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On-line membrane extraction liquid chromatography for monitoring semi-volatile organics in aqueous matrices

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Abstract

Membrane extraction is an attractive alternative to conventional extraction methods, such as liquid–liquid extraction and solid phase extraction, because the analytes can be isolated in a continuous fashion. On-line detection can be carried out using a suitable analytical instrument. The objective of this study is to study the enrichment of semi-volatile organic compounds (SVOCs) from an aqueous matrix by on-line membrane extraction, to be followed by liquid chromatographic (ME-LC) analysis for continuous monitoring. The membrane serves as an interface across which liquid–liquid extraction takes place. The SVOCs transfer from the aqueous phase and are concentrated in an organic extractant. The enriched solvent is intermittently injected into an HPLC for analysis. In this paper, the enrichment into the organic phase under different operating conditions and the performance characteristics of the instrumentation are presented.

Keywords: Membrane extraction; Water analysis; Semi-volatile organics

1. Introduction

Contamination of ground water and surface water resources in the last few decades have posed a major threat to public health. From an analytical perspective, the organic pollutants in water can be classified as volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). The US Environmental Protection Agent (USEPA) has listed numerous VOCs, such as BTEX (benzene, toluene, ethylbenzene and xylene), and SVOCs, such as pesticides, polycyclic aromatic hydrocarbons and substituted phenols as regulated compounds. Conventional analytical methods for VOCs include headspace analysis, purge and trap and solid-phase microextraction. Purge and trap is the most common method where an inert gas purges the VOCs from water. The purged organics are focused on a sorbent trap and then are thermally desorbed for GC or GC–MS analysis. The conventional measurement methods for SVOCs include liquid–liquid extraction (e.g. EPA method 1625), solid-phase extraction and large volume injection. Of these, solid-phase extraction has evolved to be the method of choice due to lower solvent use and shorter analysis time.

All the above measurement processes involve sampling at site, sample transportation storage, sample preparation and analysis. These independent

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steps increase the probability of analytical errors due to contamination and sample loss. In addition, these techniques are not designed for automated on-line analysis. Automated solid-phase extraction, liquid–liquid extraction and purge and trap have been developed for on-line analysis [1–10]. These techniques show promising results, and are used in process and environmental monitoring. In general, there is a need for instrumentation for on-line water monitoring that incorporates simple, rugged design while providing low detection limits for trace analysis.

Semi-permeable membranes have been used for extracting and analyzing VOCs from water [11–16]. Membrane extraction is attractive because analytes can be isolated on-line from an aqueous stream in a continuous fashion and the whole process can be automated. The membrane has served as an interface between the water and an inert gas (for GC analysis) or a vacuum (for a mass spectrometer). The organics migrate from the aqueous phase across the membrane to the permeate side of gas (or vacuum) under a concentration gradient. The membrane interface with GC or GC–MS for continuously monitoring water and air has been reported [15–17].

The SVOCs offer additional challenges in on-line membrane extraction because these compounds are not easy to volatilize and can not be introduced easily into an analytical instrument. Limited studies on analytical membrane extraction of SVOCs has been reported. Recently laser desorption has been used in membrane introduction mass spectrometry to recover semi-volatile compounds from the membrane [17]. Dialysis with semi-permeable membranes has been used to selectively remove lipids during the analysis of bioaccumulative compounds [18]. A membrane concentrator for SVOCs in water has been reported [19] where the water stream continuously flows through a membrane module and a certain volume of organic solvent is continuously circulated on the permeate side. After about 110 min of equilibration, an 80-fold enrichment is obtained. Recently, phenol analysis has been carried out via membrane extraction followed by HPLC separation [20,21].

The membrane serves as an interface across which liquid–liquid extraction takes place. This is governed by partition of the analyte between the aqueous phase and the membrane and also by the diffusion through the membrane. The diffusion occurs because the analyte molecules utilize the active energy to rotate a polymer segment to create a suitable size vacancy to jump into. The activation energy is a function of polymer structure and the analyte [22]. The direction of the jump is along the concentration gradient. The diffusion process can be described by Fick's law:

$$J = -DA\,\mathrm{d}C/\mathrm{d}x$$

where J is the membrane flux, D is the diffusivity, A is the membrane surface area and C is the analyte concentration in the membrane.

