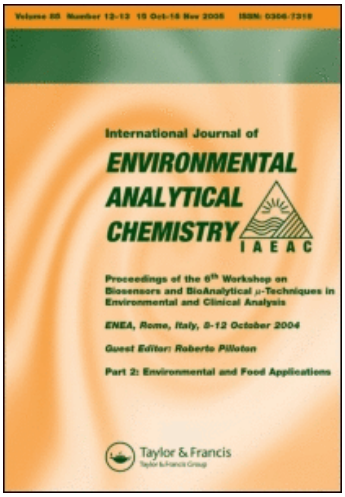


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# SUPPORTED LIQUID MEMBRANE ENRICHMENT STUDIES OF NATURAL WATER SAMPLES APPLIED TO LIQUID CHROMATOGRAPHIC DETERMINATION OF TRIAZINE HERBICIDES

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A method for sample work-up and enrichment using Supported Liquid Membrane (SLM) and liquid chromatographic determination of triazine herbicides in natural waters was investigated. A porous PTFE membrane was impregnated with a water immiscible organic solvent, forming a barrier between two aqueous phases. With a flowing donor and a stagnant acceptor solution, an enrichment of the triazines was obtained. The various factors that influence the extraction efficiency and selectivity of the extraction procedure were experimentally studied. The obtained results were in good agreement with the developed theoretical model. The pH of the acceptor solution was found to be the critical limiting factor in obtaining higher extraction efficiencies and led to an extraction efficiency decrease with an increase in enrichment time. By increasing both the trapping capacity of the acceptor solution and the donor flow rate, the method detection limit of the triazines ranged from 0.03 to 0.16 $\mu g L^{-1}$ in natural waters with 20 minutes extraction time.

*Keywords:* Extraction; supported liquid membrane; triazines; donor flow rate

## INTRODUCTION

The use of semi-permeable membranes as an alternative to liquid-liquid extraction and solid phase extraction methods in sample preparation procedures has gained attention in the last decade because of their minimum use of organic solvent and the possibility of being automated. One such approach in which

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extraction and preconcentration take place in a flow system is the supported liquid membrane (SLM) technique introduced by Audunsson[1]. The SLM technique uses a thin porous membrane immobilised with an organic liquid, forming a barrier between two aqueous phases, the donor and acceptor phase. The analytes are extracted from the flowing aqueous donor stream into the organic fluid followed by a back-extraction into the acceptor phase, which is usually stagnant. By careful choice of pH in the donor and acceptor phases, as well as the composition of the liquid membrane, selective extraction and enrichment can be achieved in one step for the diffusing species. The SLM technique is well suited for ionisable compounds such as medium to weak acids and bases which may be shifted in their aqueous/organic partitioning ratio by pH adjustments. The technique has been used for various applications such as determinations of amines in urine,[2] of herbicides in water[3,4] and of acids in manure,[5] and on-line to either liquid[6] or gas[7] chromatography.

Since their introduction, triazine herbicides have been widely used in agriculture as selective herbicides in many parts of world. These herbicides and their degradation products are highly persistent and hence their analysis in environmental samples is important. The concentration of triazines in aquatic environments like ground water, rivers and estuaries is often found to be close to the lower detection limits of most elaborate analytical procedures.[8] Methods of determination of these herbicides have, therefore, to cope with low levels and one way to improve the detection is to have an efficient sample clean-up and/or preconcentration step.



Many methods have been developed for the determination of triazines; extraction with organic solvent[9,10] or solid phase extraction[11,12] followed by gas[13,14] and liquid chromatographic[15,16] analysis have been recommended Martinez et al.[17] and Trocewicz[18] have recently reported methods for the enrichment of triazines from oil and natural waters in a supported liquid membrane followed by liquid chromatography determination with UV detection. The determination limit of the triazines in natural water was at 0.1 $\mu gL^{-1}$ after 60 minutes extraction time.[18] However, in neither of the above methods have carry over effect occurring in such a system nor the possibility of increasing the donor flow rate in order to lower the detection limit with minimum extraction time been investigated.

The objective of this paper was to investigate on the enrichment of some triazine herbicides, namely; atrazine, simazine and terbuthylazine from natural waters in a supported liquid membrane, to study the carry-over effects and to compare the detection limits by working at different donor flow rates while keeping the extraction time constant.

## EXPERIMENTAL

### Chemicals

Atrazine, 2-Chloro-4-ethylamino-6-isopropylamino-S-triazine (99%), simazine, 2-Chloro-4,6-bis(ethylamino)-S-triazine (99%), and terbuthylazine, 2-chloro-4-ethylamino-6-ter-butylamino-S-triazine (99%) were purchased from Larodan Fine Chemicals AB, (Malmö, Sweden). The $pK_a$ for the triazines studied are 1.68 for atrazine, 1.65 for simazine and 2.0 for terbuthylazine.[19]

The organic chemicals used as membranes were n-undecane, 99% and di-n-hexylether, 99% both purchased from Sigma, (Sigma Chemical Co., St Louis, MO, USA). All other chemicals used were of analytical grade. Reagent water was purified with a Milli-Q/RO4 unit (Millipore, Bedford, MA, USA).

