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Determination of organophosphorus pesticides using membrane-assisted solvent extraction combined with large volume injection–gas chromatography–mass spectrometric detection

Manuela Schellin[a,*], Barbara Hauser[b], Peter Popp[a]

[a] *Department of Analytical Chemistry, UFZ-Centre for Environmental Research, Permoserstrasse 15, 04318 Leipzig, Germany*
[b] *Bruker-Daltonik, Fahrenheitstrasse 4, 28359 Bremen, Germany*

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Abstract

Eight organophosphorus pesticides (parathion-methyl, fenitrothion, malathion, fenthion, bromophos, bromophos-ethyl, fenamiphos and ethion) in aqueous samples were analysed by means of membrane-assisted solvent extraction. First a 20 ml extraction vial was filled with 15 ml of aqueous sample. Then the membrane bag consisting of nonporous polypropylene was put into the vial and filled with 800 μl of organic solvent. The analytes were separated from the aqueous layer by transporting them through the membrane material into the small amount of solvent. The technique was fully automated and successfully combinable with large volume extraction and GC–MS. To achieve an optimum performance several extraction conditions were investigated. Cyclohexane was chosen as acceptor phase. Then the impact of salt, methanol, pH value, as well as working parameters like stirring rate of the agitator and extraction time, were studied. Moreover, the influence of matrix effects was examined by adding different concentrations of humic acid sodium salt. Detection limits in the ng/l level were achieved using large volume injection with the injecting volume of 100 μl. The recovery values ranged from 47 to 100% and the relative standard deviation for three standard measurements was between 4 and 12% (except for bromophos-ethyl: 22%). The linear dynamic range was between 0.001 and 70 μg/l. The applicability of the method to real samples was tested by spiking the eight organophosphorus pesticides to red wine, white wine and apple juice samples.

Keywords: Membrane-assisted solvent extraction; Extraction methods; Large-volume injection; Matrix effects; Wine; Fruit juices; Food analysis; Organophosphorus compounds; Pesticides

1. Introduction

Nowadays, besides carbamates and pyrethroids, organophosphorus compounds are the most applied pesticides in agriculture. They cause a non-reversible phosphorylation of esterases in the central nervous system of insects and mammals and act as cholinesterase inhibitors [1,2]. The usage of organophosphorus pesticides (OPPs) is preferred to the usage of other pesticides such as, for example, organochlorine compounds, because organophosphorus pesticides degrade much faster in the environment. Hence, there is an increasing demand for developing methods for the determination of such contaminants in food analysis and environmental analysis. For the analysis of OPPs in environmental samples preparation steps are required in order to isolate the analytes from complex matrices, remove interfering compounds and achieve a sufficient sensitivity. The European Union (EU) set the maximum level to a concentration of 0.5 μg/l for the sum of all pesticides and to a concentration of 0.1 μg/l for a single compound. Therefore, the analytical methods need to achieve detection limits below 0.1 μg/l [3].

Sample preparation methods like liquid–liquid extraction (LLE) and solid phase extraction (SPE) have been recently amended by newer, solvent-free or solvent-reduced methods. The technique of solid-phase microextraction (SPME) combined with chromatographic systems for analyzing organic compounds in water samples has become more and more popular [4]. SPME has been used for determining pesticides in the environment, for instance in natural water samples [5–8], in white wine [9,10], in fruit samples (strawberries and cherries) [4], in cucumber [11], and in honeybees [12]. The detection limits range from the μg/l to the ng/l level. Stir bar sorptive extraction (SBSE) is another new sorp-

* Corresponding author. Fax: +49-341-2352625.
E-mail address: manuela.schellin@ufz.de (M. Schellin).

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tive technique which has been applied to pesticides in water samples [13,14]. Due to a larger volume of coating material (polydimethylsiloxane) in comparison to SPME, detection limits in the low ng/l range can be reached for volatile and semivolatile compounds [15].

Membranes can also be employed as a selective barrier between two phases in sample preparation [16]. The separation is achieved when some components are transported to a greater extent than others from a donor phase through the membrane into an acceptor phase. When porous membranes are used the separation is based on the size of the molecule only. Sufficiently small molecules can permeate through the membrane material and molecules which are larger than the pore size of the membranes are retained in the donor phase.

