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Talanta 64 (2004) 101–108
Talanta
www.elsevier.com/locate/talanta

Carrier-mediated extraction of bipyridilium herbicides across the hydrophobic liquid membrane

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Received 12 August 2003; received in revised form 21 November 2003; accepted 27 November 2003

Available online 18 May 2004

Abstract

Supported liquid membrane (SLM) method for preconcentration and enrichment of the two bipyridilium herbicides, namely diquat and paraquat, from environmental water samples has been developed. The permanently charged cationic herbicides were extracted from a flowing aqueous solution to a stagnant acidic acceptor solution across a liquid membrane containing 40% (v/v) di-(2-ethylhexyl) phosphoric acid dissolved in di-*n*-hexyl ether. The mass transfer of analytes is driven by the counter-coupled transport of hydrogen ions from the acceptor to the donor phase. The efficiency of the extraction process depends on the donor solution pH, the amount of the mobile carrier added to the liquid membrane and the concentration of the counter ion in the acceptor solution. The applicability of the method for extraction of these quaternary ammonium herbicides from environmental waters was also investigated by spiking analyte sample solutions in river water. With 24 h sample enrichment concentrations of diquat and paraquat down to ca. 10 ng/L could be detected in environmental waters.

Keywords: Bipyridilium herbicides; Supported liquid membrane; Counter-coupled transport; Regeneration; Environmental waters

1. Introduction

The use of pesticides has improved agricultural productivity by offering quick and convenient way to eliminate annoying or destructive organisms. Bipyridilium herbicides are one of the commonly used chemicals for the control and management of terrestrial and aquatic vegetation. Diquat (1,1′-ethylene-2,2′-bipyridylium) and paraquat (1,1′-dimethyl-4,4′-bipyridylium) are among the chemical compounds grouped under this class of herbicides. Diquat mainly acts against broadleaf weeds whereas paraquat may be used to remove both broadleaf and grass weeds [1]. These quaternary ammonium ions are also effective contact desiccants widely used to aid harvesting of potato, cotton, sugarcane and other oil seed crops [1,2].

A serious drawback in connection with the use of these chemical substances is that the measures taken to increase productivity in agriculture may cause an array of undesirable effects on the environment, as they are highly toxic [3,4]. Considering the aquatic environment, for example, they can reach surface and ground waters through various means such as leakage, runoff and leaching [5,6]. Thus, the water bodies may contain a considerable quantity of the residues of these pesticides sufficient to affect their quality. Therefore, it is of paramount importance to determine the level to which the residues of these substances are accumulated in water bodies for the well-being of the human and aquatic lives.

The extent of release and thus distribution of these polluting substances into the environment is monitored through chemical analysis. Since the pesticides and their degradation products are found in various complex matrices at very low concentrations, preconcentration of the chemical compounds is highly desirable, prior to their analysis [7–9]. This calls for the use of efficient and selective sample handling processes [10]. To this end, numerous sample preparation techniques, that make use of various mechanisms to isolate the analytes of interest from the sample matrix, have been developed [11–15]. The supported liquid membrane (SLM) extraction methodology, introduced by Audunsson [16], is one format of membrane-based extraction technique that can be used to achieve a selective enrichment early in the sample analysis scheme. The technique utilizes a porous

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doi:10.1016/j.talanta.2003.11.049

polytetrafluoroethylene (PTFE) support material on which a water-immiscible membrane solvent or a mixture of solvents is immobilized. The immobilized membrane forms a selective barrier between two aqueous phases in a flow system. The analytes from a continuously flowing aqueous donor phase are extracted into the organic membrane liquid and then diffuse to the other side of the membrane, where they are irreversibly trapped in a second aqueous solution, the acceptor phase. The acceptor is kept stagnant during the extraction period and thereafter removed for identification. The more flexible nature of liquid membrane extraction allows tuning of selectivity by changing the organic solvent, changing or modifying the extraction process using carriers in various modes, adjustment of the pH in the donor and acceptor phases and changing the support materials. Reviews of the recent developments of the technique and comparison with other existing sample preparation methods have been discussed in detail in several publications [17–19].

