

Improved Preconcentration of Triazines from Aqueous Samples in a Supported Liquid Membrane with Electric Field

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Abstract

In the present work, an electric field was attached to a home-made supported liquid membrane cell to enhance the efficiency of the extraction; the analytical manifold consisted of a flow injection-UV-Vis spectrophotometry system. A homologous series of herbicides (atrazine, ametryn, and atraton) was used as target analytes. The solvent 1,2-DCE was found to be a promising supporting liquid in the membrane, even without the imposition of the electric field. Under the optimized conditions, an enrichment factor of 16.1 for ametryn, of 10.0 for atrazine and of 7.7 for atraton were obtained, with a sampling rate of 3.3 samples h⁻¹.

Keywords: SLM, triazines, pre-concentration, electric field, potential driven.

Introduction

Water quality is of major concern for the actual society¹⁻⁵, due to the presence of numerous pollutants such as metals⁶, dyes⁷, agrochemicals⁸⁻¹⁰, among others. Particularly, triazine herbicides are the chemicals most widely used for agricultural control around the world, recognized as photosynthesis inhibitors. These compounds have a structure of one ring with six members, with three C-atoms and three N-atoms alternating symmetrically or asymmetrically. Among these are the symmetrical triazines known as atrazine (ATRA), ametryn (AME), and atraton (ATN), which differ in the substituent of position 2 of the ring (Figure 1), a condition which determines their activity, as well as their physicochemical characteristics such as pK_a or water solubility¹¹. According to the US Environmental Protection Agency (US EPA), ATRA is the most representative compound of the group, with approximately 70 million pounds of active ingredient applied in the United States per year¹².

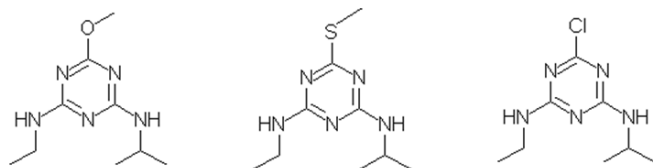


Figure-1

Chemical structures of the triazines studied, from left to right: atraton, ametryn, atrazine

The persistence of triazines in the environment varies between four to twelve months, depending on climatic conditions and the characteristics of the soil, as well as the dose that is used¹³. In

general, these pesticides are considered of moderate risk to humans; no cancer risk following acute or chronic exposures have been demonstrated with any certainty. However, at present the Environmental Protection Agency is re-evaluating the human health and ecological risk assessment associated with atrazine, owing to emerging scientific evidence in animal toxicology and human epidemiology studies that relate some types of cancer to this triazine¹⁴.

Due to the trace levels of concentration of triazines in water, it is necessary to apply preconcentration techniques prior to their quantification, like Solid Phase Extraction (SPE), Liquid-Liquid Microextraction (LLME) and the extraction with Supported Liquid Membranes (SLM)¹⁵⁻¹⁷. Among the separation techniques used during the determination of contaminants in water, SLM stands out for its simplicity, low cost and minimum consumption of organic solvents (μL), which converts it into an especially attractive technique from an environmental viewpoint¹⁸.

In SLM, the organic solvent is subjected to the pores of an inert hydrophobic membrane (support) through a capillary force, which has been named "liquid membrane". In turn, this is in contact with two liquid phases of distinct characteristics: a) the donor phase where the analyte is found originally, and b), the acceptor phase where the analyte is taken with a much lower volume than in the beginning¹⁹. In the transfer phenomenon of mass involved, the impulse force is a concentration gradient, which is why the preconcentration tends to happen across large time periods, ranging from several minutes to hours²⁰.

On the other hand, in electrochemical studies carried out through immiscible liquid interfaces (Interface of Two Immiscible Electrolyte Solutions, ITIES), it has been proposed

by our group that it is possible to control the transfer of atrazine, ametryn, and atraton by imposing a potential through the interface²¹. Following this principle, it can be expected that the attachment of an electric field to a liquid membrane would accelerate such transfer, which would make the preconcentration faster. For this reason, the present study evaluated the feasibility of enhance the separation through an electric field across the supported liquid membrane, for the preconcentration of symmetrical triazines in water.

