



Preparation of new polymeric phases for thin-film liquid phase microextraction (TF-LPME) of selected organic pollutants

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ABSTRACT

Thin films made of a polymer (cellulose triacetate, CTA) and a plasticizer have been studied as novel sorptive phases for chlorpyrifos, triclosan and tonalide. The preparation is reproducible and only requires the plasticizer to be added into an organic dispersion containing CTA. The evaporation of the solvent leaves an easy to manipulate continuous and homogeneous thin film, which has been investigated in terms of both composition and extraction efficiency for the different compounds. Six different plasticizers (namely dibutyl sebacate, bis(2-ethylhexyl) sebacate, bis(2-ethylhexyl) phthalate, bis(1-butylpentyl) adipate, 2-nitrophenyl octyl ether and 2-fluorophenyl 2-nitrophenyl ether) with different chemical structure and physical properties, such as lipophilicity, dielectric constant and viscosity, have been incorporated in the CTA matrix and the resulting polymeric membranes have been characterized by different techniques (scanning electron microscopy, thermal techniques, and contact angle). Preliminary tests were undertaken in 0.01 M NaCl solution enriched with 100 $\mu\text{g L}^{-1}$ of each analyte to study the kinetics and efficiency of extraction. All analytes were effectively extracted after 6 h with all the polymeric phases, with different kinetics. Among the different elutants tested, ethyl acetate provided satisfactory recovery values. The membrane made of CTA and dibutyl sebacate has been selected and successfully applied for the microextraction of pollutants in simulated natural water, river water and a wastewater effluent with trace concentrations added (0.2–2 $\mu\text{g L}^{-1}$) before GC–MS determination. The overall method is easy to perform and provides good reproducibility (RSD < 10%) and recoveries higher than 80%.

1. Introduction

The contamination of aquatic environments by organic species, their toxicity even at low concentrations, and their bioaccumulation in living beings, is an important environmental problem that needs to be addressed. These organic contaminants are continuously released into the global environment and only partially removed by wastewater treatment plant (WWTP) systems. For this reason, reliable analytical methods are required to determine the actual concentration of the pollutants in the different environmental compartments. Moreover, due to the low concentrations detected in aquatic systems and the complexity of these environmental matrices, a preconcentration step is required before chromatographic analysis.

Microextraction techniques have been developed to address the need for efficient sample treatment for organic compounds because they require a low consumption of organic solvent, are simple, and which can be miniaturized. [1,2]. The term liquid phase microextraction (LPME)

was introduced in 1996 [3] to describe two-phase systems in solvent-microextraction processes, using immiscible liquid films in contact with water samples [1,2]. Depending on how the liquid organic phase comes into contact with the sample, the techniques are divided into three main groups: single-drop microextraction (SDME), hollow fibre liquid-phase microextraction (HF-LPME), and dispersive liquid-liquid microextraction (DLLME) [4–7]. In HF-LPME, the immiscible organic film is impregnated in the pores of an inert support, a hollow fibre, with a receiving solution placed in the lumen of the fibre constituting a three-phase extraction system. The application of liquid phase microextraction techniques to the determination of organic contaminants in water has been revised by many authors [8–10].

The use of polymeric materials as thin films has evolved as a new methodology for microextraction techniques, namely thin-film microextraction (TFME), to overcome the limitations of both LPME (the loss of the liquid film in HF-LPME) and of solid phase microextraction, SPME (limited surface for the extraction of analytes). In TFME the extraction

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process occurs by exposing the film directly in the solution; afterwards the analytes are either thermally desorbed or an additional elution step with an appropriated solvent is required [11]. Among the polymers, polydimethylsiloxane (PDMS) has mainly been used for this purpose, but new materials have been synthesized providing balanced coverage of analytes with a broad range of properties from complex sample matrices [12–17]. Moreover, the synthesis of polystyrene (PS) films over lab-paper support has also been described; the procedure for film preparation is simple and does not require any polymerization of monomers [18]. A combination between solvent impregnated resins and LPME (solvent-impregnated agarose gel liquid phase microextraction), where the agarose gel disc functions as a three-dimensional solvent holder to protect the acceptor phase that is immobilized within its framework, has been used for polycyclic aromatic hydrocarbons (PAH) determination in water [19].

The idea of protecting the liquid phase has also been exploited in the fabrication of liquid membranes with the components entrapped in a polymeric matrix, called polymer inclusion membranes (PIMs) [20,21]. Among other advantages, the stability and easy preparation of PIMs particularly stand out. Additionally, the low consumption of organic solvent and the absence of conditioning steps make these film materials attractive for TFME. PIMs are usually made of three components: a polymer, a plasticizer and the extractant [20]. The polymer is responsible for the mechanical strength of the membrane, whereas the plasticizer acts as a solvent and provides plasticity and flexibility to the membrane film. The extractant interacts selectively with the species of interest allowing the transport and preconcentration in three-phase extraction systems. Although PIMs have mainly been applied to inorganic species, including toxic metal, organic compounds can also be preconcentrated with PIMs [22]. Phenol, formate, bisphenol A, and antibiotics have been extracted from aqueous matrices using PIMs [23–26]. Moreover, electromembrane extraction (EME) with PIMs have been applied to the determination of non-steroidal anti-inflammatory drugs with Aliquat 336 (a mixture of ammonium chlorides) as the extractant [27].

The choice of an adequate plasticizer is of paramount importance in the extraction of organic contaminants with polymeric membranes, although this has yet to be fully exploited. In any case, the influence of plasticizer on membrane performance has been discussed by several authors and it is well known that the plasticizer influences the membrane polarity. The focus of the plasticizer selection should not only be on the lipophilicity which is related to the water penetration coefficient and to the water flux across the sensing membrane, but also on the viscosity and the dielectric constant [28,29]. The role of the plasticizer in the PIM formulation has been reviewed by Almeida et al. [20]. In general, it can be observed that NPOE (dielectric constant 21, and viscosity 11.1 cP) provides higher fluxes than other plasticizer, but the correlation between PIM fluxes with the dielectric constant and viscosity must be interpreted with caution. The type of plasticizer also has a significant influence on the potentiometric response of sensors using plasticized membranes [29], and in EME with liquid membranes for the extraction of acidic and basic organic analytes: the choice of the plasticizer is crucial to ensure the partitioning of the substance into the membrane, especially for polar substances with $\log P < 0$ [30].

In our group, a PIM-based extraction phase was tested for the first time for the determination of organophosphorus pesticides [31]. The PIM was used as a thin film (TF-LPME), with the plasticizer being the liquid phase where the organic pollutant was extracted (no extractant was used for this application). The results were promising for the determination of the target compounds in surface water.

Based on these findings, in the present study, we have explored the use of polymeric films for TF-LPME of three organic compounds which are representative of different classes of emerging pollutants, namely chlorpyrifos (CPS), tonalide (AHTN) and triclosan (TCS). CPS is an organophosphorus insecticide, classified as a priority substances in Directive 2013/39/EU [32–34]. Its use has become restricted due to its

toxicological profile [35,36]. AHTN and TCS are used in personal care products and are usually released into domestic wastewater without any metabolic alteration. Levels of AHTN and TCS ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ have been detected in wastewater treatment plants (WWTPs) [37,38].

