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Review

Analytical applications of membrane extraction in chromatography and electrophoresis

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Abstract

An overview of the analytical applications of membrane-based systems for sample enrichment in chromatography and capillary electrophoresis is presented. A brief introduction to the different types of membranes and the main forces related to the transport through them is also given.

Keywords: Reviews; Membrane extraction; Sample enrichment; Preconcentration

Contents

1. Introduction

The analytical applications of membrane separation processes have attracted considerable attention during the last years. In most cases, the analytical applications of membrane processes aim at simplifying the sample preparation step.

Many papers reporting the work done in this field have been published and excellent reviews presenting the analytical strategies by which membranes simplify the sample preparation steps have also appeared [1]. The reviews of van de Merbel and co-workers [2,3], devoted to the coupling of membrane processes to separation techniques, and those of Jönsson and Mathiasson [4,5], reporting the principles and applications of supported liquid membranes, deserve special attention.

The present review focuses on the analytical applications of membranes as a way to extract and preconcentrate chemical species prior to chromatographic and electrophoretic separations. After the introduction, three parts are dedicated to liquid

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chromatography (LC), gas chromatography (GC) and capillary electrophoresis (CE).

In simple terms, a membrane can be thought of as a selective barrier between two phases [6]. The phase from which the transfer of mass occurs is called the donor or feeding phase and the phase that receives the flow is called the acceptor or permeate phase (Fig. 1). Although synthetic membranes may be of a very different chemical nature and may display different properties, they can be classified into four groups: microporous, homogeneous, ion-exchange and asymmetric. This classification, however, is not exclusive and in some cases doubts may arise as regards the structure of certain membranes.

In membrane-based processes, separation is the result of differences in the transport rates of the chemical species through the interface. It is possible to consider three basic types of mass transfer through membranes: passive, facilitated and active [7,8]. In the first, which is the one most commonly used in analytical applications, the membrane acts as a barrier through which the components are transported under the influence of a gradient in their electrochemical potential. In facilitated transport, together with a gradient in the electrochemical potential a carrier is present in the membrane that increases permeability to a considerable extent. Finally, active transport, mainly produced in cellular membranes, is produced against the gradient of electrochemical potential of the compounds via a reaction inside the membrane.

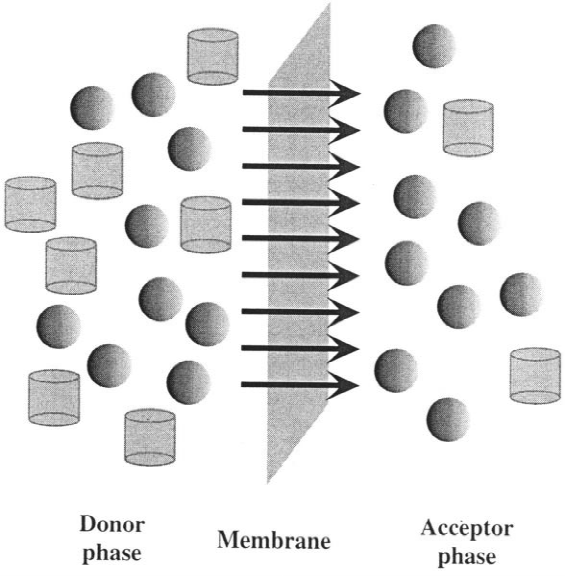

Fig. 1. Schematic representation of the transport through membranes.

From a practical point of view, the forces able to generate transport through membranes are directly related to differences in pressure, electrical potential and concentration. The mass flow brought about by differences in concentration is determined by the Fick law [$J_m = -DA(dC/dx)$]; differences in pressure produce a volume flow related to the Hagen–Poiseuille equation [$J_v = -KA(dP/dx)$], and the charge flow related to differences in electrical potential is governed by Ohm's law [$J_c = -RA(dE/dx)$]. In each of these cases there is a proportionality constant that corresponds, respectively, to the diffusion coefficient (D), hydrodynamic permeability (K), and electrical resistance (R). In all three expressions the term A represents the area of the membrane available for diffusion.