Material and Methods

Instrumentation: The cell with the supported liquid membrane was constructed in the laboratory with two polytetrafluoroethylene (PTFE) modules (5 x 3 cm), which correspond to the acceptor and donor phases, as well as PTFE tubing of 0.5 mm of internal diameter for the entrance and exit of the solutions from the modules (figure 2). The internal volume of each cavity was approximately 150 μL . Platinum electrodes were placed in the cavities of each block in order to produce an electric field through the cell, by means of a power source for laboratory use with a voltage interval of 0.1 to 35 V (Goodwill Instruments, model GPR-3510HD). A pair of seals was put on either side of the membrane, as well as six screws on their periphery in order to ensure hermetic closure.

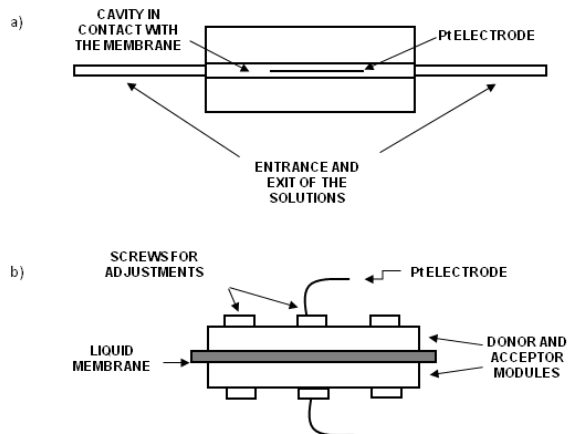


Figure-2

Prototype of the polarizable supported liquid membrane: a) top view of one of the modules, and b) front view of the cell

The detection was carried out with a UV-Visible spectrophotometer (Perkin-Elmer, model lambda EZ 210) and controlled by a PC while using the program PESSW v 1.2. by Perkin-Elmer. The package Microcal Origin 6.0 by Microcal Software Inc. was used for the treatment of data.

For the continuous management of the sample, a flow injection (FI) system was constructed (see figure 3), integrated by the following components: a) a peristaltic pump (Gilson, model Minipuls 3); b) an injection valve for low pressure (Rheodyne, model 512); c) PTFE tubing of 0.5 mm in internal diameter; and

d) a flow cell with a 10 mm optic path and 18 μL of internal volume (Hellma).

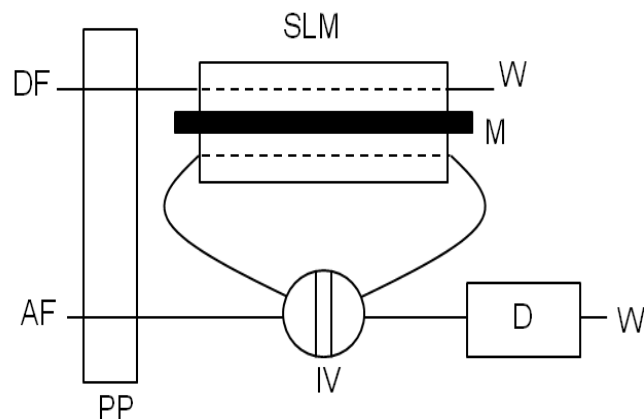


Figure-3

Representation of the FI system used: DF, donor phase; AF, acceptor phase; IV, injection valve; PP, peristaltic pump; SLM, polarizable cell; M, liquid membrane; D, detector; W, waste

An ultrasonic bath with timer and temperature control (Branson, model 55OR-DTH) was also used. For the cyclic voltammetry and ac impedance spectroscopy studies, a potentiostat/galvanostat (Autolab PGSTAT30, Eco Chemie) was employed.