Since it is necessary to pay particular attention to the selection of the appropriate plasticizer, we evaluated the role of six different plasticizers, namely 2-nitrophenyl octyl ether (NPOE), dibutyl sebacate (DBS), 2-fluorophenyl 2-nitrophenyl ether (FPNPE), bis(1-butylpentyl) adipate (BPA), bis(2-ethylhexyl) phthalate (DOP), and bis(2-ethylhexyl) sebacate (DOS), taking into account characteristics such as lipophilicity, dielectric constant, viscosity, and chemical structure. The membrane films have been characterized with scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) techniques, and contact angle. The extraction efficiency of the new films has been tested and polymeric films consisting of DBS plasticizer were finally selected for the determination of the target compounds in river waters and wastewaters.

2. Experimental section

2.1. Chemicals and materials

All chemicals were reagent grade or higher in quality. Chlorpyrifos (CPS) and Triclosan (TCS, Certified Reference Material) were supplied by Sigma Aldrich (Steinheim, Germany), and Tonalide (AHTN) was obtained from LGC Standards GmbH (Teddington, Middlesex, UK). The chemical structure and the physicochemical properties of the studied compounds are shown in Figure S1 in Supplementary Material.

Stock solutions (760 mg L^{-1} for AHTN, 928 mg L^{-1} for CPS, and 1020 mg L^{-1} for TCS) were prepared in methanol. These solutions were stored in the dark (4°C) and used to prepare multiple standard solutions at different concentrations. Cellulose triacetate (CTA) was obtained from Acros Organics (Geel, Belgium). DBS ($\geq 97\%$), DOS ($\geq 97\%$), and DOP ($\geq 97\%$) were purchased from Fluka. NPOE, BPA ($\geq 98\%$), and FPNPE ($\geq 98\%$) were supplied by Sigma Aldrich (Steinheim, Germany). Ultra-pure water from a Milli-Q Plus water purification system (Millipore Ibérica S.A., Barcelona, Spain) was used. HPLC gradient grade methanol (MeOH) and n-hexane (95%) were acquired from PanReac AppliChem (Castellar del Vallès, Spain). Ethyl acetate ($\geq 99.8\%$) and trichloromethane ($\geq 99.8\%$) were supplied by Romil Pure Chemistry (Sant Cugat del Valles, Barcelona, Spain). Sodium chloride (ACS, ISO analysis), sodium hydrogen carbonate (99–105%), sodium carbonate (99–105%), calcium chloride 6-hydrate ($\geq 98\%$) were supplied by PanReac AppliChem (Castellar del Vallès, Spain) and sodium sulfate anhydrous (GR for analysis, ACS, ISO) was purchased from Merck KGaA (Darmstadt, Germany).

2.2. Preparation and characterization of the thin films

Different polymeric films were prepared by the solvent casting method. CTA (200 mg) was dissolved under magnetic stirring in trichloromethane (20 mL) for 4 h before the addition of the plasticizer (90 mg) and stirring was then continued for two more hours. The solution was poured into a 9.0 cm diameter flat bottom glass Petri dish which was set horizontally and covered loosely. The solvent was evaporated over 24 h at room temperature. The resulting film was then carefully peeled off the bottom of the Petri dish and cut in square pieces of 2.89 cm^2 . Six different plasticizers with different chemical structures and properties (lipophilicity, solubility, viscosities and dielectric constants [29,39]) were tested, as outlined in Table S1 and Figure S2 in Supplementary Material.

The different membrane films were prepared containing 30% (w/w) of plasticizer and 70% (w/w) of CTA, resulting in the membranes labelled as M1 (NPOE), M2 (DBS), M3 (FPNPE), M4 (BPA), M5 (DOP), and M6 (DOS).

Different techniques were used for the characterization of the films. The morphology of the prepared thin films was appraised by scanning electron microscope. The instrumentation makes use of a high-resolution scanning electron microscope (TESCAN Mira 3, Brno, Czech Republic) operated at 20.0 kV. The film samples were mounted with carbon tape on metal stubs and then coated with Pt by sputtering, performed by a Cressington coater HR 208 (Watford, England, UK).

Thermogravimetric analysis was performed on a TGA 1STAR^e System (Mettler Toledo, Novate Milanese, Italy) to determine the thermal behaviour of the cellulose triacetate membranes. Samples were heated in N₂ from 25 °C up to 800 °C (20 °C min⁻¹).

Differential scanning calorimetry was performed on a DSC Q2000 from TA Instruments (New Castle, DE, USA): the scan range was from 30 °C to 310 °C (CTA) or 295 °C (CTA with additives), with a heating rate of 10 °C min⁻¹, in N₂ atmosphere (50 mL min⁻¹).

Changes in the hydrophobic character of the film surface associated to its composition were determined from contact angle measurements, which were performed by the tensile drop method using distilled water drops of 5 µL and a DSSA25 drop-shape analyzer (Krüss GmbH, Hamburg, Germany) equipped with a video system. The value given is the average of 120 measurements (60 s).

2.3. Thin-film microextraction procedure

Preliminary extraction studies were undertaken on NaCl solution (100 mL, 0.01 M) enriched with 100 µg L⁻¹ of each analyte evaluating the influence of different parameters, *viz.* membrane composition, extraction time and elution conditions.

Samples were maintained in contact with a square piece of the film with an area of 2.89 cm², under orbital agitation (250 rpm) for different times (2–4–6–8 h). The amount of analyte that remained in aqueous solution was determined by SPME-GC-FID under the following conditions: direct immersion SPME extraction was performed using a commercially available fibre with a 65 µm PDMS/DVB coating, at room temperature, under magnetic stirring for 30 min. A sample volume equal to 7 mL was placed in a 15 mL glass vial closed with a plastic cap furnished with Teflon-faced septum. After extraction, the SPME device was removed from the vial and inserted into the injection port of the gas chromatograph. The fibre was previously conditioned at 250 °C for 5 min.

Extraction efficiency, EE (%), was calculated from the ratio of peak areas, *i.e.*, the peak area after extraction divided by the peak area before extraction. Blank experiments were performed to ensure that no matrix effect was present in the SPME method.

Before elution, the thin film was washed with ultrapure water and dried. Different organic solvents (methanol and ethyl acetate) compatible with CTA polymer were then tested for elution. Finally, 1 mL of ethyl acetate was selected, added to the vial containing the film, and maintained for 15 min in the ultrasound bath, in accordance with a previous study [31]. The eluate was analysed without any derivatisation. The efficiency of the elution step was calculated using the following equation (1):

$$\text{Elution efficiency (\%)} = \frac{\text{amount of eluted compound (ng)}}{\text{amount of compound extracted in the film (ng)}} \times 100 \quad (1)$$

where the amount of eluted compound was obtained from the peak area measured in the direct injection of 1 µL of the elution solution, and then interpolated in a calibration curve in ethyl acetate (GC-FID).