### Standards

Stock solutions of each triazine for calibration of 200 $mgL^{-1}$ were prepared in acetonitrile. Standard aqueous solutions of each triazine of 2 $mgL^{-1}$ for extraction were prepared by dissolving them in water at pH 1.0 (adjusted with 0.5 mol/L sulphuric acid) and finally adjusted to pH 3.0 with 1 mol/L sodium hydroxide. The concentrations of aqueous solutions were later verified from a calibration curve. The lower pH was necessary to improve the aqueous solubility of the compounds. Stock solutions are stable for several months when stored at 0°C.



### Equipment

An Iso Chrom LC pump (Spectra Physics, San Jose, CA, USA) was used to pump the mobile phase for reversed phase separation of triazines. The analytical column was a 100 RP-18 column 5 $\mu$m × 125 mm × 4 mm Merck (Darmstadt, Germany) followed by UV detection (Model 757, Kratos Analytical Instruments, Ramsey, NJ, USA) at 235 and 254 nm.

The membrane unit (Figure 1) consisted of two circular PTFE (polytetrafluoroethylene) blocks (diameter = 120 cm, thickness = 8 mm) with grooves arranged as an Archimedes' spiral, (depth = 0.25 mm, width = 1.5 mm, length = 2.5 m) each with a total volume of 0.95 mL. Aluminium blocks with 6 mm thickness were used on both sides of the PTFE blocks to stabilise the construction.

A supported liquid membrane was prepared by soaking a porous PTFE membrane with pore size 0.2 $\mu$m, total thickness of 175 $\mu$m with 115 $\mu$m

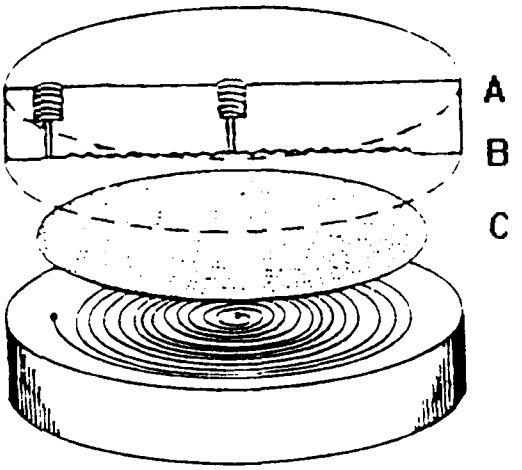


FIGURE 1 Membrane separator A: Aluminium back up B: PTFE block C: Impregnated liquid membrane



polyethylene support and a porosity of 70%; Millipore FG, Millipore (Bedford, MA USA) in an organic solvent to be immobilised for a period of 30 minutes. The membrane was then placed between the two PTFE blocks with the rough side of the membrane facing the donor side and the whole construction was clamped tight together with eight screws. After the membrane had been placed between the PTFE blocks and clamped, any remaining organic solvent on the outside of the membrane was flushed by pumping 20 and 10 mL water through the donor and acceptor channels, respectively.

A peristaltic pump (Minipuls 3; Gilson Medical Electronics, Villiers-Le-Bel, France) was used to pump solutions at constant flow in acid resistant tubings (Acid-Flexible; Elkay Products, Shrewsbury, MA, USA) with internal diameters of 2.0 mm for the sample and 1.0 mm for the buffer. The flow system (Figure 2) was connected with 0.5 mm i.d PTFE tubing and Altex screw fittings. A mixing coil and a tee connector used in the experimental set up were also made of PTFE.

## Membrane Enrichment

The sample and buffer (0.1 mol/L $NaH_2PO_4$ $H_2O$) were pumped with a peristaltic pump. Sample and buffer were mixed in the PTFE tee and the mixing coil (Figure 2). When the sample entered the donor channel in the membrane separator, the triazines were uncharged because of the pH-value (pH 4.0) and they pass by diffusion through the impregnated hydrophobic liquid membrane

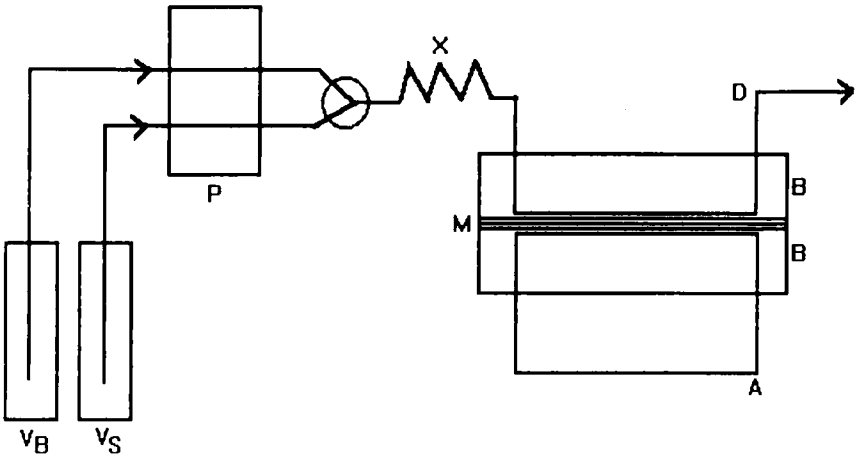


FIGURE 2 Set up for membrane enrichment; $V_B$: Vessel for buffer; $V_S$: Vessel for the sample; P: Peristaltic pump; C: Confluence point; X: Mixing coi;l B: Machine blocks of PTFE; D: Donor loop; M: PTFE membrane impregnated with organic liquid; A: Acceptor loop



to the acceptor channel. The triazines were trapped (ionised) and enriched in a stagnant 1 mol/L sulphuric acid solution. Most of the interferents, including smaller molecules which are protonated at the donor pH value and macromolecules pass through the donor channel to waste while small neutral molecules distribute between the two phases without any enrichment. For more details on the extraction process see ref.[20].

