Sample preparation using liquid membrane extraction techniques

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Abstract

A brief review is given of membrane extraction techniques that are seen as suitable for the extraction of various chemicals in water samples. Membrane-based extraction methods have now gained popularity as methods of choice in the extraction of both ionisable and non-ionisable molecules from different samples. The main attractive features for these techniques include the use of minimal organic solvents, high selectivity and clean-up efficiency, with high enrichment factors. In most cases the overall cost involved is low due to the simplicity of the techniques which normally involve relatively fewer steps and handling procedures as compared to many other sample-preparation techniques. The various forms and the configurations of membrane-based techniques are another attractive feature which allows the possibility of hyphenation with separation instruments such as gas/liquid chromatographs and even capillary electrophoresis.

Keywords: liquid membrane extraction techniques, sample preparation, water monitoring, organic and inorganic compounds

Introduction

Sample preparation is among the most important steps in any analytical process. This is due to the fact that sample preparation plays an important role in the removal of macromolecules and other matrix constituents that may adversely interfere with the detection system. In addition to that, sample-preparation methods bring about a possibility of enrichment of the analytes in very dilute samples or where low detection limits are required (Jönsson, 1992; 1993; 1999). Sample-preparation processes therefore have a direct impact on accuracy, precision and quantification limits and are often a limiting step for many analytical methods (Majors, 2003). Many sample-preparation techniques (Tadeo et al., 2004; Mitra and Kebbekus, 1998; Patnaik, 1997) that have been in use all along include head space analysis, purge and trap, solid-phase micro-extraction (SPME) (Eisert et al., 1997; Pawliszyn, 2003), liquid-liquid extraction (LLE) and solid-phase extraction However, the oldest and most widely used technique is liquid-liquid extraction. The limitations of this traditional extraction technique (liquid-liquid extraction) include the lengthy extraction times, automation challenges and use of large organic solvents which are not environmentally friendly.

Recently, sample preparation employing liquid membranes has been reported in many applications, a sign that liquid membranes are a preference over many others. The use of membrane techniques for selective extraction of analyte molecules was first introduced by Audunsson who used it for the extraction of amines in urine (Audunsson, 1986) and further developed by Jönsson and Mathiasson research groups to cover a wider application to both environmental as well as biological samples (Jönsson, 1992; 1993; 1999). Membrane extraction techniques have been used for the extraction of molecules in biological matrices (Jönsson et al., 2003; Pálmarsdóttir et al., 1997; Lindegård et al., 1992; Basheer and Lee, 2004; Msagati and Nindi, 2001; 2004a; 2004b; 2005a; 2005b; 2006; Drapala et al., 2005).

Liquid membranes have also been used extensively in the extraction of both organic molecules such as pesticides and herbicides in waters and wastewaters (Chao et al., 2002; Megersa et al., 2001; Dżygiel and Wieczorek, 2001) and metals in water and wastewater matrices (Ndungù et al., 1998; Yang and Cussler, 2000; Juang and Huang, 2000; Juang et al., 2000; 2004; Ortiz et al., 2003; Ho, 2002) as well as other organic pollutants (Berhanu et al., 2006; Khrolenko et al., 2002; Qin et al., 2002). Membrane-based techniques have been coupled to a variety of other analytical instruments such as ion chromatography (Amara and Kerdjoudj 2007) liquid chromatography (Sandahl et al., 2000; 2002), gas chromatography (Luthje et al., 2004; Mitra et al, 1996), capillary electrophoresis (Palmarsdottir et al., 1997) and atomic absorption spectrophotometers (Juang et al., 2004; Fontas et al., 2005; Van de Voorde et al., 2004; Arous et al., 2004a; Arous et al., 2004b).

Generally, liquid membrane extraction techniques may be applied in many different ways, employing different types of membranes and a variety of set-ups and configurations or designs. This review discusses the different types of liquid membrane extraction techniques in their various designs.