The partition process is similar to liquid–liquid extraction, it determines the system's selectivity and affects the sensitivity. Unfortunately, no data is available on the partition coefficient between the aqueous phase and the membrane (K_p). However, from its nature, it can be assumed to be constant for a given analyte–membrane system. The octanol–water partition coefficients from the literature may be used as a reference to approximate the partition process. Assuming the concentration gradient to be linear and the concentration at the permeate side is zero, the extraction flux can be described as:

$$J = DAK_pC^*/L$$

where K_p is the partition coefficient between the aqueous phase and the membrane, C^* is the analyte concentration in water and L is the membrane thickness. At a sufficiently low concentration, D is constant for a given analyte.

The objective of this study was to study the enrichment of SVOCs from an aqueous matrix by on-line membrane extraction, to be followed by HPLC analysis for continuous monitoring. The SVOCs transfer from the aqueous phase and are concentrated in the organic phase. The enriched solvent continuously flows into the sample loop of an injection valve that intermittently injects the sample into an HPLC for analysis. In this paper, continuous monitoring of a simulated aqueous stream is demonstrated. The enrichment into the organic phase under different operating conditions and the performance characteristics of the instrumentation are presented. The effects of water flux across the membrane and into the solvent were also studied.

2. Experimental

The instrumentation includes a hollow fiber extraction module, a six port injection valve, HPLC with a UV detector and pumps for the delivery of the extraction solvent and water. The schematic diagram of the instrumentation is shown in Fig. 1. The water sample and extraction solvent flowed counter-current on either side of the hollow fiber. Two flow-modes were tested. In ''flow-over'' mode, the water flowed outside and the solvent flowed inside the membrane fiber. In ''flow-through'' mode, water flowed inside while the solvent was outside. The flow-over configuration is shown in Fig. 1. The flow-rates were between 1.5 and 5 ml/min for the aqueous sample, while the extraction solvent flowed at 0.03–0.24 ml/min. This provided an enrichment of the organics into the solvent phase. A syringe pump (Waters, Millford, MA, USA) was used for water sample delivery, and model QG 150 (Fluid Metering, Orchard Oyster Bay, NY, USA) reciprocating pump was used for solvent delivery. In practice, the membrane module was spiraled to reduce the boundary layer effects and to make it compact. The enriched solvent phase flowed through the 100-μl sample loop of the six port valve (Valco Instruments, Houston, TX, USA). Injections were made at regular intervals onto the HPLC column for separation. Corresponding to each injection a chromatogram was obtained.

The membrane module was made using seven pieces, and is a 121 cm long composite membrane.

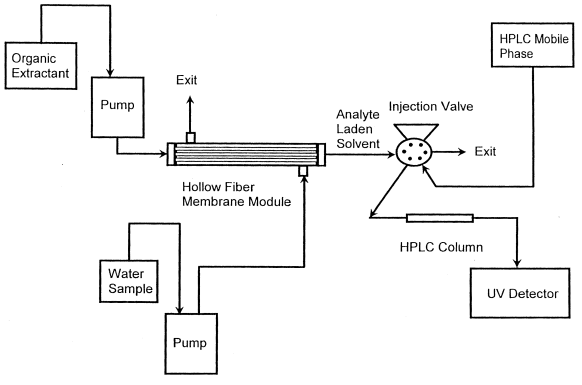

Fig. 1. Membrane extraction with liquid chromatography interface. Flow-over mode is shown here.

The composite membrane was 0.260 mm O.D.×0.24 mm I.D. (Applied Membrane Technology, Minnetonka, MN, USA) and is comprised of a microporous polypropylene support coated with 1-μm thick film of homogenous siloxane. The membrane pieces were inserted into a 1/8″ I.D. Teflon tubing. A ''T'' unit (Components & Controls, Carlstadt, NJ, USA) was used at each end of the tubing to connect the solvent and the water line. Epoxy was used to seal the ends so that the water and solvent did not come in contact with one another.