After a sample processing time of usually 20 minutes, the acceptor solution containing the organic herbicides was transferred by displacement for 5 minutes (1 mol/L $H_2SO_4$) using a peristaltic pump (while the donor channel was washed with donor buffer) into a graduated glass tube. 2.0 mL was collected and 0.7 mL of 7.0 mol/L sodium hydroxide was added to bring the final pH to 3.0. The collected extracts were analysed as soon as possible. A volume of 100 $\mu$L was injected into the HPLC. After enrichment, the membrane unit was further washed for 20 minutes with donor buffer for the donor channel and acceptor solution for acceptor channel before the next use.

For the reversed-phase liquid chromatographic separation of the three triazines, a mobile phase consisting of 50% 0.05 mol/L sodium acetate and 50% acetonitrile adjusted to pH 6.5 with 0.5 mol/L sulphuric acid at a flow rate of 1.0 mL per min was used. The mobile phase was degassed for 30 minutes on ultra sonic bath (Bransonic, Connecticut, USA) before use.

Calibration curves for the three triazines were made daily in the range 0.02–1.0 $mgL^{-1}$ based on replicate injections. Aqueous standards were injected with

a 100 $\mu$L loop at flow rate of 1.0 mL/min which gave linear correlation coefficients over 0.999 with insignificant intercepts at a 95% confidence level. The relative standard deviation based on replicate injections of 1 $mgL^{-1}$ of the triazine mixture were below 4.0% of peak heights.

### Extraction Efficiency

The extraction efficiency, E is defined as the fraction of analyte extracted from the donor phase to the acceptor phase.[20] At a specified extraction time, flow rate, phase compositions and ionic strength it is constant and it is a measure of the rate of mass transfer through the membrane. It is given by:

$$E = n_A / n_l = (c_A v_A)/(c_l v_l) \quad (1)$$

or

$$E = 1 - n_w / n_l \quad (2)$$

Here, $n_A$ and $n_l$ are the total amounts of analyte found in the acceptor and present in the extracted sample, respectively, $c_A$ and $c_l$ are the corresponding concentrations of analyte found in the acceptor and present in the extracted sample. $v_A$ is the volume of the stagnant acceptor phase and $v_1$ is the volume of the extracted sample that has passed through the donor channel. $n_W$ is the total number of moles in the donor waste accumulated from the start of the experiment. The extraction efficiency can be calculated from experimentally measured quantities using both of these equations. Deriving eqn (2), the possible presence of a fraction of the analyte in the membrane or adsorbed to various surfaces is neglected, and comparisons between the two ways of calculation can give information about such losses.

## RESULTS AND DISCUSSION

### Membrane Optimisation

#### *Carry-over effects*

In some SLM-applications,[6,21] notable carry-over effects were observed i.e. when a second portion of the acceptor is taken out before the next enrichment, significant amounts of analytes are found. Solute molecules physically adsorbing

onto the membrane surface in the acceptor side and slow mass transfer kinetics at the interface between the membrane and acceptor solution have been identified as possible causes of carry-over effects in the system. The former carry-over effect is reduced by pumping a larger volume of collecting solution while the latter is time dependent. A collecting period of 5 minutes for the acceptor solution after enrichment was used in this application while washing the donor channel with donor buffer, followed by further washing of the channels for 20 minutes to reduce both effects of memory effect.

To estimate the carry-over effects in the system occurring during the enrichment, a standard solution (0.6 $mgL^{-1}$ of the triazines) was enriched for 20 minutes followed by 5 minutes collection and 20 minutes washing. This was followed by a blank enrichment of reagent water in the same way. Thereby the carry-over effect from one enrichment to the next could be estimated. This procedure was repeated two times and gave carry-over effects of less than 0.5% except for terbuthylazine which had a carry-over effect of 2%.

To study the carry-over effect caused by slow kinetics at the membrane and acceptor interface, 1 $mgL^{-1}$ of triazine mixture was enriched as before but the acceptor solution was kept stagnant for various times ranging from 10 to 40 minutes after enrichment before collecting the enriched plug. The results indicated that the longer time the enriched plug was further kept stagnant after enrichment, the higher was the recorded amount of terbuthylazine until after 35 minutes when it reached a steady state and became constant. The extraction efficiency for other triazines remained more or less constant even with longer time of waiting before collecting the enriched plug. It therefore means that more time of further keeping the enriched plug stagnant allowed more terbuthylazine molecules in the membrane to diffuse into the acceptor solution. Carry-over effects in the SLM system for some analytes has been noted elsewhere.[6] This carry-over effect can be attributed to slow kinetics in the membrane and especially at the membrane\acceptor interface for more hydrophobic compounds with highest solubility in the organic liquid. If samples with unknown analyte concentrations are extracted a waiting time of 35 minutes before collecting the enriched plug is recommended to ensure that most of the terbuthylazine diffuses into the acceptor solution.