In some processes, a given flow may be due to more than one force. Thus, volume flow may be generated by a difference in pressure or, as in osmotic processes, by a difference in concentration. Mathematically, the relationship between flows and forces is expressed as the Onsager equation, in which each flow is expressed as the sum of the different forces originating it $J_i = \Sigma_j c_{ij} F_j$.

Among the processes generated by pressure differences are microfiltration, ultrafiltration and inverse osmosis. Microfiltration and ultrafiltration are based on processes of size exclusion, whereas in inverse osmosis (or hyperfiltration) it is also necessary to take into account the affinity of the solvents and solutes for the membrane. One drawback in this type of process is the polarization that arises due to solute concentration next to the membrane: to avoid this stirring is employed or the sample is made to flow parallel to the membrane.

Electrodialysis and Donnan dialysis are two separation processes through membranes generated by differences in electrical potential. In the case of electrodialysis, charge flow is determined by a combination of diffusional flows and flows due to electrical migration and is defined by the Nernst–Planck equation [$J_c = -DA(dC/dx) - DAczF/RT(dE/$

d*x*), where *c* is the concentration of the analyte, *z* its valency, *F* is the Faraday constant, and *R* is the gas constant]; the membranes can be neutral or charged. With the former (neutral), flows higher than in conventional dialysis are achieved while in the latter selectivity is increased because the membrane retains the species that have the same charge as it.

In Donnan dialysis, charged membranes are employed but no difference in the external potential is applied. In this process, the concentration of all the species on one side of the membrane is lower than on the other, which produces a flow of the species able to cross the membrane owing to their charge. The generated difference in potential must be compensated by the passage of ions against the gradient.

Finally, according to IUPAC, separation processes brought about by differences in concentration are generically known as dialysis and include processes of gas separation, dialysis through porous films and extraction processes. In the processes of gas separation the membranes most commonly used are homogeneous: polymeric and liquid and, in some cases, microporous membranes with extremely small pore sizes. In this case, in the Fick law – which regulates the general process – it is necessary to include a term *S* (the solubility constant), which represents the specific interactions of the species with the material of the membrane. To explain dialysis through porous membranes one introduces in the general law (Fick) a new term called tortuosity (τ), which is related to the additional resistance of the membrane to the passage of analytes. In this process hydrophilic membranes are used and the critical parameter is the maximum size of the species able to cross the membrane.

In liquid–liquid extraction processes, analyte transfer occurs through two immiscible phases. The use of microporous or homogeneous membranes is an alternative to traditional methodology. When hydrophobic microporous membranes are used, the membrane acts as a support which allows the contact between the phases without these merging. With homogeneous membranes the separation of analytes is directly related to their transport rate within the membrane phase, which is determined by their diffusivity and solubility in the membrane matrix. The main advantages over conventional liquid–liquid extraction are the avoidance of emulsion formation, the lack of the phase separation step and the use of modules with a high surface-area-to-volume ratio.

Although membrane processes may vary widely as regards how they function and in their different applications, they all have some common characteristics that make them attractive as alternatives in the field of separation. Often, they are faster, more efficient and cheaper than other separation techniques. Additionally, in most cases the processes are carried out at room temperature, which has undoubted advantages in the handling and separation of heat-sensitive species.

Among the fields of application of membranes is analytical chemistry, where separation processes using membranes are able to solve, in a simple and elegant fashion, problems in sample preparation that would otherwise require highly complex treatments. One essential characteristic of membrane-based separation processes is the ease with which they can be automated.

From the point of view of analytical applications, the most important groups of homogeneous membranes used for extraction processes are those made of polymer and liquid membranes [9], specially supported liquid membranes (SLMs). In both cases, separation is accomplished in two consecutive extraction processes between the membrane and the donor phase and between the acceptor phase and the membrane.