SLM extraction technique has been employed successfully for the sample preparation and enrichment of residues of various pesticides [20–25], anionic surfactants [26], metal ions [27,28], phenoxy acids [29,30] and amines [31–34] for the purpose of determining these substances at trace levels, in samples of different origins. So far no work has been reported on the preconcentration and enrichment of bipyridilium herbicides using this extraction technique. The objective of this study is, therefore, to develop method for sample preparation and enrichment of bipyridilium herbicides in environmental waters based on SLM technique and determination of the analytes using HPLC with UV-detection.

2. Experimental

2.1. Chemicals, reagents and working solutions

The bipyridilium herbicides used were diquat dibromide monohydrate (99.0%) and paraquat dichloride trihydrate (98.0%) purchased from Promochem (Wesel, Germany). Di-*n*-hexyl ether (Sigma, St. Louis, MO, USA) was used as a membrane solvent and di-(2-ethylhexyl) phosphoric acid (Fluka, Buchs, Switzerland) as a mobile carrier. The chemicals used for preparing donor buffers, *viz.*, H_3PO_4, $NaH_2PO_4{\cdot}2H_2O$ and Na_2HPO_4, were all from BDH (Poole, England). HPLC grade methanol and sodium salt of 1-heptane sulfonic acid (both form Sigma, St. Louis, MO, USA), and diethyl amine (Merck, Germany) was used to prepare the mobile phase utilized in the chromatographic analysis.

Stock solutions of diquat and paraquat (100 mg/L) were prepared in reagent water. Working solutions of the analytes mixture were prepared by diluting the required volumes of the stock solutions with reagent water. Solutions of the phosphate buffer were prepared from H_3PO_4-$NaH_2PO_4{\cdot}2H_2O$ (pH = 3), $NaH_2PO_4{\cdot}2H_2O$ (pH = 4.0) and $NaH_2PO_4{\cdot}2H_2O$-Na_2HPO_4 (pH = 5.0–8.0) in reagent water [35]. All stock, standard and extracted solutions were stored in a refrigerator when not in use.

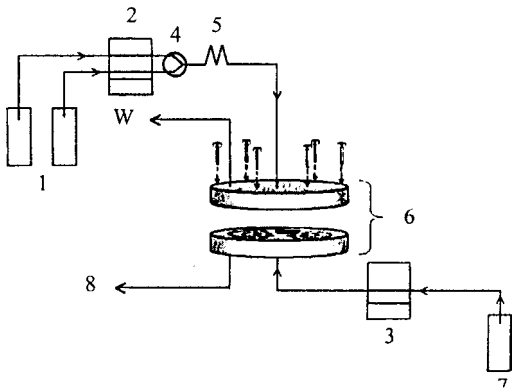

Fig. 1. Set-up of the flow system for liquid membrane extraction. (1) Containers for sample solution and donor buffer; (2) and (3) peristaltic pumps for the donor and acceptor solutions, respectively; (4) PTFE tee connection; (5) mixing coil; (6) the membrane unit; (7) container for the acceptor solution, (8) container for extract collection and (W) waste.

2.2. Experimental set-up

The details of the experimental set-up is described elsewhere [21], and its configuration is depicted in Fig. 1.

2.3. Membrane preparation and extraction procedures

The liquid membrane was prepared by immersing the porous polymeric membrane support in a mixture of di-*n*-hexyl ether (DHE) and di-(2-ethylhexyl) phosphoric acid (DEHPA) (60%/40%, v/v) for 30 min [33]. After installation of the membrane unit, its acceptor and donor channels were flushed with distilled water to remove excess organic solvent from the surface of the support material. The acceptor channel was then filled with the trapping (acceptor) solution and kept stagnant. Following this, samples of the bipyridilium herbicides and the buffer were pumped into the donor channel of the membrane unit with a peristaltic pump, in a 1:1 volume ratio. The solutions were merged in a PTFE tee connection and they were further mixed in a mixing coil. After the sample enrichment, the buffer solution was pumped alone through the donor channel to wash the flow tubing and the system was left to stand, to give sufficient time for the analytes to diffuse across the membrane to the acceptor phase where they are trapped irreversibly. Finally, the acidic acceptor solution, that may contain the extracted analytes, was transferred to a graduated cylinder by displacing with fresh acceptor solution at a flow rate of 0.2 mL/min for 10 min. The pH of the extracted solution was adjusted to 7.0 using 3.0 M NaOH and 1.0 M HCl solutions. The acceptor channel was then washed with 10.0 mL distilled water before using the membrane for the next extraction.