Principles of liquid membrane extraction techniques

In liquid membrane extraction techniques, the analyte molecules diffuse across the hydrophobic porous membranes impregnated by organic solvent under a gradient which may be created due to either concentration differences (ΔC) between the two phases, the feed (or donor) and the stripping (or acceptor) or differences in the electrical potential (ΔE).

The process of diffusion in liquid membranes is governed by Fick's first law of diffusion (Smith, 2004):

$$J = -D\frac{\partial\Phi}{\partial\chi} \qquad [1]$$

where:

J denotes the extent of flux of the analyte molecules per given area and time (e.g., $g \cdot cm^{-2} \cdot s^{-1}$ or $mol \cdot cm^{-2} \cdot s^{-1}$)

D gives the diffusibility measure of the analyte across the membrane (diffusion coefficient), with units of $cm^2 \cdot s^{-1}$ and is proportional to the velocity of the diffusing particles

Φ is the concentration in dimensions of amount of substance per volume e.g., $mol \cdot cm^{-3}$;

χ is the position e.g., cm or metre (m).

The concentration gradient is given by the ratio of the change in concentration $(\partial\Phi)$ to the change in position $(\partial\chi)$, that is, $\frac{\partial\Phi}{\partial\chi}$.

The term D depends on the temperature, viscosity of the fluid and the size of the particles according to Stokes-Einstein equation,

$$D = \frac{k_B T}{6\pi a \eta} \qquad [2]$$

where:

D is the diffusion constant
A is the radius of solute
η is the solution viscosity = mobility of the particles
k_B is Boltzmann's constant,
T is the absolute temperature.

Integrating the Fick's equation gives Eg. (3):

$$J = D\frac{(C_{is} - C_{jl})}{L} \qquad [3]$$

where:

c_{is} is the concentration of analyte i at the outer membrane interface
c_{il} the concentration of analyte i in acceptor phase
L is the membrane thickness.

From the equations above, several parameters need to be adjusted to speed up the diffusion process in order to increase the flux across the membrane. Factors which control the D term (diffusion coefficient), such as temperature and partition coefficient are normally adjusted to optimal conditions for that purpose. The effect of temperature increase on the rate of diffusion and flux can be approximated by the Stokes-Einstein equation, such that by increasing T, D will increase and hence the analyte's flux.

Partition coefficient (K) is another important factor, which controls the diffusion (flux) of analyte molecules across the membrane. The partition coefficient is defined as the ratio of the concentration of analyte in the membrane to that in the matrix as indicated by Eq. (4):

$$K = \frac{C_{membrane}}{C_{matrix}} \qquad [4]$$

where:

$C_{membrane}$ is the analyte concentration in the membrane
C_{matrix} is the analyte concentration in sample matrix.

The partition coefficient plays an important role mostly in liquid membranes where analytes cross the membrane in steps, because the analyte species in the donor (feed) phase has to be dissolved first in the membrane, diffuse through passing the membrane-acceptor interface into the bulk of the acceptor phase. The analyte is thus extracted into the membrane from the donor side and then re-extracted into the acceptor phase.

Typical materials used in fabricating membranes

The types of materials used to fabricate membranes are diverse and these include polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF), polypropylene (mainly for hollow fibres), silicone, and polysulphone (PS) (Hylton and Mitra, 2007). These materials are known to have some qualities that give them an edge over others. The materials are known to be stable at all pH ranges and they are inert to many other chemicals and have high temperature stability (Hylton and Mitra, 2007).

Classification of liquid membrane techniques

Membrane techniques exist in various forms and may be classified into several groups depending on the mode of classification (Jönsson and Mathiasson, 1999). Morphologically they may be classified into porous and non-porous (though almost all liquid membrane techniques are non-porous), but geometrically they may be classified into film/flat sheet or hollow fibre configurations. In all these configurations, the analyte molecules are selectively partitioned between two or three phases. At least from the context of this review, the geometric forms of membrane techniques will be discussed.

