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# MEMBRANE EXTRACTION IN ENVIRONMENTAL CHEMICAL ANALYSIS

## EKSTRAKCJA MEMBRANOWA W ŚRODOWISKOWEJ ANALIZIE CHEMICZNEJ

**Summary:** Membrane extraction techniques permit the application of classical liquid-liquid extraction (LLE) chemistry to instrumental and automated operation. Various shortcomings of LLE are overcome by membrane extraction techniques as they use none or very little organic solvents, high enrichment factors can be obtained and there are no problems with emulsions. A three phase SLM system (aq/org/aq), where analytes are extracted from the aqueous sample into an organic liquid, immobilized in a porous hydrophobic membrane support, and further to a second aqueous phase, is suitable for the extraction of polar compounds (acidic or basic, charged, metals, etc.) and it is compatible with reversed phase HPLC. A two-phase system (aq/org) where analytes are extracted into an organic solvent separated from the aqueous sample by a hydrophobic porous membrane is suitable for more hydrophobic analytes and is compatible with gas chromatography. The experimental format can be based on either flat membranes and on hollow fibre membranes in various ways. Using hollow fibers, it is possible to perform extractions for sample clean-up and enrichment with very cheap and simple equipment, leading to high enrichment factors (easily thousands of times) for ultra trace analysis. Membrane extraction can be a basis for environmental field sampling. Such sampling can be performed in two different regimes, with different purposes. One aim is to attempt a complete extraction of the analytes in a sample, in order to determine the total concentration of these analytes. This is similar to what is attempted with classical techniques such as LLS, and SPE (*solid phase extraction*). An alternative and complementary way of working is to attempt equilibrium between the sample and the sampler, with minimum disturbance of the sample. These are the principles of "equilibrium extraction through membranes" (ESTM) as recently was developed. This technique leads to the determination of the freely dissolved concentration (*ie* not complexated or otherwise bound fraction) of the analyte. This is related to the bioavailability, fugacity and chemical potential of a pollutant in the sample and is therefore significant for the evaluation of toxicity and transport processes of the pollutant in the environment, both for polar organic compounds, and for metal ions.

**Keywords:** extraction, enrichment, sample preparation, sampling, hollow fiber, speciation, free fraction

For the analysis of environmental water samples, a number of extraction techniques, such as the classical liquid-liquid solvent extraction (LLE), solid phase extraction (SPE) or solid phase microextraction (SPME) are used for sample preparation and sometimes also sampling. The emerging novel technology of liquid membrane extraction offers a number of advantages over other techniques. The membrane extraction techniques are in principle variants of LLE but various shortcomings of LLE are overcome as membrane extraction techniques use none or very little organic solvents, high enrichment factors can be obtained and there are no problems with emulsions. Also, they can provide unsurpassed cleanup efficiency and high extraction selectivity [1, 2].

There are in principle two variants of liquid membrane extraction, three-phase systems and two-phase systems. The three phase system (aq/org/aq), also called Supported Liquid membrane extraction (SLM), where analytes are extracted from the aqueous sample into an organic liquid, immobilized in a porous hydrophobic membrane support, and further to

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a second aqueous phase, is suitable for the extraction of polar compounds (acidic or basic, charged, metals, etc.) and it is compatible with reversed phase HPLC. The two-phase system (aq/org), also called Microporous Membrane Liquid-Liquid Extraction (MMLLE) where analytes are extracted into an organic solvent separated from the aqueous sample by a hydrophobic porous membrane is suitable for more hydrophobic analytes and is compatible with gas chromatography. The experimental format can be based on either flat membranes (as was described in most of the literature on liquid membrane extraction) and on hollow fibre membranes in various ways. With flat membranes, it is possible to perform the extraction in automated flow systems, leading to fully automated systems. A number of papers have described such systems [1, 2] and they will not be discussed further here. Using hollow fibers, it is possible to perform extractions for sample cleanup and enrichment with very cheap and simple equipment, leading to high enrichment factors (easily thousands of times) for ultra trace analysis. Such systems are usually referred to as Liquid phase MicroExtraction (LPME) systems (either 2-phase or 3-phase LPME). In pharmaceutical application, these techniques are especially developed by Rasmussen and Pedersen-Bjergaard [3].