2.4. Method validation and recovery tests at low concentration level

The TF-LPME at low concentration level was validated with M2 film using GC-MS for the quantification.

Method detection limit (MDL), method quantification limit (MQL),

relative standard deviation (RSD), linearity and coefficient of determination were obtained at the low concentration range of the analytes (0.2–1 µg L⁻¹ for CPS, 0.2–2 µg L⁻¹ for AHTN, 2–10 µg L⁻¹ for TCS). MDL and MQL were calculated using a signal to noise ratio of 3 and 10, respectively. A matrix-matched calibration [31,40] was used to calculate absolute recoveries according to the following equation (2):

$$AR(\%) = \frac{B}{A} \times 100 \quad (2)$$

where A is the response signal of the analyte recorded for the matrix-matched standard solution, and B is the response signal of the analyte recorded for the sample after TF-LPME, spiked with the target compound before extraction.

Recovery tests were carried out using simulated natural water, Llémena River water, and a WWTP effluent, enriched at different concentration levels and maintained in contact with M2.

A simulated natural sample was obtained by dissolving NaHCO₃ (0.168 g), Na₂SO₄ (0.0355 g), CaCl₂ • 2 H₂O (0.1642 g) in ultrapure water. Llémena River water was collected in May 2019 at 30–50 cm depth, whereas WWTP effluent from Quart (Girona, Spain) was collected in amber glass bottles in December 2019. Samples were stored in the dark (-20 °C) before analysis. The chemical characteristics of water samples are shown in Table S2 in Supplementary Material. The absence of CPS and TCS in water samples was determined by the Technical Services of the Catalan Institute for Water Research (ICRA, Girona, Spain) following a lab developed procedure. For AHTN, an in-house SPME method (immersion mode, 30 min extraction at room temperature, and PDMS/DVB coating) was developed to check its presence at about 2 µg L⁻¹ in the WWTP water sample.

2.5. Instrumental analysis conditions

2.5.1. GC-FID

Preliminary studies evaluating extraction conditions and the composition of the membrane were performed with a Trace GC coupled to an FID detector (Thermo Scientific, Waltham, MA, USA). For chromatographic separation, a HP-5 capillary column (30 m × 0.32 mm i.d.; 0.25 µm film thickness, Agilent) was used and He (99.9990% pure) was selected as the carrier gas. The split/splitless injection port was equipped with a 0.75 mm ID liner and operated in splitless mode maintained at 250 °C for 1 min for automatic injection and for 5 min for SPME experiments. The sample injection volume was 1 µL. The thermal programme was started at 60 °C, maintained for 1 min, ramped up to 150 °C at 25 °C min⁻¹ and then up to 270 °C at 10 °C min⁻¹, and held for 4 min. The chromatographic run ended in 20.6 min. Table S3 (Supplementary Material) reported the retention time of the target compounds.

2.5.2. GC-MS

The second part of this work about the application of TF-LPME procedure was performed using a Trace GC 2000 coupled to a PolarisQ Ion Trap or to a DSQ single quadrupole mass spectrometer detector (Thermo Scientific, Waltham, MA, USA). For chromatographic separation, a TG-5SILMS capillary column (Thermo Scientific, 30 m × 0.25 mm i.d., film thickness 0.25 µm) was used and He (99.9990% pure) was selected as the carrier gas, with a 1.0 mL min⁻¹ flow rate. The split/splitless injection port was equipped with a 0.75 mm ID liner and operated in splitless mode maintained at 250 °C for 1 min for automatic injection and for 5 min for SPME experiments. The sample injection volume was 1 µL. The thermal program was the same as was reported in Section 2.6.1. Ionization was done in the impact mode at 70 eV. The transfer line temperature was set at 250 °C and the ion source temperature at 225 °C. For the ion trap, the quantitative analysis of the target compounds was performed from the extracted ion chromatogram (see Table S3 in Supplementary Material) after full-scan mode acquisition in the *m/z* range from 50 to 340 amu. In the experiments where the single quadrupole was used, the acquisition was in selected ion monitoring

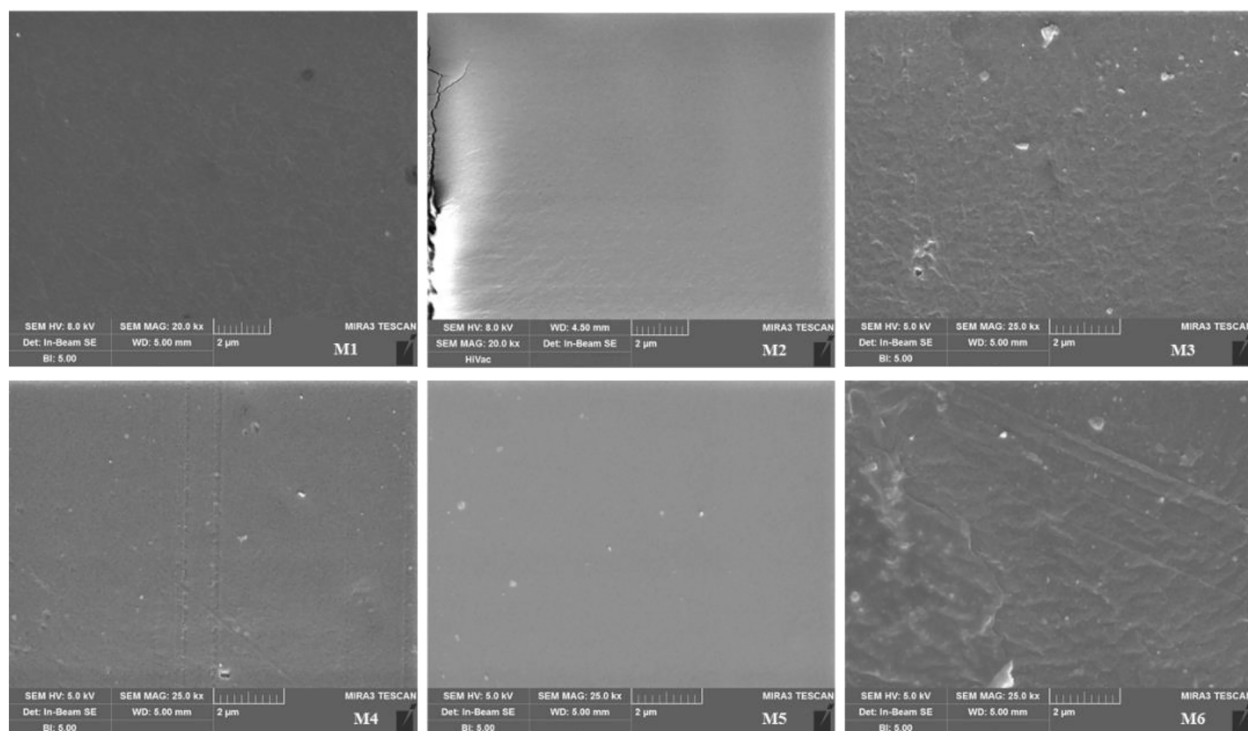


Fig. 1. SEM images on the films M1-M6.