Porous membrane extraction techniques

In actual sense these may not qualify fully as liquid membrane techniques and therefore their discussion in this review will be brief. In porous membrane techniques, the analyte molecules are partitioned from one phase which forms the feed (upstream phase) through the porous hydrophobic liquid membrane to the second phase which forms the stripping/acceptor (downstream phase) (Fig. 1) (Jonsson and Mathiasson, 2001).

The driving forces in the porous membrane extraction include temperature, concentration, pressure, heat flux, volume flux, momentum flux and electrical flux. The selectivity in the extraction process is governed mainly by the membrane properties, as well as the physical-chemical properties that exist between the membrane and the permeate components. Dialysis and electrodialysis are among the examples of porous membrane extraction techniques (Chimuka et al., 2004).

Non-porous liquid membrane techniques

Non-porous membranes do not have pores as the name suggest, therefore analytes movement in these setups is controlled mostly by diffusion. In the non-porous membrane systems, liquids are held in the pores of polymeric membranes to form what may either be called, two-phase or three phase supported liquid membrane extraction. Different configurations of non-porous membrane extractions are known to exist such as supported liquid membrane extraction (SLM) technique, micro-porous mem-
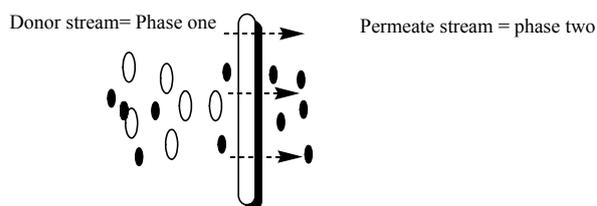
Donor stream= Phase one   Permeate stream = phase two

Figure 1
Porous membrane extraction process. The arrows show the direction of the movement of the different molecules under a concentration gradient.
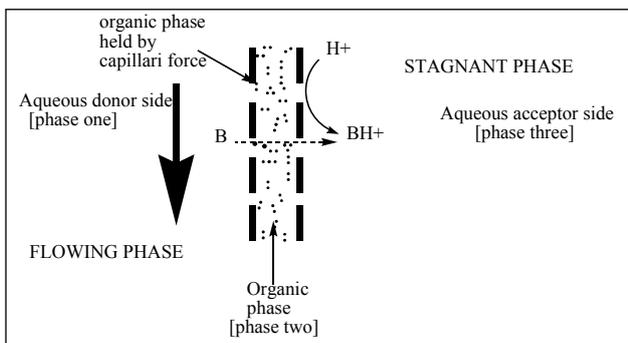
Figure 2
Schematic representation of the extraction of basic organic compounds by SLM technique. Acidic compounds cannot be extracted, and the neutral species can only transfer by diffusion, without enrichment. Equivalent chemistry is implemented for extraction of organic acids.
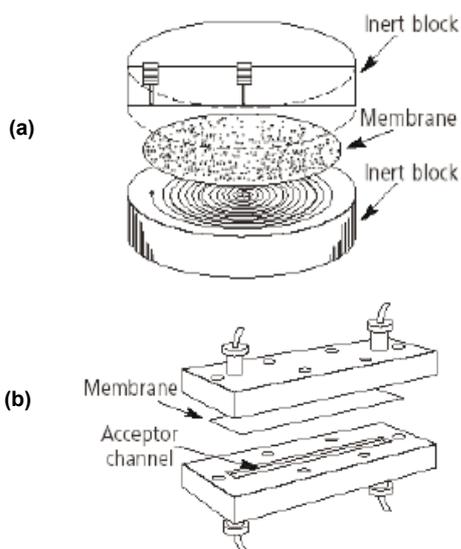

Figure 3
SLM technique performed in film/flat sheets:
(a) is a 1 mℓ channel and (b) is a 10 µℓ channel

brane liquid-liquid extraction (MMLLE) technique, emulsion liquid membranes (ELM) and stabilised liquid membrane device (SLMD) extraction techniques.