2.4. Chromatographic analysis and detection

The high performance liquid chromatography (HPLC) system used for the analysis of the bipyridilium herbicides consisted of a high pressure LC pump (LKB, Stockholm, Sweden) and a manual sample injection unit (VICI AG, Valco Europe, Schenkon, Switzerland) fitted with a sample loop. Separation of the analytes was performed on a C18 analytical column (Genesis C18 120 A, 2.1 mm i.d., Jones Chromatography Ltd., Hengoed, UK). For isocratic reversed-phase separation of the herbicide compounds, a mobile phase was prepared by mixing orthophosphoric acid (11.2 mL, 0.2 mol), diethyl amine (10.2 mL, 0.1 mol) and sodium heptanesulfonate (2.002 g, 0.01 mol) and diluting the mixture to 1.0 L with aqueous methanol (25%, v/v) [36]. The eluent was degassed before introducing into the HPLC system. A 10.0 μL aliquot (or a 25.0 μL aliquot, when lower concentration analytes were extracted) of the enriched samples were injected and analyses were carried out at a mobile phase flow rate of 0.2 mL/min. Detection of the compounds was carried out with a variable wavelength UV-Vis detector (Model 118, Gilson Medical Electronics, Villiers-Le-Bel, France). Eluents were monitored at a wavelength of 290 nm [36] and signals were recorded on a BD 111 chart recorder (Kipp and Zonen, Partille, Holland). Evaluation of the peaks was made manually.

2.5. Carry over effect

The carry over effect (COE) in the present system was studied as follows: an aqueous solution 0.5 mg/L in both the herbicides, was mixed with phosphate buffer (pH 7.0) and enriched for 40 min at a sample flow rate of 0.5 mL/min. At the end of the enrichment time, the donor channel of the flow system was washed with the buffer and the extraction system was allowed to stand for 10 min without pumping any of the channels. After collecting the extract from the acceptor, a reagent water blank was enriched in the same way and the extracts were analyzed. Effect of the length of washing time of the donor phase on the transfer of analyte molecules adsorbed on the flow channels to the membrane was studied by rinsing the flow system for 5, 10 and 20 min after processing the standard samples. The COE was calculated from the heights of the peaks of the sample and blank extractions using the equation $\mathrm{COE} = P_b/(P_b + P_s)$, where P_b and P_s are peak heights of the blank and sample extractions, respectively [37].

2.6. Optimization of the extraction system

The liquid membrane system developed for the extraction of the two bipyridilium herbicides was optimized in terms of the amount of the extractant dissolved in the membrane solvent, and pH of the acceptor and sample solutions. In all the optimization processes, 10.0 mL sample solutions containing 0.5 mg/L of each of the herbicides were mixed with donor buffer and processed at a flow rate of 0.5 mL/min for 40 min.

2.7. Determination of the extraction efficiency (E)

Extraction efficiency, in SLM extraction, is defined as the fraction of analytes extracted from the donor solution to the acceptor phase. It measures the rate of mass transfer through the membrane. The value of E can be determined from experimentally measured quantities. In the liquid membrane extraction described in this work, the quantity has been calculated from the enriched sample collected from the acceptor phase using the equation $E = n_A/n_I$, where n_I and n_A are the number of moles of analytes entering the donor channel and collected in the acceptor solution, respectively.

3. Results and discussion

3.1. Enrichment of analytes with the developed method

The transport mechanism of the quaternary ammonium ions in the present system is depicted in Fig. 2. The bipyridilium herbicides (A^{2+}) are positively charged when entering the donor channel of the membrane unit. DEHPA (RH), dissolved in the membrane solvent, reacts with the charged analyte at the donor-membrane interface forming an ion-pair while releasing a proton. The formed neutral ion-associate diffuses across the membrane and the analyte is exchanged for a hydrogen counter ion at the membrane-acceptor interface thereby the analyte is irreversibly trapped in acceptor phase in its charged form. The complex formed between the carrier and the counter ion diffuses back to the donor-membrane interface and repeats the analyte transport process. The total effect of this counter-coupled transport is transfer of analyte molecules from the donor to the acceptor and hydrogen ions in the opposite direction.