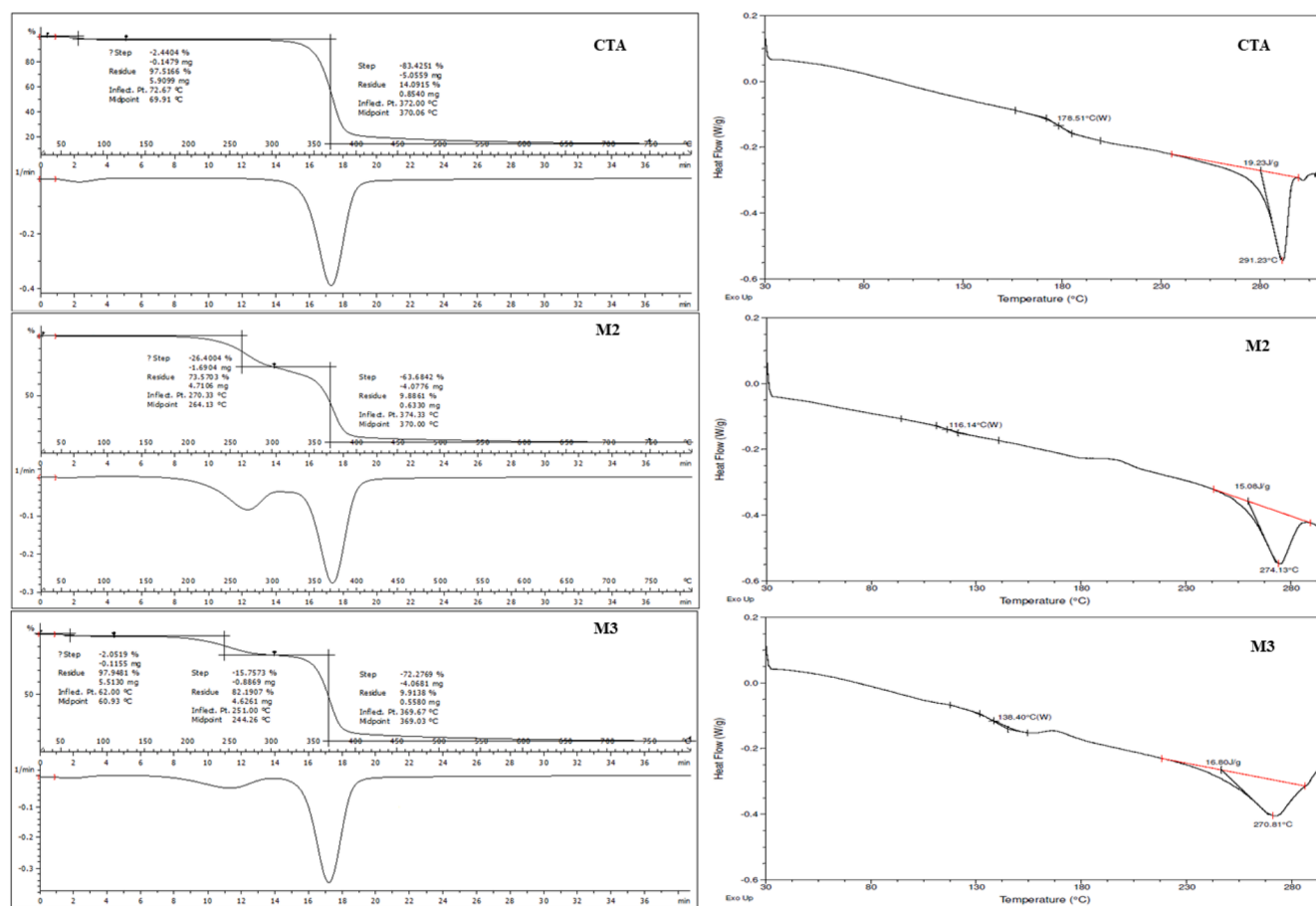


Fig. 2. TGA and DSC curves on CTA film and the films M2 and M3.

