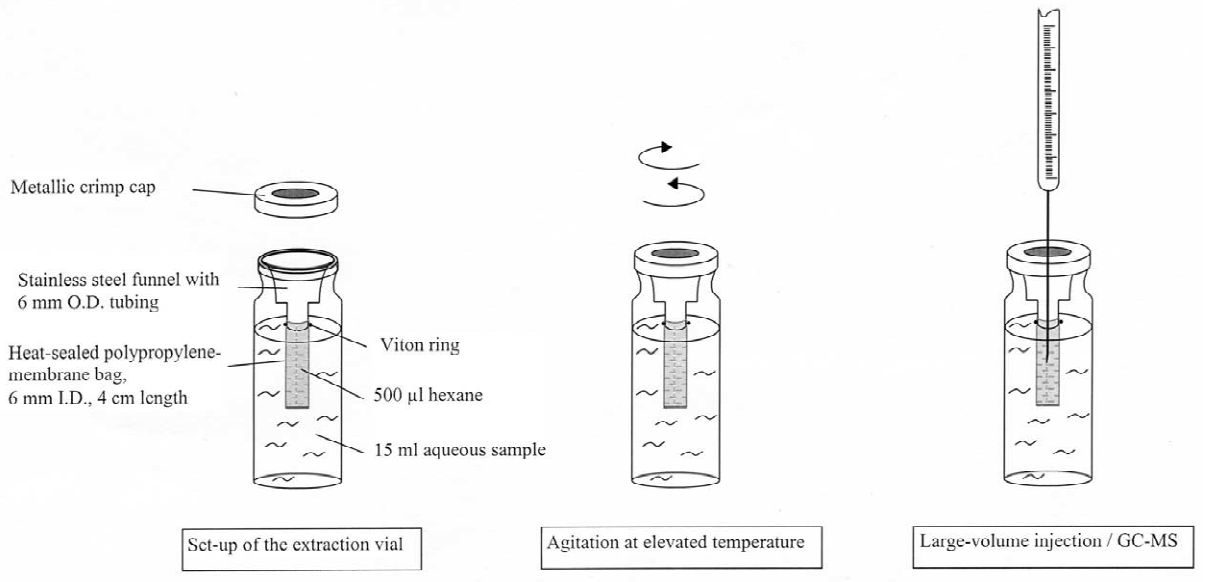

Fig. 1. Experimental setup for membrane-assisted solvent extraction.

For conditioning, eight to 10 membrane bags were extracted three times with 50 ml hexane at room temperature. The vial was filled with 15 ml of aqueous sample. The membrane bag was attached to the metal funnel, fixed with a viton ring, and the funnel was suspended in the opening of the vial. Subsequently, the membrane bag was filled with 500 μl hexane, 1 μl of the internal standard simetryne was added, and the vial was closed with a metallic crimp cap. Extraction vials were placed in the agitator of the multi-purpose sampler and orbitally shaken at a defined temperature. After the preset extraction time, the vials were magnetically removed from the agitator by the sampler and transported to the sample tray. Organic extracts were taken from the membrane bags manually by a microliter syringe and transferred to 2 ml autosampler vials. This not-fully-automated procedure was chosen because, when the study was performed, the software of the multi-purpose sampler did not allow the sequential automated membrane-assisted LLE of several samples, but only a single-shot procedure.

2.4. LVI–GC–MS

All analyses were performed using an HP 6890 Series gas chromatograph equipped with a mass-selective detector HP 5973 (Agilent Technologies, Waldbronn, Germany). The gas chromatograph was fitted with an HP5-MS capillary column, 30 m×0.25 mm I.D., 0.25 μm film thickness (Agilent Technologies). Helium 6.0 was used as carrier gas at a flow-rate of 1 ml/min (constant flow); the initial column head pressure was set to 53 kPa. The GC oven temperature programme was as follows: 50 °C for 2 min, 10 °C/min to 160 °C, hold for 1 min, 3 °C/min to 200 °C, hold for 1 min, 10 °C/min to 250 °C, hold for 2 min. The mass-selective detector was operated at 70 eV with electron impact ionization. The transfer line was set to a temperature of 280 °C, the quadrupole to 150 °C and the ion source to 230 °C. The mass-selective detector was operated in full-scan mode for ion selection and determination of background (30–350 u) and in single ion monitoring for quantification. The following time windows and diagnostic ions were used: ions m/z 161, 162 for 2,4-dichloroaniline from 10 to 16.5 min; m/z 181, 219 for α-HCH from 16.5 to 18.1 min; m/z 201, 210, 200, 214 for simazine, prometone, atrazine and propazine from 18.1 to 19.1 min; m/z 178 for phenanthrene from 19.1 to 21.8 min; and m/z 213, 227, 241, 226 for simetryne, ametryne, prometryne and terbutryne. When using pentachlorobenzene as internal standard, an additional time window from 13.5 to 16.5 min with m/z 250, 252 was included.