The analytical HPLC system (Waters, Millford, MA, USA) used in this study was comprised of a model 600E pump and a model 484 tunable UV detector. A 150×3.2 mm HPLC column with a 5-μm Pinnacle Cyano stationary phase (Restek Corp., Bellefonte, PA, USA) was used for separation. A Minichrom data system was used to acquire and analyze the data. The model compounds studied here were purchased from Aldrich Chemicals (Milwaukee, WI, USA). The HPLC mobile phase and the extraction solvents were purchased from Fisher Scientific. The HPLC mobile phase, extraction solvents and water used to prepare the working standards were filtered and left in an ultrasonicater for 30 min. The μg/ml (ppm) level stock solutions were prepared by spiking a known amount of analyte into the water and then sonicated 24 for h. The stock solutions were stored at 4°C and working standards were prepared daily from the stock solutions.

3. Results and discussions

A stagnant liquid boundary layer forms on each surface of the membrane due to poor mixing of the fluid phase and the membrane. The mechanism of liquid–liquid extraction across the membrane is shown in Fig. 2. The extraction process comprises of five distinct steps: (1) analytes diffuse from water and through the nearly stagnant boundary layer; (2) dissolve in membrane; (3) permeate through membrane; (4) desorb from membrane and dissolve in the solvent; (5) migrate through solvent boundary layer into the solvent. In steps (1), (3) and (5), the analytes are in a homogeneous phase and the migration is governed by concentration gradients. The thickness of the boundary layers is determined by the

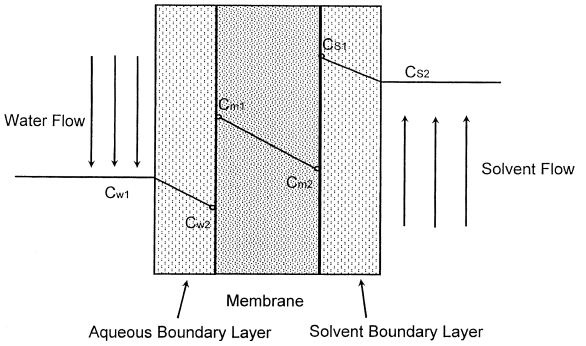

Fig. 2. Concentration profile in membrane extraction process. C_w, C_m, C_s are organic concentration in water, membrane and solvent phases, respectively.

degree of mixing of the fluid with the membrane surface. Thicker the boundary layer, the larger the mass transfer resistance is. In steps (2) and (4), the transfer of analytes from one phase to another is driven by the partitioning from the water to the membrane and from the membrane to the organic solvent.

The continuous monitoring of SVOCs in water involves carrying out the analysis at a relatively high frequency. The analytes were continuously extracted in the membrane. The enriched solvent was injected into the HPLC column every few minutes, and the operation is demonstrated by monitoring a spiked sample stream. A series of chromatograms were obtained (as shown in Fig. 3) corresponding to a sequence of equally spaced injections. The concentration of phenol, aniline and nitrobenzene in the stream were 2.58, 0.818 and 0.957 ppm, respectively. Good reproducibility of peak shape, peak height and retention time was observed. Here, the analysis frequency was limited by the separation time on the HPLC column.

Linear calibration curves were obtained for phenol, aniline and nitrobenzene with their respective equations being: $y=8.7C-94.4$ ($r^2=0.9999$), $y=3.7C-150$ ($r^2=0.9997$), $y=29.2C+308.5$ ($r^2=0.9999$). This was using acetonitrile as an extractant at a flow-rate of 0.027 ml/min. The linear curves demonstrate the linearity of the extraction process. The precision and method detection limits (MDLs) are presented in Table 1. Excellent repeatability and relatively high sensitivity were demonstrated. The