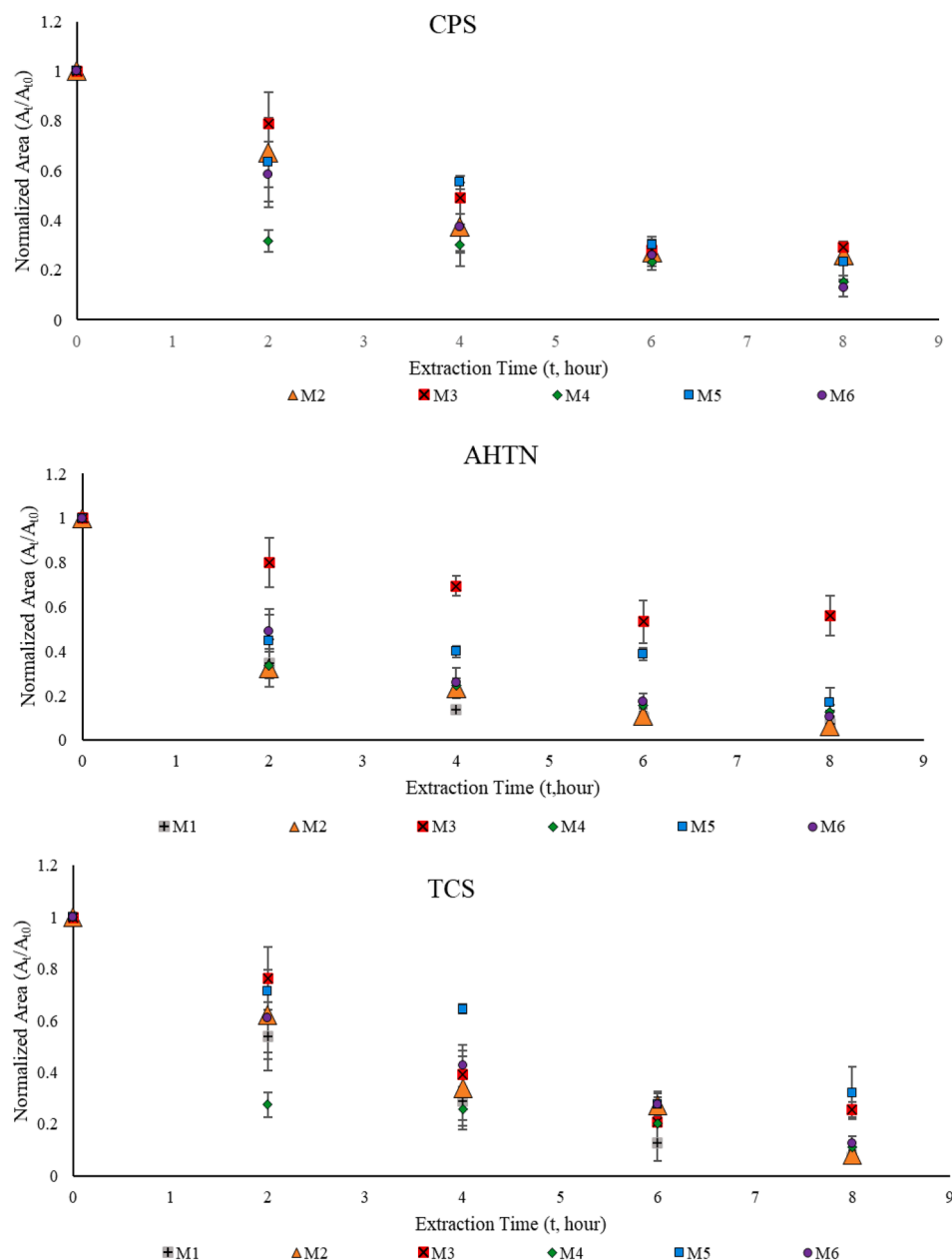


Fig. 3. Kinetic behaviour of the extraction of CPS, AHTN and TCS for the different films.

mode (SIM) using the m/z fragment shown in Table S3 in Supplementary Material. Xcalibur 1.4 software (Thermo Scientific, Waltham, MA, USA) was used for obtaining the chromatographic data.

In Table S3, the retention time of the target compounds is also shown.

3. Results and discussion

3.1. Characterization of the polymeric films

The plasticizer in PIMs is necessary to improve the mechanical properties, stability, and analyte solubility as previously described. Moreover, the plasticizer increases the fluidity/plasticity of the membrane and can improve its permeability due to the plasticization effect [20]. For these reasons, the membranes tested here have been deeply characterized by different techniques. The tested plasticizers are

commonly evaluated in polymeric membrane studies [41], and from the chemical structure point of view, they can be classified as aliphatic (DBS, BPA, DOS) or aromatic compounds (NPOE, FPNPE, DOP), bearing different functionalities. It should be highlighted the high viscosity of DOP (50 cP) and the high dielectric constant of FPNPE (50).

With regards to the morphologic characterization of the films, to avoid damaging of the membranes, only SEM images (Fig. 1) at low electric potential (5–8 kV) could be obtained, where a dense structure with the pores of CTA filled by the plasticizer molecules achieving a thick, homogeneous and less porous membrane is clearly visible. In Figure S3 in Supplementary Material the SEM image of bare CTA film is also shown. These data confirm what is reported in literature regarding the SEM analysis of CTA-based membranes [42].

The thermal behaviour of the membranes was studied by TGA and DSC analyses (Fig. 2 and Figure S4 in Supplementary Material). The thermogravimetric curve shows that CTA film is stable up to 370 °C. On

Table 1

Extraction efficiencies (with standard deviation) for the extraction of the target compounds in the thin films that were studied (n = 3).

Film	EE(%) CPS				AHTN				TCS			
	4 h	6 h	8 h		4 h	6 h	8 h		4 h	6 h	8 h	
M1 (NPOE)	n.a	n.a	n.a		86(2)	90 (3)	93(3)		71(11)	87 (7)	93(1)	
M2 (DBS)	62 (11)	73 (5)	74(3)		77(4)	89 (2)	94(2)		66(12)	73 (5)	92(1)	
M3 (FPNPE)	51 (6)	72 (5)	71(1)		30(5)	47 (10)	44(9)		61(9)	79 (6)	74(3)	
M4 (BPA)	70(8)	77 (3)	85(2)		76(2)	84 (1)	87(3)		74(7)	80 (6)	89(1)	
M5 (DOP)	44(3)	70 (2)	77(8)		60(3)	61 (3)	83(6)		35(2)	72 (3)	68(10)	
M6 (DOS)	62(10)	74 (3)	87(3)		74(7)	83 (3)	90(3)		57(8)	72 (5)	88(3)	

n.a. = data not available

the other hand, films M1 to M6 are thermally degraded in two steps: the first represents the main thermal degradation of the plasticizer (245 °C for NPOE, 264 °C for DBS, 244 °C for FPNPE, 271.5 °C for BPA, 293 °C for DOS), whereas the second represents the main thermal degradation of CTA chains. It is also possible to observe that in the case of M5 and M6, the two steps are not well separated probably because the degradation temperature of the plasticizer (DOP and DOS, respectively) is close to that of the cellulose chains. The presence of a degradation step around 60 °C for some films (CTA, M1, M3) ascribable to solvent residues can also be seen.

These data are sufficient to ensure the use of the films in environmental separation processes without any risk of membrane degradation or deterioration.

The DSC analysis provides information on the miscibility and possible interactions between the components of the polymer which, in turn, may affect the behaviour of the films with respect to microextraction of target compounds. In Fig. 2, DSC curves for bare CTA, M2 and M3 are presented. The value of the glass transition temperature (T_g) of a polymer is an important criterion for the compatibility of the components. In the case of bare CTA, T_g is found at 178.51°C, while for the films with plasticizers M2 and M3, the T_g moves to lower values, indicating the degree of the plasticizing effect, which is more accentuated in the case of M2 with DBS.

Contact angles of the films' surfaces were also measured, achieving the following results ($n = 120$): 39.6°(0.5) for M1, 49.4° (0.2) for M2, 49.5° (0.2) for M3, 52.1° (0.5) for M4, 60.8° (0.3) for M5, 51.9° (0.3) for M6. As can be observed, the addition of a plasticizer produces a decrease in the contact angle compared to the values found for bare CTA (69.2° (0.5)). This means that the hydrophilic character of the film is increased, favouring the interaction of the film with water, achieving the highest value for M5, while the lowest was for M1. According to these results, M1 to M4 and M6 would be the best choice for the TF-LPME procedure developed in the present work. M1 was previously used in the work of Vera et al. [31] for the extraction of three organophosphorus pesticides from water samples with good results, although a partial solubilisation of NPOE was observed.

3.2. TF-LPME: Evaluation of extraction conditions

The similar results obtained in the characterization of the different membranes prompted us to test all the prepared films in the TF-LPME application. The extraction kinetics was studied for each film composition at different extraction times (2 h ÷ 8 h), working with NaCl solution

(100 mL, 0.01 M) enriched with 100 µg L⁻¹ of each analyte. Each extraction time was evaluated in triplicate. A blank experiment with a CTA film (without plasticizer) was run to confirm the absence of extraction.

After microextraction, the amount of analyte remained in aqueous solution was determined by SPME, in accordance with the procedure reported in Section 2.3. The resulting kinetic graph (Fig. 3) was obtained plotting the extraction time in the x axis and EE (%), calculated as normalized area (Area of sample after TF-LPME/ Area of initial sample), in the y axis. As a summary, EE (%), at three different times (4–6–8 h) for the each membrane is shown in Table 1.