Large-volume injections were carried out using the multi-purpose sampler MPS 2 (Gerstel) with a 10 μl syringe set at an injection speed of 1 μl/s. The injection volume was 10 μl; only for validation data was it increased to 100 μl using a 100 μl syringe. The injection system consisted of a septumless head and a temperature-programmable injector (cooled injection system CIS 4, Gerstel) equipped with an empty baffled deactivated glass liner. During large-volume injection the inlet temperature was held at 20 °C by cooling with liquid nitrogen, while the column head pressure was reduced to 5 kPa and the flow-rate through the split vent was set to 100 ml/min in order to purge out most of the solvent. At a vent end time of 0.08 min, the split valve was closed for 1.5 min. The temperature programme of the injector started just after injection was finished and was chosen as follows: 20 °C for 0.12 min, 12 °C/s to 250 °C, hold for 1 min, 12 °C/s to 330 °C, hold for 3 min.

2.5. Validation of the method

All optimization data were based on peak area measurements versus the peak area of the internal standard simetryne. Every data point was recorded in duplicate; the average of the resulting extraction yields is given. The extraction yields were calculated by spiking the same amount and volume of methanolic composite standard used for preparation of aqueous standards directly in 500 μl hexane. Membrane-assisted solvent extraction was calibrated by extracting each 15 ml aqueous standard saturated with 5 g NaCl (333 g/l) containing 0.1–100 μg/l (subsequent 10 μl injection) or 0.005–10 μg/l (subsequent 100 μl injection) of each analyte and 1.3 μg/l pentachlorobenzene as internal standard. After extraction, 10 or 100 μl of the hexane extract was injected and analysed. To determine the detection limits, the mean ($\bar{w}$) and the standard deviation (σ) of six blanks (extraction of bidistilled water) were measured at the retention time of each analyte and

the detection limit was defined as the peak area corresponding to $\overline{w} + 3\sigma$. The reproducibility of the extraction was determined by the five-fold extraction of an aqueous standard containing 6.7 μg/l of each compound.

Membrane bags could be reused after three-fold extraction with hexane at room temperature. This procedure ensured the removal of memory effects and decreased the amount of interfering alkanes, esters and phthalates originating from the membrane material. For this reason, reusing membrane bags proved to be superior to using new ones.

2.6. LLE of river water

In order to compare the quantitative results of membrane-assisted LLE with an in-vial LLE without membrane, 15 ml of river water was spiked to 1 and 5 μg/l with each analyte and 1.3 μg/l pentachlorobenzene as I.S. within a 20 ml headspace vial. A volume of 1 ml hexane was added, the vial was closed with a magnetic crimp cap and then orbitally shaken at 750 rpm and 35 °C in the agitator of the MPS 2 for 30 min. The organic layer was then carefully withdrawn by a microliter syringe and transferred to an autosampler vial. Large-volume injection and GC–MS analysis were performed as described in Section 2.4 with an injection volume of 100 μl. For calculation of the content of spiked river water a direct calibration of LVI–GC–MS using composite standards in hexane and an injection volume of 100 μl was performed.