Membrane extraction can be performed in two different regimes, with different purposes. The most common aim is to attempt a complete extraction of the analytes in a sample, in order to determine the total concentration of these analytes. This is similar to what is attempted with classical techniques such as LLE, and SPE. An alternative and complementary way of working is to attempt equilibrium between the sample and the sampler, with minimum disturbance of the sample. These are the principles of “equilibrium extraction through membranes” (ESTM) as recently was developed [4]. This technique leads to the determination of the freely dissolved concentration (*ie* not complexated or otherwise bound fraction) of the analyte. This is related to the bioavailability, fugacity and chemical potential of a pollutant in the sample and is therefore significant for the evaluation of toxicity and transport processes of the pollutant in the environment, both for polar organic compounds, and for metal ions.

**Chemical principles for membrane extraction**

In *3-phase LPME* (SLM), the membrane consists of an organic solvent, which is held by capillary forces in the pores of a hydrophobic porous membrane. Typical solvents are long-chain hydrocarbons like *n*-undecane or kerosene and more polar compounds like dihexyl ether, dioctyl phosphate and others. Various additives to the membrane phase are often used for facilitating the extraction process.

Figure 1a illustrates the principle of SLM extraction, applied to extraction of acidic compounds, *eg* phenols. First, the pH of the sample is adjusted to a sufficiently low value so the acids are uncharged. When the hollow fibre is in contact with the sample, the uncharged acids (HA) are partitioned into the organic membrane phase.

To obtain an efficient transport of the acids through the membrane wall, the acceptor solution inside the hollow fibre membrane is filled with a basic buffer. Then an acid molecule, which has diffused through the organic membrane, is immediately deprotonated at the membrane-acceptor interface and thereby it is trapped, *ie* prevented from re-entering the membrane. The result is a transport of acid molecules from the sample to the acceptor phase.

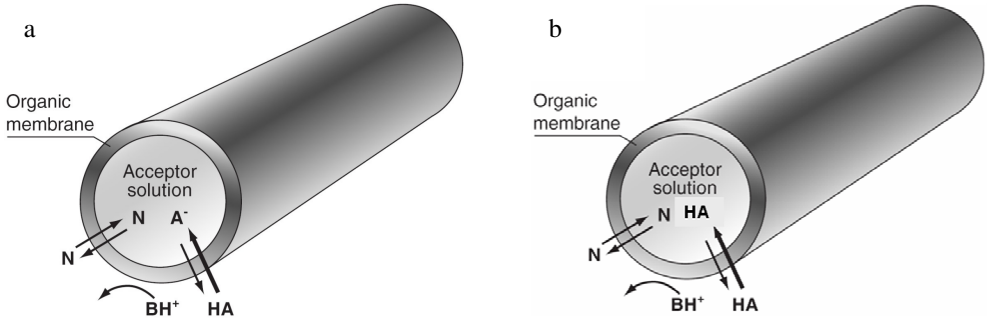


Fig. 1. Principles of liquid membrane extraction of acidic compounds: a) 3-phase LPME (SLM); b) 2-phase LPME (MMLLE) (Pictures by Lars Toräng)

Referring again to Figure 1a, it is obvious that basic compounds (B) will be charged already in the acidic sample phase and will therefore be completely excluded from the membrane. The same is true for permanently charged compounds. Neutral compounds (N) may be extracted, but will not be trapped in the acceptor, so the concentration in the acceptor phase will never exceed that in the sample and no enrichment is obtained. Further, hydrophilic neutral compounds will be very reluctant to partition into the membrane, while hydrophobic neutral compounds might accumulate in the membrane but not continue to the acceptor. Charged macromolecules, as proteins or humic acids will be rejected and the extraction rate of uncharged macromolecules will be very low due to their low diffusion coefficients. In summary, with the conditions mentioned, the SLM extraction will be highly selective for small, acidic molecules.

Obviously, basic compounds may be extracted in a similar way as acids by reversing the pH conditions. It is clear that the concept of trapping in a stagnant acceptor is central in the SLM technique. The maximum enrichment possible with such a system crucially depends on the pH gradient between the two aqueous phases; the aqueous/organic partition coefficients have no influence.

The *2-phase LPME* technique (MMLLE) is a complement to the SLM extraction as it permits membrane-based extraction to be extended to other classes of compounds. The acceptor phase is here an organic solvent, also filling the pores of the hydrophobic membrane. This forms an aqueous/organic two-phase system, with the organic phase partly in the membrane pores and partly in the acceptor channel. Such systems are best applicable to hydrophobic, preferably uncharged compounds *ie* those that cannot be extracted with SLM. The extract is organic, not aqueous as with SLM. Thus MMLLE is easier interfaced to gas chromatography than SLM, which is best compatible with reversed-phase HPLC. With MMLLE no trapping reactions are used in the organic acceptor phase. The maximum enrichment is in MMLLE equal to the distribution coefficient as in LLE, the only driving force for the mass transfer being the attainment of distribution equilibrium between the aqueous and organic phases. The extraction efficiency will be higher if the hydrophobicity of the analyte is large; *ie* if the partition coefficient is large.