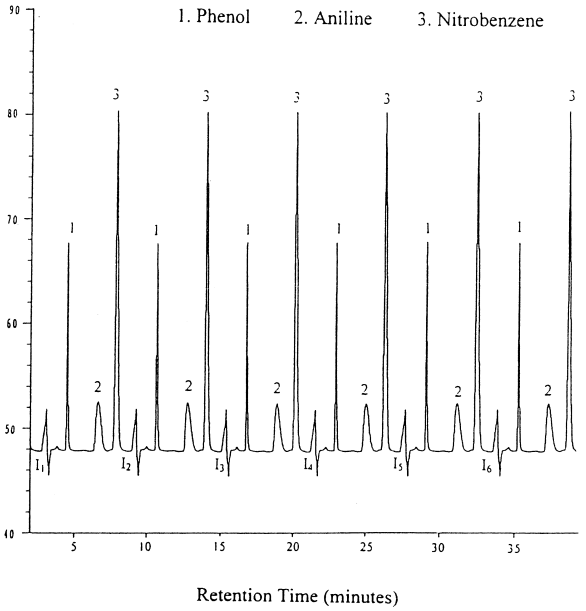

Fig. 3. Series chromatogram for continuous monitoring of a water stream. A water stream containing 2.58 ppm of phenol, 0.818 ppm of aniline and 0.957 ppm of nitrobenzene was used. Acetonitrile was used as the extractant at a flow-rate of 0.04 ml/min. A sample flow-rate of 2.5 ml/min and the flow-through mode were used.

relative standard deviations (RSD) were based on six repeat injections of the sample in Fig. 3. The MDLs were evaluated according to standard EPA method [23]. These results presented here were obtained in the flow-through mode at a water flow-rate of 2.5 ml/min. Methanol, at a flow-rate of 0.4 ml/min, was the extraction solvent. The system response, consequently the MDLs, are a function of extraction solvent, operating parameters like water flow-rate,

Table 1
Method detection limits and precision of several SVOCs

Compounds	MDLs[a] (μg/L or ppb)[b]	RSD[a,c] (%)
Phenol	15.2	0.32
Aniline	8.2	0.78
Nitrobenzene	2.0	0.14

[a] Methanol was used as the extractant at flow-rate of 0.04 ml/min. Sample flow-rate was 2.5 ml/min in the flow-through mode.

[b] Method detection limits based on standard EPA method.

[c] Relative standard deviation based on six replicates at concentration corresponding to Fig. 3.

Table 2
Enrichment factor for different compounds using different solvents in the flow-over mode

Solvents[a]	Compounds			
	Benzyl alcohol	Phenol	Nitrobenzene	Phenyl ether
Octanol at 0.07 ml/min	28	3	9	38
Hexane at 0.09 ml/min	35	5	11	63
Acetonitrile at 0.027 ml/min	2	3	2	3
Methanol at 0.05 ml/min	1	2	10	26
Log *P*(hexane)[c]	−0.76	−0.96	na[b]	na[b]
Log *P*(octanol)[c]	1.1	1.46	1.88	4.4

[a] Water flow-rate was 1 ml/min for methanol extraction and 5 ml/min for the other solvents.
[b] Not available.
[c] Partition coeffcients in the octanol–water or hexane–water system.

solvent flow-rate and membrane module design. Although no attempts were made to achieve lower MDLs, that would have been desirable for drinking water applications. However, based on the discussion that follows, it may be prudent to extrapolate, that, significantly lower detection limits could be obtained using hexane as the solvent and in the flow-over mode.

3.1. Enrichment factor

The objective of the membrane extraction was to concentrate the organics from the aqueous phase into the solvent phase. The enrichment factor was defined as:

$$\mathrm{EF} = \frac{\text{concentration in solvent}}{\text{concentration in feed water}}$$

The enrichment factor was evaluated for different flow-conditions as well as for different extraction solvents. The results are presented in Table 2 and Figs. 4 and 5. The enrichment factor was different for different analytes, was a function of the extraction conditions, and was found to be as high as 62. From Table 2, it can be seen that polar compounds such as phenol had low enrichment factors due to their strong affinity for water, and relatively