The main advantage of liquid homogeneous membranes as compared with polymeric membranes is the greater transport velocity through them, which is due to the greater diffusivity of species in a liquid medium. Additionally, in these membranes it is easier to incorporate carriers with a view to selectively increasing the permeability of certain species, giving rise to facilitated or coupled transport processes [10]. However, the membrane lifetime is usually longer for polymeric membranes, due to solvent leakage out of the liquid membranes, which becomes more pronounced as the polarity of the solvent increases; *n*-undecane and di-*n*-hexylether have shown the best stabilities.

2. Liquid chromatography

Membrane sample preparation represents an effec-

tive way of coupling on-line this part of the analytical procedure to chromatographic analysis. In this sense, different processes, generated by differences in concentration, pressure or electrical potential, are used. The main objectives of this technique are the removal of interfering compounds, present in complex sample matrices, and the preconcentration of target analytes. Regarding the first objective, dialysis through microporous membranes has frequently been used for sample clean-up with excellent results, especially in the biomedical and food analysis fields [11–17], although dilution of the analytes requires a later concentration step when low detection limits are needed. Pre-columns, packed with different materials, such as C_{18} or cation-exchange sorbents have been used for this purpose.

Regarding the use of membranes for analyte enrichment, membrane extraction has been addressed for a large number of samples and analytes. A separation module, containing the membrane is coupled to the liquid chromatograph, as shown in the scheme in Fig. 2. The separation system comprises two lines, one of them for the sample (donor) and the other for the acceptor. These are driven to the separation unit, each of them passing across one side of the membrane. After the transfer of analytes through the membrane, the acceptor, usually kept stagnant for a given extraction time (stop-flow mode), is displaced to the loop of the chromatographic injection valve. The Fig. 2 set-up shows a planar membrane, habitually used in extraction coupled to LC, although hollow fibre membranes have also been used. Fig. 3 shows separation units with different geometries and membranes. The donor and acceptor volumes can also change although, apart from some miniaturized devices coupled to capillary column chromatography [18], volumes are typically in the range of 10 to 1000 μl.

With the proper choice of conditions of the donor and the acceptor channels, the analytes are irreversibly trapped in the acceptor side, thus generating high enrichment factors in the stagnant acceptor. For acidic or basic compounds, the pH can be adjusted in the two phases in order to keep the analytes in their neutral form before they diffuse through the membrane and become ionised in the acceptor side. For permanently charged compounds, it is possible to add ion-pairing or chelating reagents to the sample. Another option, when using silicon membranes, consists of adding an organic solvent to the acceptor. This is not feasible with supported liquid membranes, because they are also made of an organic solvent, insoluble in water, which impregnates the pores.

Jönsson and co-workers have described the principles of the SLM extraction process [4,19] and have also reported a study [20] defining the factors (mainly pH and ionic strength) that limit the enrichment in SLM systems when analyte trapping in the acceptor is incomplete because ionisation cannot be fully accomplished.

Membrane extraction coupled to liquid chromatog-

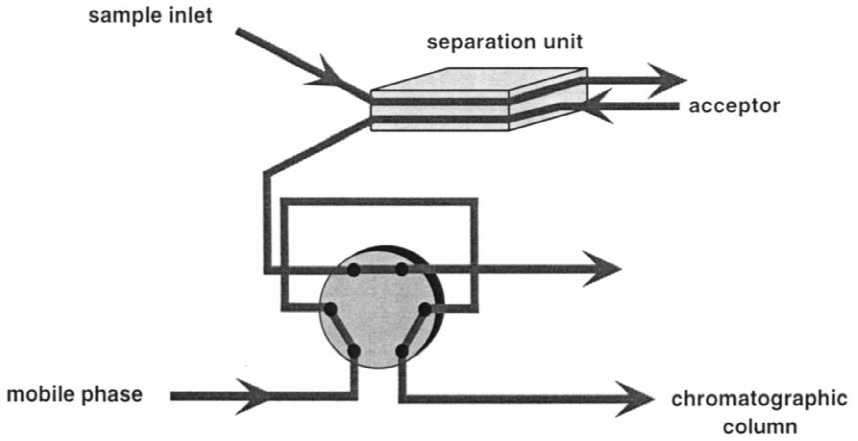

Fig. 2. Schematic set-up for a membrane extraction module coupled on-line to a liquid chromatographic system.