### *Condition of the acceptor pH*

Triazines are basic secondary amine compounds which can be protonated in acidic solutions making them suitable for trapping in the acceptor side of the membrane. In order to study the effect of pH on the degree of trapping of the triazines in the acceptor phase, 1.0, 0.5, 0.2, 0.08 and 0.025 mol/L of sulphuric

acid were used to vary the pH between 0.0 and 1.5. It was observed that the extraction efficiency for the pesticides of study were dependent on acceptor pH which increased with decrease in pH (Figure 3). Since simazine has a $pK_a$ value of 1.65,[19] the acceptor pH should be at least $-1.65$ according to the requirement for complete trapping ($\alpha_A < 0.0005$). The extraction efficiency in Figure 3 therefore increased with decrease in pH because the degree of trapping was also increasing. If the analytes are incompletely trapped, the extraction efficiency decreases with time as the analytes are accumulated in the acceptor phase, consequently decreasing the flux.[20] To study this behaviour, the dependence of extraction efficiency on enrichment time was monitored at two different trapping capacities of the acceptor solution (at different concentrations of sulphuric acid). The extraction efficiency was calculated according to equation 2. The results (Figure 4) show as expected a decrease of efficiency with extraction time. The rate of decrease was very dependent on the degree of trapping for the acceptor solution.



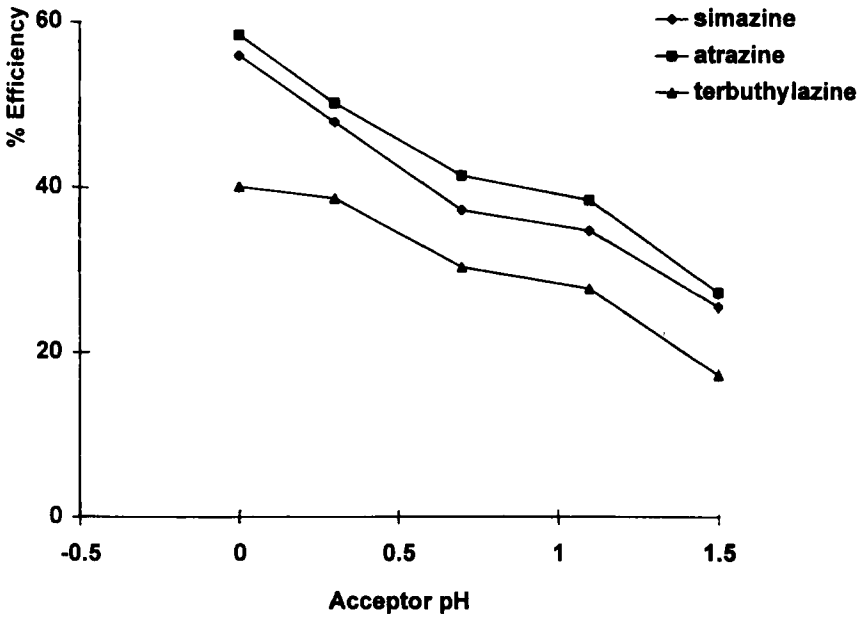


FIGURE 3 Extraction efficiency vs acceptor pH (different concentrations of sulphuric acid). Membrane composition; 50% n-undecane in di-n-hexyl ether, donor pH of 4.0 with 0.1 mol/L $NaH_2PO_4$ $H_2O$, 20 minutes extraction time of 0.6 mL/min.