This work presents the method of membrane-assisted solvent extraction. Since the system is combined with large volume injection–gas chromatography–mass spectrometry, the use of dense membrane material is favored in order to exclude any traces of water in the organic phase. When non-porous polymers are applied, the efficiency of the transport for a particular analyte depends strongly on its partition coefficient between the different parts of the membrane system (donor phase, membrane material, acceptor phase). The organic analytes in the aqueous phase are dissolved in the membrane material and diffuse through the polymer into the acceptor solvent, hence the selectivity can be influenced by choosing appropriate membrane materials and organic acceptor phases [17,18].

Membrane-assisted solvent extraction was successfully used for the determination of chlorobenzenes, triazines and polychlorinated biphenyls [19–21]. A big advantage of this fully automated technique is the exclusion of salt and particles. Since formation of emulsion—a problem of liquid–liquid extraction—does not occur a clear phase separation is achieved. The analytes are enriched by the transfer into a small organic volume and additionally in the inlet of the gas chromatograph during large volume injection (LVI). When LVI is used, the differences between the boiling point of the solvent and the boiling point of the most volatile analyte should be about 150 °C. The boiling points of the OPPs range between 109 °C (parathion-methyl) and 165 °C (ethion) and, therefore, this criteria could not be fulfilled. Nevertheless, LVI was applied although losses of the analytes were expected during the first step of large volume injection when the split valve is opened and the solvent is removed. The purpose of this work was to optimize the membrane-assisted solvent extraction in combination with LVI–GC–MS for OPPs in water, juice and wine samples.

2. Experimental

2.1. Chemicals and standards

Parathion-methyl, fenitrothion, malathion, fenthion, bromophos, bromophos-ethyl, fenamiphos and ethion were obtained from Riedel-de Haen (Seelze, Germany). Reagent water for optimization and validation consisted of deionised tap water. The internal standard parathion-([$^2H_{10}$]diethyl) was supplied from Promochem (Wesel, Germany). A stock solution in water was prepared with a concentration of 100 μg/l for each compound and diluted to a concentration of 1 μg/l for each OPP. Different volumes of the undiluted and diluted stock solution with concentrations in the range of 1 ng/l–70 μg/l were prepared for calibration. An appropriate amount of internal standard was added to each sample to give a final concentration of 3 μg/l.

2.2. Samples

Spanish red wine “La Corrida” (Baron Pilars de Pilar, Weinkellerei GmbH, Bernkastel-Kues, Germany), German white wine “Müller Thurgau” (Rheinsberg Kellerei GmbH Bingen, Germany) and apple juice (Libehna Fruchtsaft, Raguhn, Germany) were bought in a supermarket. The samples were analyzed before spiking. All samples were kept in darkness at 10 °C.

2.3. Membrane-assisted solvent extraction

The device of membrane-assisted solvent extraction produced by Gerstel (Mühlheim, Germany) is shown in Fig. 1. The extraction cell consists of a conventional 20 ml headspace-vial and is filled with 15 ml of the aqueous sample. The membrane bag is 4 cm long, has a thickness of 0.03 mm and an i.d. of 6 mm. It is attached to a metal funnel and fixed with a PTFE ring. The material of the membrane bag is dense polypropylene. This synthetic solid polymer is resistant to most organic solvents and stays stable during agitation. The membrane bag is placed into the vial which is then closed with a metallic crimp cap. All further steps are carried out automatically with the multi purpose sampler (MPS 2, Gerstel). The membrane bag is filled with 800 μl of organic solvent and transferred into an agitator. After the optimized agitation time, the organic phase is withdrawn with a syringe from the membrane bag and transferred to a 2 ml autosampler vial. Then large volume injection is performed.

2.4. Apparatus

Chromatographic analyses were performed on an HP 6890 gas chromatograph with an HP 5973 mass selective detector (Agilent technologies, Waldbronn, Germany) equipped with an MPS 2. Large volume injection was carried out with a temperature-programmable injector (CIS 4, Gerstel) provided with a septum-less head. Hundred microlitres of the extracted sample were injected with a 1000 μl syringe. The injection speed was optimized to 0.8 μl/s. During large volume injection the inlet temperature was maintained at 45 °C by cooling with liquid nitrogen.