Supported liquid membrane extraction (SLM) technique

Supported liquid membrane (SLM) is a three-phase system in which an organic phase is sandwiched (interposed) between two aqueous phases (Figs. 2, 3a and 3b). This liquid is immobilised in the pores of a supporting porous material and is held by the capillary action. One of the two aqueous phases is actually the test or sample solution containing the analyte of interest, while the other one forms the stripping solution to accept the extracted analyte (stripping/acceptor solution). In the SLM technique, the volumes of the stagnant strip solutions that are used are normally much smaller than the sample solution volumes pumped through and this ensures high preconcentration factors. Therefore, with the SLM technique, sample cleanup and enrichment can be achieved simultaneously (Jönsson, 1992; 1993; 1999; Chimuka et al., 1998).

SLM extraction technique is suitable for polar and ionic compounds such as organic acids, bases and metals. In the extraction of basic or acidic analytes, the pH of the donor solution must be such that the compounds are in their neutral or uncharged forms, thus allowing them to enter the membrane. The pH of the acceptor is maintained such that once in the membrane, the analytes are extracted into the acceptor in a charged form and cannot be back-extracted into the donor. The pH gradient therefore provides the driving force (Hylton and Mitra, 2007; Chimuka et al., 1998).

Facilitated transport in liquid membranes

To enhance the selectivity of the liquid membrane during the extraction of ionising compounds, a suitable carrier molecule with a high affinity for the analytes may be incorporated (Jönsson et al., 1994). Under these conditions, carrier mediated transport involves the reversible complex formation between the carrier and the analyte (Jönsson et al., 1994). For instance, in the extraction of metals, a complexing agent (ligand) stronger than organic carrier is normally incorporated into the strip solution and the metal ion transport from the donor via the hydrophobic membrane to the stripping solution is then driven by either proton gradient or by counter anion/cation (Figs. 4a and b) (Parthasarathy et al., 1997). The mobile carrier in the membrane complexes the metal in the donor side, diffuses across the membrane to the acceptor side where it is exchanged for a proton or taken up by a much stronger carrier (Fig. 4b). Mulugeta and Megersa extracted bipyridilium herbicides from water samples whereby di-(2-ethylhexyl) phosphoric acid was used as a carrier (Mulugeta and Megersa, 2004). Chimuka et al., (2005) have also reported the use of tri-n-butyl phosphate (TBP) as an extractant in the monitoring of uranium in complex matrix samples.

Supported liquid membranes involve the distribution of analyte in three phases to bring about clean-up/separation as well as enrichment of the extract (permeate). There are two main parameters that are of paramount importance to evaluate the performance of the SLM extraction process. These factors are the enrichment factor (E_f) and extraction efficiency (E_e). The
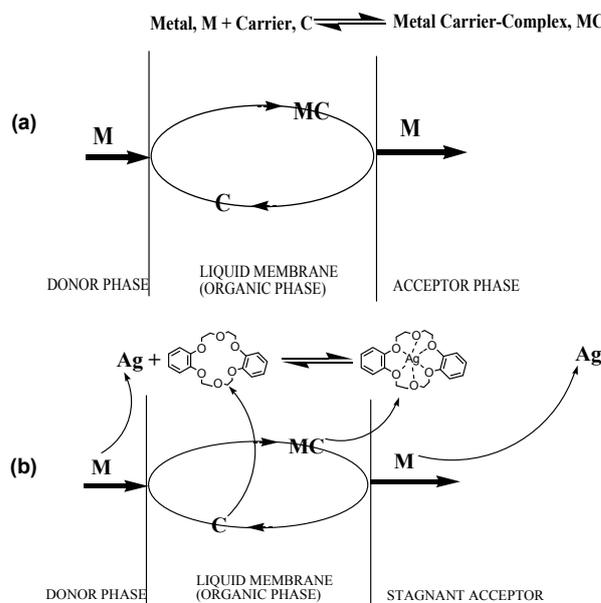

Figure 4
Facilitated transport in liquid membranes: (a) general example; (b) a typical illustration of how complexation may occur.

enrichment factor (E_f) refers to a ratio of analyte concentration in the extract in the acceptor phase to that in the donor phase. The mathematical relationships that exist between the concentrations of the analyte in the acceptor and donor phases and the extraction efficiency are given by the following equations:

$$E_f = \frac{C_a}{C_d} \qquad [5]$$

where:

C_a is the analyte concentration in the acceptor phase
C_d is the analyte concentration in the donor phase
E_f is the enrichment factor.