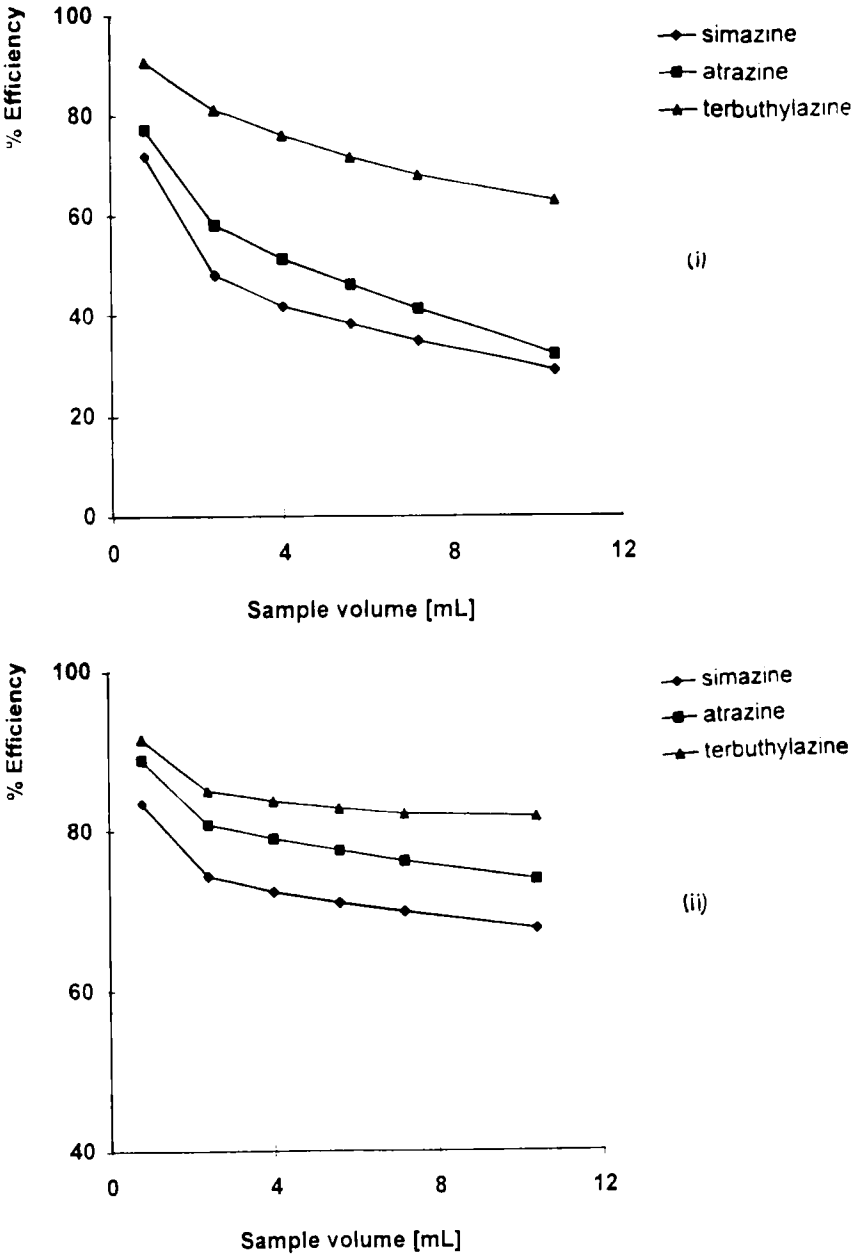


FIGURE 4 Plots of decrease in the extraction efficiency with time, donor pH of 4.0 with 0.1 mol/L $NaH_2PO_4H_2O$. Membrane composition; di-n-hexylether, (i) acceptor solution of 0.2 mol/L $H_2SO_4$, (ii) acceptor solution of 1.0 mol/L $H_2SO_4$,

### *Condition of the donor pH*

The influence of the donor pH on the extraction efficiency is not very critical but should be at least 2 pH units more than the highest $pK_a$ for basic triazines to allow complete dissolution into the membrane.[20] To study the influence of donor pH on the extraction efficiency, the pH was varied between pH 0.4 and 12. The results show that the extraction efficiency first increased with donor pH up to about 2. Then the extraction efficiency remained almost constant as almost all the solutes are in non-ionic form. A donor pH of 4.0 was taken for further work as it represented the theoretical optimum pH.

### *Choice of liquid membrane*

The extraction efficiency and selectivity are also known to depend on the composition of the organic liquid. Generally, it is desired that the affinity of the solutes for the organic liquid as measured by the partition coefficient be large as compared to interferents giving the required selectivity but not too large to give difficulties in stripping into the acceptor solution. For fairly polar compounds as the ones investigated, a polar liquid in the membrane is desirable. However, since polar liquids tend to be somewhat water soluble and less selective, a trade off must be reached between membrane stability and extraction efficiency.

In Table I, extraction efficiencies are given for three triazines with different membrane liquids under same conditions. The results show the obvious influence of the nature of the immobilised organic liquid on the recovery. Since the di-n-hexylether membrane gave considerably higher extraction efficiencies except for terbuthylazine, it was chosen as a membrane liquid. Terbuthylazine was exceptional in that the extraction efficiency did not differ in the three membranes perhaps due to its high solubility in all three membranes as it is the most hydrophobic.

TABLE I Extraction efficiencies after 20 minutes extraction of 0.1 $mgL^{-1}$ of the triazines for different liquid membranes, Donor pH 4.0, 0.2 mol/L $H_2SO_4$ as acceptor solution and donor flow rate of 0.6 mL/min. Numbers in brackets are relative standard deviation with three extractions.

| *Membrane/Compound* | *Simazine* | *Atrazine* | *Terbuthylazine* |
|---|---|---|---|
| Dihexylether | 0.50 (5.2%) | 0.53 (6.2%) | 0.32 (10.9%) |
| 50% dihexylether in undecane | 0.38 (2.7 %) | 0.43 (5.2%) | 0.32 (6.2%) |
| Undecane | 0.25 (4.4%) | 0.37 (1.4%) | 0.33 (3.6%) |

## Influence of Nonstagnant Acceptor Solution on Extraction Efficiency

The decrease in extraction efficiency with increase in enrichment time was further studied but with a nonstagnant acceptor solution slowly pumped at different flow rates in a countercurrent way. Results in Figure 5 show that the extraction efficiency was constant over the entire extraction time as the concentration gradient across the membrane was maintained by the continuous removal of the analytes from the acceptor compartment. The extraction efficiency was also much higher and depended on the flow rate of the acceptor solution. In a similar system but with pH of the acceptor solution well below the $pK_a$ of basic solutes, the extraction efficiency for nonstagnant acceptor solutions were also much higher but independent of acceptor flow rate.[1] Possible causes of greater extraction efficiency for nonstagnant acceptor solutions were attributed to the enhanced mass transfer caused by agitational effects of the fluttering membrane set in more motion when both phases are flowing. The extraction efficiency being dependent on acceptor flow rates could be attributed to the problem of incomplete trapping discussed above. However, assuming that protonation in the acceptor phase is instantaneous, then theoretically the extraction efficiency for stagnant and nonstagnant acceptor phases should be equal and independent of the acceptor flow rate.[1]

The concentration in the flowing acceptor waste was also monitored at various flow rates. The results in Figure 6 show the concentration increasing with enrichment time until steady state conditions are reached as expected. However, the steady state for terbuthylazine with the highest memory effect in the system was to some extent lately reached, suggesting that it was difficulty to strip into the bulk acceptor solution especially at the lower acceptor flow rate.