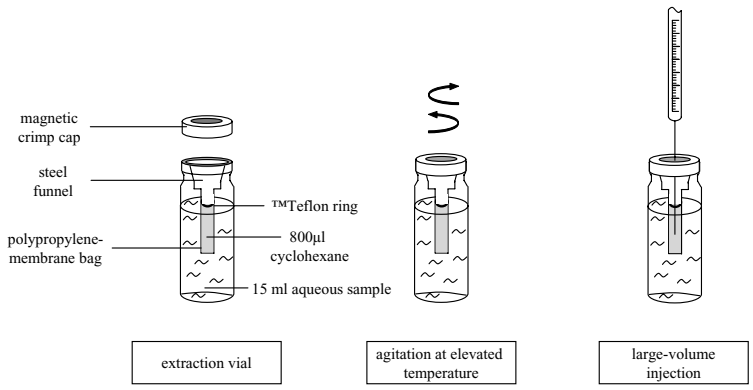


Fig. 1. Device of membrane-assisted solvent extraction.

The vent pressure was reduced to 5 kPa and the split vent was set to 100 ml/min. After 4.8 s the split valve was closed for 1.6 min and the liner was heated at a rate of 12 °C/s to 280 °C. This temperature was held for 1 min, then the spilt valve was opened and heating was continued with 12 °C/s to a final temperature of 330 °C (cleaning step). Separation was carried out with a 30 m × 0.25 mm, 0.25 μm fused silica column (SPB 5, Supelco, Bellefonte, PA, USA). Helium was used as carrier gas at a flow rate of 1 ml/min (constant flow) and an initial pressure of 53 kPa. The oven temperature program was as follows: 100 °C (1 min), 5 °C/min to 180 °C (3 min), 8 °C/min to 280 °C. The ion source temperature of the mass selective detector was set to 230 °C, the quadrupole to 150 °C and the transfer line was kept at 280 °C. The MS operated at 70 eV with electron ionization. Samples were analyzed in the full scan mode (35–400 u) for ion selection and determination of the background and in single ion monitoring mode (SIM, Table 1) for optimization and quantification.

2.5. Method validation

For optimization an aqueous standard spiked at a concentration of 1 μg/l was used and 100 μl of the organic extract were injected. The extraction temperature was set at 45 °C for all experiments. The extraction yields were calculated by spiking the same amount of each analyte used for preparation of aqueous standard directly into 800 μl of organic solvent. The precision was measured by a threefold extraction using three different membrane bags. The calibration graphs were based on the peak areas of the analytes versus the peak area of the internal standard parathion-([$^2H_{10}$]diethyl). The detection limits were determined by measuring blank samples (reagent water) six times. The mean and the standard deviation of the peak area at the retention time of each analyte were determined and the detection limit was defined as the concentration corresponding to the mean plus three times the standard deviation. Every data point was recorded in triplicate.

3. Results and discussion

3.1. Optimization of the working parameters

3.1.1. Comparison of different types of liners

When injecting a large amount of a liquid sample into a cold injection system it can happen that droplets of the sample fall through the liner and are removed through the split outlet. To overcome this problem, empty baffled glass liners can be used. The baffles which are arranged on one half off the liner extend the surface and lead to a better adhesion of the compounds during LVI. The liner has to be installed with the baffles pointing into the direction of the insert in order to ensure the contact of the syringe with the liner. Such liners are commercially available (Gerstel). During the above-mentioned application the liners were compared with self-made continuously baffled liners which have even a larger surface area. Except for fenamiphos, the enrichment of the analytes was in average about 10% greater when the continuously baffled liners were used. Therefore, they were used in all further experiments.

