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Trace enrichment and sample preparation of alkylthio-*s*-triazine herbicides in environmental waters using a supported liquid membrane technique in combination with high-performance liquid chromatography

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Sample pre-treatment and enrichment using the supported liquid membrane (SLM) technique for the determination of alkylthio-*s*-triazine herbicides in river water samples was investigated. The uncharged herbicide molecules from the flowing aqueous donor solution diffuse through a porous poly(tetrafluoroethylene) membrane, which is immobilized with a water-immiscible organic solvent, and are trapped in a stagnant acidic acceptor phase since they become protonated. Using undecane as a membrane solvent, the SLM methodology was successfully used for the enrichment and separation of seven alkylthio-*s*-triazine herbicides in environmental waters with extraction efficiencies of 60% or better. The LC results obtained on spiking the pesticides in river water samples further confirmed the selectivity of the method. The influence of the various SLM extraction parameters on the extraction efficiency was studied. In this system, the partition coefficient, K_p, between the donor and the membrane phases is large, and effects due to carry over and membrane memory are very small. Detection limits of about 0.03 μg l^{-1} were obtained by extraction of 1.0 μg l^{-1} samples in both reagent and river water at a donor flow rate of 7.0 ml min^{-1} for about 70 min. Further advantages of the procedure are the reduced analysis time and an increase in the sample accumulation rate in the acceptor phase.

Keywords: *Sample handling; supported liquid membrane; alkylthio-*s*-triazine; environmental waters; detection limit; extraction efficiency; enrichment factor*

Triazine herbicides, introduced in the 1950s,[1] are one of the largest class of agrochemicals produced, and are also one of the most commonly used for pre- and post-emergence weed control for a variety of crops including green vegetables. A report indicates that about 30% of all herbicides produced are triazines.[2] Consequently, they are also the herbicides most frequently found in environmental samples, particularly soil, surface water and groundwater owing to their relative persistence and easy transport. Their presence and distribution in environmental waters has the effect of lowering the quality of drinking as well as surface water.

Water quality has received considerable attention in recent years and stringent regulations have been issued by legislation agencies.[3] For instance, the current European Union (EU) directive dictates that the concentration of individual pesticides should not exceed a maximum admissible concentration of 0.1 μg l^{-1} in drinking water for single pesticide and 0.5 μg l^{-1} for total pesticide concentration.[3,4]

Often, the residues of pesticides and their degradation products, produced by a combination of hydrolytic, photochemical and microbial processes, are found in various complex matrices at very low concentration levels. The nature of the samples necessitates the use of preconcentration, clean-up and separation techniques.[5] The detection level of these residues, especially in environmental waters, seems to depend more on the isolation and enrichment procedure chosen than on the method used for final determination.[6] Selection of the procedure mainly depends on the sample character, the presence of other trace compounds and the concentration of the analyte.

Various preconcentration and isolation methods which are employed for the enrichment of triazines from different samples have recently been reviewed by Pacakova *et al.*[5] The advantages and drawbacks of each of the systems in the process of extraction have been discussed. The most common techniques used for sample processing of triazines are liquid–liquid extraction, supercritical fluid extraction and solid-phase extraction either off- or on-line with various analytical separation methods.

The supported liquid membrane (SLM) technique as an alternative approach to sample handling was developed by Audunsson in the mid 1980s.[7] The technique utilizes a porous poly(tetrafluoroethylene) (PTFE) membrane, on which a water-immiscible solvent or a mixture of solvents is immobilized. The membrane forms a barrier between two aqueous phases in a flow system. The principles of SLM extraction, *viz.*, selectivity, extraction efficiency and operational characteristics, and also comparisons with existing sample preparation methods have been discussed in detail by Jönsson and Mathiasson.[8]

Liquid membrane extraction has been applied to a variety of samples of environmental and biological origin. Low concentrations of amines in complex matrices such as urine,[9] blood plasma[10] and animal manures[11] have been preconcentrated and quantified. Permanently charged aromatic anionic surfactants[12] and metal ions[13] were transported across the liquid membrane on forming ion pairs with suitable complexing agents. The SLM technology was also found suitable for the sample preparation and enrichment of sulfonylurea herbicides,[14,15] phenoxy acids,[16,17] and chlorophenols[18] from water samples.

Limited information is available about the sample work-up of triazines using an SLM. Martinez *et al.*[19] recently reported an on-line enrichment method with a liquid membrane for *s*-triazines from oil samples. In a similar way, chloro-*s*-triazines[20,21] have been determined in natural waters, although problems of incomplete trapping in an acidic acceptor phase were encountered.[20]

In this work, we describe a method for sample preparation and enrichment of alkylthio-*s*-triazine herbicides with a wide range of polarity using the SLM technique. The influence of parameters such as donor flow rate, available sample volume

and time on the detection limit of the herbicide compounds under study was investigated.