3. Results and discussion

3.1. Membrane-assisted solvent extraction

In membrane-assisted solvent extraction, hydrophobic organic compounds are extracted through a dense polypropylene membrane into a small volume of organic solvent. Polypropylene (PP) was chosen as membrane material because of its known chemical resistance to most organic solvents. In a previous study [18], LDPE was successfully applied to the extraction of organochlorine compounds with subsequent GC–electron-capture detection (ECD) analysis of the extracts. The use of an MSD for detection now revealed a higher amount of matrix compounds—such as higher alkanes, esters and phthalates—to be coextracted from LDPE than from PP. Another advantage of PP for the application presented here is its stiffness, ensuring that the shape of the membrane bag remains stable during agitation. The organic solvent should have a low solubility in water in order to minimize solvent losses via passage through the membrane. At the same time it has to be sufficiently volatile to be effectively removed via the split outlet during large-volume injection. Analyte enrichment occurs firstly due to the lower volume of the organic solvent (500 μl) in relation to the sample volume (15 ml), and secondly in the insert liner of the GC–MS due to large-volume injection.

3.2. Optimization of extraction parameters

3.2.1. Influence of matrix compounds

The impact of salt, an increased methanol content and a basic pH on membrane-assisted solvent extraction can be seen in Table 1. As triazines are relatively polar analytes, the saturation of the aqueous sample with salt proved to be very effective in increasing the extraction yield of triazines in membrane-assisted LLE. The salting-out effect was most pronounced for triazines with a relatively high water solubility. By contrast, the addition of salt slightly reduced recovery for the non-polar compounds α-HCH and phenanthrene. The increase in the methanol content to 6.66% (v/v) did not have any significant impact on the extraction of most compounds compared to an aqueous sample without additives except for *s*-triazines, where a decrease in recovery of 10–20% was observed. In this case the higher methanol content seems to have increased the solubility of the analytes in the aqueous sample. The p*K* values of triazines range from 1.6 (simazine) to 4.3 (prometone). For this reason the pH of the aqueous sample should be above 6 to ensure the neutrality of the analytes. A further increase in the pH to 8 by adding sodium hydroxide did not improve the extraction yield of any compound. According to these results the saturation of the aqueous samples with salt (5 g NaCl per 15 ml water) was included in all subsequent extractions.

Table 1
Influence of matrix compounds on extraction yield of membrane-assisted solvent extraction (spiked to 6.7 μg/l each compound, extraction time 1 h, 35 °C, 750 rpm, injection volume 10 μl)

Compound	Extraction yield (%)			
	Spiked in pure water	333 g/l NaCl added	6.6% (v/v) MeOH added	Adjusted to pH 8
2,4-Dichloroaniline	66.1	90.6	58.5	68.2
α-HCH	107.6	96.2	104.5	69.2
Simazine	1.7	30.3	1.5	1.5
Prometone	6.4	74.5	5.0	4.5
Atrazine	5.0	69.4	3.9	4.5
Propazine	16.7	85.1	10.7	14.1
Phenanthrene	107.1	92.9	103.4	107.6
Ametryne	21.4	94.5	14.8	19.1
Prometryne	54.8	85.9	38.1	48.9
Terbutryne	76.0	89.3	57.9	71.2

3.2.2. Optimization of agitation speed

To facilitate the transport of analytes through the membrane into the organic solvent, the efficient mixing of the sample and the minimization of boundary layers around the membrane bag are necessary. The agitation speed of the MPS 2 was varied from 250 to 750 rpm. From 250 to 500 rpm a distinct increase in extraction yield of 30–50% was observed for all compounds, which then weakened from 500 to 750 rpm. The mixing effect was more important for triazines than for the nonpolar compounds α-HCH and phenanthrene. Consequently, the maximum agitation speed of 750 rpm of the MPS 2 was chosen for all further experiments.

3.2.3. Optimization of temperature

The agitator of the MPS 2 can be operated at a defined temperature. Without cryocooling, which was not installed in the agitator used for this study, the lowest temperature possible is 35 °C. Increasing the extraction temperature from 35 to 55 °C during agitation improved the recovery of all compounds by about 10–30%. This effect was again more pronounced for triazines with a higher water solubility than for 2,4-dichloroaniline, α-HCH and phenanthrene. As the boiling point of hexane is 69 °C, temperatures higher than 55 °C were not tested. The application of elevated temperatures can lead to solvent losses if the vial is not absolutely tight. Due to excessive pressure after agitation at 55 °C, the extract has to be withdrawn carefully using several syringe pumps. To ensure optimal extraction yield, the validation data for subsequent 10 μl injection were acquired using an extraction temperature of 55 °C.