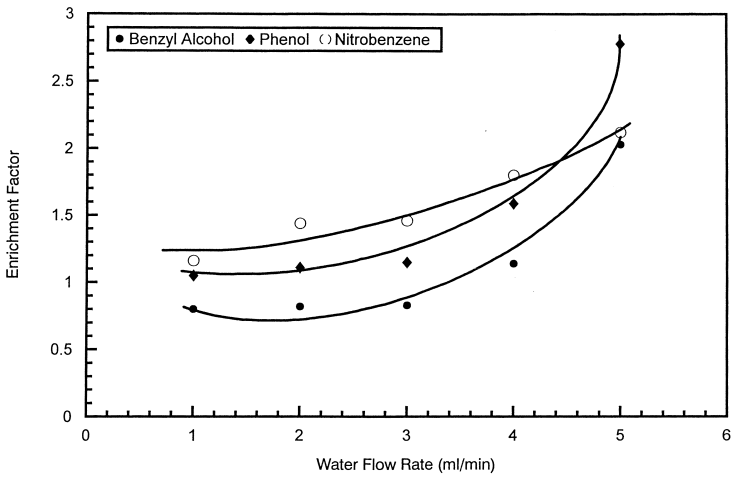

Fig. 4. Enrichment factor as a function of water flow-rate. Acetonitrile was used as the extractant at a flow-rate of 0.027 ml/min in the flow-over mode.

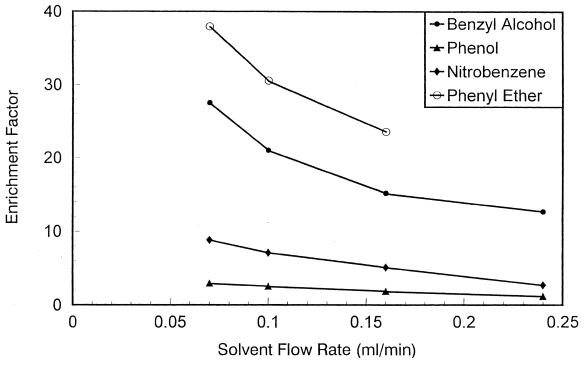

Fig. 5. Enrichment factor as a function of extractant flow-rate. Octanol was used as the extractant. Water flow-rate was 5 ml/min in the flow-over mode.

low partition coefficients in the hydrophobic membrane used here. These results are consistent with other studies [12,13,22]. Non-polar compounds such as phenyl ether showed much higher enrichment factors. Comparison of Tables 1 and 2 demonstrates that analytes with low enrichment factors had high detection limits and vise versa.

The extraction solvent played an important role in determining the enrichment factor. Four solvents, methanol, acetonitrile, octanol and hexane were evaluated here. These represented a wide range of polarity. The enrichment factor was relatively lower in the polar solvents methanol and acetonitrile and higher in non-polar solvents. Even a polar analyte such as phenol had the highest enrichment factor in hexane, the most non-polar of the solvents used here. The octanol–water and hexane–water partition coefficients from the literature [24] are also presented here. Although the partition coefficients of the analytes are higher in the octanol–water system than in the hexane–water system, the enrichment factors in hexane were found to be higher than that in octanol. The presence of the membrane is the obvious cause of this anomalous behavior. A possible reason is that when the solvent came in contact with the membrane, the polymeric material swelled. This resulted in a more open structure that allowed rapid diffusion of analytes through the membrane. Hexane having a polarity that is similar to silicone, swelled the membrane more than octanol did. Consequently, the permeability was higher when hexane was used. Another possible explanation is as follows: Octanol could more easily extract these compounds directly from water than hexane. However, octanol being more polar did not readily extract organics from the non-polar polysiloxane layer. Therefore, hexane as a non-polar solvent turned out to be a stronger extractant in step (4) of the extraction process.

Another variable in the extraction process is the flow-mode. Both flow-over and flow-through modes were effective in on-line extraction. The enrichment factors were found to be consistently higher in the flow-over mode. For example, at a water flow-rate of 2.9 ml/min and a methanol flow-rate of 0.023 ml/min, the enrichment factors for benzyl alcohol, phenol and nitrobenzene were around one. Where as, in the flow-over mode at a water flow-rate of 2.9 ml/min and a methanol flow-rate of 0.035 ml/min, the enrichment factors for the same three compounds were 13, 7 and 6, respectively. The internal volume of the membrane was small as the fiber I.D. was only 0.240 mm. The volume outside of the membrane was much larger because the I.D. of the module was 3 mm. Thus in flow-over mode, a small volume of organic solvent was involved in the extraction so that the analytes could be concentrated into a smaller volume.