Experimental

Chemicals, reagents and working solutions

The alkylthio-*s*-triazine herbicides used were ametryn (99.7%), desmetryn (99.8%), dimethametryn (94.0%), dipropetryn (99.2%), metoprotryn (98.9%), prometryn (98.8%) and terbutryn (99.5%), all from Promochem (Wesel, Germany). The structures and pK_a values are shown in Table 1.[1]

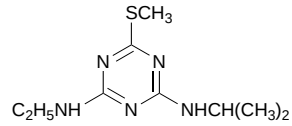
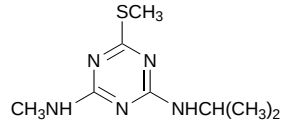
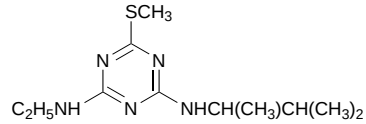
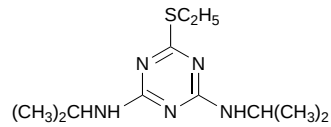
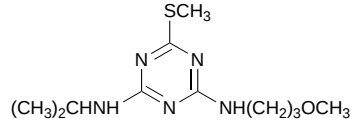
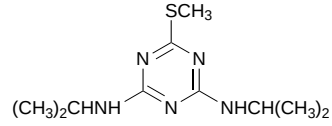
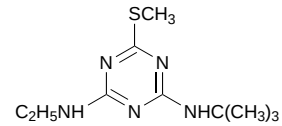
The organic solvents used for impregnation of the membrane were undecane and dihexyl ether (Sigma, St. Louis, MO, USA). Acetonitrile (Merck, Darmstadt, Germany) used for the chromatographic system was of HPLC grade. Sodium dihydrogenphosphate monohydrate ($NaH_2PO_4 \cdot H_2O$, 0.02 mol l^{-1}) and disodium hydrogenphosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$, 0.01 mol l^{-1}), both from Merck, were used as buffer (with a volume ratio of 13.96 : 24.04)[22] to give a pH of 7.0. Apart from sodium hydroxide (NaOH), obtained from Eka Nobel (Bohus, Sweden), all other chemicals were from Merck and were of analytical-reagent grade. All standard solutions were prepared in reagent water purified by a Milli-Q/RO4 unit (Millipore, Bedford, MA, USA).

Stock solutions of the herbicides (100 mg l^{-1}) were prepared in acetonitrile. A series of solutions for calibration in the range 0.1–2.0 mg l^{-1} was obtained by diluting the required volume of the stock solution with water. An aqueous solution (5.0 mg l^{-1}) of the triazine mixture was prepared by dissolution in water at pH 4.0 (the pH was adjusted with sulfuric acid). Stock solutions were stable when stored at 0 °C for at least 6 months. River water samples for spiking were collected from the Kävlinge river located about 20 km north of Lund, Sweden.

LC equipment

Separation of the herbicide mixture was effected by LC with UV detection. The mobile phase was pumped with an Iso Chrom LC pump (Spectra-Physics, San Jose, CA, USA) for reversed-phase separation of the triazines. Samples were introduced into the separation system with an autosampler (Waters, WISP Model 710B, Milford, MA, USA). The separation was performed on a C_{18} column (Techsphere 5ODS, 250 mm × 4.6 μm id; HPLC Technology, Macclesfield, Cheshire, UK), followed by UV detection (Model 757, Kratos Analytical Instruments, Ramsey, NJ, USA). The peaks were recorded on a 2210 recorder (LKB, Stockholm, Sweden) and evaluated manually.

Table 1 Alkylthio-*s*-triazine herbicides used, their structures and dissociation constants

Common name	Systematic name	Structure	pK_a
Ametryn	2-Methylthio-4-ethylamino-6-isopropylamino-*s*-triazine		4.1
Desmetryn	2-Methylthio-4-methylamino-6-isopropylamino-*s*-triazine		4.0
Dimethametryn	2-Methylthio-4-ethylamino-6-(1,2-dimethylpropylamino)-*s*-triazine		4.0
Dipropetryn	2-Ethylthio-4,6-bis(isopropylamino)-*s*-triazine		4.3
Metoprotryn	2-Methylthio-4-isopropylamino-6-(3-methoxypropylamino)-*s*-triazine		4.0
Prometryn	2-Methylthio-4,6-bis(isopropylamino)-*s*-triazine		4.1
Terbutryn	2-Methylthio-4-ethylamino-6-*tert*-butylamino-*s*-triazine		4.3

Membrane equipment

The membrane holder (Fig. 1, upper box) consisted of two circular PTFE blocks (diameter 120 mm, thickness 8 mm) with machined grooves (depth 0.25 mm, width 1.5 mm, length 250 cm, each with a total volume of about 0.95 ml) so that they formed channels that were arranged in the form of Archimedes spirals. Both sides of the holder were backed with aluminium blocks (Fig. 1; A in the box) of 6 mm thickness, in which threads for the clamping screws were machined, to make the assembly stable. In addition, the donor channel of the PTFE block was equipped with an O-ring, outside the grooves, for sealing the flow system.