From the results on the studies on the influence of nonstagnant acceptor solutions on extraction efficiency, one may suggest the possibility of combining SLM and a solid phase trace enrichment column in situations where stagnant acceptor solution limits the mass transfer rate because of incomplete trapping problem so that stripped analytes are slowly pumped but are later trapped on the pre-column. This is a similar technique as described for dialysis (ASTED).[22]

## Natural Water

The influence of sample matrix and various concentrations on the extraction efficiency were determined by spiking natural water from Kävlinge river, situated about 20 km north of Lund, Sweden. Blank natural water was extracted for 20 minutes. Natural water was then spiked at 100, 20 and 5 $\mu gL^{-1}$ of the

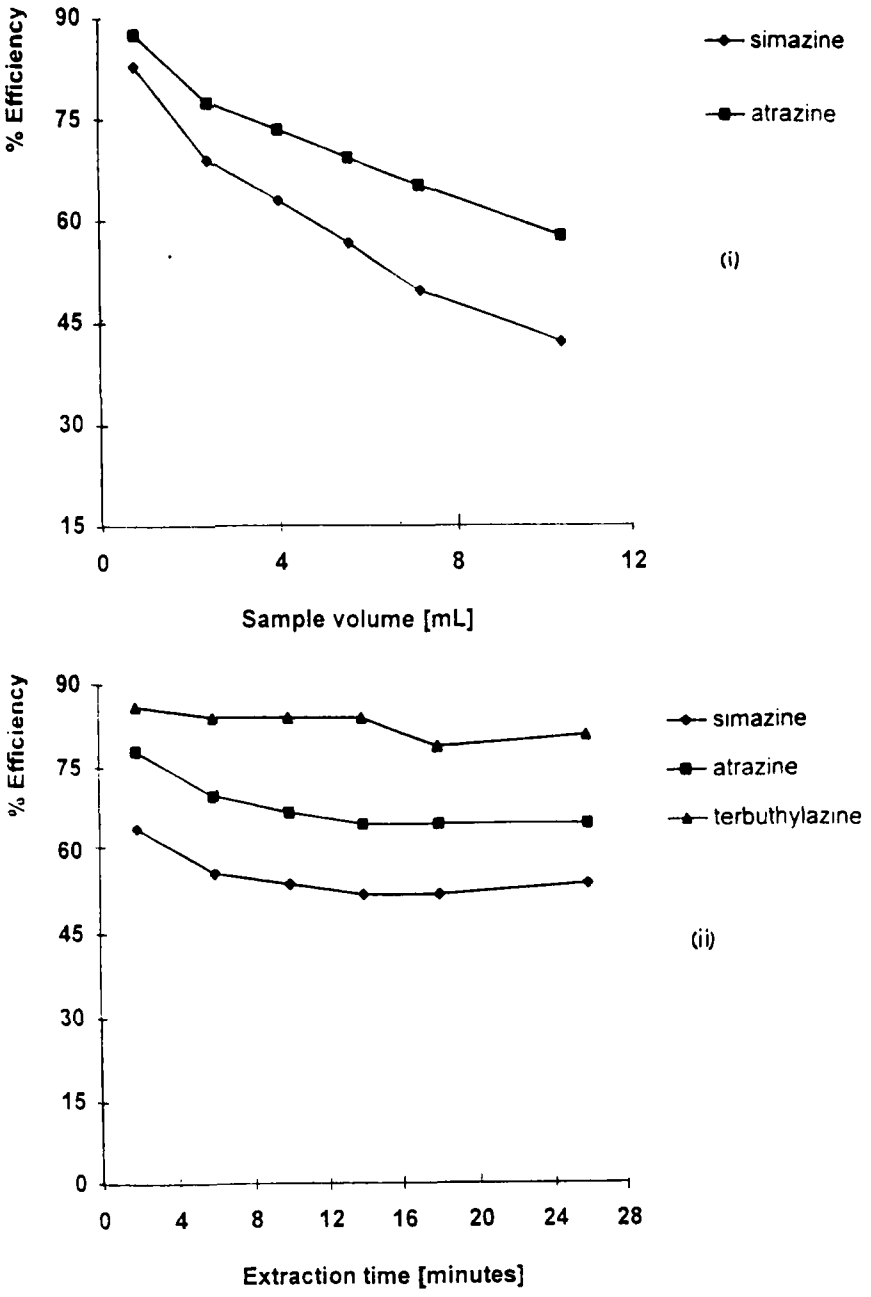


FIGURE 5 (i & ii) Plots of decrease in the extraction efficiency with extraction time with a 0.2 mol/L $H_2SO_4$ as an acceptor solution. Membrane composition; 50% di-n-hexylether in undecane (i) stagnant acceptor solution (ii) nonstagnant acceptor solution at flow rate of 0.08 mL/min (iii) non-stagnant acceptor solution at flow rate of 0.2 mL/min