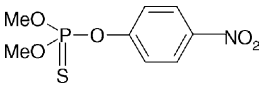
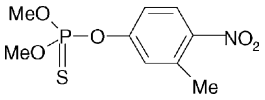
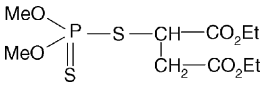
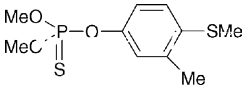
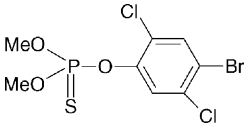
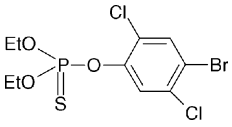
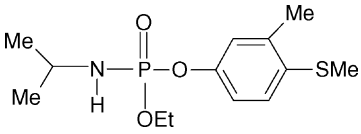
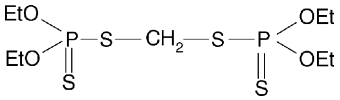
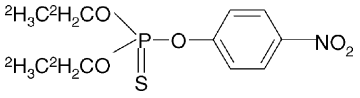
3.1.2. Preconditioning of the membrane bags

Before application the membrane bags underwent a twofold extraction with hexane in order to reduce interfering substances in the chromatogram which were coextracted from the membrane material. Despite this cleaning, alkanes and phthalates were found in the chromatogram when scan mode was applied (Fig. 2). However, when the SIM mode was used, the interfering compounds did not affect the analysis. In a former work it had been shown that after cleaning with hexane polypropylene membrane bags can be reused up to seven times without losing efficiency [21].

3.1.3. Optimization of extraction solvent

Since the lowest possible extraction temperature in the agitator is 35 °C, the boiling point of the solvent should be higher than this temperature. On the other hand the solvent

Table 1
The eight OPPs and the internal standard with their K_{ow} values, water solubilities and the selected SIM ions

OPP	log K_{ow}	H_2O solubility (mg/l)	SIM ions	Structure
Parathion-methyl	2.94	50	263, 125, 109	
Fenitrothion	3.40	30	277,260, 125	
Malathion	2.84	145	173, 125, 93	
Fenthion	4.09	55	278, 125, 109	
Bromophos	4.88	40	331, 125, 47	
Bromophos-ethyl	5.68	2	359, 242, 97	
Fenamiphos	3.23	700	303, 288, 154	
Ethion	5.09	1	231, 153, 97	
Parathion-([$^2H_{10}$]diethyl) internal standard			301, 115, 99	

has to be volatile enough to be removed through the split outlet during the large volume injection. Methanol, cyclohexane and heptane were tested. Methanol is not suitable, because it diffuses through the membrane into the aqueous phase and the volume of the organic phase is strongly reduced after the agitation process. Using cyclohexane, the best extraction yields were achieved, therefore it was applied for all analysis. It had been employed successfully before to determine polychlorinated biphenyls in water samples [21].

3.1.4. Impact of salt, pH value and methanol

When the pure sample was extracted, the standard deviations of the peak areas ($n = 3$) were between 10% (parathion-methyl) and 40% (bromophos-ethyl). The addition of 5 g NaCl to each sample to give a saturated solution resulted in lower standard deviations (4% for malathion, 22% for bromophos-ethyl, $n = 3$). Moreover, due to a salt addition the extraction yields increased significantly (Fig. 3), which can be explained by the salting out effect. Because of the increasing ionic strength of the aqueous phase, the water molecules solvate the electrolyte ions and therefore the water solubility of the OPPs decreases. This effect is strongest for analytes with a small octanol–water partitioning coefficient (K_{ow} value); parathion-methyl, fenitrothion, malathion and fenamiphos. For extraction of triazines with membrane-assisted solvent extraction a strong salting out effect has been noticed as well [20]. In Headspace-SPME the addition of salt to give a concentration of around 30% (w/v) improved the extraction efficiency of high water soluble OPPs [22,23]. Using direct SPME for determining insecticides in water, the presence of salt led to a decrease of the extraction yield when the salt content was higher than 15% (w/v) [9]. Mestres et al. [24] explained this effect