Reagents: All reagents used were at least analytical grade. ATN, ATRA and AME were PESTANAL grade by Riedel-de Hën; 1,2-dichloroethane (1,2-DCE), dihexil ether (HXE), and undecane (UND) by Sigma Aldrich were used as solvents to prepare the SLM. Tetraphenylarsonium tetrakis_4-chlorophenyl_borate (TPAsTPBCl) was precipitated from the corresponding chemicals and recrystallized twice from acetone (BDH, AnalaR). Water purified with an EasyPure equipment (Barnstead) was used throughout. For the formation of the liquid membrane, a PTFE one from Sartorius, with a thickness of 65 μm and a pore size of 0.2 μm , was used.

Stock solutions of individual ATRA, AME and ATN containing 100 $\mu\text{g mL}^{-1}$ were prepared in methanol and stored at 4°C. The working solutions were prepared daily by adequate dilution. A buffer solution of $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ (0.1 mol L^{-1} , pH 7) was also prepared.

FI manifold and procedure: For the SLM-FI system, the acceptor module was placed in the loop of the two-way injection valve, while the sample was introduced directly into the donor module. With the valve in position I, the acceptor phase was carried through the acceptor module until reaching the detector, in order to register the baseline signal. The change of the valve to position II made it possible to retain a specific volume of the acceptor phase within the acceptor module and to carry out the

preconcentration of the analyte during a certain period of time (stop-flow mode). Returning the valve to position I enabled to send the enriched acceptor phase to the detector, where the analytical signal was registered. Finally, the acceptor module was washed before the next sample was introduced.

For the optimization of each variable related with the SLM-FI system, a new supported liquid membrane was prepared and its behavior studied in the course of a workday. The SLM was prepared by introducing the PTFE membrane in the organic solvent, sonicating it for 20 minutes, and removing the excess of solvent before securing it in the cell. In all cases the herbicides were prepared at a concentration of $0.5 \mu\text{g mL}^{-1}$ in a buffer solution of $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ 0.1 mol L^{-1} pH 7 for the donor solution. The transient signal was registered at the absorption maximum for each of the compounds of interest: 221 nm for ATN and AME, and 210 nm for ATRA.

Also, the following strategies were applied: i. evaluations in triplicate of experimental conditions for each variable in random order throughout the workday; ii. the Dixon test for the identification of suspicious samples ($\alpha=0.05$); iii. the calculation of the peak height of the FI transitory signal, and finally iv. the normalization of signals with regard to the highest results from each trial.

Results and Discussion

Some physicochemical parameters related to the transfer of the triazines of interest through an interface of water/1, 2-DCE are shown in table 1. The partition of the neutral and protonated species in this bifasic system is proportional to its partition in a water/octanol system. According to these data, the transport of triazines from an organic phase like 1,2-DCE to an aqueous phase in the following order $\text{ATN} > \text{AME} > \text{ATRA}$.

Table-1
Physicochemical parameters of the triazines studied²¹

	<i>pKa</i>	<i>Log P_{DCE}^a</i>	<i>Log P_{DCE+}^b</i>
Atrazine	1.7	0.38	-3.55
Ametryn	4.0	0.69	-1.09
Atraton	4.1	1.58	-0.50

Logarithm of the separation coefficient of the neutral^a and ionic^b species in the water/1,2-DCE system.

The phenomenon can be considered equivalent to the limiting step of SLM in the conventional modality. It was used the homologous series in order to establish if this behavior coincided with the experimental results obtained throughout. Table 2 includes the variables considered in this study as well as the optimal conditions founded, using ATN as analyte in all cases; AME and ATRA were considered just for the optimization of variables related to the SLM cell.