In flow-through mode where the water flows inside of the membrane, smaller fiber diameter leads to a lower Reynolds Number (Re) which determines the degree of mixing:

$$\mathrm{Re} = (\rho \nu d/\mu)$$

where ρ is the density, ν is the velocity, d is the fiber I.D. and μ is the viscosity. The higher the Re, the better the mixing is. Less mixing at the surface of the membrane results in a thicker boundary layer. Since the organics had higher solubility in the membrane than in water, a concentration depletion zone was formed. This increased the mass transfer resistance in step (1) and resulted in a lower enrichment factor. The boundary layer was not as critical for the organic solvent in which the analytes had very high solubility and high diffusivity. In flow-over mode, the diameter of membrane module was much larger than the hollow fiber I.D., thus, a higher Re was obtained. Also the presence of membrane fiber in the module shell acted as a barrier to the flow-path that

introduced more turbulence and better mixing of the aqueous phase with the membrane.

The enrichment factor was also a function of water and solvent flow-rates. Faster water flow lead to a higher Re number forming a thinner boundary layer and faster mass transfer in step (1). A higher flow-rate also brought more sample and, consequently, a larger amount of analyte into the module. Using the enrichment factor as a function of water flow-rate (in the flow-over mode) using acetonitrile as the extractant is shown in Fig. 4. It can be clearly seen that as the water flow-rate increased, the enrichment factor increased. The effect of extractant flow-rate at a constant water flow-rate is shown in Fig. 5. The lower the flow-rate, less was the solvent involved in the extraction process. Thus, a higher enrichment factor was achieved. On the whole, higher water and lower extraction solvent flow-rates are favorable for high enrichment factors.

3.2. The effects of water permeation across the membrane

The membrane acts as a barrier between the aqueous phase and the organic extractant. Ideally, it ought to facilitate selective extraction while preventing the leakage of either phase to the other side. Being small molecules, water and the solvents have relatively high diffusion coefficients in the membrane material. Consequently, these molecules may be expected to permeate through the membrane along with the analyte molecules. The permeation of water across the membrane and its effects were investigated here in the flow-through mode. The results are presented in the Table 3. The flow-rate of water was increased from 1.5 to 5 ml/min. Since the fibers were narrow (0.24 mm I.D.), this resulted in higher pressure drops and, consequently, higher pressures inside the membrane (from 32 to 99 p.s.i.). This further increased the flux of water across the membrane. When the water flow-rate was 1.5 ml/min (assuming negligible water flux at this flow-rate), the solvent flow-rate was 0.026 ml/min. When the water flow-rate was increased to 5 ml/min, the permeate side flow-rate increased to 0.26 ml/min. The water flux was an equivalent of 0.234 ml/min. The mixing of water with the solvent did not interfere in the analysis, but diluted the solvent stream.

At a higher flow-rate, a larger amount of sample is brought into the membrane per unit time and one would expect the system response to increase. However, according to Table 3 that was not the case. As flow-rate increased, the system response (normalized with respect to a flow-rate of 1.5 ml/min) increased. The response leveled off beyond a flow-rate of 3 ml/min, even though more sample was brought in. Although more sample permeated through, the leakage of water diluted the solvent phase. There was no net increase in the enrichment factor and, consequently, no enhancement in sensitivity. At higher flow-rates, the water flux may even dilute the solvent phase to the point that the enrichment factor would decrease. Flow rates higher than 5 ml/min were not tested here because higher pressure could rupture the membrane.

This also demonstrates another advantage of the flow-over mode. Since the internal diameter of the module shell is significantly larger than that of the membrane, an increase in flow-rate does not translate

Table 3
Effects of water flux in flow-through mode

Water flow-rate inside membrane (ml/min)	Normalized[a] response for phenol	Normalized[a] response for nitrobenzene	Pressure in the membrane (p.s.i.)	Flow-rate in the permeate side (ml/min)
1.5	1.00	1.00	32	0.026
2.0	1.61	1.68	38	0.069
3.0	2.03	2.26	55	0.07
4.0	2.16	2.36	74	0.13
5.0	2.15	2.34	99	0.26

[a] Response at flow-rate of 1.5 ml/min was considered to be one.

to higher pressure on the membrane. Consequently, the leakage problem is significantly less.