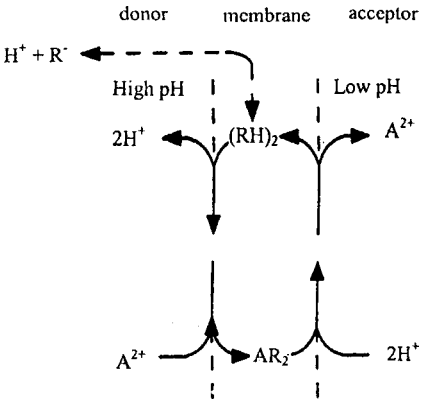

Fig. 2. Schematic representation of the transport mechanism of the bipyridilium herbicides in the SLM extraction system.

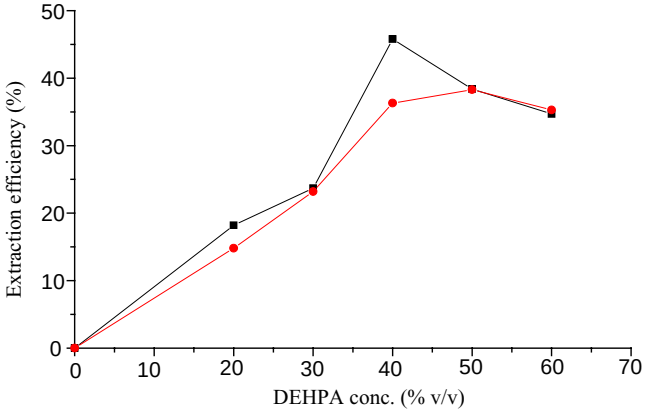

Fig. 3. Extraction efficiency versus carrier concentration in the membrane liquid. Donor pH: 7.0 with phosphate buffer; acceptor solution: 0.1 M HCl. A 10.0 μL aliquot of the enriched sample was injected into the separation system. Symbols: (■) diquat and (●) paraquat.

3.2. Optimization of the extraction system

3.2.1. Effect of carrier concentration on extraction efficiency

For carrier-mediated liquid membrane extraction systems, the carrier is a vital component in the membrane formulation. Fig. 3 shows how the extraction efficiency is influenced by the quantities of DEHPA dissolved in the membrane solvent, DHE. From the results of this study it is evident that the participation of a carrier is necessary for the transport of the quaternary ammonium compounds across the membrane. There is a steady increase in extraction efficiency with carrier concentration up to a level of about 40–50% (v/v) of DEHPA, after which a downward trend is observed for both the analytes. This observation might be the result of the influence of two factors on the mass transfer of the solutes through the liquid membrane, namely, the concentration gradient of the solute-carrier ion associate and the viscosity of the organic liquid membrane phase [38].

The flux of the compound through the membrane, J, is related to the concentration gradient, ΔC, and the membrane thickness, l, through Fick's first law as $J = -D\,\Delta C/l$, where D is the solute diffusion coefficient. In this case, high fluxes can be achieved when a large diffusion coefficient as well as a large concentration gradient is maintained. On the other hand, the analyte diffusion is dependent on the viscosity of the organic phase, η, according to the Stokes–Einstein relationship as $D = kT/6\pi\eta r$, where k is the Boltzman constant, T is the absolute temperature and r is the molecular radius of the species. Therefore, increasing the carrier concentration generally increases the driving forces as well as the viscosity of the liquid membrane. Even if the flux of the analytes is increased for higher DEHPA concentrations in the organic phase, the effect of increase in viscosity on the mass transfer prevails above a carrier concentration of 40% (v/v) and as a result, the extraction efficiency of the examined compounds decreases.