Table-2
Variables optimized throughout the present study

Subsystem	Variable	Studied Interval	Optimal condition
SLM Cell	Voltage of transfer, V	0.1 - 35	35
	Impregnation time of membrane, min	1 - 30	20
	Supported solvent	1,2-DCE, HXE, UND	1,2-DCE
FI System	Nature of acceptor phase	HCl, H ₂ SO ₄ , HNO ₃	HCl
	Concentration of acceptor phase, mol L ⁻¹	0 - 1	1
	Preconcentration time, min	1 - 15	15
	Flow rate of the acceptor phase, MI min ⁻¹	0.2 - 1.5	1.1
	Flow of the donor phase, mL min ⁻¹	0.5 - 3.2	0.5

SLM cell: As initial conditions, 1,2-DCE was selected as the supported solvent, owing to the same reasons considered in ITIES: the solvent is immiscible with water, thus enabling the formation of a well-defined interface that can be polarized easily due to its favorable dielectric constant (10.36). Each herbicide with a concentration of $0.5 \mu\text{g mL}^{-1}$ in the buffer solution at pH 7 were used as the donor phase, with a flow rate of 1.8 mL min^{-1} ; the acceptor phase consisted of $150 \mu\text{L}$ of HCl 0.1 mol L^{-1} (pH 1), owing to the cell dimensions. According to the results reported by several authors, both pH conditions were satisfactory for a transfer of triazines in a conventional SLM^{20,22-24}. The initial preconcentration time was five minutes.

The use of platinum electrodes located in the donor and acceptor chambers was proposed to impose an electric field across the liquid membrane, in order to enhance the stripping into the acceptor solution. The analytical signal obtained during the preconcentration of ATN under the action of the electric field is presented in figure 4. As can be observed, the normalized signal increases as the potential is augmented, a tendency which was also observed with AME and ATRA. Due to the fact that the analytical signal is proportional to the concentration of the analyte in the acceptor phase, it can be established that the imposition of a potential through the system favors the preconcentration of herbicides with 35 V as the best value for the three pesticides. This value was imposed by the characteristics of the power supply used.

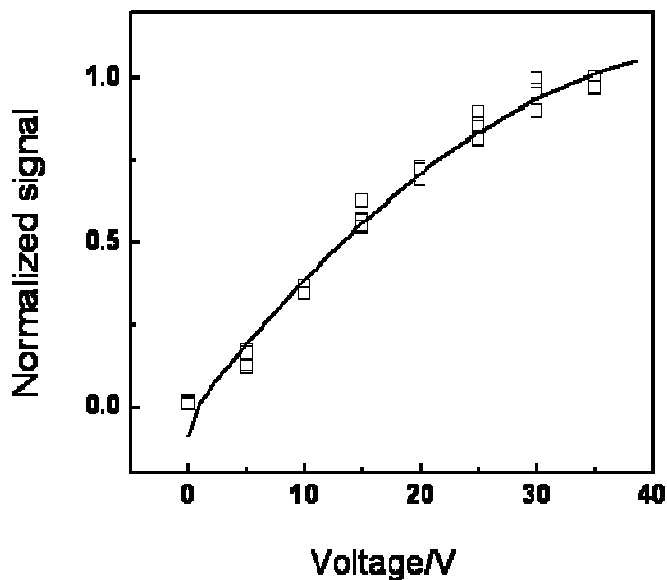


Figure-4

Influence of the voltage applied in the SLM during the preconcentration of ATN 0.5 mol L^{-1} , using 1,2-DCE as solvent. Other experimental conditions: flow rate of the donor phase 1.8 mL min^{-1} ; HCl 0.1 mol L^{-1} as acceptor phase in a stop-flow mode; preconcentration time of five minutes

The large electric field value applied across the SLM, can be explained due to the high resistivity of the membrane and the absence of the supporting electrolyte in the organic phase. However, the electrical current present in the system is probably quite small. In order to proof this issue, a cyclic voltammetry in a potential range of -1 to 1 V and ac impedance for the system was carried out, by using ATN as the target compound. For that, a small amount of the TPAsTPBCl was added to the organic phase previous to its support in the membrane, since TPAsTPBCl is the typically supporting electrolyte employed in the ITIES studies²¹. The process was carried galvanostatically. The results are observed in Figure 5. When ATN was alone, the current was small compared to that observed once the addition of the TPAsTPBCl in the organic phase. This shows that the salt enhanced the conductivity across the membrane.