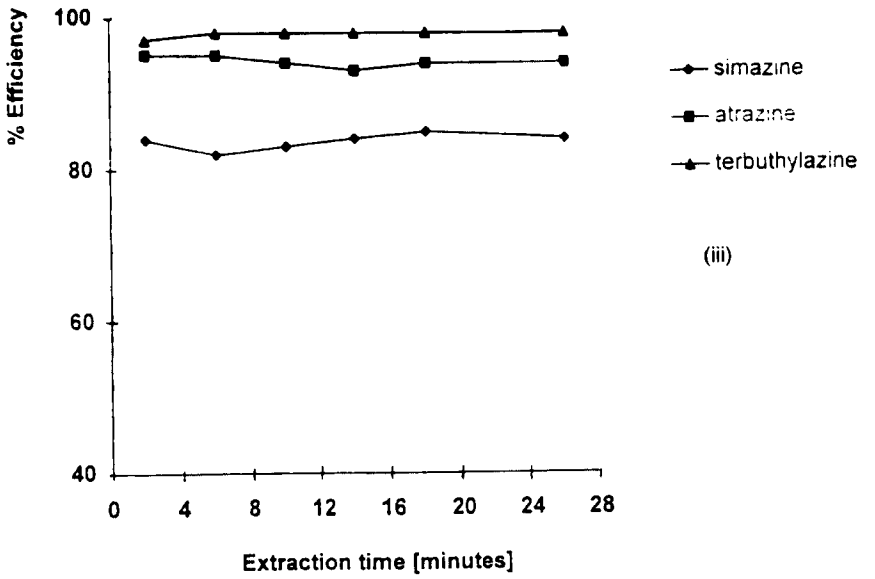


FIGURE 5 (iii) Plots of decrease in the extraction efficiency with extraction time with a 0.2 mol/L $H_2SO_4$ as an acceptor solution. Membrane composition; 50% di-n-hexylether in undecane (**i**) stagnant acceptor solution (**ii**) nonstagnant acceptor solution at flow rate of 0.08 mL/min (**iii**) non-stagnant acceptor solution at flow rate of 0.2 mL/min



triazine mixture and extracted in the same way. The results were compared to those of reagent water extracted under similar conditions. No major differences could be seen at the chosen concentrations (Table II). The chromatograms of the blank and spiked natural water extracts are shown in Figure 7.

In other similar systems,[6,20] it has been shown that the extraction efficiency decreases while the amount of analyte extracted per unit time increases with increasing flow rate. To study this effect, the extraction time of 20 minutes was kept constant while the donor flow rate was increased from 0.6 to 5.0 mL/minute. The corresponding method detection limits are shown in Table III. The results shown in the table indicate that by increasing the sample volume extracted while keeping the extraction time constant, the method detection limit could be lowered by a factor of about 7 for all the compounds. This is attractive for environmental natural water where sample volumes are often unlimited. The only obvious draw back is reduced membrane stability due to processing of larger liquid volumes, increasing the rate of dissolution of the membrane liquid. The detection limit with a UV detector at 235 nm was therefore dependent on the donor flow rate and extracted sample volume.

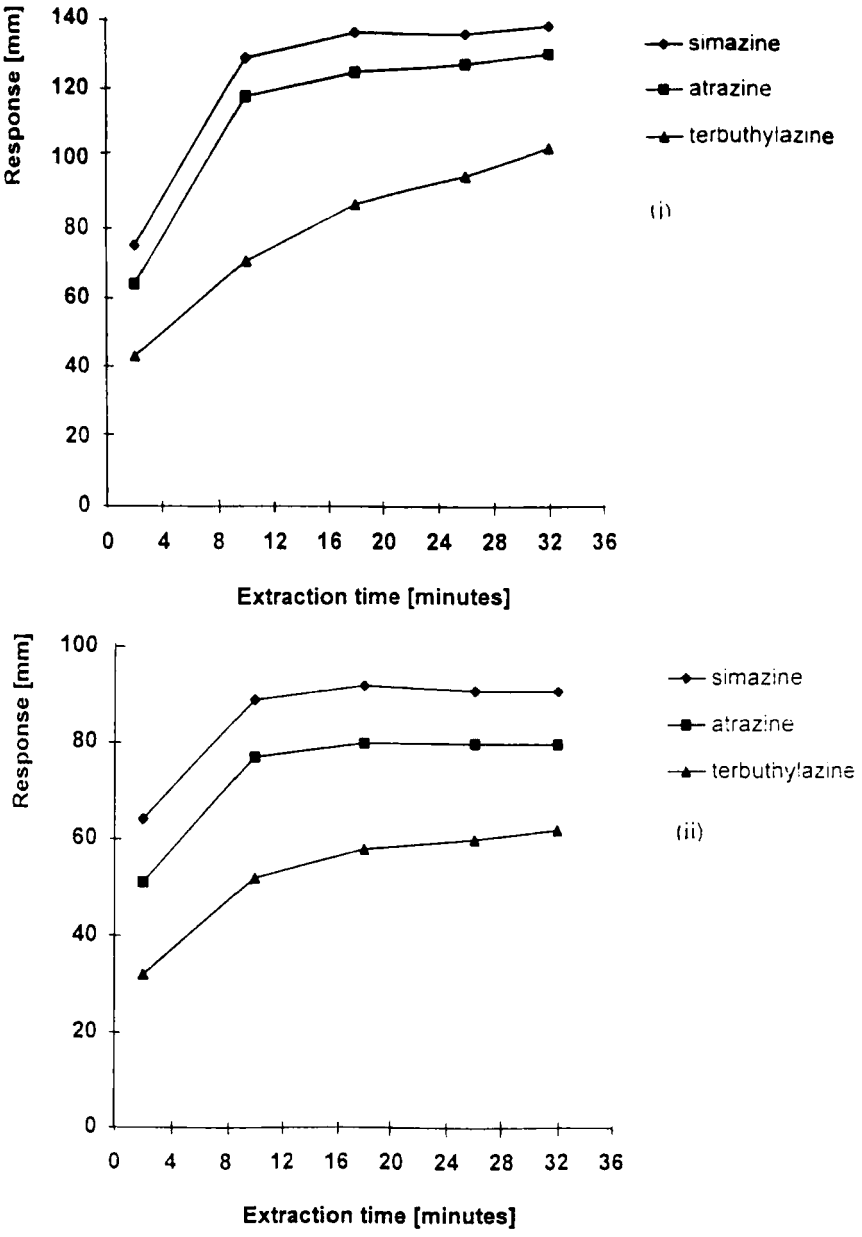


FIGURE 6 Plots of concentration profile in the acceptor outlet at different times with 0.2 mol/L $H_2SO_4$ as an acceptor solution. Membrane composition; 50% di-n-hexylether in undecane (i) 0.08 mL/min as an acceptor solution flow rate (ii) 0.2 mL/min as an acceptor solution flow rate