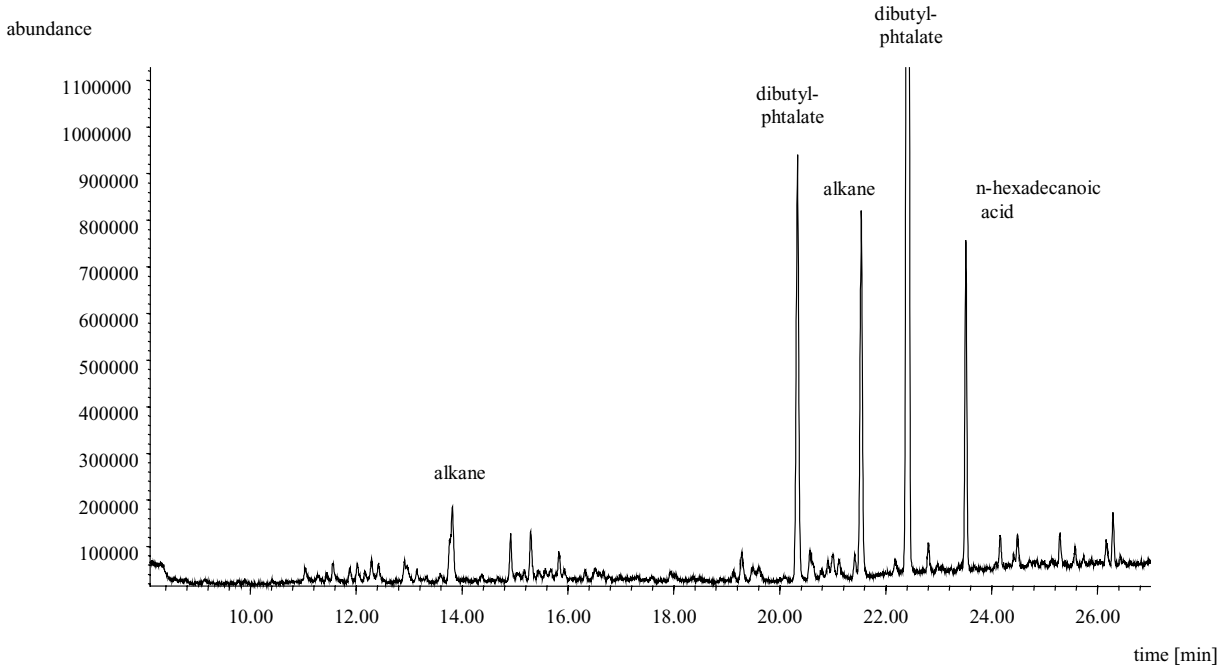


Fig. 2. Coextracted matrix compounds by extraction of reagent water, 45 °C, 30 min, injection volume 100 μl, scan mode.

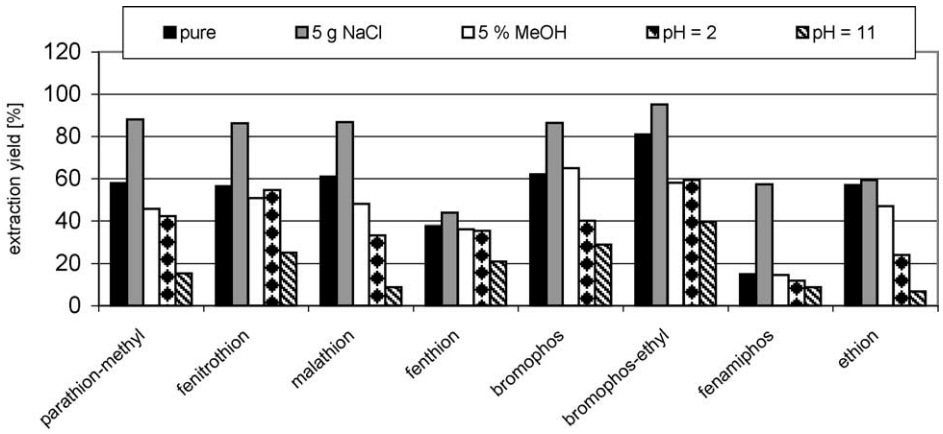


Fig. 3. Influence of matrix compounds, spiked to 1 μg/l of each OPP, 30 min extraction time, 45 °C, 750 rpm, injection volume: 100 μl.