As outlined in Fig. 3 and Table 1, the kinetic curves are quite different depending on both, the analyte and the plasticizer. As a first approach, the different behaviour of the films can be related to the changes in the hydrophilicity of the material itself and to the plasticizing effect, observed in the DSC analysis.

It is possible to witness that the slowest kinetics were observed for all the compounds with M3 and M5. FPNPE (M3) is the plasticizer with the lower LogP values (3.69, see Table S1), although the contact angle value is similar to that of other films (M2 or M4). In this case, the less hydrophobic plasticizer weakly interacts with the target compounds (LogP values around 5) resulting in a not favourable extraction. On the other hand, DOP (M5) presents the highest viscosity value hindering mass transport within the membrane with a consequent decrease in extraction efficiency [26]. These findings justify the worst results for M3 and M5 that were discarded. M1, bearing the lower contact angle, shows good results for AHTN and TCS. However, extraction profiles for CPS with M1 could not be measured due to the presence of the NPOE peak in the chromatogram due to the higher solubility of NPOE in water (Table S1).

M2, M4, and M6 (all of them with aliphatic chains in the structure of the plasticizer) show similar properties and no significant differences in the EE were obtained for these films, except at 4 h where M2 and M4 are slightly better, especially for the case of TCS. However, leaching of the plasticizer in the aqueous solution is noticed with M4 (at a retention time around 11.2 min).

3.3. TF-LPME: Evaluation of elution conditions

After 6 h microextraction, ultrasound assisted extraction (UAE) was applied during 15 min to recover the analytes from the polymeric film [31], and in preliminary trials ethyl acetate and methanol (1 mL) were tested. Quantitation was carried out through an external calibration since no matrix effect was observed in GC-FID. In the case of methanol,

Table 2

Analytical parameters of the TF-LPME coupled with GC-MS.

Compound	Working range(µg L ⁻¹)	Intercept	Slope	R ²	MDL(µg L ⁻¹)	MQL(µg L ⁻¹)
CPS	0.2–1	+2810.8	104,858	0.9980	0.05	0.17
AHTN	0.2–2	+823.6	26,294	0.9935	0.04	0.14
TCS	2–10	–61140	59,443	0.9917	0.42	1.41

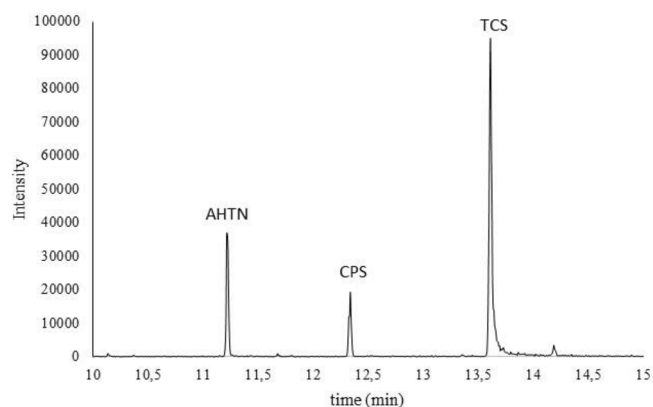


Fig. 4. Extracted ion chromatogram (GC-ITMS) for the standard prepared at the highest concentration level after TF-LPME and elution with ethyl acetate.

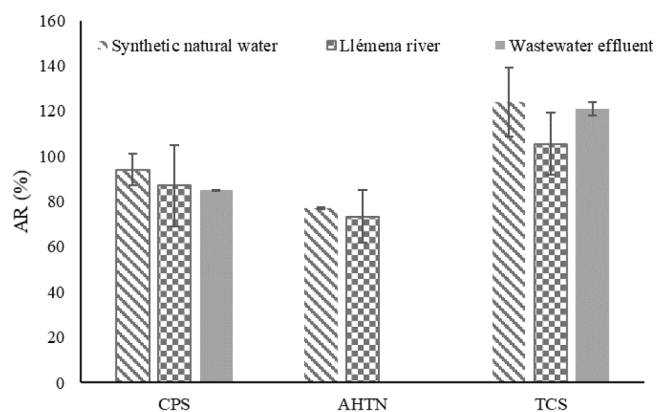


Fig. 5. Absolute Recoveries, AR(%), from simulated and real water matrices.

the eluate was evaporated under N_2 and then reconstructed with 1 mL of hexane. Although similar performances were obtained for both solvents, elution with ethyl acetate is more convenient as it avoids the evaporation step. For this reason, ethyl acetate was selected as the eluent solvent, ensuring high elution efficiency (68–110 %) for all the compounds in all the tested film. Only for TCS with M6 the elution efficiency was lower (31%).

The results obtained for characterization, extraction, and elution efficiency made it possible to identify M2 as the most suitable phase for the simultaneous preconcentration of these analytes, also at low concentration levels (low $\mu g L^{-1}$) as discussed below.

3.4. TF-LPME: Analytical performance at low concentration levels

The final analytical procedure (6 h extraction with orbital agitation with M2 and a subsequent elution step of 15 min UAE with 1 mL of ethyl acetate) was performed on 100 mL 0.01 M NaCl solution. Linearity was checked within the following concentration ranges: 0.2–1 $\mu g L^{-1}$ for CPS, 0.2–2 $\mu g L^{-1}$ for AHTN, 2–10 $\mu g L^{-1}$ for TCS. A good correlation was found between the spiked concentration of pollutant in NaCl solution and peak area determined after elution. In Table 2, the quality parameters of the method are depicted. Determination coefficients were higher than 0.99 and MDL were below 0.1 $\mu g L^{-1}$, except for TCS. TCS, a polar compound bearing a hydroxyl group, is usually determined by liquid chromatography or GC with derivatization. The fact that this compound could be monitored together with CPS and AHTN with the present method is of great interest from the environmental point of view.

A chromatogram of the three analytes at the highest concentration level is reported in Fig. 4.

It is worth mentioning that by decreasing the final volume of solvent used in the elution step, there is the possibility that the method developed could be applied to even lower concentration of the target analytes.

Moreover, repeatability of the method expressed as RSD values resulting from three independent analyses were better than 10% for the lowest concentration tested.

3.5. Recovery studies with simulated natural water, river water and wastewater

Recovery experiments were performed using three different matrices: simulated natural water, Llémena River water and WWTP effluent. The samples were spiked at 0.5 $\mu g L^{-1}$ for CPS and AHTN and at 2 $\mu g L^{-1}$ for TCS. As reported in Fig. 5, satisfactory recoveries, calculated according equation (2), ranging from 73% to 124% were achieved for the three compounds, except for AHTN in WWTP effluent. AR(%) for AHTN in WWTP water sample was not calculated since, as mentioned in the experimental part, this compound was determined in the raw water from the WWTP at 2 $\mu g L^{-1}$, higher than the selected spiked level. AR(%) values are acceptable for the environmental application of the method.