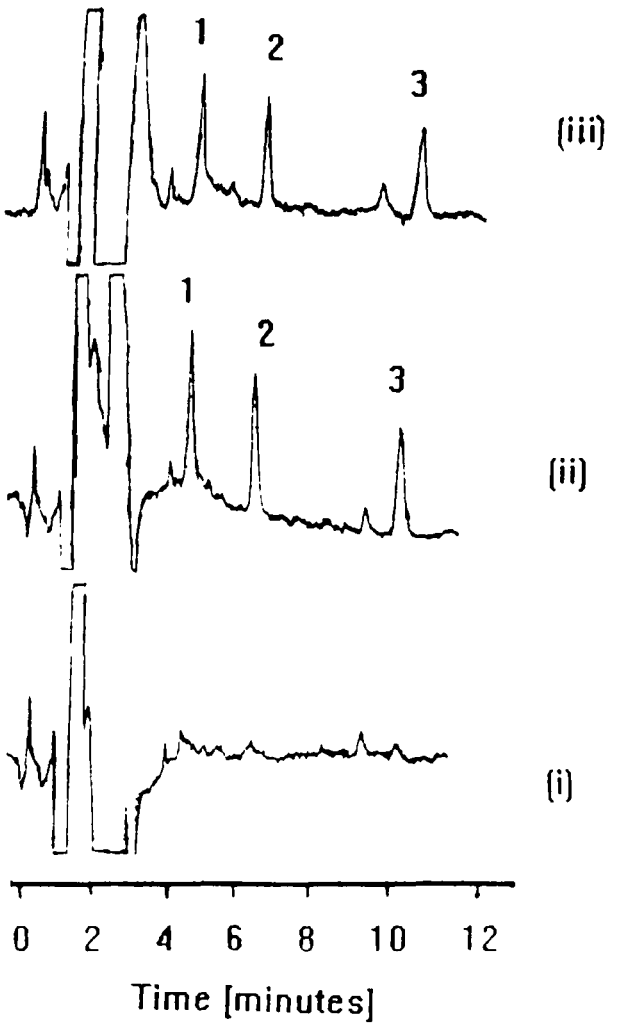


FIGURE 7 Chromatograms (LC-UV) of three triazines at 20 minutes extraction time (**i**) extraction of blank natural water (**ii**) natural water extract spiked with 10 $\mu gL^{-1}$ simazine (1), 5 $\mu gL^{-1}$ atrazine (2), and 5 $\mu gL^{-1}$ terbuthylazine (3) at donor flow rate of 0.6 mL/min (**iii**) natural water spiked with 1.5 $\mu gL^{-1}$ simazine (1), 0.7 $\mu gL^{-1}$ atrazine (2) and 0.7 $\mu gL^{-1}$ terbuthylazine (3) at donor flow rate of 5.0 mL/min.

## CONCLUSION

We have demonstrated in this paper that SLM extraction with HPLC and UV detection can be used for the determination of triazine herbicides in natural waters. We have also shown that by the use of higher flow rate, it is possible

TABLE II Extraction efficiencies of triazines from different concentrations spiked in natural water. Donor pH 4.0, 1 mol/L sulphuric as acceptor solution, Di-n-hexylether as membrane liquid, 20 minutes pumping time of 0.6 mL/min. Numbers in brackets are relative standard deviations with corresponding number of extractions

| *Concentration* | *Simazine* | *Atrazine* | *Terbuthylazine* |
|---|---|---|---|
| 100 $\mu gL^{-1}$ (reagent water) | 0.65 (7.8%, 6) | 0.72 (3.9%, 6) | 0.52 (9.1%, 4) |
| 100 $\mu gL^{-1}$ (river water) | 0.68 (1.2%, 4) | 0.72 (2.1%, 4) | 0.47 (6.5%, 3) |
| 20 $\mu gL^{-1}$ (river water) | 0.67 (8.2%, 3) | 0.74 (2.8%, 3) | 0.50 (8.3%, 3) |
| 5 $\mu gL^{-1}$ (river water) | 0.63 (7.2%, 3) | 0.65 (4.7%, 3) | 0.52 (6.1%, 3) |

TABLE III Method detection limit (3 times the standard deviation of the blank) of the herbicides in spiked natural water at two donor flow rates in $\mu gL^{-1}$.

| *Donor flow (mL/min)* | *Simazine* | *Atrazine* | *Terbuthylazine* |
|---|---|---|---|
| 0.6 | 1.0 | 0.2 | 1.1 |
| 5.0 | 0.15 | 0.03 | 0.16 |

to lower the detection limit for these herbicides while maintaining the same extracting time.



## *Acknowledgements*

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