3.2.2. Effect of acceptor and donor solution pH on extraction efficiency

To study the degree of extraction of the bipyridilium herbicides in the acceptor phase, the concentration of hydrochloric acid was varied between 0.01 and 1.0 M while the pH of the donor solution was kept constant at 7.0. As can be seen from Fig. 4(a), maximum extraction efficiencies for diquat and paraquat were obtained at an acceptor pH of 1.0. The lower extraction efficiencies of both analytes at an acceptor pH below 1.0 might be due to their instability in strongly acidic media [2]. In addition to this, as the pH of the trapping solution becomes too low, the carrier may be protonated and becomes unable to transport the charged analytes. When the proton concentration approaches 0.01 M, the extraction efficiencies of both analytes was much lowered in spite of a pH difference of five units between the donor and the acceptor phases. This is most likely due to the fact that DEHPA is partially dissociated in this pH region. This prevents the back extraction of the carrier as undissociated acid from the

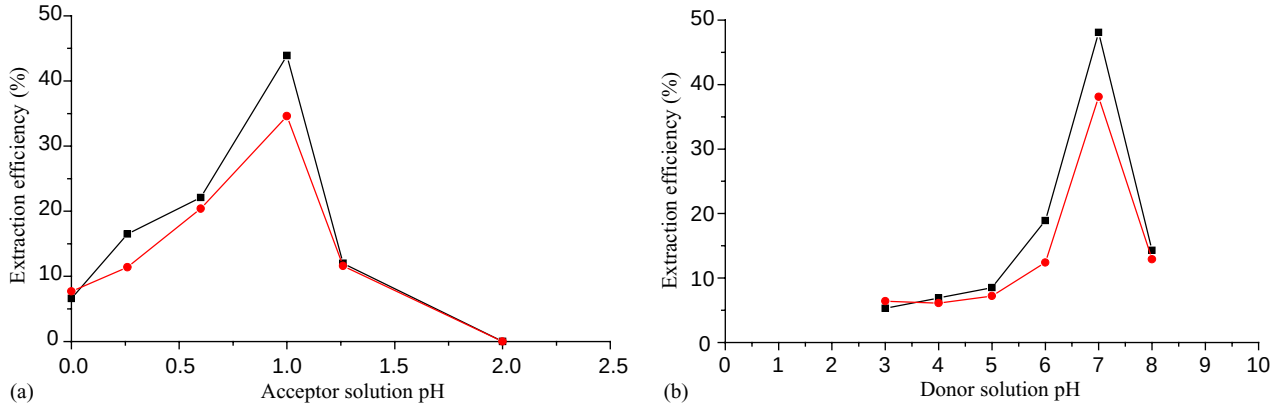

Fig. 4. (a) Extraction efficiency versus acceptor solution pH, and (b) extraction efficiency vs. donor solution pH. Membrane liquid: DHE/DEHPA (60%/40%, v/v); for (a) donor solution pH: 7.0, with phosphate buffer; for (b) acceptor solution: 0.1 M HCl. A 10.0 μL aliquot of the enriched sample was injected into the separation system. Symbols: (■) diquat and (●) paraquat.

acceptor solution to the membrane liquid, thereby inhibits the mass transport of the analytes in the other direction [39].

In the study of the influence of donor solution pH on *E*, sample solutions were mixed with phosphate buffers, ranging in pH from 3.0 to 8.0, before entering the donor channel of the extraction system and enriched for 40 min. The results of this experiment are shown in Fig. 4(b). It is clear that increase in pH in the donor phase leads to higher extraction of the analytes as it is required to create a proton concentration gradient over the membrane. Therefore, the increase in fraction of analytes extracted in the acceptor phase with the decrease in hydrogen ion concentration in the donor solution can be attributed to this criterion. On the other hand, the decrease in *E* above a donor solution pH of 7.0 might be due to the decomposition of the analytes in basic media [2]. Furthermore, the solubility of DEHPA in the donor solution increases with pH and this could lead to lower extraction efficiency as a result of formation of complexes with the analyte molecules in the donor solution which pass to the waste instead of being dissolved in the membrane [39].

3.3. Carry-over effect

Transfer of fraction of analyte molecules adsorbed on the flow tubing and the surface of the support material to the acceptor channel can be effected by washing the flow system between each extraction, and in the present system this was studied as described in Section 2.5. The results of this study, given in Table 1, clearly show the adsorption of higher fraction of analyte molecules in the flow system during the extraction. The COE's determined for both analytes, after a 20 min washing and 10 min equilibration time, are less than 3%, showing that effective transfer of maximum fraction of the adsorbed analytes to the acceptor phase is possible by rinsing the flow system with a fresh donor buffer. Leaving the extraction system to stand for some time after the washing period, without pumping any of the channels, is also required to complete the diffusion of analytes across the membrane liquid.