As a summary, it can be stated that the method proposed herein is simple, cost-effective, easy to perform, and, apart from the GC, does not require any additional equipment. Further work is in progress to prepare new films with biodegradable polymers and greener modifiers to increase the sustainability of the process.

4. Conclusions

In this study, we have demonstrated the application of self-prepared polymeric films for TF-LPME of selected organic contaminants. The results show that the membranes made of a polymer and a plasticizer exhibit satisfactory extraction properties, although this is dependent on the composition of the polymer matrix. The significant contribution of plasticizer to the extraction process, allowing the solubility of the target compounds in the membrane, can be seen. As a result, we have given great importance to the selection of the appropriate plasticizer, carefully evaluating the membrane performance in relation to properties such as lipophilicity, viscosity and contact angle. The final method involves a membrane made of CTA and DBS as two-phase system for the TF-LPME of CPS, AHTN and TCS in river waters and WWTP effluents.

CRediT authorship contribution statement

Francesca Merlo: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Antonella Profumo:** Formal analysis, Methodology, Writing – review & editing. **Claudia Fontàs:** Formal analysis, Methodology, Writing – review & editing. **Enriqueta Anticó:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2021.107120>.

References

- [1] M. Rutkowska, J. Plotka-Wasyłka, M. Sajid, V. Andruch, Liquid-phase microextraction: A review of reviews, *Microchem. J.* 149 (2019) 103989, <https://doi.org/10.1016/j.microc.2019.103989>.
- [2] M. Sajid, J. Plotka-Wasyłka, Combined extraction and microextraction techniques: Recent trends and future perspectives, *TrAC - Trends Anal. Chem.* 103 (2018) 74–86, <https://doi.org/10.1016/j.trac.2018.03.013>.
- [3] H. Liu, P.K. Dasgupta, Analytical chemistry in a drop, *TrAC - Trends Anal. Chem.* 15 (9) (1996) 468–475, [https://doi.org/10.1016/S0165-9936\(96\)00065-9](https://doi.org/10.1016/S0165-9936(96)00065-9).
- [4] E. Psillakis, N. Kalogerakis, Developments in liquid-phase microextraction, *TrAC - Trends Anal. Chem.* 22 (9) (2003) 565–574, [https://doi.org/10.1016/S0165-9936\(03\)01007-0](https://doi.org/10.1016/S0165-9936(03)01007-0).
- [5] L. He, X. Luo, H. Xie, C. Wang, X. Jiang, K. Lu, Ionic liquid-based dispersive liquid-liquid microextraction followed high-performance liquid chromatography for the determination of organophosphorus pesticides in water sample, *Anal. Chim. Acta.* 655 (1–2) (2009) 52–59.
- [6] M.T. Pena, M.C. Casais, M.C. Mejuto, R. Cela, Development of an ionic liquid based dispersive liquid-liquid microextraction method for the analysis of polycyclic aromatic hydrocarbons in water samples, *J. Chromatogr. A.* 1216 (36) (2009) 6356–6364.
- [7] Y.-u. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, Determination of four heterocyclic insecticides by ionic liquid dispersive liquid-liquid microextraction in water samples, *J. Chromatogr. A.* 1216 (6) (2009) 885–891.
- [8] E. Carasek, J. Merib, G. Mafra, D. Spudeit, A recent overview of the application of liquid-phase microextraction to the determination of organic micro-pollutants, *TrAC - Trends Anal. Chem.* 108 (2018) 203–209, <https://doi.org/10.1016/j.trac.2018.09.002>.
- [9] M.I. Pinto, G. Sontag, R.J. Bernardino, J.P. Noronha, Pesticides in water and the performance of the liquid-phase microextraction based techniques. A review, *Microchem. J.* 96 (2) (2010) 225–237, <https://doi.org/10.1016/j.microc.2010.06.010>.
- [10] C. Mahugo-Santana, Z. Sosa-Ferrera, M.E. Torres-Padrón, J.J. Santana-Rodríguez, Application of new approaches to liquid-phase microextraction for the determination of emerging pollutants, *TrAC - Trends Anal. Chem.* 30 (5) (2011) 731–748, <https://doi.org/10.1016/j.trac.2011.01.011>.
- [11] S. Seidi, M. Tajik, M. Baharfar, M. Rezazadeh, Micro solid-phase extraction (pipette tip and spin column) and thin film solid-phase microextraction: Miniaturized concepts for chromatographic analysis, *TrAC - Trends Anal. Chem.* 118 (2019) 810–827, <https://doi.org/10.1016/j.trac.2019.06.036>.
- [12] N. Reyes-Garcés, E. Gionfriddo, G.A. Gómez-Ríos, M.N. Alam, E. Boyacı, B. Bojko, V. Singh, J. Grandy, J. Pawliszyn, Advances in Solid Phase Microextraction and Perspective on Future Directions, *Anal. Chem.* 90 (1) (2018) 302–360, <https://doi.org/10.1021/acs.analchem.7b04502>.
- [13] R. Jiang, J. Pawliszyn, Thin-film microextraction offers another geometry for solid-phase microextraction, *TrAC - Trends Anal. Chem.* 39 (2012) 245–253, <https://doi.org/10.1016/j.trac.2012.07.005>.
- [14] E. Carasek, J. Merib, Membrane-based microextraction techniques in analytical chemistry: A review, *Anal. Chim. Acta.* 880 (2015) 8–25, <https://doi.org/10.1016/j.jaca.2015.02.049>.
- [15] O. Posada-Ureta, M. Olivares, A. Delgado, A. Prieto, A. Vallejo, M. Irazola, A. Paschke, N. Etxebarria, Applicability of polydimethylsiloxane (PDMS) and polyethersulfone (PES) as passive samplers of more hydrophobic organic compounds in intertidal estuarine environments, *Sci. Total Environ.* 578 (2017) 392–398, <https://doi.org/10.1016/J.SCITOTENV.2016.10.194>.
- [16] I. Bruheim, X. Liu, J. Pawliszyn, Thin-film microextraction, *Anal. Chem.* 75 (4) (2003) 1002–1010, <https://doi.org/10.1021/ac026162q>.
- [17] C.J. Golding, F.A.P.C. Gobas, G.F. Birch, Characterization of polycyclic aromatic hydrocarbon bioavailability in estuarine sediments using thin-film extraction, *Environ. Toxicol. Chem.* 26 (5) (2007) 829, <https://doi.org/10.1897/06-378R.110.1897/06-378.S1>.
- [18] J. Ríos-Gómez, R. Lucena, S. Cárdenas, Paper supported polystyrene membranes for thin film microextraction, *Microchem. J.* 133 (2017) 90–95, <https://doi.org/10.1016/j.microc.2017.03.026>.