3.2.4. Optimization of extraction time

The time profile of membrane-assisted solvent extraction under optimized conditions (55 °C, 750 rpm, 333 g/l NaCl) is shown in Fig. 2. An increase in the extraction time resulted in higher enrichment of all compounds from 10 to 30 min. Further prolongation failed to further improve extraction yields. After 30 min, recoveries of 60–100% were obtained; consequently, extraction equilibrium was reached after this relatively short time. Hence, an extraction time of 30 min was chosen for the acquisition of validation data.

3.3. Validation of the method

The performance of membrane-assisted solvent extraction was evaluated under optimized extraction conditions; the validation data are listed in Table 2. When using an injection volume of 10 μl, the extracted amounts of the selected analytes were linear in the range 0.05–100 μg/l with correlation coefficients of 0.9965 or better. Detection limits of 10–100 ng/l were achieved after an extraction time of only 30 min. Hence, the requirements of the German drinking water decree [19] (0.1 μg/l for individual pesticides) as well as the recommendations of the World Health Organization (WHO) for drinking water [20] (2 μg/l atrazine and simazine)

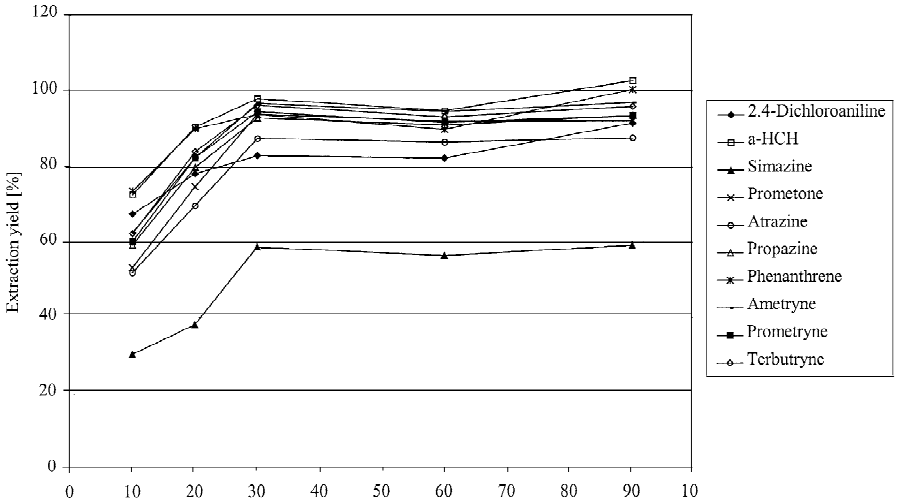

Fig. 2. Optimization of extraction time (6.7 μg/l each compound, 333 g/l NaCl, 55 °C, 750 rpm, injection volume 10 μl). *x*-Axis: extraction time in minutes.

were met. Detection limits were restricted by blanks from coextracted matrix components originating from the heat-sealed polypropylene membrane bag. These coeextracted compounds were also registered in the single ion monitoring data acquisition mode and became more important when the injection volume was increased to 100 μl. A chromatogram of an extract obtained after membrane-assisted solvent extraction of water spiked to 50 ng/l is shown in Fig. 3, demonstrating the high background resulting from a 100 μl injection, which reduced the accuracy of peak integration at lower concentrations. The whole extraction procedure proved to be well reproducible. The relative standard deviation of five consecutive extractions varied from 2.1 to 13.3%. In order to further improve detection limits, a final injection volume of 100 μl extract was chosen. This resulted in detection limits of 1–10 ng/l and a linear