The liquid membrane support was Millipore FG (Millipore) with an average pore size of 0.2 μm, a total thickness of 175 μm of which about 115 μm is polyethylene backing, and a porosity of 70%. The liquid membrane was prepared by immersing the membrane support in the organic solvent to be immobilized for a period of 30 min. The soaked membrane was placed between the two PTFE blocks, with the rough side of the membrane facing the donor side (Fig. 1; B in the box) and the whole construction was clamped together tightly and evenly with six screws. Thus, the two channels are separated by the liquid membrane, forming the donor (feed) and the acceptor (receiving) compartments. After installation of the impregnated membrane in the separator, both channels were flushed with water to remove excess of the organic solvent from the surface of the membrane.

The configuration of the flow system is shown in Fig. 1. Two peristaltic pumps (Minpuls 3; Gilson Medical Electronics, Villiers-Le-Bel, France) were used to control the flow rates of the donor and acceptor phases independently. The tubes used for pumping solutions were acid-resistant (Acid-Flexible; Elkay Products, Shrewsbury, MA, USA) with internal diameters of 2 mm for the donor and 1 mm for the acceptor. The various parts of the flow system were connected with 0.8 mm id PTFE tubing and Altex screw fittings. The sample and buffer in the donor stream were merged in a PTFE tee connection, and then mixed in a coil (1.0 m × 0.8 mm id coiled PTFE tubing) before entering the donor channel of the membrane device.

Enrichment and separation procedures

Aqueous samples of triazine mixture and the buffer were pumped with a peristaltic pump and delivered to the extraction system with a total donor flow rate of 1.0 ml min^{-1} (sample-to-buffer volume ratio of 1 : 1), for 20 min, which was followed by pumping of the channel with the donor buffer solution for another 20 min, while the acceptor phase was kept stagnant. The system was left to stand for 10 min to allow diffusion of the analytes from the membrane to the acidic acceptor phase. The same procedure was followed throughout except in some experiments at a higher flow rate (7.0 ml min^{-1}), where 500 ml of a 1.0 μg l^{-1} sample solution were extracted. At the end of 10 min, the contents of the acceptor channel were quantitatively transferred into a 10 ml calibrated glass tube, by displacement with 0.1 mol l^{-1} sulfuric acid to a final volume of 2.0 ml. The flow rate of the acceptor used was 0.4 ml min^{-1}. The extracts collected were adjusted to pH 7.0 with about 0.4 ml of 1.0 mol l^{-1} sodium hydroxide. A 20 μl aliquot of the enriched sample was introduced into the HPLC system, except at lower concentrations, below 5 μg l^{-1}, where 50 μl were injected.

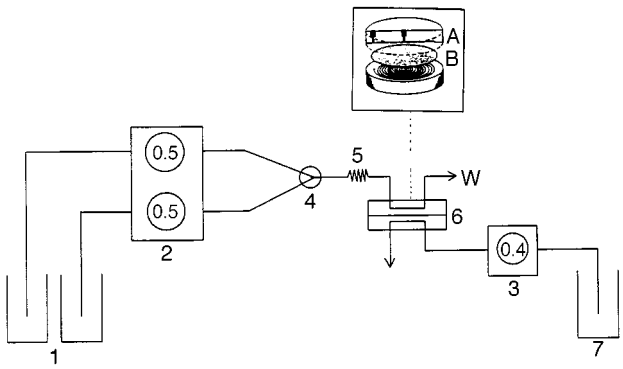


Fig. 1 Set-up of the flow system for liquid membrane extraction. 1, Containers for sample solution and donor buffer; 2 and 3, peristaltic pumps for the donor and acceptor phases, respectively (numbers in circles are flow rates of the channels); 4, PTFE tee connection; 5, mixing coil; 6, membrane extraction unit (in the box above the flow system: A, PTFE block; and B, impregnated membrane support); 7, container for acidic acceptor solution; and W, waste.

For the reversed-phase chromatographic separation of the triazine mixture a mobile phase consisting of 56% acetonitrile and 44% 0.05 mol l^{-1} sodium acetate, adjusted to pH 7.0 with 0.5 mol l^{-1} sulfuric acid, was utilized. The mobile phase was de-gassed for 30 min either on an ultrasonic bath (Bransonic, Danbury, CT, USA) or by bubbling with helium. All analyses were carried out at a mobile phase flow rate of 1.0 ml min^{-1}. The analytes were monitored at 235 nm.