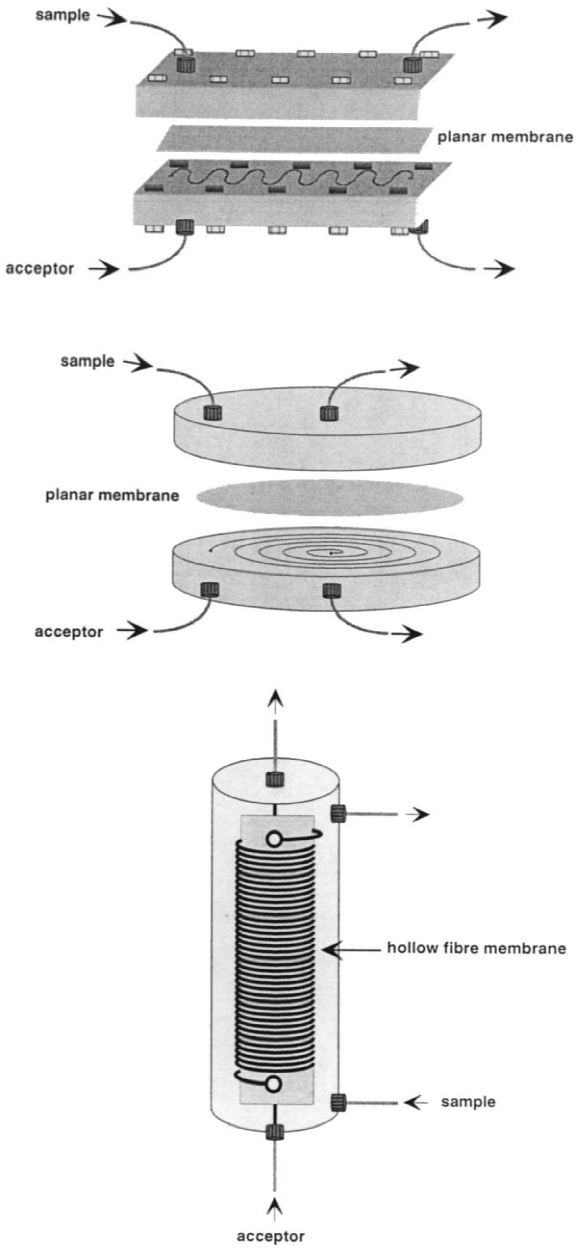

Fig. 3. Several separation modules with different geometries and types of membranes.

raphy has basically been performed with supported liquid membranes and with silicone membranes. Table 1 shows a summary of both approaches, classified according to their fields of application: biomedical, environmental, food and agricultural analysis, and the petroleum industry. In general, high selectivity is achieved with this technique, because only the components of the sample that are soluble in the acceptor and in the membrane are able to cross it, so that it is frequent to obtain comparable chromatograms from synthetic standards and from samples, as shown in Fig. 4 which depicts the chromatograms obtained after separation through a silicone membrane of different phenols, from a standard prepared in hexane (Fig. 4a) and from a crude oil sample [56]. Regarding sensitivity improvement, the enrichment factors are increased by increasing the enrichment time (extraction time, maintaining the acceptor flow halted). However, a later preconcentration step can be performed by using a pre-column [34,42] prior to the chromatographic system.

Additionally, when only very small sample volumes are available and high extraction efficiency is needed, recirculation of the sample through the separation unit has been proposed. Such is the case of the determination of drugs in blood plasma [22] or herbicide residues in matrices with high lipid contents [29].