## Examples of hollow fibre membrane extraction formats

Several different formats for hollow fibre extraction have been presented. Practically all of them are based on the Accurel®PP fiber materials produced by the company Membrana GmbH (Wuppertal, Germany; www.membrana.de). These fibres are made of polypropylene and come in different sizes, most commonly inner diameters of 600 µm or 300 µm are used. The price for such membrane material is very reasonable and permits disposable operation.

In Figure 2 are shown some commonly used set-ups for hollow fibre membrane extraction in environmental context. Sometimes the fibre is attached to a syringe, syringe needle or a micropipette tip during the extraction for support and convenient filling of the fibre, in other cases the fibre is freely floating in the sample and then some manual handling involving microsyringes is necessary, which has been shown to pose no practical problems.

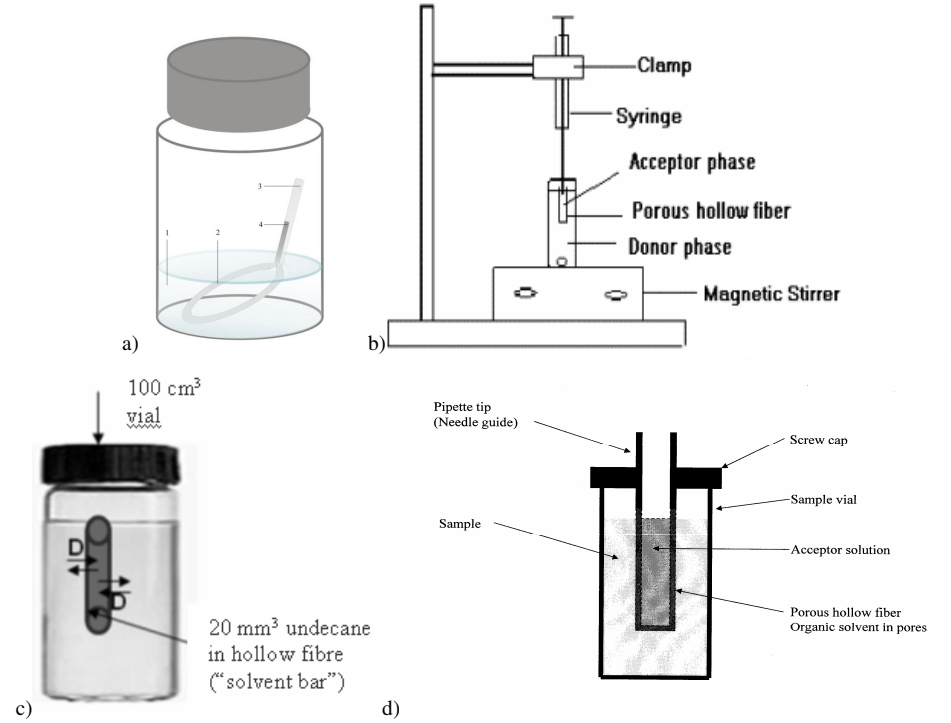


Fig. 2. Experimental arrangements of hollow fibre membrane extraction; a) single loop, made by 10÷100 cm of 0.3 mm i.d. hollow fibre, closed together with a piece of aluminium foil, freely moving in a sample bottle [4]; b) setup according to Lee [5], 0.6 mm fibre connected to an HPLC syringe; c) "solvent bar" [6] - a short (ca 2 cm) fibre with 0.6 mm i.d. and closed by heat in both ends, floating in the sample; d) arrangement with a micropipette tip according to Rasmussen and Pedersen-Bjergaard [3]

## Applications

In Table 1 are listed some recent applications from the Lund group of 2- or 3-phase hollow fibre extraction in environmental and biological applications.