Calibration graphs for the triazines under study were prepared daily in the concentration range 0.1–2.0 mg l^{-1} (and 2.5–20 μg l^{-1} when lower concentration analytes were extracted), at five points, based on triplicate injections and measurements of peak heights. All the graphs gave linear correlation coefficients of 0.9998 or better with insignificant intercepts at the 95% confidence level.

Results and discussion

Enrichment with supported liquid membrane extraction

The triazines in the extraction system, pH 7.0, are largely uncharged when entering the donor channel in the membrane separator. They then diffuse through the hydrophobic liquid membrane to the acceptor channel which contains 0.10 mol l^{-1} sulfuric acid. The acceptor phase was kept stagnant during the whole extraction period, and the protonated triazines were trapped and enriched. Smaller interfering molecules that are protonated at the donor pH and larger molecules are not extracted into the membrane but instead pass the donor channel to waste. Neutral molecules distribute themselves between the two phases and thus enrichment for them is unlikely to occur.

Selection of the membrane solvent

The mass transfer through the liquid membrane depends on the extent of diffusion of the solute molecules from the flowing donor phase to the acidic acceptor, where they will be irreversibly trapped. One of the most important parameters that can influence the efficiency and selectivity of extraction is the membrane solvent through which permeation will occur.[7,8] Choice of the membrane solvent may be governed by, among other things, the partition coefficient, K_p, of the analyte molecules between the organic solvent and the aqueous donor phase. K_p should be as large as possible for the target molecules, while for the interfering compounds, it should be low.

The extent of analyte extraction from the sample matrix can be expressed as the extraction efficiency, *E*. It is defined as the fraction of the analyte extracted into the acceptor phase to the total amount of analyte in the sample. The values of *E* obtained for the alkylthio-*s*-triazines with two membrane solvents and a mixture of them are given in Table 2 (in the order of analyte elution). A higher efficiency was observed with undecane. As has been indicated elsewhere,[7,15] undecane has good selectivity towards other organic substances in natural water samples,[15] and also has long-term stability as a membrane solvent.[7] In the extraction of these compounds, more than 100 samples have

been processed with this membrane, without significant decrease in the extraction efficiency. The other solvents, *viz*., dihexyl ether and a mixture of undecane and dihexyl ether, are also good alternatives except that their lifetime as a membrane solvent is shorter, which might be due to gradual dissolution of the more polar dihexyl ether into the aqueous flow system.

The undecane solvent was also used for the extraction of various concentrations of the herbicide compounds, Table 3. The extraction efficiencies are nearly independent of the analyte concentration, *cf.* the RSD values in Table 2. A slight lowering of the efficiencies for the late eluting compounds might be due to adsorption of the compounds, at lower concentrations, on the donor side.

Carry over effect

Whenever possible, complete extraction and quantitative transfer of the analyte in question through the membrane is needed to obtain as high an efficiency of extraction as possible. In some practical applications, the transfer was not complete as notable fractions of the samples have been found when a second portion of the acceptor is taken before the subsequent enrichment.[12,23,24] These residual amounts might be from one of the following two sources. Firstly, solutes adsorbed on the connecting tubes, flow system or the membrane surface can constitute some amount of the portion, when they are carried to the membrane system. The effect due to this first portion can be termed the carry over effect (COE). COE may be defined as the fraction of the analyte compounds, charged or uncharged, that is being adsorbed in the flow system during the SLM extraction and can be determined in the subsequent blank extractions.

To investigate the COE with the present system, a 0.5 mg l^{-1} aqueous standard solution of the herbicide mixture was enriched for 20 min followed by a 20 min wash with the donor buffer, and a 10 min waiting time, *i.e*., without pumping any of the channels. After sample collection from the acceptor, a reagent water blank was enriched in the same way. The fraction of the analyte adsorbed varied from about 0.50 to 5.0% of the extracted sample; the highest values found were for the late eluting compounds. It was observed that washing of the flow system for 20 min can lead to effective transfer of the analyte to the acceptor.

The second source of the analyte molecules that can be determined after the first extraction may be from slow diffusion of the target molecules through the liquid membrane. The effect due to this portion of the left over sample can be termed the membrane memory effect (MME).