Another mode of membrane extraction, recently used for analytical applications, is the MMLLE technique: microporous membrane liquid–liquid extraction. In a way this is similar to the SLM system, because an organic solvent impregnates the pores of a microporous membrane. The difference lies in the fact that the same solvent forms the acceptor phase. Thus, the technique is comparable to an aqueous–organic extraction, with the advantage that the formation of emulsions is avoided. This procedure has permitted the automatic extraction and determination of triazines in complex matrices such as corn, sunflower and olive oil [26] or the selective enrichment of up to 250 times for cationic surfactants in river and wastewater [57] after ion-pairing with heptanoic acid, which also serves as counter-ion for ion pair normal-phase chromatographic separation of the surfactants.

Another recently proposed technique is solvent microextraction with simultaneous back-extraction (SME/BE) [58,59] employing a microlitre-size liquid membrane. It is different from the classic bulk liquid membrane (BLM) technique, which uses volumes ranging from a few millilitres to over 100 ml and has had little analytical application. SME/BE

Table 1
Applications of membranes for sample enrichment in liquid chromatography

Application field	Supported liquid membranes	Silicone membranes
Biomedical	Bambuterol in plasma [18] Drugs in water [21] and plasma [22] Phenols in plasma [23] Dansylated amino acids in water [24] Ropivacaine metabolites in urine [25]	
Food and agricultural analysis	Phenolic acids in nutrient solutions [27]	Vitamin E in butter [28] Herbicides in egg [29] Vitamin E isomers in vegetable oil [30]
Environmental	Phenoxy acids in water [31,32] Herbicides in natural water [33–37] Amines in air [38] and rainwater [39] Carboxylic acids in air [40,41] Chlorophenols in river water [42] Surfactants in natural water [43] Carboxylic acids in soil [44,45] Triazines in natural water [46–48] Anilines in natural water [49] Metal ions in river water [50]	Trace organics in water [51] Phenols in wastewater [52]
Petroleum industry		Phenols in crude oil and fuel [53–55]

employs an unsupported liquid membrane, with a $\leq$80 μl volume of organic solvent, held within a PTFE ring and layered between two aqueous phases. The sample solution is stirred for a given extraction time and then an aliquot or a microdrop of the aqueous acceptor phase is injected into a high-performance liquid chromatography (HPLC) system. The authors have reported enrichment factors of about 500 for methamphetamine, mephentermine and methoxyphetamine, and of about 160 for 2-phenylethylamine, when using a 1.0-μl drop of aqueous acceptor and a 15 min extraction time [59]. Like the SLM system, the technique could be used for ionisable compounds, with the advantage of not generating memory effects, because a fresh organic membrane is used for each extraction; however automation of the process is more complicated and to date, it has only been applied off-line.

3. Gas chromatography

Many of the applications of membrane extraction coupled to GC correspond to the MESI technique: membrane extraction with a sorbent interface. It has mainly been developed to carry out the sampling and continuous monitoring of organic volatile (VOCs) [60–67] and semivolatile [68,69] compounds in environmental aqueous or atmospheric samples. Planar membranes were initially used, but later developments have focused on hollow fibres, which provide a higher surface-area-to-volume ratio [70]. Mathematical modelling of the extraction system has been made by Pawliszyn and co-workers [71–73].