On the other hand, the extraction efficiency refers to the fraction of analyte that is extracted into the acceptor phase and is defined mathematically as:

$$E_e = \frac{m_a}{m_b} = \frac{C_a V_a}{C_d V_d} \qquad [6]$$

or

$$E_e = E_f \frac{V_a}{V_d} \qquad [7]$$

where:

m_a = mass of analyte in the acceptor phase
m_d = mass of the analyte in donor phase
V_d and V_a are the volumes of the donor and acceptor respectively.

Supported liquid membranes have been used mostly in the extraction of ionisable pollutants in water and wastewater samples. This technique has been used extensively in the extraction of agrochemical residues in natural waters (Chimuka et al., 1997; Megersa and Jönsson, 1998), environmental and biological samples (Megersa et al., 2001) and in fruit juices (Khrolenko et al, 2002, 2005). Supported liquid membrane application in the extractions of metals in waters is well documented and has shown great success which is evidenced by numerous reports covering a wide range of metals (Smith, 1997; Djane et al., 1997a; 1997b; 1998; 1999; Papantoni et al., 1995; Soko et al., 2003; Romero and Jönsson 2005; Valenzuela et al., 2007).

Micro-porous membrane liquid-liquid extraction (MMLLE) technique

Unlike in the SLM technique which is a three-phase system, MMLLE technique is a two-phase system whereby analytes are extracted from an aqueous solution into an organic phase (Fig. 5).
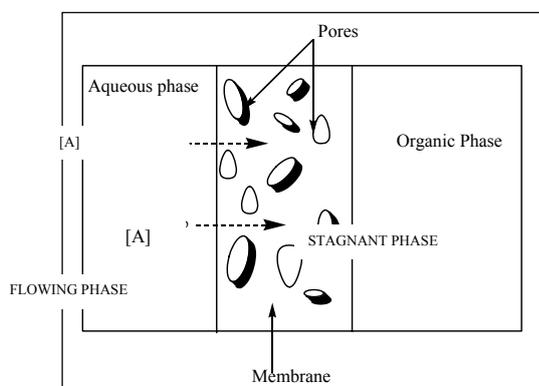

Figure 5
Schematic diagram of MMLLE schematic showing how analytes diffuse across a micro-porous membrane

The performance of the MMLLE technique is to a large extent dependent on partition coefficient, K_p such that:

$$K_p = \frac{C_o}{C_a} \qquad [8]$$

where:

C_o and C_a represent the equilibrium analyte concentration in the organic and aqueous phases, respectively.

For an analyte to be efficiently extracted with MMLLE, it should have low solubility in the aqueous phase as well as volatility. Non-polar organic compounds and non-ionising compounds usually extract well with high efficiencies and preconcentrate higher than the polar and ionising molecules due to the solubility factors. In MMLLE, the migration of molecules from aqueous to organic phase is driven by the concentration gradient of the analyte and is limited by its partition coefficient.

MMLLE has been reported in the extraction of environmental pollutants such as the extraction of dinitrophenolic compounds [Bartolome et al., 2007], isobutylicetophenone (Zorita et al., 2007), organo tin compounds (Cukrowska et al., 2004), and organo lead compounds (Cukrowska et al., 2007) from aqueous samples.

Hollow fibre micro-extraction technique

The hollow fibre micro-extraction technique is also known as liquid phase micro-extraction (LPME). In this technique a porous polypropylene hollow fibre strand is used and to it a very small volume of acceptor solution (in micro-litre ranges) is filled. The filled hollow fibre is then exposed to an organic liquid to impregnate the pores and then placed in an aqueous sample where extraction will proceed. Liquid phase micro-extraction can be carried out in either a two phase (MMLLE) or a three phase (SLM) depending on the analyte being extracted. The application of LPME has been reported in a wide variety of analyses of environmental pollutants such as the PAHs, drugs and pesticides (Hou et al., 2003; Hou and Lee 2002; Ma et al., 2006, Dziarkowska, 2007).