MME has been observed in some SLM applications,[23] mainly due to slow mass transfer kinetics across the membrane/acceptor interface, which led to incomplete transfer of the analytes out of the membrane. To study this effect, 0.5 mg l^{-1} of the sample mixture was enriched, as above. After collection of the sample plug, the system was allowed to stand for a further 20 min to allow diffusion of the molecules retained in the membrane during the first extraction. The same procedure was repeated three times and gave MMEs ranging from 0.11 to

Table 2 Extraction efficiency (*E*) for 20 min extraction of 0.5 mg l^{-1} samples of alkylthio-*s*-triazine herbicides in various membrane solvents. Donor pH: 7.0 with phosphate buffer; acceptor pH: 0.70; donor flow rate: 1.0 ml min^{-1}. A volume of 20 μl was introduced into the separation system (table is in the order of analyte elution)

Herbicide	Undecane	RSD* (%)	Dihexyl ether (DHE)	RSD* (%)	DHE–undecane (50 + 50)	RSD* (%)
Desmetryn	0.639	3.25	0.584	3.98	0.591	4.00
Metoprotryn	0.620	1.94	0.557	3.79	0.561	2.41
Ametryn	0.650	1.92	0.553	4.07	0.540	2.90
Prometryn	0.572	1.23	0.473	3.15	0.470	2.33
Terbutryn	0.489	0.82	0.401	2.71	0.406	2.19
Dimethametryn	0.480	1.09	0.393	2.51	0.403	2.11
Dipropetryn	0.457	0.88	0.356	2.90	0.376	2.42

* RSD is the relative standard deviation for $n = 5$.

Table 3 Extraction efficiencies of the samples of herbicides at concentration levels of 1.0, 2.0 and 5.0 μg l^{-1} in both reagent and river water. A 50 μl aliquot of the enriched sample was introduced into the LC separation system except for 500 μg l^{-1} where 20 μl were injected

	Concentration of the sample extracted/μg l^{-1}					
Herbicide	1.0 μg l^{-1} sample in reagent water	1.0 μg l^{-1} sample in river water	2.0 μg l^{-1} sample in reagent water	5.0 μg l^{-1} sample in reagent water	500 μg l^{-1} sample in river water	500 μg l^{-1} sample in reagent water
Desmetryn	0.632 ($n = 4$)	0.627 ($n = 6$)	0.638 ($n = 6$)	0.631 ($n = 6$)	0.626 ($n = 3$)	0.643 ($n = 3$)
Metoprotryn	0.621 ($n = 4$)	0.618 ($n = 6$)	0.612 ($n = 6$)	0.613 ($n = 3$)	0.608 ($n = 3$)	0.623 ($n = 3$)
Ametryn	0.637 ($n = 4$)	0.626 ($n = 6$)	0.643 ($n = 6$)	0.643 ($n = 4$)	0.645 ($n = 3$)	0.651 ($n = 3$)
Prometryn	0.572 ($n = 4$)	0.588 ($n = 6$)	0.606 ($n = 4$)	0.580 ($n = 5$)	0.579 ($n = 3$)	0.587 ($n = 3$)
Terbutryn	0.502 ($n = 4$)	0.531 ($n = 5$)	0.536 ($n = 4$)	0.507 ($n = 6$)	0.542 ($n = 3$)	0.549 ($n = 3$)
Dimethametryn	0.494 ($n = 4$)	0.488 ($n = 4$)	0.517 ($n = 5$)	0.509 ($n = 5$)	0.510 ($n = 3$)	0.517 ($n = 3$)
Dipropetryn	0.470 ($n = 4$)	0.484 ($n = 4$)	0.497 ($n = 6$)	0.485 ($n = 4$)	0.492 ($n = 3$)	0.490 ($n = 3$)

0.80% of the extracted sample for the seven herbicides studied. This is well below the uncertainty of the measurements.

Effect of the acceptor pH

When the SLM technique is applied to either acidic or basic compounds, the pH of the stagnant acceptor phase plays an important role in controlling the degree of extraction of the target analytes. According to theoretical considerations,[25] to achieve a nearly complete extraction for the basic compounds, the pH on the acceptor side should be at least 3.3 pH units below the pK_a of the analytes in question. Alkylthio-*s*-triazines are basic secondary amine compounds having pK_a values between 4.0 and 4.5 (Table 1) and thus can be protonated and trapped in acidic acceptor solutions.

To study the degree of extraction of the analytes in the acceptor phase, the concentration of sulfuric acid in the range 0.005–0.5 mol l^{-1}, at five points, was used to vary the pH between 0 and 2.0, while the pH of the donor solution was kept constant at 7.0. It was observed that the extent of enrichment, and thus the extraction efficiency of the herbicide compounds under study, was dependent on the acceptor pH. Fig. 2 shows the influence of sulfuric acid concentration on the trapping capacity of the acceptor. The extraction efficiency increases when the pH of the acidic acceptor solution decreases, although it seems to be largely unaffected by decreasing the pH beyond 0.70. In contrast to the chloro-*s*-triazines,[20] whose pK_a values are less than 3.0, it is possible experimentally to reach a plateau for the extraction efficiency which is again in good agreement with the theoretical derivations.[25] On decreasing the pH below 0.7 an increase in efficiency was not obtained, and thus a concentration of sulfuric acid corresponding to pH 0.7 was chosen in all the subsequent extractions.