Fig. 5 shows a scheme of the procedure, including a membrane module and a sorbent interface, directly connected to the GC system. The membrane is in contact with the sample or its headspace, and the extraction takes place in two steps: analyte extraction from the matrix by the membrane material and analyte stripping from the membrane by an inert gas phase, such as N_2 or He, for volatile compounds, and high-density CO_2 for semivolatile ones. The sample is typically pumped through the centre of the fibre and the stripping phase flows countercurrently around the exterior of the fibre, towards the sorbent

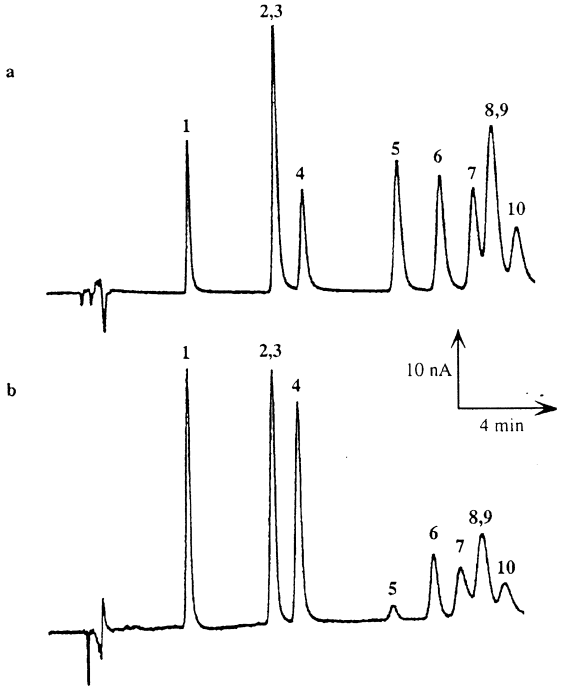

Fig. 4. Chromatograms with amperometric detection of a standard prepared in hexane (a) and a crude oil sample, diluted with hexane (b). Mobile phase: acetonitrile–water (30:70, v/v) to which 1 g/l of KNO_3 and 0.025 g/l of H_2SO_4 had been added as supporting electrolyte (Q=1.0 ml/min). Peaks: (1) phenol, (2) *m*-cresol, (3) *p*-cresol (4) *o*-cresol, (5) 3,4-dimethylphenol, (6) 3,5-dimethylphenol, (7) 2,3-dimethylphenol, (8) 2,4-dimethylphenol (9) 2,5-dimethylphenol, (10) 2,6-dimethylphenol.

interface, where the analytes are concentrated and, finally, thermally desorbed onto a GC system for analysis. The whole process is computer-controlled.

Microporous polypropylene membranes and, more usually, homogeneous silicon membranes have been used in the membrane module. Different sorbent interfaces have been proposed: a bed of activated charcoal [60], cryogenic trapping [61,62], a poly(dimethylsiloxane) polymer [63,64] or a silicon membrane positioned inside a deactivated silica tubing [65].

With this approach the membrane acts as a selective barrier, keeping water and high molecular mass compounds from entering the GC column, while enrichment is performed at the sorbent interface, although the sensitivity of the method is also dependent on the flow-rate and the membrane size, in such a way that better detection limits are obtained with higher sample flow-rates and longer membranes.

Additionally, coupling to GC has been performed with membrane modules similar to those used in LC. Since the mechanism is similar to a liquid–liquid extraction, this procedure is suitable for compounds of moderate and low volatility. Two modes of membrane operation, on-line coupled to GC analysis, are possible: the continuous-flow mode and the stop-flow mode. Examples of this approach are the use of silicone rubber membranes for the determination of trace organics in aqueous samples [74,75], with concentration factors of 50–200, and of supported liquid membranes for polycyclic aromatic hydrocarbons (PAHs) in environmental waters [76], amines in urine [77], and plasma [78] and anaesthetics in blood plasma [79]. Determination of anaesthetics in this matrix has recently been proposed by the same authors, simplifying the process

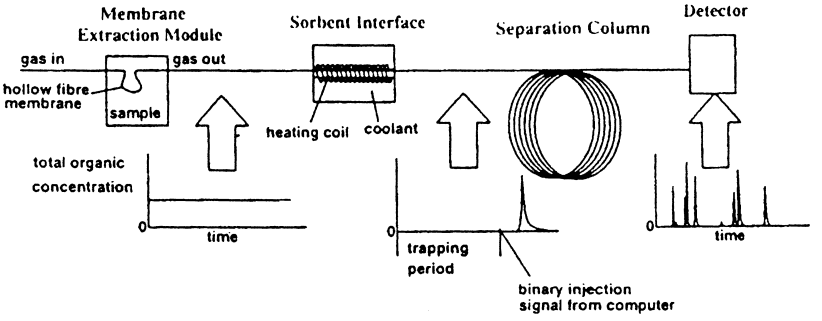

Fig. 5. Components of the MESI system coupled to a gas chromatograph. Reprinted from Ref. [70], with permission from Elsevier Science.