There are two modes of LPME that have been reported thus far and these include the static LPME and dynamic LPME (Figs. 6a and b) (Zhao and Lee, 2002). In static mode, the acceptor solution remains in the lumen throughout the entire extraction. In dynamic mode, however, the acceptor is repeatedly introduced and withdrawn from the lumen. Some researchers
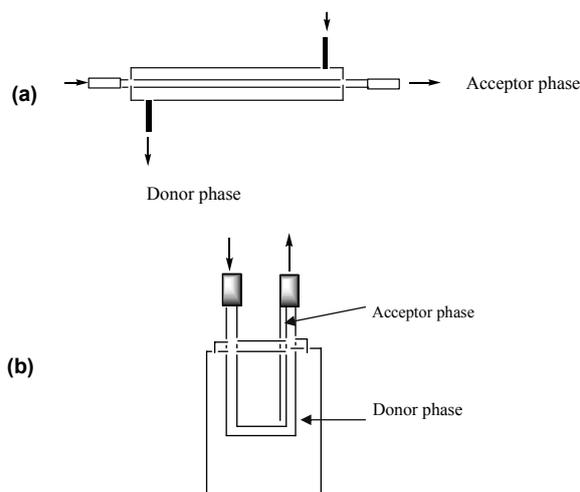

Figure 6
Hollow fibre configurations; a = dynamic mode; b = static mode

have indicated that the dynamic mode has an edge over the static mode in that it can result in much higher enrichment factors (Hou et al., 2003; Hou and Lee, 2002; Basheer et al., 2003).

An example of the application of HFSLM static mode was reported by Kou et al. (2004) in the analysis of haloacetic acids in water, where they analysed 9 haloacetic acids to sub $\mu g \cdot \ell^{-1}$ detection limits, low RSD values between 1.5 to 10.8% and high enrichment factors ranging between 300 to 3 000. Nora-adisak and Varanusupakul (2006) have also reported the use of a similar configuration to determine trihalomethanes in water samples.

Emulsion liquid membrane (ELM) technique

The emulsion liquid membrane (ELM) (Fig. 7) is designed to have a large surface area per unit sample volume, which gives it an advantage of high flux rates across the membrane as well as high preconcentration factors. ELM technique has several disadvantages, all related to the formation of emulsion and these are:
- Controlling the factors that affect emulsion stability such as ionic strength, pH, etc.
- If for any reason, the membrane does not remain intact during use, the separation that has been achieved is destroyed
- In order to recover the receiving phase and also to replenish the carrier phase, one has to break the emulsion. This is a difficult task, since in order to make the emulsion stable; you have to work against the ease of breaking it back down.

Despite the above cited drawbacks, several applications of ELMs have been reported both for speciation of metal ions (Kumbasar and Tutkun, 2001; Gasser et al., 2007; Fonad and Bart 2008; Sengupta et al., 2007; Sabry et al., 2007; Garmeiro et al., 2007) and organic compounds (Lee, 2008; Kaghazch et al., 2006).
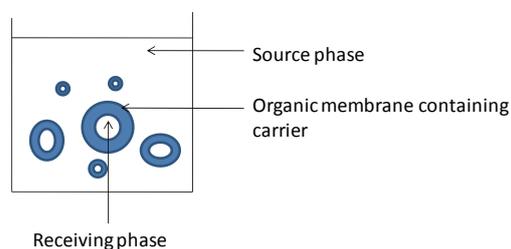

Figure 7
ELM extraction set-up

Conclusions

Liquid membrane extraction techniques in various forms and configurations have many sample-preparation applications and a potential to be extended to even more different pollutants in the water samples. Depending on the type of analyte and possible extraction process, it is possible to select the most appropriate liquid membrane technique.

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