Effect of the donor pH

Solutions of the herbicides containing 0.5 mg l^{-1} of each of the triazines under study were mixed with phosphate buffer, ranging in pH from 3.0 to 8.0, before entering the donor channel. The buffers were prepared from H_3PO_4–NaH_2PO_4 (pH = 3.0), NaH_2PO_4 (pH = 4.0) and NaH_2PO_4–Na_2HPO_4 (pH = 6.0–8.0).[26] All buffers were freshly prepared and used throughout this work. The results shown in Fig. 3 indicate that below pH 4.0, which is also below the pK_a of the compounds of interest, the herbicides rarely cross the hydrophobic membrane, since most of the fraction entering the donor channel is in protonated form.[8] As has been theoretically predicted by Jönsson *et al.*,[25] for basic compounds such as triazines, the pH of the flowing donor solution should be at least 2 pH units more than the highest pK_a value to facilitate their dissolution into the membrane. In the extraction of the alkylthio-*s*-triazines, as shown in Fig. 3, analyte permeation through the membrane, *i.e.*, the extraction efficiency, seems not to be affected much between pH 6.0 and 8.0. One further observation here is that at pH 8.0 the results are less reproducible, which might be due to some chemical reaction, *e.g.*, hydrolysis, that may occur in the donor phase.[1] Therefore, pH 7.0, at a constant ionic strength of 0.05, was observed to be suitable, and this pH was used for all subsequent analyses.

Influence of the donor flow rate

One of the advantages of liquid membrane extraction is the possibility of increasing the amount of sample passing the donor channel per unit time, especially when large sample volumes are available, so as to increase the total amount of analyte accumulated in the stagnant acceptor solution. This is primarily useful when the extraction system is limited by the mass transfer in the donor channel, *i.e.*, if the partition coefficient, K_p, between the organic membrane liquid and the aqueous donor phase is relatively large ($K_p > 1$). Under these circumstances the decrease in the extraction efficiency with increase in donor flow rate is small, while the accumulation factor, E_a (defined as moles per concentration and time units), may increase with the donor flow rate. Further experimental benefits of such a procedure are shortening of the extraction time used and also lowering of the detection limit with the same extraction time.

The influence of the donor flow rate on the extraction efficiency, and therefore on the enrichment of the herbicide compounds, was investigated over a wide range of flow rates, from 0.6 to 7.0 ml min^{-1}. The enrichment factor, E_e ($E_e = C_a/C_d$; where C_a is the concentration of the enriched sample from the acceptor and C_d is the concentration of the sample entering the donor channel for enrichment), increases with increasing donor flow rate for all of the compounds studied, Fig. 4.

The problems associated with increasing the donor flow rate are the decrease in the lifetime of the membrane and reduced extraction efficiency for the subsequent extractions. This may be caused by dissolution of the membrane liquid into the flowing large volume of the aqueous donor phase. In fact, the donor flow rate can be increased up to 3.5 ml min^{-1}, without causing pronounced effects on the lifetime of the membrane. However, in order to obtain a relatively high extraction efficiency from a limited sample volume and to prolong the

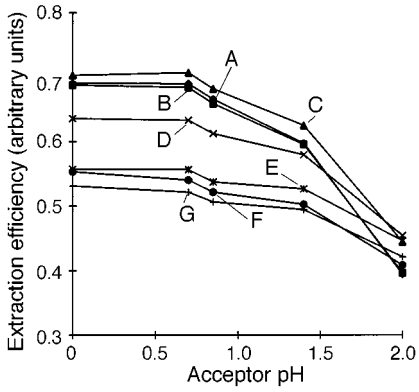


Fig. 2 Extraction efficiency *versus* the acceptor pH. Membrane composition: 100% undecane; donor pH: 7.0 with phosphate buffer; 20 min extraction of 0.5 mg l^{-1} of the herbicide mixture at a donor flow rate of 1.0 ml min^{-1} and an acceptor flow rate of 0.4 ml min^{-1}. A 20 μl aliquot of the enriched sample was injected into the separation system. A, Desmetryn; B, metoprotryn; C, ametryn; D, prometryn; E, terbutryn; F, dimethametryn; and G, dipropetryn.