- [19] S.H. Loh, M.M. Sanagi, W.A. Wan Ibrahim, M.N. Hasan, Solvent-impregnated agarose gel liquid phase microextraction of polycyclic aromatic hydrocarbons in water, *J. Chromatogr. A.* 1302 (2013) 14–19, <https://doi.org/10.1016/j.chroma.2013.06.010>.
- [20] M.I.G.S. Almeida, R.W. Catrall, S.D. Kolev, Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs), *J. Memb. Sci.* 415–416 (2012) 9–23, <https://doi.org/10.1016/J.MEMSCI.2012.06.006>.
- [21] M.I.G.S. Almeida, R.W. Catrall, S.D. Kolev, Polymer inclusion membranes (PIMs) in chemical analysis - A review, *Anal. Chim. Acta.* 987 (2017) 1–14, <https://doi.org/10.1016/J.ACA.2017.07.032>.
- [22] A. Olasupo, F.B.M. Suah, Recent advances in the removal of pharmaceuticals and endocrine-disrupting compounds in the aquatic system: A case of polymer inclusion membranes, *J. Hazard. Mater.* 406 (2021) 124317, <https://doi.org/10.1016/j.jhazmat.2020.124317>.
- [23] X. Meng, C. Gao, L. Wang, X. Wang, W. Tang, H. Chen, Transport of phenol through polymer inclusion membrane with N, N-di(1-methylheptyl) acetamide as carriers from aqueous solution, *J. Memb. Sci.* 493 (2015) 615–621, <https://doi.org/10.1016/j.memsci.2015.06.037>.
- [24] P. Pantůčková, P. Kubán, P. Boček, In-line coupling of microextractions across polymer inclusion membranes to capillary zone electrophoresis for rapid determination of formate in blood samples, *Anal. Chim. Acta.* 887 (2015) 111–117, <https://doi.org/10.1016/j.aca.2015.07.004>.
- [25] A.M. Balahouane, N. Benosmane, B. Boutemour, S.M. Hamdi, M. Hamdi, Removal of bisphenol A from synthetic wastewater solutions using a polymer inclusion membrane, *Desalin. Water Treat.* 208 (2020) 367–376, <https://doi.org/10.5004/dwt.2020.26470>.
- [26] A. García-Rodríguez, V. Matamoros, S.D. Kolev, C. Fontàs, Development of a polymer inclusion membrane (PIM) for the preconcentration of antibiotics in environmental water samples, *J. Memb. Sci.* 492 (2015) 32–39, <https://doi.org/10.1016/j.memsci.2015.05.037>.
- [27] C. Román Hidalgo, M.J. Martín Valero, R. Fernández Torres, M.A. Bello López, Use of Polymer Inclusion Membranes (PIMs) as support for electromembrane extraction of non-steroidal anti-inflammatory drugs and highly polar acidic drugs, *Talanta.* 179 (2018) 601–607, <https://doi.org/10.1016/j.talanta.2017.11.066>.
- [28] A. Mancilla-Rico, J. de Gyves, E. Rodríguez de San Miguel, Structural characterization of the plasticizers' role in polymer inclusion membranes used for indium (III) transport containing IONQUEST® 801 as carrier, *Membranes (Basel)* 11 (6) (2021) 401, <https://doi.org/10.3390/membranes11060401>.
- [29] N. Sakač, D. Madunić-Čačić, M. Karnaš, B. Durin, I. Kovač, M. Jozanović, The influence of plasticizers on the response characteristics of the surfactant sensor for cationic surfactant determination in disinfectants and antiseptics, *Sensors.* 21 (10) (2021) 3535, <https://doi.org/10.3390/s21103535>.
- [30] F.A. Hansen, S. Tirandaz, S. Pedersen-Bjergaard, Selectivity and efficiency of electromembrane extraction of polar bases with different liquid membranes—Link to analyte properties, *J. Sep. Sci.* 44 (13) (2021) 2631–2641, <https://doi.org/10.1002/jssc.202100167>.
- [31] R. Vera, S. Insa, C. Fontàs, E. Anticó, A new extraction phase based on a polymer inclusion membrane for the detection of chlorpyrifos, diazinon and cyprodinil in natural water samples, *Talanta.* 185 (2018) 291–298, <https://doi.org/10.1016/j.talanta.2018.03.056>.
- [32] P.E. Rosenfeld, L.G.H. Feng, Risk of Hazardous Wastes (2011), <https://doi.org/10.1017/CBO9781107415324.004>.
- [33] European Commission (EC), Directives of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, *Off. J. Eur. Union.* 2013 (2013) 1–17. doi:http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32013L0039.
- [34] J.C.G. Sousa, A.R. Ribeiro, M.O. Barbosa, M.F.R. Pereira, A.M.T. Silva, A review on environmental monitoring of water organic pollutants identified by EU guidelines, *J. Hazard. Mater.* 344 (2018) 146–162, <https://doi.org/10.1016/j.jhazmat.2017.09.058>.
- [35] S. Soares, T. Rosado, M. Barroso, D.N. Vieira, E. Gallardo, Organophosphorus pesticide determination in biological specimens: bioanalytical and toxicological aspects, *Int. J. Legal Med.* 133 (6) (2019) 1763–1784, <https://doi.org/10.1007/s00414-019-02119-9>.
- [36] R.I. Krieger, Hayes' Handbook of Pesticide Toxicology (2010), <https://doi.org/10.1016/C2009-1-03818-0>.
- [37] A. Godayol, E. Besalú, E. Anticó, J.M. Sanchez, Monitoring of sixteen fragrance allergens and two polycyclic musks in wastewater treatment plants by solid phase microextraction coupled to gas chromatography, *Chemosphere.* 119 (2015) 363–370, <https://doi.org/10.1016/j.chemosphere.2014.06.072>.
- [38] T.E.A. Chalew, R.U. Halden, Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban, *J. Am. Water Resour. Assoc.* 45 (2009) 4–13, <https://doi.org/10.1111/j.1752-1688.2008.00284.x>.
- [39] L. Nghiem, P. Mornane, I. Potter, J. Perera, R. Catrall, S. Kolev, Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), *J. Memb. Sci.* 281 (1–2) (2006) 7–41, <https://doi.org/10.1016/j.memsci.2006.03.035>.
- [40] F. Merlo, F. Maraschi, D. Piparo, A. Profumo, A. Speltini, Simultaneous pre-concentration and HPLC-MS/MS quantification of phycotoxins and cyanotoxins in

- Inland and coastal waters, *Int. J. Environ. Res. Public Health*. 17 (2020) 1–10, <https://doi.org/10.3390/ijerph17134782>.
- [41] E. Rodríguez de San Miguel, J.C. Aguilar, J. de Gyves, Structural effects on metal ion migration across polymer inclusion membranes: Dependence of transport profiles on nature of active plasticizer, *J. Memb. Sci.* 307 (1) (2008) 105–116, <https://doi.org/10.1016/j.memsci.2007.09.012>.
- [42] O. Arous, H. Kerdjoudj, P. Seta, Comparison of carrier-facilitated silver (i) and copper (ii) ions transport mechanisms in a supported liquid membrane and in a plasticized cellulose triacetate membrane, *J. Memb. Sci.* 241 (2004) 177–185, <https://doi.org/10.1016/j.memsci.2004.04.024>.