Moreover, in carrier-mediated liquid membrane extraction processes, the problem of incomplete transfer of analyte molecules from the membrane liquid to the acceptor phase (membrane memory effect, MME) can be lowered by designing extraction conditions that enhance the extent of breaking of the ion-associates, formed between the analyte molecules and the extractant, at the membrane-acceptor boundary. This can be done by properly optimizing the composition of the acceptor solution.

Table 1
Fraction of analytes (%) detected in the blank extract after washing the donor channel of the flow system

Herbicide	Washing time (min)		
	5	10	20
Diquat	11.8 (8.5)	7.8 (9.6)	2.6 (15.6)
Paraquat	8.5 (5.7)	5.7 (14.1)	2.4 (15.2)

Numbers in bracket are percent relative standard deviation values for $n = 4$.

3.4. Donor flow rate dependence of extraction efficiency

The effect of the flow rate at which sample solutions pass through the donor channel on the efficiency of the extraction was studied by processing samples at different flow rates in the range between 0.2 mL/min and 4.0 mL/min. The most efficient extractions were obtained when samples were processed at lower flow rates. This is mainly because the lower sample flow rates provide longer contact time for the analyte molecules with the membrane liquid via increasing their residence time in the donor channel of the membrane [19].

On the other hand, increasing the donor flow rate increases the amount of analytes introduced into the extraction system and the net result often is an increase in the amount of solute molecules accumulated in the acceptor phase (E_e) in a given period of time [19]. The results obtained in this study are also in agreement with this theoretical prediction. A downward trend in E_e above a donor flow rate of *ca.* 3.0 mL/min was observed which might be due to the decrease in the lifetime of the membrane and reduced extraction efficiency for the subsequent extractions which may be caused by dissolution of the membrane liquid into the flowing large volume of the aqueous sample, and these factors are cited as the major problems of increasing the donor flow rate.

3.5. Lifetime of the membrane

Evaluation of the lifetime of the liquid membrane was carried out by extracting sample solutions prepared in reagent water for 60 h at a flow rate of 1.0 mL/min. Two milliliter of the contents of the acceptor channel were collected every 3 h and analyzed. It was observed that the membrane could be used for about 18 enrichment cycles of 3 h duration each, without a significant decrease in the extraction efficiencies of both analytes Fig. 5. This observation was also found to be in a good agreement with the results described elsewhere [39].

After 60 h of continuous extractions, when the extraction efficiencies of diquat and paraquat drop to 16.2 and 13.9%, respectively, the support material was demounted from the membrane assembly, washed with distilled water and dried. It was then reimpregnated in the organic liquid membrane for 30 min. Further extractions were performed using the reimprignated membrane and practically the same results, as the newly prepared supported liquid membrane, were obtained suggesting the convenient regeneration of the membrane.

3.6. Applications

3.6.1. Performance of the extraction method at lower analyte concentrations

The performance of the developed method for the extraction of trace quantities of diquat and paraquat was

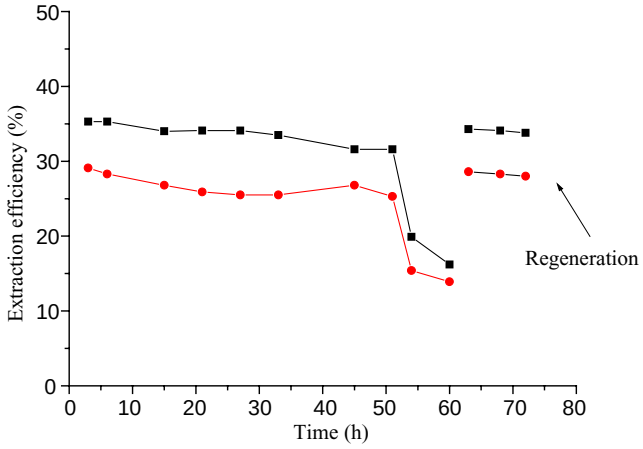

Fig. 5. Extraction efficiency versus time. Extraction of 0.5 mg/L of the herbicide mixture; membrane liquid: DHE/DEHPA (60%/40%, v/v); donor pH: 7.0, with phosphate buffer; donor flow rate: 1.0 mL/min; acceptor solution: 0.1 M HCl; acceptor flow rate: 0.2 mL/min. A 10.0 μL aliquot of the enriched sample was injected into the separation system. Symbols: (■) diquat and (●) paraquat.