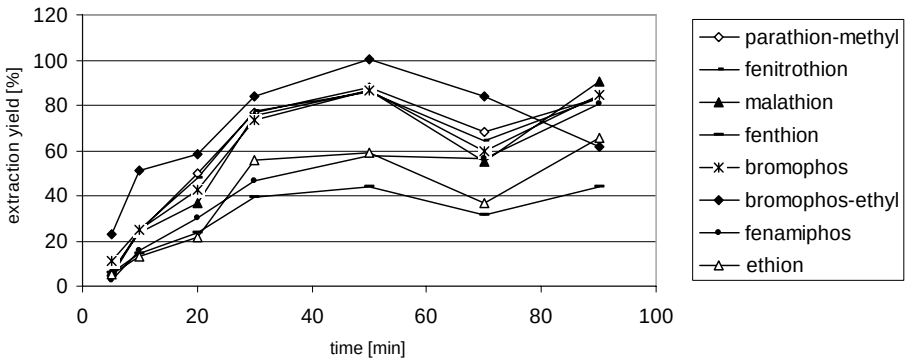


Fig. 4. Optimization of extraction time, spiked to 1 μg/l of each OPP, 45 °C, 750 rpm, 5 g NaCl, injection volume: 100 μl.

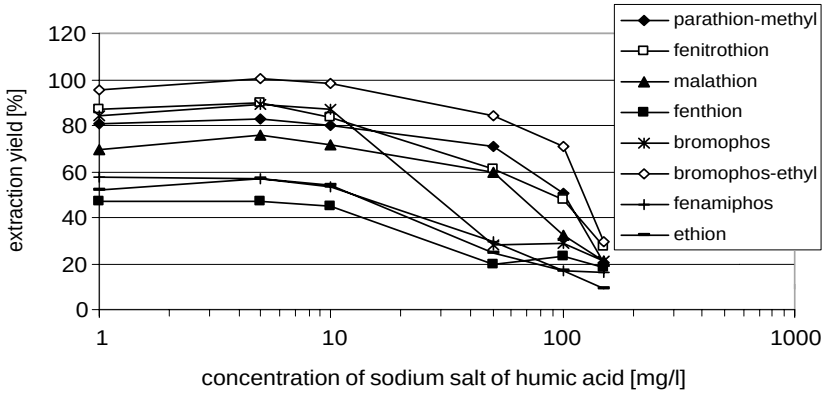


Fig. 5. Impact of different concentrations of humic acid sodium salt, 1 μg/l each OPP, 50 min extraction time, 45 °C, 750 rpm, 5 g NaCl, injection volume: 100 μl.

by the possible formation of a thin salt layer around the SPME fiber which has a negative influence on the extraction process.

Furthermore, the influence of the pH value for the eight OPPs was tested. A variation of the pH value between 2 and 11 did not lead to better results, alkaline conditions even decreased the extraction yields. The presence of methanol to avoid glass adsorption of the analytes did not have a significant impact. Thus, in all further optimization steps 5 g NaCl were added to the sample.

3.1.5. Stirring rate and extraction time

To improve the transport of the target compounds through the membrane material, the vials were stirred in the agitator at different stirring rates ranging from 250 to 750 rpm. Increasing stirring rates gave rise to a larger extraction yield for all OPPs (between 20 and 80% larger). Thus, the highest possible stirring rate of 750 rpm was applied.

The extraction time varied between 5 and 90 min, the standard deviations of the peak areas ($n = 3$) ranged between 3 and 15%. A significant increase of the extraction yield for all OPPs from 5 to 50 min was observed (Fig. 4). After 50 min the extraction yields decreased and for all compounds but bromophos-ethyl the 50 min level was reached again after 90 min. It is supposed that after 50 min the equilibrium was nearly achieved. An extraction time of 50 min, resulting in extraction yields between 47 and 100% was chosen for all further analyses.

3.1.6. Effect of humic acid

The presence of humic acids can have a considerable influence on environmental samples. In this work the impact of matrix compounds has been investigated by adding different concentrations of sodium salt of humic acid (1–150 mg/l) to the water sample. The results demonstrate that the presence of humic acid had an insignificant effect in the range of 1–10 mg/l. When adding 150 mg/l of sodium salt of humic acid the extraction yields decreased between 30 and 60% (Fig. 5). In former works where SPE and SPME were applied, it has also been shown that the presence of natural or xenobiotic contaminants in water affects the extraction process by reducing the recovery efficiency [7,25–27]. Interaction processes of the pesticides and the humic acid, e.g. adsorption, may cause this effect. These results imply that membrane-assisted solvent extraction can be applied successfully to water samples with low to medium organic matter content.