[80] by using the MMLLE technique, which uses an organic solvent as acceptor phase, thus allowing direct transfer of the solution to the injection loop in the gas chromatograph. MMLLE has also been applied to the enrichment of organotin compounds in aqueous samples after off-line derivatization [81].

4. Capillary electrophoresis

In recent years CE has become a technique of separation of considerable potential, especially in the separation of complex samples coming from biological matrices. The need to inject small sample volumes is translated into high detection limits; for this reason, a process of enrichment of the analytes is usually required.

On the other hand, the complexity of the injected samples demands, in many cases, an effective clean-up process. Several studies have been carried out aimed at the improvement of the detection limits by means of preconcentration prior to the separation step [82]. The use of solid-phase extraction microdevices requires high solvent volumes to desorb the retained analytes, thus producing a reduction in the electroosmotic flow, peak broadening, and a loss of resolution [83–85]. As an alternative to solid-phase extraction, membranes have been used as systems for the preconcentration and introduction of samples [86]. The coupling of dialysis with CE was proposed by Bao and Dasgupta [87]. The sample is pumped through the outside of a hollow fibre dialysis membrane that connects two sections of a capillary and, after diffusion of the analytes to the interior, an appropriate voltage is applied to introduce them into the electrophoresis system. A different module with a planar membrane, coupled in a continuous flow system, has also been proposed [88]. However, with these devices only a small part of the sample is introduced in the system, and in order to increase sensitivity, the dialysate preconcentration has been proposed. Veraart et al. [89,90] used a polymeric sorbent to trap the analytes; 200 μl of a tetrahydrofuran–water (3:1, v/v) mixture are sufficient for the elution of the preconcentrated analytes. This device has been used for the determination of sulfonamides and acidic antiinflammatory drugs in serum and urine.

Purification and clean-up of the samples prior to their injection into the electrophoresis system have also been carried out by means of electrodialysis units [91,92]. However, to achieve analyte enrichment it is necessary to use an electrodialysis unit with three compartments separated by two membranes; the first membrane retains the macromolecules and the second one only allows the passage of small ions, thus producing enrichment of the analytes of interest in the intermediate compartment. The analytes are later electrokinetically injected into the electrophoresis system [93].

Most of the applications of membrane extraction for sample preparation and enrichment are based on the use of off-line coupled supported liquid membranes [94–96]. An on-line coupling has been proposed [97] using a miniaturized hollow-fibre module, with an acceptor volume of only 1.3 μl. After analyte enrichment, this small volume is injected into the capillary using the double-stacking procedure for large volume-injection; the method involves a manual step to insert the capillary in the electrode vessel. The process of clean-up and enrichment carried out with the SLM allows the determination of bambuterol in blood plasma at nanomolar detection limits.

Also, copper electrodes coated with liquid membrane phases in which carrier molecules are included, have been used for the potentiometric detection of organic acids [98].

A new approach to preconcentration prior to separation by CE is the use of polymeric membranes impregnated with chromatographic stationary phases of the type C_4, C_8, C_{18}, etc. [99]. After adsorption and concentration of the analytes, the membrane is washed with a buffer solution and elution is carried out with the minimum possible volume of an organic or aqueous–organic solution. Then, the appropriate voltage is applied for the separation of the analytes. This strategy has been used for the determination of different compounds in biological fluids [100–103].

Acknowledgements

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