investigated by processing samples containing the two analytes in the concentration range of 1.0–5.0 μg/L for 20 min at a donor flow rate of 1.0 mL/min. The results obtained, Table 2, for all samples were not significantly different indicating that the variation of concentration of analytes has no effect on the magnitude of the mass transport and the parameters influencing the extraction were constant in the examined range.

The applicability of the method for the extraction of the analytes from environmental water samples was also tested by spiking and processing water samples collected from Awash river (100 km south of Addis Ababa, Ethiopia). First, blank reagent and river waters were extracted under similar conditions for 20 min, and their extracts were analysed. No major differences can be seen between their chromatograms, Fig. 6(a) and (c). River water was then spiked at concentration levels 1.0 to 5.0 μg/L of the two herbicides. The experimental results summarized in Table 2 clearly show the possibility of utilizing the developed method for trace enrichment of the bipyridilium herbicides from water samples that may contain matrices of various types and concentrations. Moreover, the chromatogram of the river water extract, Fig. 6(d), is very similar to that of the reagent water extract, Fig. 6(b), and is free from interfering peaks. This can be attributed to the rejection of potentially interfering solutes from entering the acceptor compartment of the membrane unit.

Table 3
Detection limits of the bipyridilium herbicides for 20 min extraction of samples at a flow rate of 1.0 mL/min

Herbicide	Detection limit (μg/L)*	
	In reagent water	In river water
Diquat	0.40 ± 0.13	0.56 ± 0.16
Paraquat	0.50 ± 0.19	0.74 ± 0.24

* Mean ± 95% confidence level for $n = 4$.

3.6.2. Detection limits

Samples containing both herbicides at concentration levels from 2.0 to 20.0 μg/L, at five points, were extracted for 20 min at a flow rate of 1.0 mL/min and calibration graphs were constructed based on peak height measurements. Both the compounds exhibited linear relationships in the examined range with correlation coefficients of 0.9986 and 0.9988 or better for diquat and paraquat, respectively, with insignificant intercepts at 95% confidence level.

The detection limits of the pesticides with the developed method were determined from the calibration curves after processing blank water samples at a flow rate of 1.0 mL/min for 20 min. For both analytes the detection limits calculated as three times the level of the baseline noise are listed in Table 3.

Further lowering of these values is possible by processing large volume of samples if the sample volume is not a limiting factor. In addition to this, much lowered detection limit values can also be obtained if each analyte is monitored at its own maximum absorption wavelength, i.e. diquat at 308 nm and paraquat at 257 nm [36].

In another series of experiments, water samples collected from Awash river were spiked at 10.0 ng/L (a concentration lower than the detection limit determined for 20 min extraction of samples at a flow rate of 1.0 mL/min) of both analytes and enriched at a flow rate of 1.0 mL/min for 24 h and analytes of interest were detected in the solutions collected from the acceptor channel. This further shows the possibility of detecting the compounds under study present at concentrations well below the limits set by the European Union for

Table 2
Extraction efficiencies of the samples of herbicides in reagent water and river water

Herbicide	Extraction efficiency (%)					
	Sample concentration (μg/L) (in reagent water)			Sample concentration (μg/L) (in river water)		
	5.0	2.0	1.0	5.0	2.0	1.0
Diquat	37.8 (10.3)	37.8 (7.1)	34.5 (5.2)	32.1 (4.6)	35.4 (3.8)	31.5 (7.6)
Paraquat	34.2 (3.1)	32.7 (9.5)	28.8 (9.0)	27.8 (3.9)	28.2 (5.3)	24.7 (8.6)

Sample solutions were enriched at a flow rate of 1.0 mL/min for 20 min and 25.0 μL aliquot of the enriched samples were introduced into the LC separation system. Numbers in bracket are percent relative standard deviation values for $n = 3$.