Fig. 6. Red wine sample and the obtained clear extract (right).

Table 2
Validation data for membrane-assisted solvent extraction

OPP	R.S.D. (%, $n = 3$)	LOD (ng/l)	Linear dynamic range (μg/l)	R^2
Parathion-methyl	6	11	0.011–70	0.9997
Fenitrothion	4	15	0.015–70	0.9945
Malathion	4	1	0.001–70	0.9945
Fenthion	5	8	0.008–70	0.9938
Bromophos	9	7	0.007–70	0.9954
Bromophos-ethyl	22	22	0.022–70	0.9953
Fenamiphos	12	20	0.020–70	0.9958
Ethion	10	23	0.023–70	0.9983

3.2. Method validation

Sample analysis was performed under the optimized conditions: the addition of 5 g NaCl to each sample, agitation speed of 750 rpm and 50 min extraction time. The results concerning precision, detection limits, linear dynamic range and calibration data are listed in Table 2. The standard deviations of the peak areas range from 4 to 12% (except for bromophos-ethyl with 22%). Linearity is given between 0.001 and 70 μg/l. The correlation coefficient of the calibration graph (R^2) is 0.994 or higher. This shows the potential and the sensitivity of the method for the investigation of organic compounds in aqueous samples.

The method of membrane-assisted solvent extraction is comparable to other extraction methods using membrane materials. Jönsson and co-workers presented the technique of supported liquid membrane extraction (SLM) and microporous membrane liquid–liquid extraction (MMLLE) for the determination of pesticides in environmental samples [28–31]. One example is the analysis of alkylthio-*s*-triazine herbicides in river water using SLM [32]. Under optimized conditions extraction efficiencies of 60% and LODs of about 30 ng/l were achieved. The determination of thiophanate-methyl and its metabolites with SLM and MMLLE in natural water showed detection limits of 100–500 ng/l [33].

3.3. Wine and juice samples

After the method development based on reagent water, the method was applied to real samples. Since OPPs are in use for agricultural purposes, two wine and one juice sample were analyzed under optimized conditions. None of the target analytes was found in the samples, hence they were spiked to a level of 0.5 μg/l for each OPP. Quantification was carried out using the calibration data for reagent water. In Table 3 the average results of three measurements are shown. Recoveries between 75 and 124% were determined, the standard deviation ($n = 3$) were in average about 10%. Matrix response enhancement can be a possible cause of higher recoveries. The obtained extracts were very clear and colourless. This was strongest noticed concerning the red wine samples (Fig. 6). A chromatogram of red whine, spiked to 0.5 μg/l in comparison to a standard solution at the same concentration is presented in Fig. 7.