The same response can be observed clearly in the ac impedance spectroscopy experiment carried out, between 50 000 to 50 Hz, according to figure 6. The higher impedance was observed for the baseline of the experiment and not supporting electrolyte was present in the organic phase, while in presence of ATN alone the impedance decreased. However, in presence of the TPAsTPBCl and ATN the impedance dropped considerably. In conclusion, the low conductivity of the SLM required a large electric field as high as 35 V, as the used in this work. No values higher than 35 V was explored, by limitations of the power supply used.

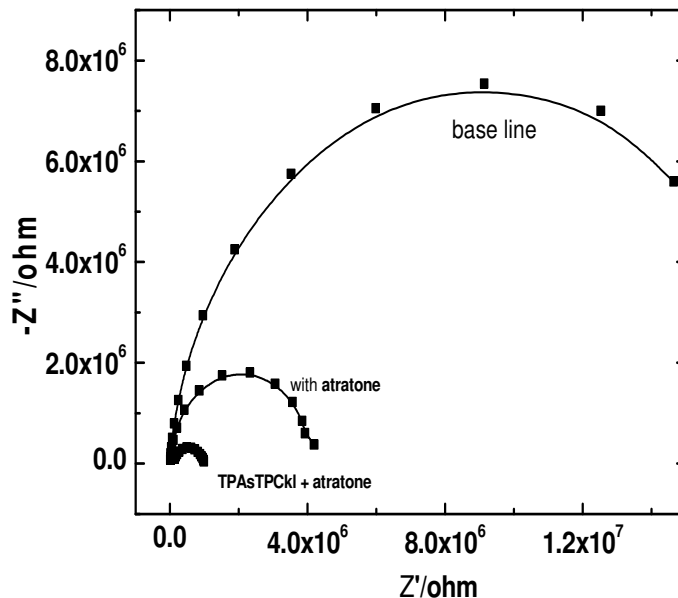


Figure-5

Cyclic voltammogram for the SLM proposed, in presence and absence of a typical electrolyte used in ITIES, with a sweep rate of 50 mV s^{-1} . Experimental conditions: $0.5 \text{ } \mu\text{g mL}^{-1}$ of ATN in a buffer solution of $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ 0.1 mol L^{-1} pH 7 as the donor phase, and HCl 0.1 mol L^{-1} as acceptor phase in a stop-flow mode

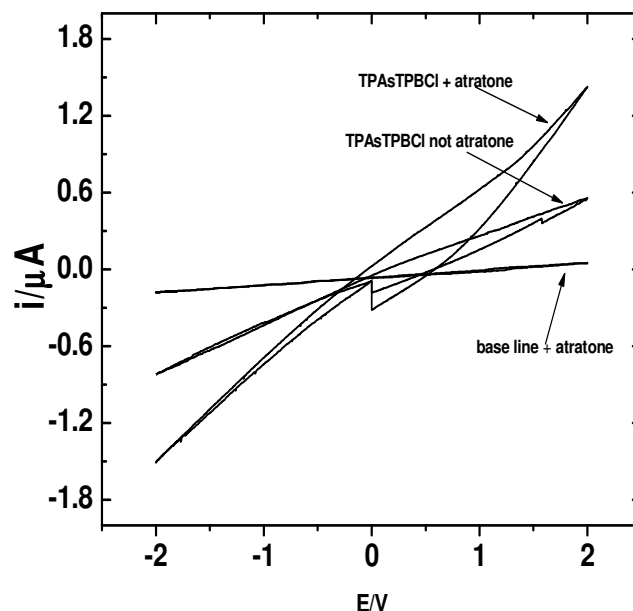


Figure-6

Complex plane impedance spectra for the SLM system at 1V

The strategy is not new for membrane systems. For platinum salts of tertiary amines and quaternary onium bases, Kulikova *et al.*²⁵ reported the back extraction of this metal from liquid membranes in an electric field by using a system where the organic solvent was supported in a cationic exchange membrane, while between the electrodes and the LM there were chambers containing HCl (five-chambered dialyzer). In that work, an increase in current density also resulted in an increase in the amount of metal in the stripping phase. By means of cyclic voltammetry experiments, it was determined that electrical conductivity of the salt in 1,2-dichloroethane did not depend of the HCl concentration, in spite of the large applied voltage field (between 0 to 600 V).