Table 2
Validation data for membrane-assisted solvent extraction

Compound	10 μl injection[a]				100 μl injection[b]		
	Reproducibility[c], 30 min extraction, RSD (%, $n=5$)	Detection limit (ng/l)	Linear dynamic range (μg/l)	Correlation coefficient (R^2)	Detection limit (ng/l)	Linear dynamic range (μg/l)	Correlation coefficient (R^2)
2,4-Dichloroaniline	2.1	10	0.05–100	0.9971	5	0.005–5	0.9971
α-HCH	5.2	25	0.05–100	0.9987	10	0.01–10	0.9990
Simazine	10.4	100	0.1–100	0.9999	5	0.005–10	0.9942
Prometone	13.3	50	0.1–100	0.9965	5	0.005–10	0.9987
Atrazine	8.4	50	0.1–100	0.9991	1	0.005–10	0.9979
Propazine	11.9	50	0.1–100	0.9984	5	0.005–10	0.9994
Phenanthrene	3.7	10	0.05–100	0.9990	1	0.1–10	0.9998
Ametryne	10.7	50	0.1–100	0.9981	5	0.005–10	0.9993
Prometryne	14.3	50	0.1–100	0.9998	5	0.005–10	0.9970
Terbutryne	13.1	50	0.1–100	0.9993	5	0.005–10	0.9973

[a] Extraction time 30 min, 333 g/l NaCl, 55 °C, 750 rpm.
[b] Extraction time 1 h, 333 g/l NaCl, 45 °C, 750 rpm.
[c] 6.7 μg/l each compound.

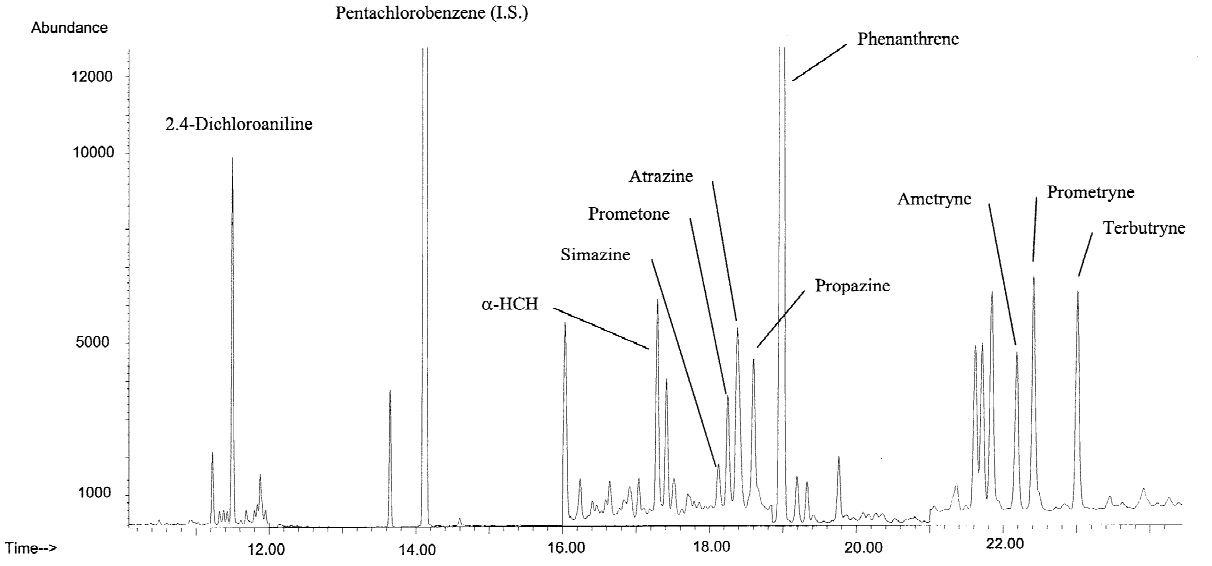

Fig. 3. Single ion monitoring chromatogram of LVI–GC–MS after membrane-assisted solvent extraction of 15 ml water spiked to 0.05 μg/l with each compound (extraction time 1 h, 333 g/l NaCl, 45 °C, 750 rpm, injection volume 100 μl). Time scale in minutes.

dynamic range of 0.005–10 μg/l with correlation coefficients of 0.9970 or better. The validation data showed that the semi-automated membrane-assisted LLE can be used as a reliable sample preparation technique for aqueous samples.

The use of an injection volume of 100 μl enables the step of solvent addition into the membrane bag to be integrated into the automatic procedure. In this case, the sampler can be equipped with a 1000 μl syringe, which can be used both for the precise addition of 500 μl hexane and after agitation for large-volume injection of 100 μl extract.