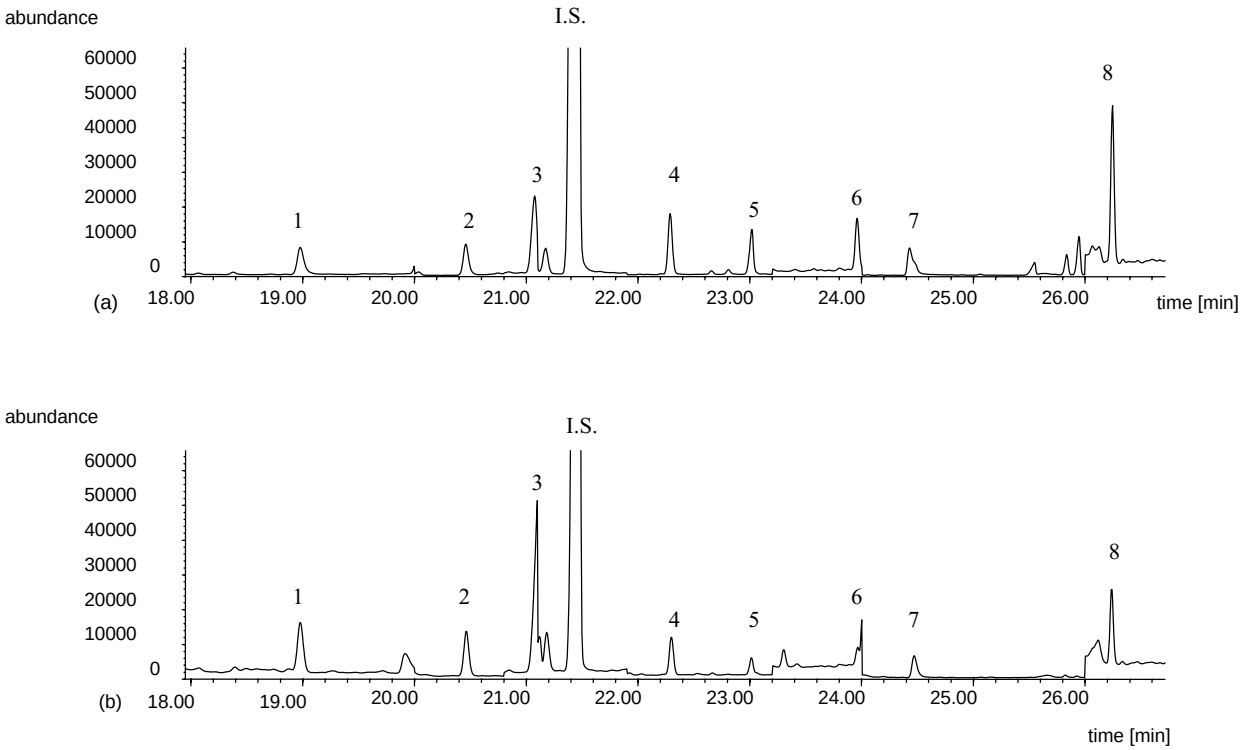


Fig. 7. Chromatograms of spiked water and red wine samples, 50 min extraction time, 45 °C, 750 rpm, 5 g NaCl, injection volume: 100 μl, SIM-mode. (a) Pure water spiked to 0.5 μg/l, (b) red wine spiked to 0.5 μg/l. (1) Parathion-methyl; (2) fenitrothion; (3) malathion; (4) fenthion; (5) bromophos; (6) bromophos-ethyl; (7) fenamiphos; (8) ethion.

Table 3
Results of the spiked samples

OPP	Spiked amount (μg/l)	White wine		Red wine		Apple juice	
		Detected amount (μg/l)	Recovery (%)[a]	Detected amount (μg/l)	Recovery (%)[a]	Detected amount (μg/l)	Recovery (%)[a]
Parathion-methyl	0.50	0.56	113	0.52	104	0.60	119
Fenitrothion	0.50	0.56	111	0.53	105	0.58	116
Malathion	0.50	0.42	83	0.59	119	0.51	101
Fenthion	0.50	0.44	89	0.40	81	0.44	88
Bromophos	0.50	0.41	83	0.45	90	0.41	83
Bromophos-ethyl	0.50	0.59	118	0.42	84	0.39	78
Fenamiphos	0.50	0.46	93	0.56	111	0.62	124
Ethion	0.50	0.41	82	0.37	75	0.49	97

[a] Percentage values obtained considering extraction yields in reagent water (Fig. 3) as 100%.

4. Conclusion

Membrane-assisted solvent extraction is a simple, solvent-reduced and fully automated technique. Due to the transfer of the analytes into a small amount of organic solvent and because of large volume injection detection limits in the ng/l range can be obtained. Thus, the maximum level for OPPs set by the EU can be verified without difficulties. The method of large volume injection can be applied successfully, although the differences concerning the boiling points between solvent and analytes are not as high as advised (150 °C). The extraction yields range from 47 to 100% under the optimized conditions. The independence of the method from matrix compounds is shown in obtaining recoveries around 100% for the wine and juice samples. This implies that the extraction process is not significantly influenced by other compounds and by the presence of humic acids to a concentration of 10 mg/l. Thus, membrane-assisted solvent extraction shows a promising applicability for complex liquid samples. The polypropylene membrane bags are robust, easy to handle and have the advantage of low cost. After a simple cleaning procedure they can be reapplied for different matrices without losing efficiency. In future to allow measuring in scan mode the pretreatment of the membrane bags should be improved in order to reduce the appearance of coextracted compounds in the chromatograms.

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