Table 1

| Compounds | Sample types | Extraction, analysis | Max. enrichment; min. LOD | Ref. |
|---|---|---|---|---|
| Dinitrophenols | Environmental waters | 3-phase, HPLC | 7000; 7 ng $dm^{-3}$ | [7] |
| Copper | Environmental waters | 3-phase (ESTM), Spectrophot. | Not applicable | [8] |
| Dinitrophenols | Environmental waters | 3-phase, HPLC | 300; 0.1 µg $dm^{-3}$ | [9] |
| Phenoxy acid herbicides | Environmental waters (very dirty) | 3-phase; HPLC | 400; 0.3 µg $dm^{-3}$ | [10] |
| PhIP (aromatic heterocyclic amine) | Urine, plasma | 3-phase; HPLC(fluorescence) | 126; 11 ng $dm^{-3}$ | [11] |
| Drugs (fluoxetine, norfluoxetine) | Sewage | 3-phase, HPLC | 1700, 11 ng $dm^{-3}$ | [12] |
| Short fatty acids | Blood serum | 3-phase, GC-FID | 155; 0.04 µM | [13] |
| Drugs (Ibuprofen) and metabolites | Environmental water, incl. sewage | 2-phase, GC-MS | 2000, 7 ng $dm^{-3}$ | [14] |
| Polybrominated diphenyl ethers | Environmental waters, incl. leachate | 2-phase, GC-MS | 5000, 1 ng $dm^{-3}$ | [6] |
| Alkyl phenols (incl. nonylphenol) | Environmental water | 2-phase (ESTM), HPLC | Not Applicable | [15] |
| Nitrophenols | Environmental water (incl. sea) | 2-phase, HPLC | 300; 0.1 µg $dm^{-3}$ | [16] |
| Drugs (Ivermecin) and metabolites | Environmental water | 2-phase; LC-MS | 80; 200 ng $dm^{-3}$ | [17] |

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## EKSTRAKCJA MEMBRANOWA W ŚRODOWISKOWEJ ANALIZIE CHEMICZNEJ


**Streszczenie:** Membranowe techniki ekstrakcji pozwalają na wykorzystanie klasycznej ekstrakcji roztwór-roztwór (LLE), stosując również techniki instrumentalne zautomatyzowane. Wady klasycznej LLE są usuwane przez stosowanie technik ekstrakcji membranowej, pozwalających na użycie bardzo małych ilości

rozpuszczalników, uzyskanie dużego współczynnika wzbogacenia i uniknięcie trudności związanych z powstaniem emulsji. Trójfazowy (woda/zw.org./woda) układ SLM (*Supported Liquid Membrane*), gdzie analit jest ekstrahowany z roztworu wodnego do cieczy organicznej unieruchomionej na porowatej, hydrofobowej membranie, a następnie do drugiej fazy wodnej, jest odpowiedni do ekstrakcji związków polarnych (kwasowych lub zasadowych, jonów) i jest odpowiednikiem chromatografii HPLC z odwróconą fazą. Układ dwufazowy (woda/zw.org.), gdzie anality są ekstrahowane do rozpuszczalnika organicznego z wodnej próbki przez porowatą, hydrofobową membranę, jest odpowiednikiem chromatografii gazowej. W doświadczeniu można wykorzystać płaskie membrany i membrany z wydrążonych włókien. Używając wydrążonych włókien, można w prosty i tani sposób poprzez ekstrakcję gruntownie oczyszczać i wzbogacać próbki, osiągając kilkutysięczne współczynniki wzbogacenia. Ekstrakcja membranowa może być wykorzystywana podczas pobierania próbek środowiskowych. Pobierania takich próbek może być wykonane dwoma różnymi sposobami, w zależności od założonych celów. Jednym celem jest ekstrakcja analitów z próbek, by określić ich całkowite stężenie. Pod tym względem metoda ta jest porównywalna z klasycznymi technikami, takimi jak: LLS i SPE (*ekstrakcja z fazy stałej*). Alternatywnym i uzupełniającym sposobem jest metoda polegająca na osiągnięciu równowagi pomiędzy próbką a sondą, z minimalnym zaburzeniem próbki. Jest to zasada „równowagowej ekstrakcji przez membrany" (ESTM - *Equilibrium Extraction Through Membranes*), metody rozwijanej w ostatnich latach. Ta technika umożliwia oznaczania stężenia wolnych form (tj. nieskompleksowanej albo inaczej związanej formy) analitu. Związane jest to z dostępnością biologiczną, lotnością i potencjałem chemicznym polutantu w próbce i dlatego jest ważne w ocenie toksyczności i transportu polutantu w środowisku przyrodniczym, zarówno polarnych związków organicznych, jak i jonów metali.

**Słowa kluczowe:** ekstrakcja, wzbogacanie, przygotowywanie próbki, próbkowanie, światłowód, specjacja, wolne frakcje