3.4. Comparison of membrane-assisted solvent extraction and in-vial extraction

The results of membrane-assisted solvent extraction were compared to an in-vial extraction of spiked river water (Table 3). The water sample was taken from the River Weisse Elster in Leipzig and spiked to 1 and 5 μg/l using methanolic composite standards. The content of spiked river water extracted by membrane-assisted LLE was calculated on the basis of a calibration using aqueous standards (0.001–10 μg/l) extracted under the same conditions as river water. In-vial LLE was performed according to Section 2.6. Recoveries of in-vial LLE were about 100%. The withdrawal of the organic extract proved to be difficult because the organic layer was very thin and the phase boundary was disturbed by particles. Therefore, for the automation of in-vial LLE, at least 4 ml hexane would have to be used to ensure clear phase separation and to enable the withdrawal of the extract by the sampler without risking the injection of water. This would decrease detection limits by a factor of eight compared to membrane-assisted solvent extraction. However, the analytical accuracy of in-vial LLE was better than that of membrane-assisted LLE, as can be seen from Table 3. The average deviation of the analytical result from the spiked concentration value was 12.4% for in-vial LLE of river water spiked to 1 μg/l and 23.9% for membrane-assisted solvent extraction. Membrane-assisted solvent extraction proved to be easier to perform; as an injection volume of 100 μl was used, some extractions could be carried out completely automatically (with solvent disposal, agitation and injection performed by the sampler). As a relatively high background originating from coextracted membrane components was registered, especially when using the full-scan mode, the preconditioning of membrane bags needs to be further optimized. Another possibility for reducing the amount of coextracted matrix is to use membrane

Table 3
Analytical results (μg/l) for spiked river water—comparison of membrane-assisted LLE and in-vial LLE

Compound	River water spiked to 1 μg/l		River water spiked to 5 μg/l	
	Membrane LLE[a] (μg/l)	In-vial LLE[b] (μg/l)	Membrane LLE[a] (μg/l)	In-vial LLE[b] (μg/l)
2,4-Dichloroaniline	0.98	1.67	4.34	6.7
α-HCH	1.18	1.33	6.04	5.68
Simazine	1.28	0.85	5.83	3.49
Prometone	1.30	1.05	6.31	4.51
Atrazine	1.33	1.07	6.10	4.53
Propazine	1.31	1.11	6.22	4.71
Phenanthrene	1.07	1.10	6.29	4.76
Ametryne	1.29	1.12	6.32	4.84
Prometryne	1.36	1.12	6.45	4.70
Terbutryne	1.25	1.10	6.23	4.69
Average of deviation from spiked concentration level (%)	23.9	18.2	22.9	12.4

[a] Extraction time 1 h, 333 g/l NaCl, 45 °C, 750 rpm, 1.3 μg/l pentachlorobenzene as I.S. in water.
[b] Extraction time 30 min, 333 g/l NaCl, 45 °C, 750 rpm, 1.3 μg/l pentachlorobenzene as I.S., 1 ml hexane as extraction solvent; injection volume 100 μl.

bags with a thinner wall. The precision of the analytical results could probably be improved by using standardized membrane bags with exactly the same size and surface.

4. Conclusions

The incorporation of a laboratory prepared polypropylene membrane bag in a conventional 20 ml headspace vial enables the complete automation of membrane-assisted solvent extraction by using a multi-purpose sampler capable of the disposal of the extraction solvent into the membrane bag, agitation of the vial at a defined temperature and subsequent large-volume injection. The method is a promising enrichment technique for various organic compounds, including more polar analytes such as triazines. Under optimized extraction conditions, extraction yields of 60–100% were obtained even for triazines after 30 min extraction. This resulted in detection limits in the low ng/l range. The exclusion of water, particles and macromolecular compounds from the organic extract by means of nonporous polypropylene makes membrane-assisted LLE particularly suitable for complex samples high in organic matter. Especially, applications in food and bioanalysis seem to be highly favorable. The method can also be interfaced to HPLC by choosing a water-miscible solvent such as acetonitrile. These polar solvents do not wet the surface of the membrane bag and cannot pass into the aqueous sample. The development of new software for the MPS 2 now also enables the automation of a sequence of membrane-assisted solvent extractions, thus increasing sample throughput and minimizing time for sample preparation. The whole technique is currently being commercialised (Gerstel, Mülheim, Germany).

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