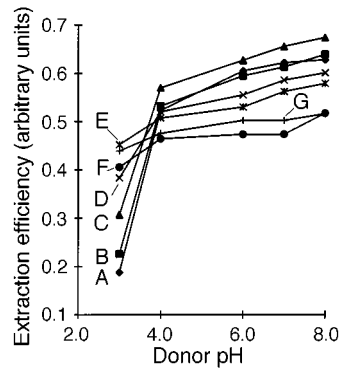


Fig. 3 Extraction efficiency *versus* the donor pH. Acceptor pH: 0.7. Donor pH was varied with 85% H_3PO_4–NaH_2PO_4, NaH_2PO_4 and NaH_2PO_4–Na_2HPO_4. Other conditions as in Fig. 2. A, Desmetryn; B, metoprotryn; C, ametryn; D, prometryn; E, terbutryn; F, dimethametryn; and G, dipropetryn.

lifetime of the membrane, a donor flow rate of 1.0 ml min^{-1} was chosen, and used throughout unless otherwise stated.

Applications

The applicability of the developed liquid membrane method to the extraction of environmental water samples, that may contain matrices of various concentrations, was tested by processing spiked river water samples collected from the Kävlinge river, situated about 20 km north of Lund, Sweden. First, the extraction efficiencies were determined by extracting blank river water for 20 min, followed by spiked river water samples at concentration levels between 1.0 and 5.0 μg l^{-1} of the triazine mixtures. Samples in reagent water were also processed under identical conditions. The results obtained, Table 3, for samples in both mixtures are not significantly different in their values. The reliability of the developed method was further assessed by extracting a higher concentration, 500 μg l^{-1}, of the analyte mixture in a similar manner. It can be seen from Table 3 that the extraction efficiencies of the compounds are unaffected when samples are processed at 1.0 ml min^{-1} for a 20 min extraction time.

In another series of experiments 500 ml of samples in both reagent water and spiked in river water were enriched at a flow rate of 7.0 ml min^{-1}. The enrichment factors, obtained from the extraction of a 1.0 μg l^{-1} sample mixture, are given in Table 4. To estimate the time required to obtain the same enrichment at a lower flow rate, the same samples were first extracted at 0.5 ml min^{-1}, for 20, 40, 60 and 120 min. Linear relationships were obtained for enrichment *versus* extraction time. By extrapolating the results for the enrichment factors at 7.0 ml min^{-1}, the time required to obtain the same enrichment at a lower flow rate was found, Table 4. The results show that the time required for both reagent and river water samples is similar.

The detection limits of the pesticides were studied first at a sample flow rate of 1.0 ml min^{-1} for a 20 min extraction. For all the compounds the detection limits, calculated as twice the noise level, were comparable in both river and reagent water ranging from 0.2 to 0.8 μg l^{-1} (Table 5). It was also of interest to ascertain how the detection limit was influenced by increasing the flow rate of the sample across the donor channel. By extracting a 500 ml sample mixture containing 1.0 μg l^{-1} of each of the compounds at 7.0 ml min^{-1}, the detection limits were lowered 5–10 times for the samples studied in both reagent and river water, Table 5. Utilizing the developed method, trace enrichment of the alkylthio-*s*-triazines can be successfully achieved when a larger sample volume is available for analysis, as also described earlier.[8] Table 4 indicates that to obtain a higher sample enrichment at lower flow rates, a longer processing time is needed. This can be useful when a limited sample volume, *e.g.*, blood plasma, is available.[10] In other applications of membrane extraction for *s*-triazines, detection limits ranging from 40 to 70 μg l^{-1} for a sample containing chloro- and methylthio-*s*-triazines[19] and of about 0.15 μg l^{-1} for chloro-*s*-triazines[20] have been obtained. In the present work, the detection limits obtained were much lower, and the possibility of lowering the detection limits further was also verified when sample volume is not a limiting factor.

Typical chromatograms of these results are shown in Fig. 5, and were obtained by first pumping blank reagent and river water, followed by extraction of the sample mixtures under identical conditions. The seven herbicides were separated in 15 min when all the HPLC parameters were optimized. To allow

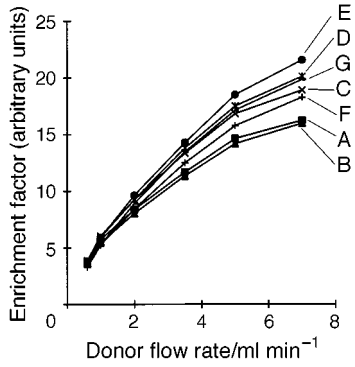


Fig. 4 Influence of the donor flow rate on enrichment factors E_e ($E_e = C_a/C_d$, where C_a is the concentration of the enriched sample from the acceptor, and C_d is the concentration of the sample entering the donor channel for enrichment) for extraction of 0.5 mg l^{-1} herbicides for 20 min. Acceptor pH: 0.7. Donor pH: 7.0. A, Desmetryn; B, metoprotryn; C, ametryn; D, prometryn; E, terbutryn; F, dimethametryn; and G, dipropetryn.