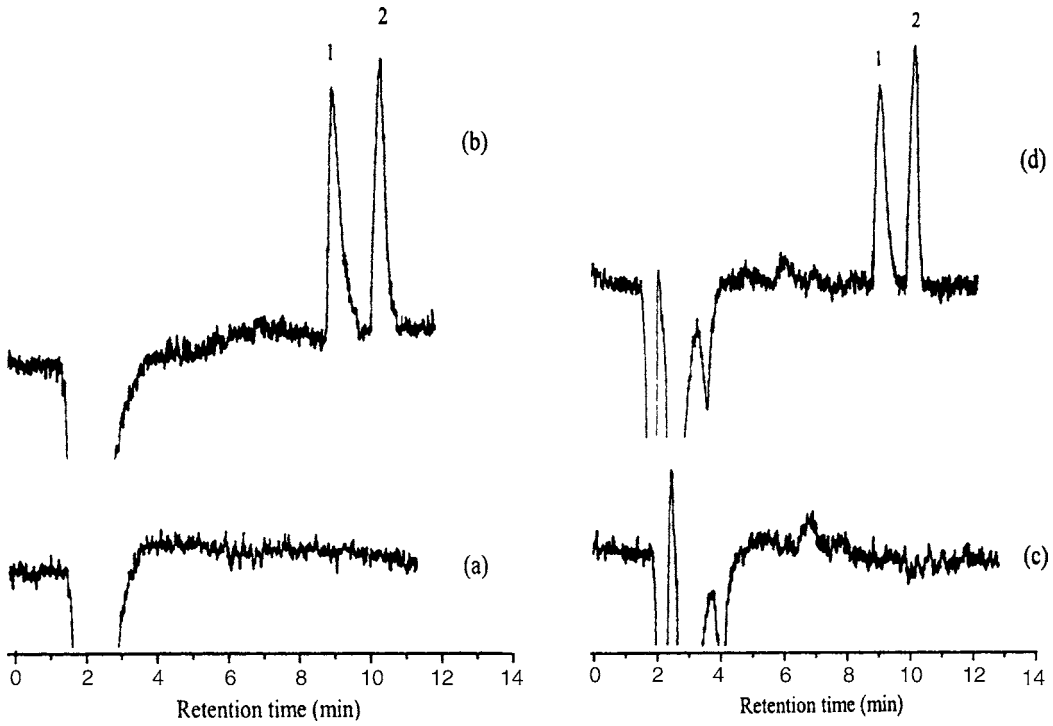

Fig. 6. Chromatograms (HPLC-UV) of extracts of (a) blank reagent water (b) 5.0 μg/L of the two bipyridilium herbicides in reagent water (c) blank Awash river water (d) 5.0 μg/L of the two bipyridilium herbicides in Awash river water. Samples (10 mL) were extracted at a donor flow rate of 1.0 mL/min and 25.0 μL of the extracts were injected. Peaks: (1) paraquat and (2) diquat.

individual pesticides in drinking and surface water, 0.1 μg/L [40].

4. Conclusion

It has been demonstrated that SLM extraction in combination with HPLC with UV detection can be utilized for the determination of trace quantities of bipyridilium herbicides in environmental water samples. The effect of various extraction parameters on the mass transfer of analytes was investigated and optimized, and under these conditions a successful sample work-up and enrichment of the compounds under study were obtained. The test for stability of the SLM indicated that it can be utilized to process samples for relatively longer durations and its regeneration also provides the possibility of using the membrane support for further membrane preparations. Amount of the analyte molecules in sub-ppb level has been determined after extraction with the liquid membrane. The possibility of lowering the detection limit of these herbicides was also investigated by extracting large volume of samples containing the analytes of interest at lower concentrations.

Acknowledgements

The authors are grateful to Prof. Jan Ake Jonsson for his material support at all levels of this research work. Financial support from the Swedish Agency for Research in Developing Countries (SAREC) and the Deutscher Akademischer Austauschdienst (DAAD) is also gratefully acknowledged. M. M. would like to thank the Department of Chemistry, Addis Ababa University for the experimental facility during the whole period of the project.

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