Temperature also effects the water flux. Higher temperature increases analyte diffusivity and reduces the partition coefficient of analytes in the membrane. Higher temperatures also tend to accelerate membrane swelling, which increases pore-flow. At a membrane temperature of 50°C, the enrichment factor was seen to drop due to enhanced leakage of water. Experiments were not carried out above the manufacturer specified upper membrane operating temperature of 60°C.

4. Conclusions

On-line membrane extraction using an organic solvent was an effective method for the continuous monitoring of semi-volatile organics in water. ME-LC demonstrated low detection limits, linear calibration curves and excellent precision. An enrichment factor as high as 62 was obtained during continuous, on-line extraction. It was a function of the analyte and extraction solvent as well as flow-conditions. The flow-over mode was found to provide higher enrichment than the flow-though mode.

References

[1] E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, Chromatographia 29 (1990) 415.
[2] G.J.H. Mols, M. Althuizen, H. Janssen, C.A. Cramers, U.A.Th. Brinkman, J. High. Res. Chromatogr. 19 (1996) 69.
[3] J.J. Vreuls, A.J.H. Louter, U.A.Th. Brinkman, J. Chromatogr. A 856 (1999) 279.
[4] D. Puig, I. Silgoner, D. Barcelo, Anal. Chem. 69 (1997) 2756.
[5] S. Chiron, S. Papilloud, W. Haerdi, D. Barcelo, Anal. Chem. 67 (1995) 1637.
[6] A.J.H. Louter, C.A. Beekvelt, P.C Montanes, J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. 725 (1996) 67.
[7] J.J. Vreuls, U.A.Th. Brinkman, G.J.D Jong, K. Grob, A. Artho, J. High Res. Chromatogr. 14 (1991) 455.
[8] E.C. Goosens, D.D. Jong, G.J.D. Jong, U.A.Th. Brinkman, J. High Res. Chromatogr. 20 (1997) 325.
[9] E.C. Goosens, D.D. Jong, G.J.D. Jong, F.D. Rinkema, U.A.Th. Brinkman, J. High Res. Chromatogr. 18 (1995) 38.
[10] A.J.H. Louter, P.A. Jones, J.D. Jorritsma, J.J. Vreuls, U.A.Th. Brinkman, J. High Res. Chromatogr. 20 (1997) 363.
[11] W.S.W. Ho, K.K. Sirkar, Membrane Handbook, Van Nostrand Reinhold, New York, 1992.
[12] X. Guo, S. Mitra, Anal. Chem. 71 (1999) 4407.
[13] X. Gou, S. Mitra, J. Chromatogr. A 826 (1998) 39.
[14] S. Mitra, L. Zhong, N. Zhu, X. Guo, J. Microcolumn Separation 8 (1996) 21.
[15] X. Guo, S. Mitra, Anal. Chem. 71 (1999) 4587.
[16] L.E. Slivon, M.R. Bauer, J.S. Ho, W.L. Budde, Anal. Chem. 63 (1991) 1335.
[17] M.H. Soni, J.H. Callahan, S.W. McElvany, Anal. Chem. 70 (1998) 3103.
[18] B. Strandberg, P.-A. Bergqvist, C. Rappe, Anal. Chem. 70 (3) (1998) 526.
[19] H. Nomura, J.H. Ahn, M.J. Foster, T.C. Thomas, Membrane Concentrator for Semi-volatile organic Compounds. NeoMecs 4832 Park Glen Road, St. Louis Park, MN 55416.
[20] M.T.G. Sanchez, J.L.P. Pavon, B.M. Cordero, J. Chromatogr. A 766 (1997) 61.
[21] M.E.F. Laespada, J.L.P. Pavon, B.M. Cordero, J. Chromatogr. A 823 (1998) 537.
[22] H. Eustache, G. Histi, J. Membrane Sci. 8 (1981) 105.
[23] 40 Code of Federal Registrar, 1994, Part 136, appendix B.
[24] A. Leo, C. Hansch, D. Elkins, Chem. Rev. 71 (1971) 6.