In relation to the preparation of the liquid membrane, it could be observed that sonication had a better effect on the impregnation with the solvent of interest than the high vacuum procedure conventionally used for the same purpose. According to the results, an increase in the time of sonication lead to a better preconcentration factor during the first 20 minutes. This phenomenon is due to the fact that ultrasound applied to a liquid forms micro-bubbles in which high pressure and energy can be attained; when a solid surface makes contact with a liquid submitted to ultrasound, the collapse of the micro-bubbles projects the liquid forcefully against its surface²⁶. However, it could not be established why the signal appeared to diminish after 30 minutes. Considering the physical appearance of the impregnated membrane, its mechanical resistance may have been affected in these conditions. A period of 20 minutes was selected as optimum in further experiments.

Chemical and hydrodynamic conditions: The influence of acidity on the extraction of triazines in the acceptor phase was studied with three inorganic acids in the interval of 0 to 1.0 mol L⁻¹. The acidity of the acceptor phase was favorable in the migration of these herbicides towards the system, which was reflected in the increase of the analytical signal, which coincides with the results reported in previous works^{20, 22-24}. This tendency is due to the fact that once in the acceptor phase, the analyte is protonated and does not return to the original solution; thus, the enrichment of the acceptor phase depends on the pH of the medium and on the acid disassociation constant of the analyte²⁷. The best results were obtained with an acceptor phase of HCl 1 mol L⁻¹, which was chosen for further studies.

Later, the influence of the preconcentration time on the separation of triazines was evaluated. Several terms can be used to measure the mass transfer across the membrane at a specified flow rate and phase composition. The enrichment factor for any extraction technique based on membranes is expressed as follows:

$$E_e = EV_d/V_a \quad (1)$$

where E is the extraction efficiency, V_d the volume of the donor phase (or the volume of the sample) and V_a is the volume of the

acceptor channel (or the extraction volume), as stated by Jönsson and Mathiasson²⁸. As can be seen from this equation, the enrichment factor is proportional to the volume of the donor phase, independently of the efficiency of the extraction. The extraction efficiency is estimated as:

$$E = n_a/n_d \quad (2)$$

where n_a and n_d are the number of moles of the analyte extracted in the acceptor phase and those entering the donor compartment, respectively.

According to the results reported by Chimuka *et al.*²⁰ and Jönsson and Mathiasson²⁷, the variation of the enrichment factor is not always a linear function of the extraction volume. In this work, the tendencies observed for the three herbicides were similar to those described by Chimuka *et al.* when representing the enrichment factor vs volume, as they reach and equilibrium across time²⁰. For further studies, a preconcentration time of 15 min was considered, in order to achieve a favorable sample throughput (3.3 samples per hour).

Also, the flow rates of the donor and the acceptor phases were evaluated. It should be highlighted that in the study of the flow rate of the donor phase, the volume of this phase was maintained constant (while varying the preconcentration times), in order to maintain the bulk of the analyte to be extracted constant. The best conditions were obtained from the extraction in the trial with the lowest flow rate (0.5 mL min⁻¹). From the perspective of the SLM, this tendency is due to the fact that with a lower flow rate the residence time of the analyte within the FI system is longer, which facilitates the transfer of mass from the donor to the membrane. However, equilibrium is reached when the diffusion of the analyte through the membrane controls the transfer of the mass of the entire system¹⁹.

In relation to the flow rate of the acceptor phase, some authors have proposed that the acceptor phase be kept static during the preconcentration so that the flow rate of the acceptor phase would not influence the enrichment factor^{29, 30}, but only determine the time required to transport the enriched solution to the detector, once the preconcentration is concluded. This strategy was chosen in the present study. Sufficiently high flow rates were searched, but without affecting the analytical signal, considering that by being a dynamic system, the noise in the analytical signal tends to be proportionate to the flow rate of the solution. Finally, the donor and the acceptor flows rates were 0.5 and 1.1 mL min⁻¹, respectively; both conditions were reached with the same impulsion system by means of tubing with different internal diameters coupled to the head of the pump.