Table 4 Enrichment factors for the extraction of 500 ml of a 1.0 μg l^{-1} sample mixture, in both reagent and spiked river water, at a flow rate of 7.0 ml min^{-1} (n = 3), and the corresponding time required if the same volume of the mixture were enriched at a flow rate of 0.5 ml min^{-1}

	Sample in reagent water		Sample spiked in river water	
Herbicide	Enrichment factor*	Time/min†	Enrichment factor*	Time/min†
Desmetryn	51	310	51	310
Metoprotryn	54	350	53	360
Ametryn	52	280	51	280
Prometryn	66	390	62	410
Terbutryn	78	490	73	460
Dimethametryn	78	480	73	510
Dipropetryn	80	490	75	530

* Enrichment factor for a 1.0 μg l^{-1} sample mixture at a flow rate of 7.0 ml min^{-1}. † Time required to obtain the same enrichment at a flow rate of 0.5 ml min^{-1}.

Table 5 Study of the detection limit of the alkylthio-*s*-triazine herbicides at a flow rate of 1.0 (20 min extraction) and 7.0 ml min^{-1} (extraction of 500 ml of 1.0 μg l^{-1} sample mixture). Other conditions as in Table 3

	Detection limit (μg l^{-1}) at 1.0 ml min^{-1} (20 min extraction)		Detection limit (μg l^{-1}) for extraction of 500 ml sample at 7.0 ml min^{-1}	
Herbicide	Sample mixture in reagent water	Sample in spiked river water	Sample mixture in reagent water	Sample in spiked river water
Desmetryn	0.3	0.2	0.04	0.04
Metoprotryn	0.4	0.3	0.05	0.05
Ametryn	0.3	0.3	0.03	0.03
Prometryn	0.5	0.4	0.04	0.04
Terbutryn	0.6	0.5	0.05	0.05
Dimethametryn	0.7	0.6	0.06	0.07
Dipropetryn	0.8	0.8	0.06	0.07

the samples adsorbed in the flow system to pass through the membrane unit, the same volume of the donor buffer was pumped as above and the acceptor was also processed in the same way. It can be seen from the results that the extraction process is selective and yields a clean chromatogram.

Conclusions

It has been demonstrated that SLM extraction in combination with HPLC with UV detection can be utilized for the determination of trace amounts of alkylthio-*s*-triazines in environmental water samples. The various SLM extraction parameters were studied and optimized, and under these conditions a successful sample work-up and selective extraction of the compounds under study were obtained. The possibility of lowering the detection limit of these herbicides was investigated by extracting lower concentrations, at a higher donor flow rate. Trapping of the compounds in the acidic acceptor phase seems complete and the extraction method is very suitable for the enrichment of this class of triazine compounds from complex matrices.

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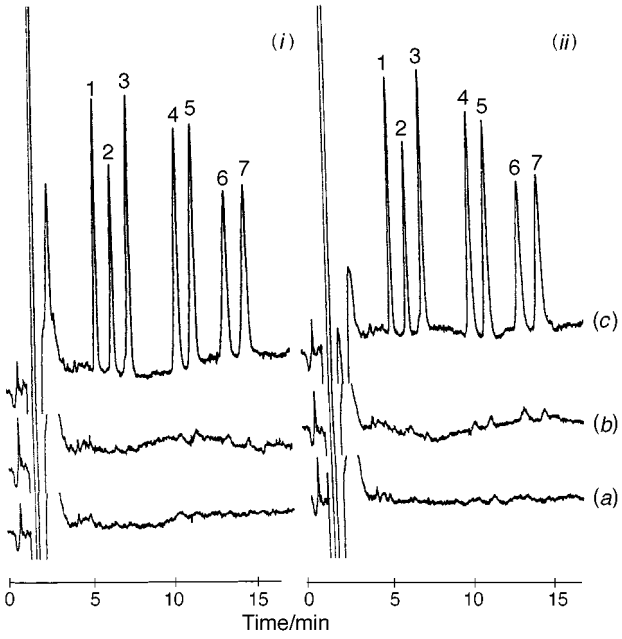

Fig. 5 Chromatograms (LC–UV) of 1.0 μg l^{-1} of the seven triazines studied (*i*) in reagent water and (*ii*) spiked in Kävlinge river water. Samples (500 ml) were extracted at a donor flow rate of 7.0 ml min^{-1} and 50 μl of the extract were injected in each case. Peaks: (1) desmetryn, (2) metoprotryn, (3) ametryn, (4) prometryn, (5) terbutryn, (6) dimethametryn and (7) dipropetryn. In both sets of chromatograms (*a*) denotes blank extraction, (*b*) extraction of buffer followed by sample extraction and (*c*) sample extraction.

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