Preconcentration of triazines under the electric field: Tests were conducted to compare different solvents in the SLM with electric field, under the optimal experimental conditions described in table 2. As mentioned before, 1,2-DCE was

considered after electrochemically checking the feasibility of the transfer of the three herbicides through a polarized interface water/1,2-DCE (ITIES)²¹. As far as HXE and UND were concerned, they had been used in other studies of SLM due to the partition coefficients that the analytes establish between organic and aqueous phases.

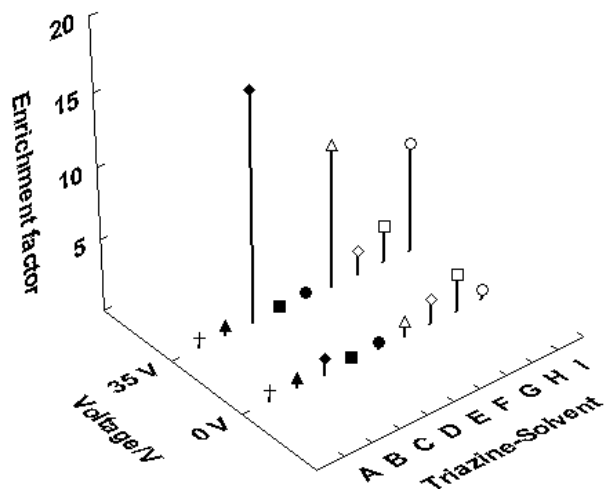


Figure-7

Enrichment factors obtained with the three solvents, under the optimal conditions detailed in Table 2: A) AME-UND, B) AME-HXE, C) AME-1,2-DCE, D) ATRA-UND, E) ATRA-HXE, F) ATRA-1,2-DCE, G) ATN-UND, H) ATN-HXE, I) ATN-1,2-DCE

Figure 7 represents the results from the extraction of the three herbicides where the different solvents were used to form the SLM. As can be seen, without the application of an electrical field there is no clear tendency as to which solvent is more appropriate for the three compounds, although the preconcentration of triazines was observed in the three cases. However, the magnitude of separation was not comparable with that reported by other authors^{20, 22-24, 29-30}, considering that the periods of preconcentration which were used here were below the previously used periods; in addition, the geometry of the cells was distinct.

In contrast, during the application of 35 V, the enrichment factor obtained with 1,2-DCE stands out above the rest, in the order AME > ATN > ATRA. These results partially coincide with those obtained through ITIES, where the hydrophobic nature of the neutral and ionic species is in the order ATN > AME > ATRA (table 1). In energetic terms, the ATRA requires more energy to be transferred from the aqueous to the organic phase, as its partition coefficient for the neutral species is small, while the partition coefficient for the ionic species has a high negative value; the more negative this value, the more similar is the molecule to the aqueous phase. On the other hand, in ITIES it can be observed that ATN and AME are more hydrophobic than ATRA, which explains their more efficient extraction by using

SLM. However, further experiments will be necessary to establish the reason for the behavior of AME and ATN in comparison to the tendencies expected according to ITIES results.

Conclusion

The operation of SLM under an electric field improved the preconcentration of these species. The observed tendencies during the evaluation of parameters like the flow rate of the donor phase and the nature of the acceptor phase were similar to those reported by other authors in the operation of SLM without polarization. The 1,2-DCE was identified for the first time as a good candidate for the formation of SLM, with or without the application of the electric field. The applicability of the solvents under study occurred in the order 1,2-DCE > HXE > UND in the proposed conditions. The enrichment factor for the triazines occurred in the order AME > ATN > ATRA; the order coincides with the hydrophobicity of the neutral or protonated species of ATRA, while it differs for AME and ATN.

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